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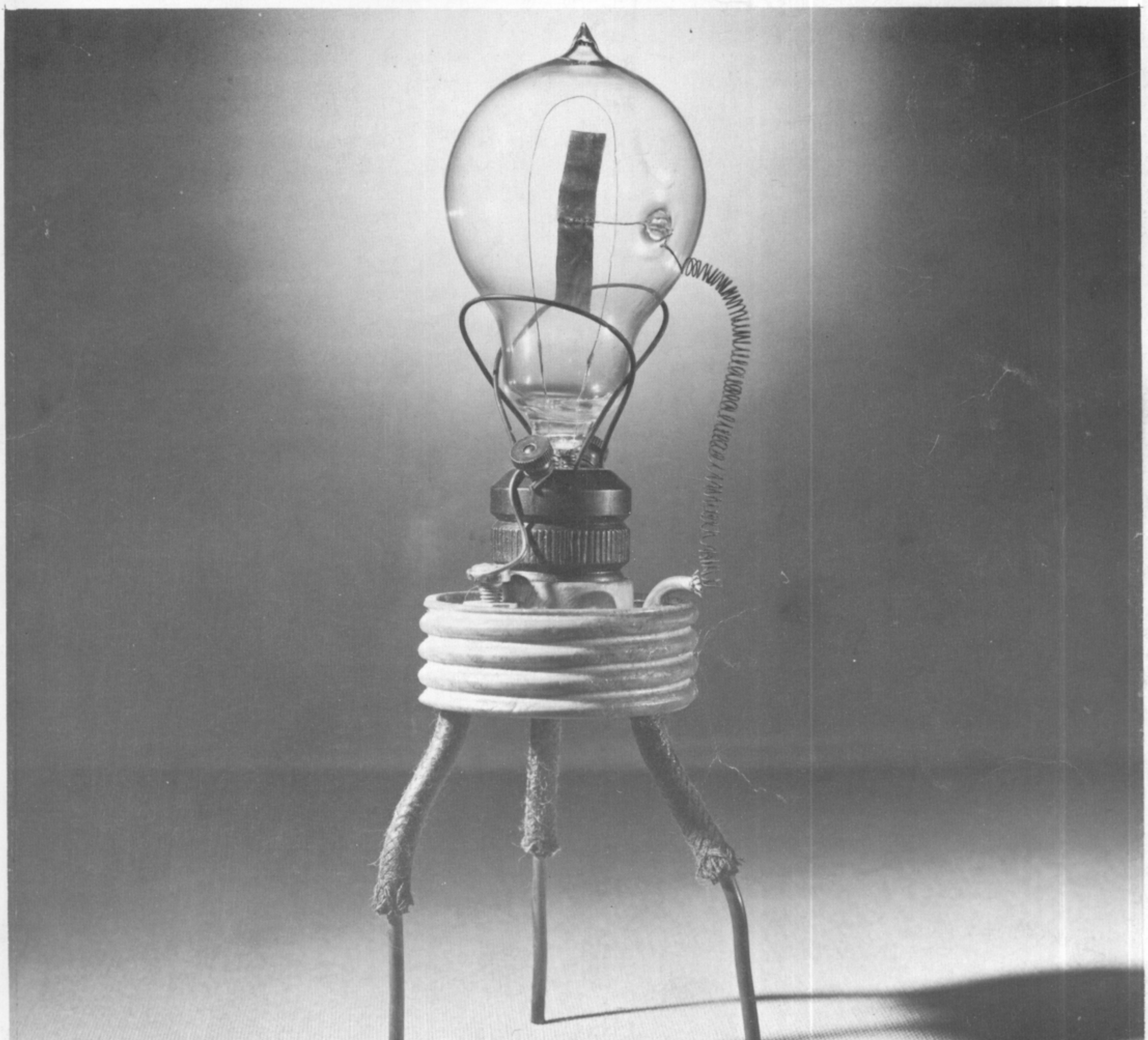

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The annual Historical Metallurgy Society conference held in Birmingham in September 1984 highlighted an important period in the history of metals which had tended to be overlooked, possibly because it is so recent.

The first half of the 20th century with two world wars and a revolution in transport and communications, resulted in intense activity by research and production metallurgists creating materials required to capitalize on the inventiveness and ingenuity of scientists and engineers.

An item which typifies 1900-1950 was the thermionic valve. Sir John Fleming (1850-1945) influenced by the work of Thomas Edison, patented his oscillation valve, a diode or two electrode device, in 1904 (illustrated on our cover) and was followed in 1907 by Lee de Forest (1873-1961) who added the 'grid' and turned the valve into a triode and the prototype of the modern radio component.

As James Bradbury records in his paper on Nickel (pages 67-68) the metallurgical contribution to the development and eventual mass-production of the thermionic valve was considerable. By mid-century there were over 1,300 types of valve available to the radio construction industry in Europe whilst production, world-wide topped 200 million units per annum. By this time however, the situation was changing with solid state research at the Bell Telephone Laboratories leading to the gradual introduction of transistors in the 1950s and the first British transistor radio set in 1956.

Thermionic valves were fitted to some radios, tape-recorders and record-players until the early 1970s whilst valves continue to be employed on the transmission side of the industry and as replacements in some television receivers. But the small heated glass bottles of the domestic wireless era have now become museum pieces with the events leading up to their dominance, technological history.

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It was the thought of so much unrecorded work which prompted Bill Alexander to suggest the idea of the 1900-1950 Alloys conference. At an early stage in pre-conference planning, a decision was made to publish the entire proceedings in a future issue of *JHMS*. Eighteen people wrote and/or presented papers, there were three shorter contributions and two further papers have been offered since. They are all printed in the *Journal* which follows and it is intended to publish metallurgical notes on some of the exhibits examined at those technological museums visited during the conference weekend in a future *Journal*. A sub-committee has been created to stimulate the study of recent metallurgical history and the Honorary Editor invites your co-operation.

Contents

The cover illustration is of Professor Fleming's original oscillation valve and is reproduced by kind permission of the Director of the Science Museum, South Kensington, London.
We gratefully acknowledge the help received by HMS Council member Sue Cackett.

The historical background to the development of **Alloys 1900-1950**

Bill Alexander

Synopsis

This review outlines the metallurgical scene at the beginning of 20th century and in 1950.

Brief references are made to past publications, present state of information, methods used at turn of the century and significance of impurities in most tonnage metals produced at that time.

The state of the art and science are compared for the two periods under the four headings of: extraction and manufacture, typical uses, test equipment properties and data and finally the state of metallurgical theory.

Examples of alloy development during this period show the range of alloying principles used. These are solid solution hardening, duplex and multiphase alloys, grain size and orientation, the range of heat treatments and the use of alloys at elevated temperature.

Finally some general observations are made on the multiplicity of properties which alloys require to give adequate service.

Introduction and Objectives

This introductory lecture is intended to outline the metallurgical scene as it was in 1900 and also again at the close of the period under review. The Conference organisers have also promised that the academic or theoretical metallurgy will be kept to a minimum. But if the Conference attains its initial objectives then in the years ahead more papers and discussions may take place on the metallurgical science behind the development of these alloys. The real aim is to endeavour to set the record straight on one facet only, namely the true origin of the first discovery or concept of an alloy during this period. A second aim is to begin documenting the initial artifacts made in such alloys.

Already there are a great number of such artifacts preserved in various engineering museums up and down the country, examples of which you will see tomorrow, but very few if any have adequate identification or documentation of their alloy composition or metallurgy. The museums which will be visited have all welcomed this chance of widening their information on the presentation of such engineering parts.

Past Publications

It is perhaps not widely realised that publication of many academic papers in the UK on metallurgical topics could during the 1920s to 1940s in the UK be delayed by anything up to three years. These were due to refereeing, limited publication facilities and in some cases discouragement by the authorities and directors of industrial firms to disclose practical knowhow and expertise. Some firms were more enlightened and looked upon publication as increasing and raising prestige and indicative of the technical and research backup to their production and to their customers. Finally, World War I and World War II delayed publication until the mid 1920s and until the late 1940s respectively.

Present State of Information

It must be admitted that many such alloys of tonnage significance and International repute in the World today are well documented historically. One has only to think of high speed steels, Duralumin, the stainless steels, Silumin, nodular or spheroidal iron, but the two latter are not mentioned in one of the best source books which reviews the science of metallurgy during this period, namely the Sorby Centennial Symposium of the History of Metallurgy, AIMME, Cleveland 1963[1]. This is a wonderful book for references and dates of academic papers on alloys during this time, but it contains very little critical analysis or record of the initial discovery and none of the manufacture of the alloys and in what particular engineering form, apart from, and to a very limited extent, the tungsten filament lamp, duralumin and iron silicon transformer sheet. Indeed the latter is the only alloy to which reasonable justice is recorded as comprehensive historical metallurgy, and by that I mean the true origins of the introduction, various modifications in practice and in theory. In this particular case theory followed the practical innovation!

Methods at the Turn of the Century

The technique for developing alloys during the first decade or so of the 20th Century was merely an extension, under more controlled conditions of the methods used by the ancients. In the latter half of the 19th Century iron and copper alloys were methodically examined by such early eminent metallurgists as:

J O Arnold, Benedicks, H C H Carpenter, G Charpy, H le Chatelier, Chernoff, L Guillet, R A Hadfield, E Heyn, C T Heycock & Neville, H M Howe, Ledebur, A Martens, F Osmond, J Riley, W C Roberts Austen, A Sauveur, J E Stead, B H Thurston, Troost, T W Turner, Wertler, to name but a few.

Other noted workers in academic and practical metallurgy were Bauer, Berthelot, Berthier, Bessemer, Deville, Hall, Héroult, Ewing, Gautier, Mond and Tammann.

The simple and largely empirical method was used of mixing various elements by melting, casting and hot and cold working where considered necessary. The range of such alloys were then tested by various mechanical, physical and chemical procedures which were available and which will be elaborated later. Heat treatment of steels had long been practised without any adequate metallurgical theory to support the methods.

This procedure could obviously be a time consuming and somewhat arduous process, particularly if, as had become desirable in the early 1900s, three and more components were being used, such as in the nickel chromium steels, cast irons and high tensile brasses. Nevertheless the procedures were objective and practical and had the advantage that at an early stage, the potential alloy was subjected to manufacturing methods which would have to be used for regular production.

The development of a new alloy therefore rarely needed significant modification in manufacture to obtain the requisite properties shown in experimental trials. In fact the manufacturing methods for wrought alloys could be thought of as a selecting procedure which in most cases tested the alloy much more than it would ever undergo in service. In short, the race was to corner the market with some real or illusionary improvement in properties of a new or old alloy, for the customer. Such new alloys were almost invariably patented, sometimes with key information not divulged. The alloys marketed were usually given brand names and occasionally house names and numbers, such as Staybrite, Broternal, Mazak, Duralumin[2], or the house names of: Hidiminium RR56 etc. Brightray G S, F & H Taurus Bronze Mark I to XXX. Catalogues of such names were published from time to time in:

The Metal Industry Handbook[3] Thurston's List of Brasses and Bronzes, USA.

but the manufacturing procedures were closely guarded secrets.

British Standards and other material specifications were beginning to emerge but the vast majority of engineering and construction metals and alloys were ordered and purchased by brand names with supervised testing and inspection in the suppliers works. Such on-site testing persists to this day and is increasing again as quality assurance becomes more essential for most products.

Impurities

Considering production metallurgy at the turn of the century, almost all so-called virgin or pure metals were despatched from the mines and smelters to their various destinations, contaminated with a range of impurities. Therefore, strictly speaking, they were already alloys and showed significant disparities in workability and properties according to where they originated. This of course was not new, and as with the newer alloys so with the virgin metals, the key impurities were well recognised, but because they were not easy to remove, or in some cases estimate, they were oxidised or reduced and slagged off and the impurities minimised but usually not completely eliminated. The entire metallurgy of copper and iron is full of examples showing the effects of impurities which were present either from the ore or from smelting and melting. Usually such impurities concentrated in the grain boundaries where they had the most detrimental influence on structural properties.

So another great watershed in the art of the metallurgist began to emerge about this period ie the advent of pure metals in significant tonnages. Copper was already being purified by electrolysis to raise the electrical conductivity. The initiation of this method of refining, after fire refining, was by Elkington, at Pembrey in South Wales in 1869[4], but it was well into the period before aluminium, zinc, cadmium, lead, nickel, tungsten and manganese were produced at better than 99.5% purity.

Consequently, one important factor in alloying during 1900-1950 was adjusting for the removal of the effects of impurities on working and properties of a range of common metals. Significant examples of impurities effects at this time were:

Silver, arsenic, sulphur, oxygen and bismuth in copper.
Antimony, arsenic, copper, silver and gold in lead.
Iron, silicon and manganese in aluminium.
Cadmium, lead and bismuth in zinc.

The effects on iron of carbon, sulphur, phosphorus and manganese were well appreciated by 1900 and several effective methods for their elimination or control had been devised.

State of the Art and Science 1900 and 1950 AD

It is perhaps now logical to outline in summarised form the state of the art and knowledge about 1900 AD under four headings, namely:

Extraction and Manufacture.
Typical Uses.
Tests, Equipment, Properties and Data.
Metallurgical Theory.

A similar brief deposition is made for 1950 AD.

1900 AD State of Extraction and Manufacture

Common tonnage metals were all impure except some copper and tungsten which had just been produced as a pure metal. Melting was by solid fossil fuel either directly using coke or long flaming coal or indirectly by gas generation from coal or coke and some electric arc. Cast shapes were mainly in sand or ingot moulds. Working was by hot and cold rolling and drawing. Extrusion had just been introduces for brasses but lead piping had been extruded from about 1800. Tungsten wire was just being made via a rudimentary powder metallurgical route. In 1892 Dr Ludwig Mond erected a large scale experimental plant at Smethwick to extract nickel shot by the decomposition of nickel carbonyl, but it took several years before this stage of the extraction of pure nickel was achieved.

1900 Typical Uses

Structural, mechanical and electrical applications were well advanced, and steam and electrical traction was being further developed. Motor cars were emerging in small numbers. By 1912 the USA had produced national specifications for steels for the automotive industry [5]. Iron and steel were predominant metallic alloys followed by copper in a wide range of alloys mainly as brasses and bronzes then lead, tin and zinc.

Exotic metals except precious metals were hardly known industrially except for tungsten filament for electric light.

1900 AD Tests, Properties and Data Available

Simple tensile tests covering YP UTS % elongation and % reduction in area were widely used for testing alloys. Wickstead had just marketed a tensile testing machine incorporating a stress/strain drum plotter. Other workshop tests in general use were hot and cold bend tests, torsion tests and occasionally drop tests, although these were only carried out at ambient temperatures. Physical tests such as electric resistivity, conductivity and magnetic properties appear to have been regularly carried out on new alloys. Chemical analysis for composition was a laborious and complicated business by a combination of wet and dry methods which were usually specific for each element analysed, and many trace impurities were ignored.

Fairbairn had long since carried out his classic original work on wrought iron girders for bridges in the 1860s. It was to be well into the 20th Century before Wohler, Gough and Moore developed the practice and theory of fatigue testing and failure of metals.

Equilibrium diagrams were beginning to be determined experimentally and used to a very limited extent by the practising metallurgist. C T Heycock and Neville published the copper tin equilibrium diagram about 1901 but without accurate solid solubility lines.

Despite Sorby's use of the microscope in 1863 for examination of metallurgical structures, the microscope was only just beginning to be used by observation on and control of the structure of alloys. F Osmond in 1880 was the first person to use the microscope at Le Creusot works to study the metallographic changes both in the science and works laboratories. He deemed it an indispensible auxiliary to chemical analysis and physical testing[6]. A H Hiorns, head of the Department of Metallurgy at the Birmingham Municipal Technical School, at the time with the largest number of students in Europe, published a book on Metallography in 1902[7]. This included some 50 microstructures, the majority only x50 magnification. Because of poor preparation of both polishing and etching, and because the majority are of cast structures showing coring, very little can be gleaned from them. It is interesting to note that Ilford dry plates and Morgan and Kidd's bromide white enamel paper were recommended for photographing the microstructures. W C Roberts Austen in his chapter on Metallography showed some 17 microstructures again mostly x50 mainly of brasses, aluminium bronzes and some steels[8].

McLean[9] in his fairly recent analysis of papers published about this period says that very few microstructures appeared. Ewing and Rosenhain had first shown that slight deformation of a polished microstructure revealed slip lines on the surface[10]. Dilatometry emerged as a technique for studying critical points in steels by 1896[11]. The Pt/PtRh thermocouple was developed by 1886[12].

1900 AD Metallurgical Theory

Several authorities stated that metals were crystalline, even after working and deformation. In 1905 the explanations of brittleness in metals and alloys ranged over the effect of impurities, to the amorphous metal theory of the structure of grain boundaries.

Willard Gibbs had propounded the Phase Rule in America in 1878 [13] but it does not seem to have been widely recognised in Europe as of great significance to the theory of alloys. For example, translations were published in 1898/99 in Germany and France and he was given the Copley Medal of the Royal Society in 1901. This gives some indication of the slow diffusion of metallurgical theory.

The concept of critical points, pioneered experimentally and theoretically by Tschernoff in 1867 were still mulled over and discussed when Roozeboom in 1899 [14] applied the phase rule to the constitution of iron and steel. Followed in 1906 by an iron carbon diagram showing the interrelation between Tschernoff's critical points and those of F Osmond. In 1913 H M Howe published papers establishing the critical point lines but this was at the end of a twenty year period where these critical points had been intensively studied by several different methods [15]. During this period also the Widmanstätten structures from: Meteorites, certain steels slowly cooled and a wide range of copper base alloys continued to be examined microscopically.

A useful idea of the confused state of the alchemy, art and little science at about this time can be obtained by perusing W C Roberts Austen's book[7]. Also the nine books published by A H Hiorns [6,14] covering the entire range of smelting, refining, working, metallurgy, alloying and metallography give vivid and accurate pictures of the state of the art/science over the period 1880/1912.

1950 AD State of Extraction and Manufacture

Most metals could be obtained in large tonnage quantities as pure or reasonably pure 99.99 to 99.5% purity. Many less common metals were also available in pure form as distinct from the various thermit reaction products available hitherto. These were normally contaminated with iron, silicon, carbon and aluminium, eg in magnesium, chromium and manganese. Even the first batches of UK chromium were contaminated with iron, silicon, copper and manganese.

Many sophisticated methods of electric melting of metals had been developed to maintain purity, avoid gas pickup and ensure homogeneity. These were HF, LF and MF induction furnaces, vacuum high frequency and arc melting.

Direct chill and semi-continuous casting of aluminium alloys had been well developed and was slowly being applied to other metals such as iron and copper.

Many new surface heat treatments of steels existed apart from carburising, aluminizing and chromising. Many varied sand mould shaping and bonding procedures were also in use such as: oil, shell, carbon dioxide/silicate, furfural/alcohol and investment.

Continuous wide strip production for motor car bodies, tin plate, galvanizing and tin cans had been pioneered in the USA in the 1920s. There had also been a revival and much larger scale manufacture of metals by various exothermic type reactions eg magnesium, uranium, thorium, titanium, and by electrolysis such as manganese and chromium.

1950 AD Typical Uses

Completely new uses in which various metals played a major part in their engineering development had occurred since 1900. Specifically the major ones were:-

motor cars, mass production thereof
aeroplanes
gas turbines, jets
power station generation of electricity
transmission of electricity over long distance grid and underground cables
wireless
radar
rocketry
atomic bombs
nuclear power

While great improvements had been made in all alloys used for the devices and machines which were in being at the end of 19th Century.

Such as:

Railways, steam and electric engines, rails and crossovers.
Power generation by steam, gas and diesel.
Electric dynamos and motors.
Ships, naval and mercantile marine.
Armament; guns, shells and armour plate.

These improvements were in significantly better performance, efficiency and durability.

1950 AD Tests, Properties and Data Available

Mechanical tests such as tensile testing, fatigue and creep tests were fully instrumented. The Diamond Pyramid and Rockwell hardness testers had been used since the late 1920s and proved of inestimable value in production control of heat treatment and also in reducing the time and material wasted on alloy research, development and control procedures. Deep drawing cupping machines by Ericson et al had also been in use for grain size and control of deep drawing in steel, copper alloys and aluminium sheet and strip.

The spectrometer was just being fully automated into the Quantomet, for speedy and accurate control of impurities and minor additions to all metals.

Accurate gas analyses were possible in works as distinct from research laboratories.

Welding was long since proven as a satisfactory method of joining metals in almost any form by wide variety of gas and arc welding techniques. But spot welding was responsible for over 50% of such joints – mainly in the motor and aircraft industries. Ship's hull construction had changed in the USA from rivetting to welding through World War II and when the impact transition temperature fracture problem had been finally solved, rivetting was eliminated.

Powder metallurgy particularly of iron, bronze and copper small parts for armaments etc received a great boost particularly in USA. But in the years immediately after World War II it reverted mainly to its pre-war usage for tungsten filaments, tungsten carbide tools and oil-less bearings.

1950 AD Metallurgical Theory

Hansen's authoritative compendium on Equilibrium Diagrams[15] was published in 1936 but contained little accurate data on the change in solid solubility limits in many binary and in very few ternary alloy systems. Alloy theory had been developed by Hume Rothery and Raynor et al[16] but it did not prove usefully applicable to improving the wide range of commercial alloys already in existence.

Crystal structures and the range of atomic positions of atoms in metallic phases had been established by X-ray techniques. Phase identification in complex alloys was also considerably facilitated and orientation of grains of cold worked and annealed strip and sheet became easy to determine. The close interrelationship between ductile/brittle fracture in steels whether welded or not, the internal stresses and the impact transition temperatures were being exhaustively studied.

From this comparison over the half century it is clear that quite revolutionary strides were made in the manufacture and use of alloys using an extremely wide range of procedures. Indeed this emerges and continues to this day as one of the great fascinations of metallurgy – namely, its great variety. The art, craft and science still calls for skill, followed by accurate and reproducible control techniques in manufacture and inspection.

In the course of these reviews it seems that insufficient tribute has been given to the team of scientists and metallurgists at the NPL who between 1911-1938 worked under Dr W Rosenhain, FRS and elucidated much of the age hardening phenomena and the significance of the addition of a range of elements to improve the engineering performances of aluminium and the original Duralumin alloy[17]. A succession of workers became famous in this team for their work over the years. These included S L Archbutt, Marie L V Gayler, D Hanson, H L Haughton and G D Preston. Their work formed the basis on which the Hiduminium-RR alloys were perfected and which are dealt with by Dr W M Doyle. Reference is made to the work of the NPL by Frank King and Mac Young.

Example of Alloy Development During 1900-1950

We must now bridge this gap between the state of the art in 1900 to how it was in 1950 with some indications of the wide range of alloying techniques which were slowly emerging and usually subsequently 'validated' by metallurgical theory. Many detailed examples will be given by my colleagues in the main lectures of this Conference. All I seek to do is, introduce metallurgical terms with which some of you may not be familiar and which are not arranged in order of historic significance.

1. Solid Solution Hardening

One of the simplest to comprehend is solid solution hardening. Probably the best and oldest example is the presence of limited amounts of zinc or tin in copper to make brasses and bronzes respectively without changing the phase, which is a face centered cubic lattice. Both additions considerably harden the base metal as annealed but they also increase the rate of work hardening of copper on cold deformation. Usually the greater the hardening per atomic percent of added element in solid solution the greater the rate of hardening on subsequent cold working. Another almost standard effect of pure metals dissolving added elements in solid solution is to increase electrical resistance and decrease thermal conductivity. An example of such combined property changes would be the use throughout the world of phosphor bronze and nickel silver leaf springs in telephone exchanges.

2. Duplex and Multiphase Alloys

Additions of most elements, beyond limits as delineated in equilibrium diagrams result in second, third and fourth phases being formed according to the number of components and treatments of the alloy system. These are usually visible microscopically and according to shape and distribution also significantly alter properties.

Good examples of such improvements are the range of bearing alloys which are almost invariably a mixture of hard and soft phases, also printing type metals which expand slightly on solidification, thus giving a good definition to the typeface. Cast irons of a wide range of grades and including innoculation and nodularising also the pearlitic structures in steels and aluminium silicon alloys as modified.

3. Grain Size and Orientation

Grain size and grain orientation became important during this time, partly because of developments in flat rolling as continuous strip, and partly through production improvements, in properties of artifacts such as transformer steel and later for deep drawing and processing operations. Both latter processes revealed variations in grain size as shown by rough surfaces or fracture on further shaping. This was because large grains or grains with directional orientation developed under certain combinations of cold rolling reduction and annealing times and temperatures. Two very good examples were the manufacture of 70/30 brasses for cartridge cases, lamp reflectors, hub caps and various deep pressings of iron silicon sheets for low magnetic losses in transformer sheets[18].

4. Heat Treatment

The possibility of altering the properties of metals and alloys by heat treatment and working had long been recognised by the ancients, but with more scientific approaches and the ability to study changes in structure metallographically, the emergence of the 20th Century initiated an increase in a range of heat treatment techniques, mainly in the ferrous industry.

Basically, these treatments by heating can be divided into five main classes which are:-

(i) **Annealing** – normally to soften and recrystallise the alloy for subsequent working.

(ii) **Transformation Heat Treating** – applicable to almost the entire range of steels. The steel is soaked until it is entirely austenitic then quenched to retain a martensitic structure and tempered to reduce brittleness and hardness to give a range of different structures from bainite-sorbite-troostite-pearlite etc. These elementary heat treatment procedures are nowadays much more accurately controlled at the quenching and tempering stages in time, temperature and rate of cooling. Time, temperature, transformation diagrams[19] and automatic control of furnaces and cooling at all time x temperature stages of heat treatment were becoming common practice by the end of this period.

(iii) **Heat Treatment for Improvement of Surface Hardness:** One of the standard methods since ancient times was by heating steel for a long time at red heat and above, in a carbonaceous atmosphere then quenching; the surface could be hardened because carbon diffused into the surface. Many different methods of diffusing in carbon, nitrogen and boron were invented during this period and a wide range of durable and hardwearing artifacts manufactured by this procedure. Good examples abound in motor car engines, aero engines where long service and good performance is essential.

(iv) **Age, Temper or Precipitation Hardening** – Age hardening, temper hardening or precipitation hardening is usually a double treatment of heating to such a temperature that the second phase completely dissolves in the basic phase. On quenching into water the basic phase is retained as a supersaturated solid solution. Subsequent heating at low temperature results in the second phase partially precipitating out and usually hardening the alloy. The principle was first discovered and widely exploited with the aluminium-copper-magnesium-silicon alloy Duralumin. Although one of our colleagues is now belatedly, but with some justification, claiming that the high speed tool steel developed by F W Taylor could fairly claim to be the first practical example of solid solution heat treatment followed by precipitation hardening of tungsten and other carbide phases to develop the strength and wear resistance at high temperatures.

(v) **Low Temperature Stress Relief Annealing** – This is carried out, as its name implies, to relieve internal stresses which can easily be retained in the finished artifact. These stresses can lead to fracture in service whether by season cracking as in brass cartridge cases or the failure of Liberty ships hulls made by welding and then sailing into Arctic waters. No significant alloy change occurs in such cases. In modern parlance dislocation arrays are disentangled thus slowly relieving internal stresses.

5. Use of Alloys at Elevated Temperatures

Throughout this period alloys in the critical parts of engines were required to perform at higher and higher temperatures, to improve their thermodynamic efficiencies. This also meant that at these high temperatures the alloys were called upon to withstand higher stresses and not suffer undue oxidation and scaling losses. Above a temperature of roughly 2/3rds of the alloys.MP in K almost all metals distort plastically, ie they show no elastic limit. One has therefore a temperature x time x load set of criteria to meet to ensure adequate dimensional stability during the life of the part. To solve these problems practically, usually means a combination of almost all the metallurgical principles enunciated.

The first example was probably the high speed tool steel shown by Taylor at the Paris Salon 1900 and then the development of the tungsten filament for lamp bulbs in the early 1900s. The best example was the development of the range of Nimonic alloys initiated in the late 1930s and continuing through to the present day for jet and gas turbine engines[20]. But our friends in Germany were short of nickel and so they developed a series of alloys for their early gas turbine engines which were iron based and economised in scarce metals. Austenitic type steels containing either 18% chromium, 9% nickel or 16% chromium and 15% nickel were used stabilised with not more than 2% of molybdenum, tungsten, tantalum and titanium.

General Observations

The main objective of the major alloy developments during this period has been to improve strength without undue sacrifice of toughness and ductility. If the latter two properties were significantly impaired then serviceability particularly under shock loading would become limited[21].

The improvements in strength and hardness are used to reduce material usage and thus costs, and also to lighten structures in the transportation industry and hence economise on running costs and energy. This statement is as all engineers and metallurgists know, a gross understatement of all the subtleties in alloy development, working and design of artifacts for use in the 20th Century. The general 'strength' term is used to cover improvements in various properties as follows, together with typical artifacts requiring that property.

Hardness: wear resistance as in bearings and ball and roller cases.

elastic limit: springs.

flexural limits Young's modulus: aeroplane wings.

toughness: railway crossings, rail carriage and wagon links.

elasticity, ductility and strength: wire ropes.

fatigue resistance: connecting rods on reciprocating engines.

corrosion fatigue: paravane cables for mine sweeping.

lower impact transition temperatures: ships hulls, pressure vessels, railway axles.

bearing properties: almost invariably two phase alloys: white metals on steel shells, copper 30% lead alloys, powdered metal/oil bronzes.

Another important improvement in properties with some alloys was that of improved fabricability, ie shaping by various means, with increased speed, lower failure rate and higher yield, all aimed at reducing costs. Typical of such improvements and examples of the alloys involved are:-

machinability: leady brass, free machining steels, ledalloy, copper with selenium, tellurium or sulphur.

weldability: spot welded steel sheets for motor cars, and alclad for aeroplanes; titanium and niobium inhibited stainless steels.

formability by hot forging, drawing, pressing, spinning: grain size and orientation control of steels and brasses for motor car body shells and parts.

Apart from so called strength properties, there have also been equally if not more important improvements in alloys, especially in:-

Electrical and thermal conductivity

Magnetic properties

Electrical resistance

Corrosion resistance for use in a wide range of natural and manufacturing experiments. For example USS Cor Ten which was introduced in 1933 and is the first example of a high strength low alloy steel with a YP 50% greater than structural carbon steel[22].

Conclusion

In conclusion, it should be re-emphasised that the objective of this Conference is to ascertain the true origin or breakthrough in developing new alloys during this period. But in almost all cases after the initial launch onto the market there has followed long periods of stepwise improvements in both design and alloy structure, before near perfection for service has been obtained. In the case of blades for jet engines alone this has amounted to millions of man hours of design and alloy testing throughout the World.

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Copper 1: Alloy to pure metal

Richard Chadwick

Synopsis

Crude copper from early smelting was made into high copper (alpha) brasses by Bristol brass-makers, and the system of cold working small pieces with intermediate anneals persisted in Birmingham into the present century. Somewhat later the Swansea smelters developed refining practices to produce metal that could be hot rolled in spite of low purity. These methods lasted into the 1920s, when systematic researches into the effect of metallic and gaseous impurities led to the development of new coppers for a multitude of applications.

The electrolytic refining of copper, first undertaken on a production scale at the turn of the century, had by mid-century largely displaced fire-refining. While the purer metal obtained thereby found its main use for electrical conductors, the absence of deleterious impurities made possible the hot rolling of a wide range of copper alloys, employing increased ingot size with substantial production economies.

Copper was mined and artefacts produced by some of the earliest civilisations. Smelting of ores, the production of metal, and its conversion into wrought forms, was developed mainly in this country, over a span of some 400 years. Yet until almost the end of our 50-year period of study, wrought copper was never available as a pure metal, which even now is a premium commodity of limited use. Indeed the large family of alloys that went under the name of copper must have involved, over the centuries, greater technical and research effort than in the creation of the several new-technology alloys referred to in other conference papers.

In no way is it possible to extract metallic copper, and convert into a tough malleable product, except by complex procedures that have taken centuries to develop, involving the acceptance of a varying degree of debasement. The early smelters of Elizabeth's reign, c1570-1590, would not have needed to produce tough copper, since the main application was in bronzes, especially for cannon, but also for coinage.[1] After a century-long gap of inactivity, smelting of copper ores was resumed c1680 in small-scale works on the Wye at Redbrook, and on the tidal reaches of the Bristol Avon. The rough metal, often granulated by pouring into water, was delivered to the Bristol brass-makers, who reacted the metal in sealed crucibles with calamine (zinc carbonate) ores from the Mendip hills, to produce an alloy of generally around 80% copper, which could be worked by cold hammering, with intermediate anneals.[2]

By contrast the Swansea smelters from c1720 operated on a larger scale, employing more elaborate, but also more efficient procedures. They had, by the early 18th century, established the conditions needed to produce tough copper that could be hot-forged, or converted into sheet by battery or rolling mill. In the last of several operations blister or pimple copper (97% Cu) was exposed on the shallow hearth of a reverberatory furnace to oxidise residual sulphur and other impurities, thereby taking up some 2/3% of dissolved oxygen.[3] The bath was then 'poled' by forcing under the surface a tree-trunk of green wood, thereby producing a boiling action. This was continued until tough-pitch was achieved, when a cast sample could be hammer forged without cracking. Tough-pitch copper, containing around 0.1% oxygen, solidified with a smooth and level surface, so that a cast flat cake could be rolled or forged directly without the need for surface dressing.

The tough-pitch condition came to be understood only in our present half-century, when it was shown that oxygen and hydrogen, dissolved in the liquid metal, reacted on solidification to produce steam. There needed to be sufficient excess of oxygen to react with the whole of the dissolved hydrogen, leaving only a minimum residue of dispersed cuprous oxide.[4] With the variable quality of copper due to adventitious impurities introduced from ores of differing origin, not only was the final oxygen content variable within a range of 0.05 to 0.15%, but bringing the copper into tough-pitch often proved difficult, and the addition of lead was an effective remedy which was widely adopted,[3] as it was indeed well into the present century. Poling with green wood is of course still employed.

With the availability of copper from a variety of sources world-wide, commonly traded as unrefined blister copper, impurities became increasingly troublesome, and systematic studies were carried out in the early 1920s to identify elements, or combinations of elements responsible for causing brittleness in hot working, or lowered ductility in the wrought metal.[5] Such impurities were of course removed by electrolytic refining, but during the 1939 war, when both high grade metal, and electro-refining capacity were in short supply, severe losses were experienced by a policy of diluting good copper with bismuth-containing material.[6] Arsenic, sometimes present in Cornish and Devon ores, had been generally considered to be beneficial, especially in high temperature applications, including the fire-boxes and stay-rods of steam locomotives. A systematic study, in which British and Continental railways collaborated, led to the adoption of specifications for arsenical coppers generally of about 0.4% arsenic content.[7] Arsenic was commonly added in the reverberatory furnace, after completing the refining cycle, as white arsenic (As_2O_3), an operation which might be thought nowadays to be unacceptably hazardous, although the furnaceman who shovelled in this substance always believed that the ambient atmosphere was beneficial to health.

Two major applications for hot-rolled copper plates were in the locomotive fire-box, and in singe-plates for the textile industry. Both involved exposure to hot reducing gases, and embrittlement, by the reaction of hydrogen with oxide particles in the copper, could lead to premature failure. Alloying with up to 1% phosphorus was shown experimentally to improve hot rolling characteristics, but relatively large additions were needed to eliminate dissolved oxygen.[8] Nevertheless phosphorus deoxidation soon came to be widely adopted, and with suitable precautions some 0.05% residual phosphorus was found to be effective. Tough-pitch coppers were cast in open moulds dressed with bone-ash in a water suspension, with considerable pick-up of oxygen by the unprotected surface during pouring (Fig 1). It was soon realised that to prevent oxygen pick-up an oil dressing, such as that used in brass casting, would be preferable. This led to problems with gas unsoundness, needing some adjustment in the poling technique. It also involved the abandonment of the flat cake, the crystal structure of which led to the formation of gas cavities of unacceptable size and shape, as well as damaging surface shrinkage.[9] The change to vertical casting involved the need for large strippable moulds, generally constructed from rolled copper plates assembled with cast iron spacers. Slabs of up to 3 tons weight could be so cast to match the shapes available from open moulds used for tough-pitch coppers.[9]

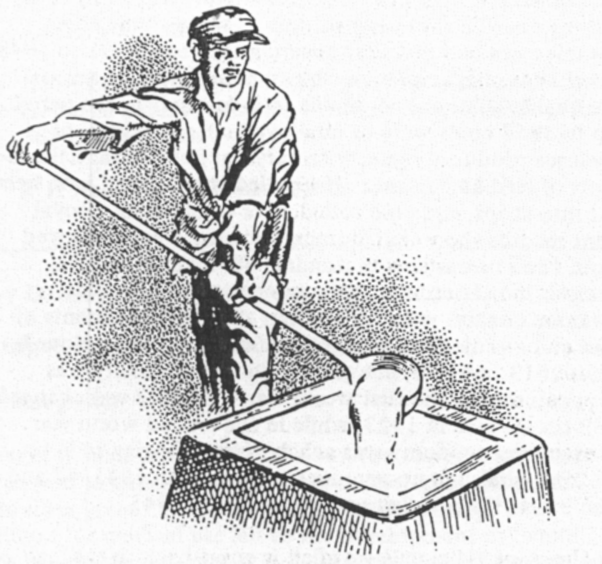

Fig 1 Lading Copper
Swansea

The copper industries of South Wales and Lancashire, based initially on smelting, and later on the fire-refining of imported blister copper, employed hot rolling throughout. After 1832, when Muntz introduced the 60 copper, 40 zinc hot-rolling alloy (yellow metal in Swansea terminology), this alloy came to replace copper in the sheathing of ships, and later to be in great demand by the craftsmen of the Indian bazaars. South Wales plants had offered plates of both copper and brass 10'6" wide, and up to 2 tons in weight, as well as hammered shapes of corresponding size, from as early as 1850.[10] In the early part of the present century Morfa, said to be the largest copper works in the UK, was capable of rolling plates of up to 5 tons with a maximum width of 13 ft.[11] Bibbys of Garston, not to be outdone, installed plant of similar capacity around 1910. This wide Bibby rolling mill was moved to Hafod in 1937, and was in continuous use until late 1980.[12]

Fabrication of alpha brasses, centered in the Birmingham area, continued in the traditional Bristol method of alternating cold rolling and annealing. In the first quarter century Birmingham practice was to melt in plumbago crucibles of 90 to 180 lbs capacity in coke-fired furnaces, with pouring into cast-iron moulds held together with rings and wedges, and employing an oily dressing, the flames from which protected the metal stream from oxidation (Fig 2). The quality of product depended upon care in applying the mould dressing, correct judgement of pouring temperature and a controlled rate of pour, leaving enough metal to feed the central shrinkage pipe in the final stages of solidification.[13] The crucial factor was the skill of the workman, who was alone responsible for quality. Inspection was carried out after the first rolling, end cropping and scalping; rejection involved remelting and casting in unpaid overtime, known as 'working for the King'.

The brass casting technique could not be employed to cast tough pitch coppers, and in the early part of the century an alloy with 2-3% of zinc was widely employed. In the molten alloy the zinc effectively deoxidised the copper, and its vapour pressure prevented hydrogen pick-up, while the rolled strip, both in appearance and in physical properties, closely resembled the pure metal. 'Cap Copper' was in effect an early de-oxidised copper, and its principal use was and still is, for the fabrication of the central percussion caps used in both military and sporting ammunition.

Fig 2 Casting Brass
Birmingham

With the introduction of new alloys generally of higher value, and with more demanding specifications, the problem of gas porosity, and associated inverse segregation, became more acute. More restricted application of flaming dressings, with better design of pouring arrangements, became necessary.[14] A suggestion that a chlorinated hydrocarbon as a mould dressing might, as with chlorine in aluminium melting, reduce dissolved gases as well as eliminating hydrogen from the vapourised dressing, proved to be impracticable because of the quantity of black smoke evolved during pouring.[15] Research into gas equilibrium conditions in the molten alloys, more particularly the tin bronzes, showed the advantages that derived from controlled oxidation by oxides within the melt, or by the use of a cover of oxidising slag, processes pioneered by Henri Lepp in France.[16]

The electrolytic refining of copper, which the Swansea smelters had pioneered from 1879 onwards, came into wider use from the beginning of the century, when it came to be realised that this provided not only a premium metal, but that the recovery of gold, silver and other valuable metals, was often sufficient to pay for the refining process. Initially the main application was for high conductivity wires for electrical generators, for current transmission, and for telegraphy. However the availability of cathode copper opened up the possibility of hot rolling the alpha brasses, and other copper-base alloys, using larger piece weights, and from about 1930 this practice was widely adopted with substantial cost savings. Furthermore cast slabs of HC quality copper could be hot-rolled at lower temperatures, with less scaling loss, and reduced edge-cracking as compared with cakes cast from fire-refined metal, which justified the extra cost. Even so, it was just not possible by remelting to establish the necessary conditions for casting slabs of HC quality copper in the normal brass foundry. These were purchased from major producers, who were able to offer slabs to specified dimensions as a by-product of a normal wire-bar casting line.[17]

The ultimate oxygen-free high-conductivity copper (OFHC) became available towards the end of the half-century. Other alloyed coppers, generally providing for some special requirement with minimum loss of electrical conductivity, included phosphorised copper (an oxygen-free alloy with a small carefully controlled residual phosphorus content), alloys with varying silver up to about 1% for high-temperature strength in generator windings, a 1% cadmium alloy for trolley wire, and high conductivity alloys with minor additions, including lead, sulphur, tellurium etc, designed to improve machinability. Thus the adventitious impurities of the earlier years had been replaced by minor additions for specified industrial applications. Copper had become a generic name for a new family of alloys.

Table 1 Analysis of UK Bronze Coins

Year	Lead %	Tin %	Iron %	Nickel %	Arsenic %	Zinc %
1806	0.03	0.01	0.01	0.02	0.44	0.01
1854	0.10	0.10	0.03	0.08	0.36	0.04
1860	0.50	3.1	0.04	0.07	0.17	2.3
1891	0.05	5.3	0.08	0.03	0.77	1.3
1900	0.06	5.6	0.02	0.01	0.37	0.9
1903	0.08	4.8	0.03	0.01	0.35	0.9
1912	0.06	5.7	0.01	0.01	0.17	1.1
1913	0.03	4.3	0.01	0.03	0.01	1.03
1916	0.03	4.3	0.01	0.18	0.01	0.90
1917	0.03	4.1	0.01	0.03	0.16	1.11
1920	0.13	4.5	0.03	0.03	0.06	1.21
1930	0.01	4.5	0.04	0.01	0.03	1.6
1940	0.02	3.4	0.01	0.01	0.01	1.41
1944	0.01	0.51	0.01	0.01	0.01	2.48
1946	0.01	3.1	0.01	0.01	0.01	1.61
1948	0.01	4.3	0.01	0.01	0.01	1.2

Table 2 'Coining Bronze' Alloys – Royal Mint

Period	Tin %	Zinc %
1860 – 1923	4	1
1923 – 1942	3	1½
April 1942 – Oct 1945	½	2½
Oct 1945 – May 1959	3	1½
June 1959 – date	½	2½

In connection with this historical study, analysis by X-ray fluorescence has been carried out on some thirty coins (pennies and half-pennies) covering the years 1791 to 1948. Some typical examples are shown in table 1, and mirror the quality of copper available to industry over the period. Up to 1859 coins were of unalloyed copper typical of Swansea produced metal with varying, but substantial contents of lead and arsenic. Hot-rolled sheet would have been cut into strips, and cold rolled prior to blanking. Royal Mint records show that 'coining bronzes' were employed from 1860 onwards with nominal 4% tin and 1% zinc, analysis indicating that the copper was still of typical Swansea quality, with varying but substantial contents of lead and arsenic. A purer grade of copper was employed from 1913 onwards, but some lowering of quality was apparent during the first world war. The alloy was changed to 3 tin 1½ zinc in 1923, while in the second world war even greater economy was achieved by changing to ½ tin 2½ zinc, although no pennies were struck in 1941, 42 and 43. The 3 tin 1½ zinc alloy was reinstated in 1945.

The present 2½ zinc ½ tin alloy is going back to the 'cap copper' of the 1920s. A very good alloy, easy to cast, and free from gas problems. It should be noted however that in the US the only 'bronze' coin, the 1 cent, is in fact a zinc blank electroplated with copper. Our own Royal Mint has already put itself in a position to compete by installing plant for electro-plating blanks, so maybe the days of the 'bronze' coin are coming to an end. An historical milestone indeed.

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Alloy Development in the Period 1900 - 1950

Contribution from: Professor Alan E W Smith

1 Carat golds:

Usually, to maintain a golden colour, the copper and silver are present in equal amount. More copper gives red gold, more silver green. In World War I, a great shortage of platinum for medical use led to the development of 'white' golds, whose colour initially matched platinum. I do not remember if platinum wedding rings were prohibited or merely discouraged; but wearing a white gold one was patriotic. Wires of these various colours woven into 'Venetian bangles' give an extremely attractive effect.

2 Sterling silver:

Normally the alloying metal is all copper; but my father (acting as consultant to Oakes, Turner in Sheffield) developed an alternative, to meet the call for a somewhat softer alloy for the spinning trade. This had half copper, half cadmium. A vase spun from a single sheet of it was presented to him in 1918 and I still have it. Data, or even the vase, are available if of interest.

3 Dental amalgams:

My father was ARSM and taught there for a short time, including the dental students, at whose request he produced his 'Dental Metallurgy' in 1898. This ran through six editions until 1947. Amalgam compositions used to be a firm's choice and their setting was uncontrolled: a contraction could give a loose filling and too much expansion would split the wall of a thin tooth. Research gradually sorted things out, especially that by Marie Gayler (1933) which led to standard alloy composition and stop-watch mixing procedures as now used. The BS 2983 covering these came only in 1957 I believe.

4 Fusible alloys:

These were a wide and wonderful range until the Tin Research Bulletin catalogued them. Wood's metal was well known; and I found its use for demonstration spoons (which melt while stirring hot tea) was valuable for popular lectures. Later on came the addition of x% indium, making the quinternary eutectic, giving a low enough setting temperature to use it as a substitute for plaster in the setting of broken arms. I have not heard of it in recent years so maybe it did not take on.

5 Recalescence:

Demonstrated very effectively by the 'hot iron wire' apparatus designed by Prof R C Gale pre-1930 (?) and later marketed by Gallenkamp (?). We used this regularly with our classes and found it invaluable.

6 Rosenhain's alloy – the zinc-aluminium eutectoid, 1912:

Quenched and held in the hand it rapidly becomes too hot to hold. We made many batches of this type of alloy and used it in our lectures.

(It was our interest in this material and its spontaneity which led to my researches, along with Tony Hare, to introduce control by adding further alloying elements – as in the case of the steel eutectoid. This resulted finally in the magnesium compositions called ZAM, to the Government patent, and my paper in the J Inst Met 1973. But this comes outside the 50 year period).

7 Graphs:

a) Collecting the dates of isolation of the elements I produced a graph 'Progress in the discovery of metals', 1700 to 1950+ and linked with it the dates of Lavoisier, Faraday, Mendeleev and the Periodic Table. In 1900 there were known 62 metals and in 1950, 74. Industrial usage might take anything up to 100 years after the isolation however.

b) The aircraft demand for Magnesium during the war led me to produce a graph of the annual output from 1909 to 1949, including the temporary wartime factories/processes and main technical books on its alloys.

Copper 2: Brasses, Bronzes and Nickel Silvers

Sam Temple

Introduction

Unlike many of the alloys being considered at this Conference, trade in brasses and bronzes had developed for at least a century before 1900 and nickel silvers for about 80 years with well-established centres in most industrialised countries. This is typified by the remark of a visitor to Birmingham in 1893 who wrote, when describing the city, 'She writes her name in brass. . .'[1]

The story of the next fifty years shows initially continuing expansion for these alloys as population, standards of living and demand increased, with peaks of activity during the two World Wars, and then the beginning of a slow decline in usage, brought about by the developments of alternative materials and new product designs, whereby their special properties were no longer unique.

Although outside the period under consideration, it is useful to mention the most famous of the pioneers in the industry, G F Muntz, who in the 1830-40 period, popularised the brass alloy, 60% copper, 40% zinc, (60/40), for the sheathing of ships. The story quoted in contemporary journals[2] that the precise composition registered by Muntz, under the trade name 'Muntz Metal', was found due to a workman's mistake, indicates the trial and error methods of making these alloys. This persisted for many years until the systematic study of the metallurgy of alloys was established and long after, as Jennifer Tann reports[3] 'neither new forms of technology nor new forms of work organisation ousted the old'. Even as late as 1923 in the introduction to a text book on the subject[4] we find the authors bemoaning the fact that 'many (manufacturers) still prefer the legacies of Tubal Cain to the wisdom of Percy and Roberts-Austen'.

However in spite of such factors, progress continued, particularly in the last two decades of the XIX Century, as new methods of casting, stamping, piercing, tube making etc were developed, so cheapening and expanding the usage of all malleable materials. This was at the same time as new industries like water, gas and electrical engineering were expanding, with inventions like the bayonet type of electric light holder by Edison in 1888. The use of Muntz Metal, for example, had declined with the application of steel plates to ship building but even in this industry there was an increased demand for ships fittings such as compasses, lamps, pumps etc. New demands for ornamental ware, both sacred and secular, for domestic articles like bedsteads, spoons and forks, etc occurred as well as increases in traditional trades, improvements in the manufacture of guns and ammunition after a rather static period from the end of the Napoleonic Wars, gave rise to the further expansion as armies re-equipped prior to the First World War.

Thus by 1900 we have a thriving industry with many end-uses.

Factors Influencing Choice of Alloy

Before considering the individual alloys, it is useful to list the significant changes which occurred in the next 50 years, which so influence selection.

a) the increased purity of copper, tin, nickel and zinc used in alloying due to improvements in refining techniques and exploiting of new ore bodies. This led both to changes in manufacturing technology and to new alloys where a specific impurity (added element) gave unique properties.

b) the application of scientific metallurgical techniques to these alloys. Until the 1880s such work had been confined to the ferrous industry. After that copper and its alloys were similarly studied by pioneers like Roberts-Austen, Carpenter and Edwards in England and Charpy and Guillet in France. The British workers published their findings under the auspices of the Alloys Research Committee of the Institution of Mechanical Engineers beginning at the third report in 1895 and concentrating on equilibrium criteria and recrystallisation phenomena from then until about 1920. Guillet and Charpy in France worked on impurity influences in the same period. During the First World War, this work was concentrated in War Office and Admiralty laboratories and from 1920 in private organisations, who set up Research Establishments, as distinct from laboratories for quality control purposes, and by the formation of the BNFMRA in 1921.

c) throughout the period, standardisation of sizes, engineering properties and alloys grew in importance. In 1906[5] the British Waterworks Association imposed general standardisation of sizes of fittings on equipment suppliers under the Supply of Water Regulations, and similar moves in the gas and electricity industries resulted from the work of the Engineering Standards Committee of the Institution of Civil Engineers from 1901. This Committee subsequently became the basis of the British Engineering Standards Association and, from 1931, the British Standards Institution. Standardisation of alloys was started by these bodies in a limited way in the First World War and continued in the next three decades but was not fully completed until after 1950.

This latter aspect was also confused by the widespread use of trade and patented names, some of which enjoyed, and still enjoy, considerable popularity. Such trade names have considerable commercial significance, as the writer can recall, when he worked for the successor company of the Muntz factory in 1937, customers were regularly asking for 'genuine Muntz Metal' – one hundred years after the name was registered!

d) from 1925-30 the accent has been to improve the manufacturing technology of these alloys rather than seek new compositions, so improving their effectiveness in combating substitution by cheaper materials. New compositions were developed, but nearly always these were by additions of other elements in such proportions that they no longer fall within reasonable definitions of brass, bronzes or nickel silvers. A few of the many names, which occur to the writer, whose work in improving techniques of production was important and which illustrate the wide scope of this work are:-

Genders and Bailey[6] on brass casting, Pell Walpole[7] for improving the chill casting of phosphor bronze and early work on applying the techniques of submerged die continuous casting to bronze and nickel silver, Guillet[8] who first described how quenching from a high temperature improved ductility and yet retained mechanical strength in bronze, Browndon, Cook and Miller for a number of papers[9,10] surveying and codifying the annealing and grain growth characteristics of all these alloys, so assisting standardisation of optimum properties.

Brasses

It is convenient to discuss the various copper-zinc alloys under five headings, viz:–

1. Brazing Solders – up to 55% copper.
2. Alloys containing between 55% and 62% copper.
3. Alloys containing between 62% and 80% copper.
4. Alloys with small additions of one or more elements other than copper or zinc.
5. Gilding Metals.

It should be noted that 55% and 62% copper are approximately the limits of the Alpha and Beta phases of the copper-zinc constitutional diagram, which so influence the properties of the brasses.

Alloys Containing Less than 55 Per Cent Copper

Brazing or Hard Soldering was a much favoured joining method in the early years of the Century and alloys based on the 50/50 and 54/36 composition became standardised in the form of wire and granules by 1930. Their use declined subsequently as copper-silver-phosphorus alloys were developed with melting points in the range 650 degrees C – 800 degrees C (compared to 860 degrees C – 880 degrees C for copper-zinc alloys). Prior to the First World War, lower copper contents were in vogue, under the names of 'Brass Solder' or 'Spelter', with 40/60 and 33/67, with melting points in the range 780 – 830 degrees C, being most popular.

Typical applications of these solders were their use for brazing steel bicycle frames and the joints in copper hot water cylinders.

Alloys Containing 55-62 Per Cent Copper

For a century or so, the 60/40 composition had been probably the most popular in this group and from 1830 onwards, manufacturers made special efforts to keep near the proportions and use pure raw materials to retain the good hot working properties of the alloy with adequate cold workability for many applications.

Major effort in this group in the period under review was directed to popularising alloys, where one or more other metals were added to the basic composition, to enhance particular properties demanded by new uses. These alloys are dealt with in a later section.

The good casting properties of brass resulted in an extensive usage for plumbers and engineering fittings – taps, joints, etc – for this composition, which persists today in the standardised ranges of 59/62% and 57/60% copper[11].

Alloys Containing 62-80 Per Cent Copper

This is the main range of binary alloys used in the forms of strip, sheet, wire and tube, because of their good workability, together with ease of polishing, plating and colouring.

The composition most in demand was the 70/30 alloy used in munition manufacture for cartridges and the larger QF shells. It is the alloy of the highest ductility, but different manufacturers claimed, no doubt due to differences in limits of impurities or in methods of manufacture, varying compositions from 66/34 to 75/25 were best. During the First World War, impartial examination resulted in no serious distinctions being established in this range, but impurity control and the avoidance of the brittle Beta phase by specific processing routes were shown to be essential. Thus Cartridge Brass was standardised by Governmental decree in the range 68/72% copper with low impurities and strict manufacturing conditions and these limits persisted during the Second World War.

During peacetime it also became established as the preferred composition for deep drawing and pressing applications where extreme demands had to be met, for example, condenser tubes, sheets for the top and bottom tanks of car radiators with assymetrical proportions, etc.

Particularly between the two World Wars, much research activity was devoted to the fabrication of these alloys and to methods of improving their properties by precise control of rolling, drawing and annealing conditions, so tailoring the properties to a precise end use. A good example of this was the use of brass strip for automotive radiator construction where determined efforts were made to substitute such strip by aluminium and steel, but generally to no avail.

Economic factors were always under consideration. The price of copper, throughout the whole 50 years, was always two to three times that of zinc, and so efforts were continually being made to lower the copper content of these alloys with minimum loss of properties. Work on the constitution of the material showed the suitability of the 62/38 alloy, with specific processing procedures, for many of the applications using 70/30 brass. This commercial brass or 'Basic brass', ie that of the basic price from which other alloys were calculated, became the most used composition in this group for peacetime usages. However considerable differences were possible between the various manufacturers due to processing difficulties, which led once again to a proliferation of trade names.

Alloys with higher copper contents were however specified in cases where products were susceptible to the phenomenon known as 'season cracking' ie where products were pressed and stored. Such alloys were also free from the Beta constituent and compositions from 72/28 to 75/25 were used in some countries for cartridge manufacture. The 80/20 alloy became popular for refrigerator parts in contact with the the liquid refrigerant, which could easily induce season cracking in other materials.

Brass Containing One or More Other Metals

Lead, tin, aluminium, iron manganese and nickel are the most common additions found in brasses.

Lead was a common impurity in commercial zinc and in fact all brass artefacts over the centuries eg ecclesiastical brasses on tombstones, invariably contained lead as an adventitious impurity. It was not until the mid 19th century that the role of lead in improving the machining characteristics of brass was understood and not until the end of the century when the extrusion press, originally developed for lead pipe, was modified by Dick and others for brass, did leaded brass alloys become widespread. The main alloys based on the 60/40 composition contained two or three per cent of lead and were provided in the form of extruded rod or wire, which were either machined to shape or hot forged in a variety of shapes, eg taps and fittings, and replaced castings of similar composition.

The property of easy machinability gave rise to many uses eg plate and wheel parts in clocks and instruments, linotype and monotype printing parts, engraving plates, etc.

A military use during both World Wars was that of primers for QF and other shells.

Interesting developments, where colour properties were exploited, together with a third element to impart another specific feature were those of adding aluminium, to impart a 'golden' colour, or manganese, to give a rich 'chocolate brown' colour. Such alloys were used for decorative purposes and older readers will recall the golden coloured brass curtain rail and the impressive 'bronze' shop front exteriors, which today are rarely found in High Street stores.

Tin. The addition of tin was shown by Muntz and others to improve the resistance to corrosion in sea water and this led to two groups of alloys containing 1% of tin viz Naval Brass 62% copper, 37% zinc and 1% tin, and Admiralty Brass 70/29/1.

These alloys were used extensively for sheet, plate and tube manufacture for marine applications. Their use was widespread until the Second World War, when alloys of superior corrosion resistance largely replaced them.

Further references to them is made in other papers to this Conference.

High Tensile Brasses. Iron, nickel, aluminium, tin and manganese all increase the tensile strength of brass and all were used in various combinations during this period.

Dick systematically studied the addition of iron to the nominal 60/40 composition, developing a reliable method of adding the higher melting point iron, and patenting his product under the name Delta metal at the turn of the century. However the firm he founded used the name more widely for alloys containing other metals in the next 50 years.

The name most associated with this group of alloys is the Frenchman, Guillet[12], who in the period 1900-1920, demonstrated that most of the added elements in the proportions of interest were in solid solution and this had the same practical effect as altering the proportions of zinc in an alloy, although the quantitative effect varied with the addition. Accordingly, he developed his 'ratios' or 'zinc replacement capacity coefficients', which are for each 1% of added element the % zinc equivalent is:-

Silicon	Aluminium	Tin	Lead	Iron	Manganese
10	6	2	1	0.9	0.5

Thus the alloy 62/37/1 — Naval Brass mentioned earlier would be equivalent in mechanical properties, etc to a brass containing 39% of zinc.

This work spearheaded much empirical work in the early years of the century on many combinations of these elements and showed that a particular set of mechanical properties could be obtained by differing proportions of the added elements, so that precise compositions could not be specified, and even today a wide combination is permitted in standard specifications although mechanical properties are usually precisely defined.

Manganese was a favourite addition, because apart from the effect on strength, it improved the soundness of castings and imparted good corrosion resistance. These alloys became known as 'manganese bronzes' but they are of course brasses and the position was further confused by a whole variety of trade names under which they were marketed. A glance at lists published in the 1910-1930 period shows names like Parson's Manganese Bronze, Rubel Metal, Turbiston's Brass, Turbadium Bronze, Durana Brass, and many others, almost all of which have fallen into disuse.

High manganese alloys – two per cent or more – were used in the cast or forged condition for large ships' propellers and shafts, often with tin and iron additions, and these alloys have only recently been superseded in the last two decades by nickel-aluminium or manganese-aluminium tin bronzes with increased strength and corrosion resistance. (See Copper 3).

More typical of the high tensile brasses is the alloy of which the author has had experience viz the 1-2-3 alloy – 1% iron, 2% manganese, 3% aluminium with 58% copper. In the cast condition it has a tensile strength of 30 tons per square inch (465 MPa) and, as worked, strengths up to 45 tons per square inch (695 MPa) ie 60-75% greater than basic brass. Unfortunately these alloys all suffered to some extent with stress corrosion cracking and while a number of usages were developed, eg non sparking tools for the mining industry, their use declined after the Second World War.

Another aspect studied systematically from 1920 was the emphasis on possible temper hardening alloys to increase strength, and a variety of alloys were developed, especially during the Second World War when tin was in short supply and alternatives to bronze were being sought. These alloys are the subject of another paper at this Conference.

Miscellaneous. The possible use of vanadium, cobalt, chromium, magnesium and silicon with or without the more common elements, was also studied, but with no lasting success.

Silicon brasses with 0.5% to 1% of silicon were used as a brazing alloy to join copper sheets in refrigerator panel manufacture until aluminium and stainless steel superseded the product.

The use of brass for coinage was limited, but reference should be made to the nickel containing alloy – 79% copper, 20% zinc, 1% nickel – used for the twelve-sided threepenny bit – from 1937 to 1967.

The Gilding Metals. The name generally given to the higher copper alloys – over 85% copper – which arose from attempts to simulate the colour of gold, so that a plated article would appear the same even when the plating wore off. Another popular name at one time was Tombac.

The range of alloys from 80% to 97% copper exhibit a wide variety of colours which can be modified both by the manufacturing process and by the subsequent surface treatment of the product. This latter aspect was particularly important in the period under review in the fancy goods and jewellery trades, where colours ranging from orange to black were imparted by chemical means, mostly acetate and sulphide solutions. The alloy with 87-88% copper was the one, which in its natural state, was the nearest colour to gold and so it was used in such applications as pen nibs, cigarette cases and cheap jewellery.

In both World Wars the 90/10 alloy was used for the bullet envelopes of cartridges and the 97/3 alloy for caps.

Small additions of lead are made to these alloys to improve their machinability and so we find use is made of such alloys as 90% copper, 1% lead, 9% zinc for name plates, memorial plaques, etc.

Generally therefore these alloys were extensively used in the decorative trades and, especially in the first 20 years of the century, when the Art Nouveau movement stimulated changing designs of ornamental work and the substitution of gold and silver articles by plated ware became commonplace.

Bronzes

The commercial alloys of copper and tin, almost invariably containing phosphorus, and often zinc and lead, to limited extents. Their variety is much less than those of the brasses because with more than 8% tin or so they become brittle, and with over about 12%, almost unworkable in any form.

A convenient classification is:-

(a) Wrought alloys

(b) Cast alloys

Throughout the period the use of bronzes has declined because the price of tin rose spectacularly throughout these years and also because in both World Wars tin was in short supply. Substitution was particularly active in Germany during the First World War, and with all combatants in the Second, and alloys like leaded 'bronzes' were developed with high lead and little or no tin.

Wrought Bronzes are in general confined to tin contents of less than 10%. In 1895 in the Third Report to the Alloys Research Committee of the Institution of Mechanical Engineers, Roberts-Austen and Stansfield showed that the best combination of ductility with strength is found in an alloy of 5% tin and in the next fifty years the range 4% to 6% tin became commonly used in the form of wire, strip and tube for springs, instrument components, high strength fasteners and applications needing higher strength and better corrosion resistance than brass. The strength comparison is typically shown by the following figures of hard rolled strip material (50% cold reduction).

	Limit of Proportionality tons per sq in (MPa)	**Ultimate Tensile Strength tons per sq in** (MPa)
Bronze 5% tin	31 (479)	46 (710)
Brass 30% zinc	13.5 (202)	30 (463)

and in fact tensile strengths up to 60 tons per square inch (927 MPa) can be obtained when the tin content is raised to 8%, which is generally accepted as a limit for cold working. The whole range of tin contents from 2% to 8% tin is in use with the 3.5%, 5% and 7.5% being the compositions most often specified. Phosphorus is invariably added to improve casting and act as a deoxidising agent.

A number of other alloys were also used. The 1% tin alloy – sometimes called Post Office Bronze – was used in the form of wire for telephone lines and tramway trolley wire, sometimes with an addition of cadmium up to 0.5%. This alloy has now been superseded completely by a copper cadmium alloy.

Foudrinier wire (usually 7% tin), used in the manufacture of wire cloth for paper making machines, illustrates well the type of application where bronze excels, viz with good corrosion and abrasion resistance.

Coinage has been an important usage for these alloys for many years. During this period in UK the favoured alloy was 4% tin with 1% zinc until the Second World War, when the tin content was reduced to 3% and since 1959, the 'bronze' coinage contains only 0.5% tin with 2.5% zinc.

Cast Alloys. The use of bronze for bells and musical instruments was developed in early times with the 25% tin alloy being considered optimum. A de-oxidiser was essential, usually phosphorus, as tin oxide gives a disagreeable sound to bells.

Nowadays lower contents than 25% are used with the 18-20% alloy being used for instruments like cymbals.

For engineering and commercial applications, tin contents of 10% or less are generally found with some additions of one or more of lead, zinc, phosphorus and nickel. Gun metal for ordnance had been replaced by steel prior to 1900, but the term continued in use with Admiralty Gun Metal – 88% copper, 10% tin, 2% zinc – being the standard for various marine uses eg pumps and valve parts until about 1920, when lower tin content alloys were substituted with larger additions of lead and zinc. These became standardised to some extent into alloys, averaging 85% copper, 5% tin, 5% lead, 5% zinc – sometimes referred to as the 'three-fives' alloy – with other popular compositions being 86% copper, 7% tin, 5% zinc and 2% lead, and 83% copper, 3% tin, 9% zinc, 5% lead. These alloys are widely employed for all types of pumps, bearings, gears, valves, etc and their use is well-illustrated in the examples to be seen in the Coventry Motor Museum, which the Conference visits during this weekend. Note especially the chemical composition of the bearings and parts analysed and how the tin contents of the alloys have fallen from 1897 to 1948 with increases in lead and zinc. During the 1940s 2% nickel was introduced often replacing tin to give improved creep resistance and better mechanical properties in these alloys.

Similar alloys to these are used for statutary and other sculpted artefacts.

Finally, mention needs to be made of Speculum Metal 66% copper, 34% tin – a hard brittle alloy formerly used for mirrors, because it takes a high lustre after polishing. Attempts were made during the period under review to popularise the alloy in plated form as a substitute for silver.

Nickel Silvers

A misnomer given to a wide range of alloys in which nickel in contents up to 30% is added to brasses. They were originally developed for decorative purposes as an economic replacement of silver and became very popular to replace silver and Sheffield Plate, when electroplating was developed about 1830. Today EPNS ware is well-known and alloys with more than 12% nickel, being white in colour, are favoured for this application. Prior to the First World War, its most popular name was German Silver, but other trade names were legion. Names like Packtong, Argentan, Tutenag, Sterlin, White Copper are still occasionally met with today.

Guillet[12] showed in his work on 'zinc equivalence' that nickel tended to replace copper rather than zinc and so the alloys were capable of good cold workability although there was a considerable increase in strength over brass.

The use of these alloys for table ware, especially spoons and forks, was developed in the XIX century and the original classifications, which date prior to the First World War, were for such applications, with Trade Quality Names like 'Best', 'A1', 'Firsts', 'Seconds', etc based on decreasing nickel contents being usual[13]. Best contained 30% nickel, 'Fifths' contained 5% nickel. This classification was continued largely into the British Standard Institution's specification 790 in the 1930s. It was only after 1950 when usage declined, because of the increased cost of nickel and competition from stainless steel became intense, and that there is little property advantage for alloys over about 18% nickel was accepted and a great reduction in variety took place, with the result that 12% and 15% nickel with approximately 60% copper became the accepted alloys for ornamental and tableware generally.

The greater strength over brass combined with better corrosion resistance and a high electrical resistance has led since about 1920 to a number of engineering applications, mainly in electrical engineering. The earliest of these was their use as tape and wire in switches, plug sockets, resistances and later in the telephone and wireless trades for contacts and springs, especially the flat springs used in telephone relays, where the 12% and 18% nickel alloys have been standardised.

The addition of 1%-2% of lead to improve machinability gave rise to an extensive industry in cylinder locks, keys and also hinges for spectacle frames. In these cases 10% nickel is usual with the copper content lowered to about 45% so permitting easier extrusion into rods and sections. This alloy was also used in structural decorative applications – window frames, shop fronts etc – but only found limited use.

A 45% nickel alloy was developed for use as parachute harness buckles because of its high shear strength.

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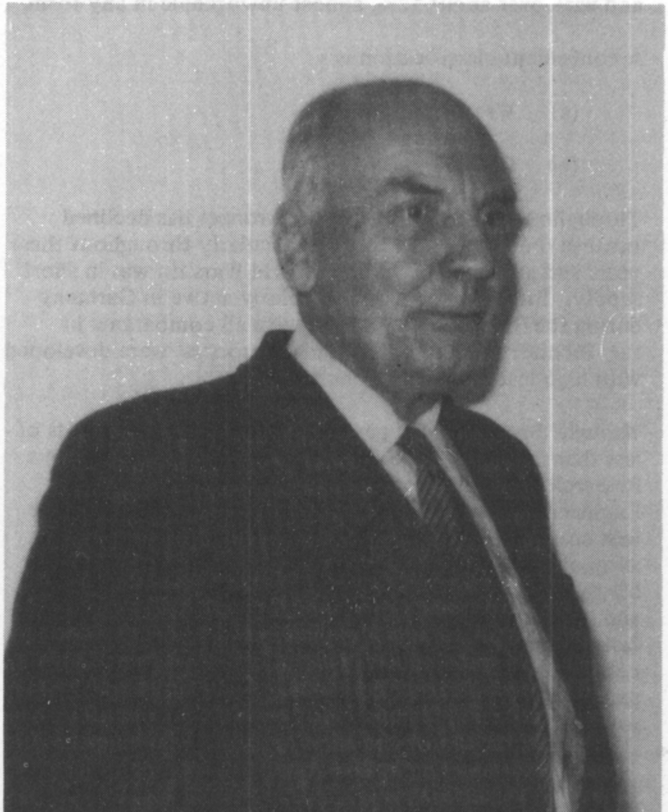

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Copper 3: The rise and decline of the **Manganese Bronze** marine propeller

Albert French

Origins: In the Field of Marine Propellers

The origin and development of this group of alloys, the use of them in large tonnages, has been inextricably involved with developments in naval architecture and the design of the marine propeller. It is true that they also found a niche in applications in general engineering, in not insignificant quantities in relation to other cast copper-based alloys in that field, but the large tonnages used were in the manufacture of marine propellers. It was for this particular application that the alloys were introduced in 1876 and it is therefore relevant briefly to review the development of the screw propeller.

Marine propellers were referred to in the literature of naval architecture in 1800 and a propeller was said to have been fitted to a submarine in 1787 during the American War of Independence. Many designs and configurations were subject of experiment using various materials and methods of manufacture; castings in iron, fabrications including wood and wrought iron. There was an Archimedes screw as early as 1794 but the important landmark with this form of propeller – the helical propeller with which people today are familiar – was the use of such a propeller on the 'Archimedes' in 1839. For the S S Great Britain, I K Brunel designed and made one of the first practical propellers. These were of wrought iron, six bladed and weighed 4 tons. The ship was laid down in 1839 and launched in 1843. In 1849 a famous trial was set up by the Admiralty when ships identical in form and in engine power were linked stern to stern, HMS Basilisk – with a 'Common paddle' and HMS Niger – with a 'Smith's screw': the 'Niger' pulled the Basilisk at 1.466 knots, thus establishing the interest of the Admiralty.

In the 1870s liners such as 'Germanic', 'Adriatic' and 'Britannic' were plying the North Atlantic routes at 16 knots driven by screw propellers made in cast steel. Because of the higher strength of steel than iron, blade sections could be considerably reduced to achieve greater efficiency and higher speeds, but the rate of deterioration due to corrosion and cavitation erosion was high: the propellers lasted only 1.5 to 2 years before being discarded and replaced. It was no doubt these circumstances which motivated Parsons to seek an alloy with the strength of steel but with more suitable resistance to the marine conditions and in 1876 Patent No 482 was published for his 'Manganese Bronze'. The sales promotional literature of the day as illustrated in Table 1 is both relevant and of general historical interest.

The Admiralty would have been most interested in the performance afforded by steel propellers but could not accept the problems associated with them because of their short life. Gunmetal would have had some advantage in strength over cast iron but be difficult to produce as satisfactory castings in the sizes required. So the Admiralty welcomed the new alloy which could be satisfactorily melted in the coal-fired reverberatory furnaces used at the time. Although the larger propellers were cast as boss and three or four blades as individual castings then machined and assembled, these castings could each be up to 2 or 3 tons finished weight.

Up to this time propellers had been manufactured by engine builders. There was however in Deptford, S E London, a Company, J Stone Ltd, engineers and founders who had been associated with marine engineering since they were founded in 1831, whose records show that they were producing propellers in 1881. In 1882, in the same district, the Manganese Bronze and Brass Company opened to produce propellers in 'Parson's Manganese Bronze'. J Stone Ltd approached Kings College in London where Professor Huntingdon undertook work on the development of the Manganese Bronzes on their behalf.

Parsons had started with Muntz Metal '60/40 brass' added 1% Sn to improve its corrosion resistance, and 1% Fe to 'strengthen' the alloy, amounts of manganese (necessary as a de-oxidizer) and aluminium were limited at low level: no doubt he discovered that with Sn at that level any significant addition of A1 would have been deleterious rather than advantageous. This was the alloy adopted by the Admiralty and used both by them and the Manganese Bronze and Brass Company through the years into the middle nineteen-forties. In 1889 J Stone Ltd registered a Trade Name 'Stone's Bronze', associated with an alloy again based on '60/40 brass' containing 0.5% Sn, 1.5% A1, 1% Fe, 1% Mn. This was their basic alloy for propeller production until about 1950 when use of the alloys declined but they are still used today for those Manganese Bronze propellers which are produced.

One wonders why the alloys were ever called 'Manganese Bronze', for they are brasses and properly known today as 'High Tensile Brasses' In the eighteen-seventies however, 'brass' was a name associated with a cheap alloy used for making simple products for everyday use, articles in which no particular engineering properties were required. 'Bronze' on the other hand was a name associated with alloys of quality, expensive, in particular tin-bronze used for important bearing and gear-wheel applications. Why **'Manganese Bronze'**? Well Mn was a necessary de-oxidant in the alloying of Cu-Fe and as far as the author is aware has been introduced in larger proportions into alloys of this type only when A1 has been included as an alloying element; the Mn addition avoided undesirable micro-structural effects of the A1 in the Cu Zn system in the cast condition.

During the first few years foundrymen must have had many problems in handling these alloys, which were different characteristically from cast iron, gunmetal, tin-bronze and brass with which they were familiar. The castings would have had to be fed using large feeding heads. Running systems would have had to be developed to minimise the effects of turbulence leading to the entrapment of oxide films. The metal had to be melted in reverberatory furnaces and caused problems in controlling composition, particularly compensating for the inevitable loss of zinc.

Early Developments to 1912: Marine Propellers

In 1897 came the successful trials with the 'Turbinia' the first ship driven by a steam-turbine engine. In succeeding years increasing numbers of ships with steam-turbine propulsion were built. As the steam-turbine developed considerably more shaft horse power than the reciprocating

Table 1

STATEMENT

Showing the estimated saving in the expense of a Propeller during the life of a Vessel by adopting **Parsons Manganese Bronze** in place of Steel: Weight of Propeller say 10 tons. Life of Vessel say 15 years.

Dr			Cr
Cost of **Manganese Bronze** propeller for 15 years –	£	Cost of Steel propeller for 15 years –	£
One Parsons Manganese Bronze Propeller, weighing 10 tons, say at £115 per ton finished	1,150.0.0	One propeller in Cast Steel, weighing 10 tons at £45 per ton	450.0.0
Approximate balance in favour of **Parsons Managnese Bronze** in 15 years working	10,600.0.0	* Say one renewal above every five years or two renewals only in 15 years in addition to the first cost £450 x 2	900.0.0
		Dock charges and labour involved in renewals and repairs, say £250 in 15 years	250.0.0
		Saving by using Manganese Bronze – in coal	
		† Say 2 tons of coal per day, at an average cost of £1 per ton, and assume vessel makes 250 working days per annum only – this would equal 500 tons of coal at £1 per ton = £500: £500 per annum for 15 years	7,500.0.0
		In speed –	
		** Say only ¼ knot per hour extra speed equals 6 knots per day which for 250 working days = 1500 knots per annum – Assuming vessel makes 10 knots per hour, or say 250 knots per day, this will mean 6 days' working expenses, ie wages, coal, wear and tear of engines etc. saved per annum, say 6 days at £25 per day = £150 per annum. £150 per annum for 15 years	2,250.0.0
		Value of old bronze blades, say 10 tons at £40 per ton	400.0.0
	11,750.0.0		11.750.0.0

* It is well known that steel propellers on Atlantic Liners wear out in from 18 months to 2 years, so that the cost of renewals in the majority of instances must greatly exceed our estimate.

† It will be remembered that Mr. Manual, Superintending Engineer of the Peninsular & Orient Steam Navigation Company, certified to a saving of 8 tons of coal per diem in the case of ss 'Ballarat'.

** We think it will be admitted that £25 per day is a very small estimate of the working expenses of an average sized steamer.

ss 'Zealandia' and 'Australia' gained 1 knot per hour by replacing their steel propellers with Manganese Bronze and many other vessels had done the same.

engine, propeller designers required alloys of strength superior to those then available. Both the propeller manufacturers went through the same experience of producing propellers in all-beta manganese bronzes: both suffered the same fate in that the early propellers shed blades after very short periods of time at sea. J Stone who by now had set up their own research laboratories produced an alloy with 2% Al, 1.2% Mn, 1.27% Fe and a zinc equivalent of 44%, with superior mechanical properties to those of 'Stone's Bronze', and registered the name 'Turbiston Bronze' in 1908. The Manganese Bronze and Brass Company had their 'Turbadium'.

Thus before the First World War the propeller alloys were established and remained the same until after 1943; for ships with reciprocating engines 'Stone's Bronze' and 'Parson's Manganese Bronze'; for turbine driven ships 'Turbiston Bronze' and 'Turbadium'; and for naval ships the Admiralty's specified alloy according to Parson's patent composition.

An important contribution to the metallurgical understanding of these alloys during this period was that of Guillet (Rev Met, 1906, Vol 3) with his work on zinc-equivalence. He found that when an alloying element was added to Cu-Zn in the range of brasses around the 60/40 composition the effect on the microstructure was equivalent to adjusting the Zn content of the binary alloy by the amount of the element added multiplied by a factor which was referred to as its zinc equivalent: for example Si 10; Al, 6; Sn, 2; Fe, 0.9; Mn, 0.5. This work has been of enormous value to those working with the manganese bronzes to this day.

1912-1950: In General Engineering

It is an aside, but not entirely irrelevant, that in the J Stone Laboratories aluminium bronzes were also being developed before the First World War and under Melt Book ref L189 in 1912 an alloy with 9.75% Al, 5% Fe, 5% Ni Bal Cu was produced. By the 1940s J Stone and Co Ltd were marketing this alloy extensively by that name, 'L189', now widely used as BS1400 AB2. Not irrelevant because throughout these years the Manganese bronzes have had to compete with the aluminium bronzes and eventually around 1950 when the problems of producing very large castings for marine propellers in those alloys had been overcome it was the aluminium bronzes which took over in the propeller field.

The manganese bronzes are good casting alloys. Oxide films become entrapped unless the castings are suitably run, ie free from turbulence, but they are much less troublesome in this regard than the aluminium bronzes. They are not as susceptible to problems associated with gas absorption as the aluminium bronzes. Both require special attention to feeding. None-the-less between the wars many non-ferrous foundries started to supply castings to the general engineering industry for applications in which strength was a particular requirement, but the manganese bronzes were not as resistant to corrosion as the aluminium bronzes. While few foundries found themselves able to make good castings in aluminium bronze many ventured into making castings successfully in manganese bronze.

Metallurgically an important landmark was the work of O Bauer and M Hansen (Z Metallkunde 1929-1934, Vols 21 to 26) who studied various ternary systems of Cu and Zn with other elements, the work with Sn and Al being particularly valuable. There followed the alloys basically containing 5% Al, 2.25% Mn, 2.25 Fe, balance Cu-Zn adjusted to give two different types of alloys, with microstructures all-beta and alpha-beta with some 35% alpha. Both were much stronger than the established alloys. The all-beta alloy was the strongest in the group, often known as '50 ton bronze', but being all-beta it was highly susceptible to stress-corrosion cracking, a fact difficult to convey to those designers who appeared to scan the specification books for alloys of the highest strength as the sole consideration.

Up to the time of the Second World War, the Admiralty, the leading manufacturers and the originators of the alloys, considered that to maintain the required standards of quality the metal should be made from virgin metals. It is particularly unfortunate, for since that time there have been considerable developments in the field of foundry technology for these alloys with high standards of technical proficiency and quality control. Similarly there are ingot makers who have advanced quality control facilities. Secondary materials are preferable whenever satisfactory standards of quality can be achieved.

There were however problems on the way. As among founders, so among Ingot Makers some were better equipped and more technically informed than others, and could better handle the alloying problems. There was a lack of knowledge on the effects of impurities, separately and in combination: work was carried out by J Stone and Co for their own information, and passed on for specification purposes. The importance of specifying a minimum alpha content in the alpha-beta structure of the alloy in general use, BS1400 HTB1 had been realized.

However probably the most important problem was that associated with the occurrence of 'hard-spots' in the alloy. When these were present the castings could not be machined. Once they were in the metal no way was found of removing them. Hard-spots were related to the iron-rich phase present in all the alloys which serves as a grain refiner. Metallurgists will be familiar with the principles involved in the separation of this phase due to Fe in the Cu Zn system and the mechanism by which it serves to refine the grain structure. The problem arises when significant amounts of Si are picked up during melting as from carborundum crucibles or from the acid linings of reverberatory furnaces. The phenomena is significantly aggravated if B is picked up from a flux used during melting, particularly in a reverberatory furnace. The iron-rich phase is so modified as to render the particles formed very hard and resistant to cutting tools. It was some time before proper studies were made and the results published.[1,2,3]

In more recent years the manganese bronzes have continued to be used in this field but in decreasing amounts because of the superior properties of the aluminium bronzes and the fact that founders have become more experienced and knowledgeable in handling them.

In connection with 'Quality Control' as applied in those days, composition and mechanical properties were specified. When the author first became involved with these alloys in 1943 two methods were in use for checking zinc loss; one was dependent upon the accuracy of the charge for other elements. The first was a quick analysis for Cu content. The second was a 'fracture-bar' test for which a sample, 5" long, 5/8" deep, tapered, 7/8" wide at top, was cast into a chill mould, knocked out immediately this was possible, and quenched by dipping alternate ends to increasing extents in water. A nick was made across the centre and the bar fractured. Metallurgists of the day were able to judge by colour and 'sparkle' in the fracture, the Zn level to within 1/2% and usually closer, of the actual amount present. It was always ensured in the charge calculation that the Zn level would not be high after melting, for the necessary Cu addition to correct would be so formidably large as to make the correction impossible: so zinc was always added as a correction. How far back either of these techniques went into the past is not known. Temperature would have been judged by pushing a rabble back from the door through the metal surface and watching the extent of the Zn flame around the rabble head as the surface was disturbed. This was remarkably reliable as found by the author who used pyrometric equipment of the day in the 1940s. In the event of a difference of opinion, one was left wondering which to rely upon – the shop foreman always won the day!

Post-casting tests would have consisted of chemical analysis and mechanical testing carried out on integrally-cast test bars. Tensile strength, elongation and a 'yield-point' were determined. 'Yield-point' was specified as for steel and the fact that manganese bronze did not 'yield', as did steel, was not noticed, or not regarded as significant. The test was carried out using dividers across the 'pop or pock-marks' for measuring elongation. Clearly the method was capable of providing a considerable range of results according to the care taken. Had considerable care been taken, the minimum specified by the Admiralty of 15 tons per square inch would have been difficult to achieve. To achieve that value the proportion of the alpha phase would have to be very low and could result in a significant scatter in results. Yet the presence of some alpha phase in the microstructure was essential. The consequences from working at low levels of alpha content in the microstructure did not become apparent until after 1943.

1943 Onwards: Marine Propellers

During the intervening years from 1912, alloys had not changed but the sizes of propellers had increased enormously. The Queen Mary and Queen Elizabeth each had four propellers of finished weight about 30 tons. Each was a 'solid' propeller, ie not 'built-up' from separate blade and boss castings. Larger coal-fired reverberatory furnaces were installed to melt 25 tons each which with smaller units, and using one or two sprues for pouring, allowed a complete range of sizes to be cast: see Table 2.

Table 2 The largest sizes of castings produced

J Stone Ltd —— J Stone & Co —— Stone Manganese Marine

Up to 1905	Up to 6 tons MB
1913	7 tons MB
1920	12 tons MB
1929	20 tons MB
1933	55 tons MB
1970	85 tons Al Bronze
1974	103 tons Al Bronze

An interesting problem which occurred about 1943 related to a disturbing effect, which affected a number of large naval ships. An area about 1 to 1.5 ft across appeared on each blade high towards the top of the casting, in the region of maximum thickness, from which whole crystals fell away as the chipping hammers were applied to remove surplus metal. The alloy was to the Admiralty composition 1% Sn, 1% Fe, 0.25% Mn, Cu+Zn with Cu about 56%.

It should be explained that as the blade cools very slowly, there is a tendency for the Fe-rich grain refining phase to gravitate downwards. This reduces the amount of this phase available in the zone of the last metal to solidify, consequently the grain structure is coarse: * Fig 1 Segregation also results in changes in composition. In each of the castings concerned inverse segregate appeared at the blade surface: see Fig 1. The microstructure of the main part of the casting was normal alpha-beta; the coarse grained structure was also of alpha-beta but with isolated all-beta grains. The boundary between the inverse segregate and the original surface consisted of a sharply defined change in microstructure from normal alpha-beta to all-beta C to B Fig 1. The microstructure of the segregate gradually changed from all-beta at this boundary to beta-gamma as the cast surface was approached B to A and C to D. This brittle structure caused the falling away of whole crystals under the chipping hammers.[4]

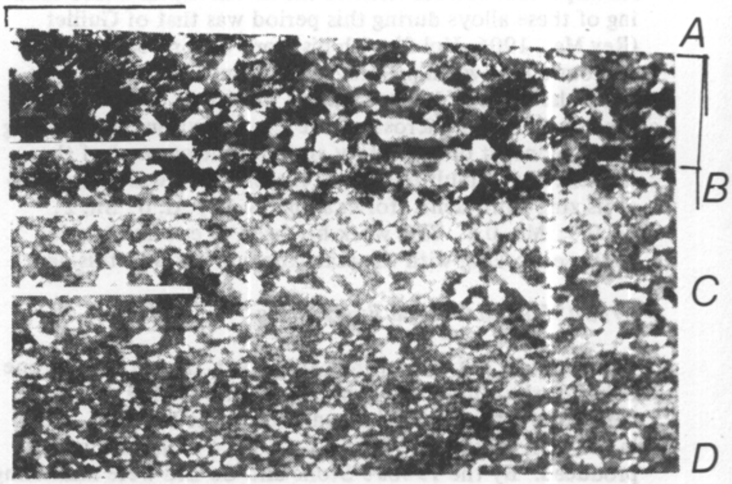

Fig 1 Admiralty Bronze Propeller Blade Cross Section, Approximately Full Size: Showing Grain Coarsening and Segregation Effects.

Further work led to the disclosure that under certain circumstances manganese bronzes could dissolve hydrogen to a small but sufficient extent to cause inverse segregation to occur on large propeller castings. If the condition were aggravated by the use of flux during melting, then the effect could be produced on very much smaller propeller castings.

Another investigation of the time related to the concern of metallurgists in naval dockyards when it was found that a number of propellers which had been in service, and were in store on the quayside, exhibited edge cracks. It was found that these were associated with welding repairs or blade straightening even though such repairs had been carried out according to correct procedure and the metal had been very slowly cooled under controlled conditions. The normal alpha-beta structure had not been restored and there were zones of all-beta structure which were subjected to stress-corrosion cracking in the marine atmosphere. It would not be surprising that if the metal were heated from the alpha-beta into the beta phase, the closer the composition were to the alpha-beta/beta boundary, the more difficult it would be to restore the original structure. But laboratory work at the time disclosed that with structures not at all abnormal for the alloy, surprisingly slow rates of cooling were necessary.

Table 3 Comparative Properties of Propeller Alloys

	0.2% proof stress MPa	Tensile Strength MPa	Fatigue Strength in 3% Sodium Chloride solution Stress at 10^8 reversals MPa
Manganese Bronze	200	510	84
Nikalium: Nickel Alum Bronze	270	680	141
Novoston: Manganese Alum Bronze	305	685	124
Martensitic Stainless Steel, 13% Cr	450	680	77
Low Carbon Steel	250	450	35

It will be recalled from an earlier section that in order to meet the Admiralty 'yield-point' requirement as laid down very many years previously, it was necessary to keep the proportion of the alpha phase low, and metallurgists of the day were content that provided alpha phase were present in the alloy as-cast then there would be no risk of propeller failure due to stress-corrosion cracking. This took no account of the possible need to effect repairs. Recent information indicates that there are limits of alpha phase content below which one should not go in order to avoid stress-corrosion. This led to the 15% low limit for alpha content now in the BS1400 HTB1 specification.

The problems which had come to light associated with the Admiralty alloy led to further development work to produce a new alloy. An alloy was required for Admiralty work which would have adequate strength and corrosion resistance at a reasonable level of alpha content in the alpha-beta structure. The basic composition of the original Parson's alloy was not at fault but the 'yield-point' requirement led to alloys having a low-alpha microstructure since there was no other way to meet it. For many years extensometers had been in use in metallurgical laboratories and had been used for 'in-house' quality control purposes and proof-stress was specified. The Admiralty 'yield-point' requirement of 15 tons/sq in min as measured was probably at best equivalent to a 0.5% Proof Stress. Alloys of that type such as 'Stone's Bronze' and BS1400 HTB1, with reasonable alpha contents of around 30%, would normally have been specified at minimum 11 tons/sq in for a 0.15% Proof Stress. So an alloy was developed with 0.15% Proof Stress specified at min 15 tons/sq in, with adequate corrosion resistance by the addition of 0.5% Sn; the composition being 0.5% Sn, 2.25% Al (for improved strength), 1.25% Mn, 1.25% Fe, with Cu+Zn to give a zinc equivalent of 43, ie 35% alpha. This was the last alloy developed in the manganese bronze family.

In this period quality control techniques also were improved. Composition basically still depended upon control of the composition of the furnace-charge which consisted of virgin metal, pre-alloyed in tilting furnaces, and scrap propellers returned from service. Composition after melting, with the furnace held, was checked using a specially designed test-piece, cast into sand, held for a given period, and then quenched. A microspecimen was prepared. The proportion of alpha to beta was measured to give a zinc equivalent value, and thus zinc loss could be established. Also the form and amount of the iron-rich phase could be seen and by using suitable etching techniques Si pick-up, and certain impurities, could be detected.

Test-bars had been the source of another problem. Being integrally cast they were liable to exhibit inclusions and from blade to blade three bars would not always be as consistent as desirable. The problem was to persuade engineers of the day that the properties given by a test-bar bore no relationship to the properties of the metal in the propeller which could fall off in strength by 20% from tip to root in the blades. In fact the test-bars served only to demonstrate that the metal was capable of giving certain properties. For this purpose with the specification suitably set, bars cast separately under standardized conditions were clearly desirable. The proposed procedure was accepted by the Admiralty and Lloyds Register, who were responsible for the inspection of propellers for commercial ships which were coming back into production at this time. Thus separately cast test-bars became more widely accepted instead of integrally-cast bars.

Many will recall that after the war expert teams went to Germany to review developments which had taken place there in various industries during the war. With marine propellers these teams found that being unable to obtain sufficient supplies of copper the Germans had turned to stainless steel, 12 to 13% Cr Martensitic. This observation immediately appealed to the Admiralty who saw advantages in the high strength which could be achieved. The propeller manufacturers could foresee the problems which would be involved in manufacturing large propellers in such an alloy, particularly if heat-treatment should be a requirement (J Stone had one made). They were of course aware of the advantages to the naval architect in enabling higher speeds and greater efficiency to be achieved. A suitable copper-based alloy was available, in the well established nickel aluminium bronze, but there would be considerable problems associated with melting this in a large reverberatory furnace because of gas pickup. The largest electrical melting unit available at the time was a medium frequency furnace of about 1 ton capacity used for melting stainless steel. So research was put in hand to develop a completely new copper-based alloy with all the desirable properties.

The final chapter in the story of manganese bronze as an alloy for propellers for high performance ships opened soon after. Developments in ship design by naval architects to produce faster, larger and more efficient ships led to a number of failures of manganese bronze propellers. These failures were experienced by many of the propeller manufacturers. There was no evidence that such failures were specific to one class of ship. The fractures were of classical corrosion fatigue appearance. Many engineers of the day found it difficult to understand how a propeller could be subjected to fatigue stresses; their concept of fatigue was usually related to the fluctuation of stress through zero, as in the classical Woehler test. (See Footnote).

The basis of the calculation used by naval architects for the determination of blade thicknesses was a cantilever beam theory first published in 1911 with some modification and refinement over the years. Very large factors of safety had been found appropriate: X12 to X14 based on the ultimate tensile strength of separately cast test bars.

According to these calculations the blades should not have broken, so clearly fatigue stresses had been increased above those normally experienced. Investigation into the corrosion fatigue properties of manganese bronze yielded interesting results. For an alloy of given basic composition, with specific amounts of Sn, Al, Mn and Fe, increasing the tensile strength by the adjustment of the Cu+Zn contents to decrease the proportion of alpha to beta, and led to a progressive drop in resistance to corrosion fatigue. To satisfy the naval architects requirements clearly an alloy of superior resistance to corrosion-fatigue was now required.

Work progressed on the development of a new copper-base alloy from which the copper-manganese-aluminium bronze (nearer to a true 'manganese bronze' than is high tensile brass!), given the trade name 'Novoston', emerged, and was put into service for the more highly stressed propellers. Then electric melting became available on a scale to permit nickel-aluminium-bronze to be used: Table 3. These alloys gradually took over and the use of manganese bronzes declined so that while in 1950 almost 100% of all propellers were made in these alloys (the balance in cast iron) today the proportion is down to about 20%.

Table 3 Comparative Properties of Propeller Alloys

	0.2% proof stress MPa	Tensile Strength MPa	Fatigue Strength in 3% Sodium Chloride solution Stress at 10^8 reversals MPa
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Low Carbon Steel	250	450	35

Conclusion

The rise in the use of manganese bronzes from their introduction in 1876 has been traced through their development and world wide application as marine propellers, running into many thousands of tons per year, to their decline for this application. This set in around 1950, when they were superseded by aluminium bronzes.

During the same period their application in general engineering increased significantly in relation to the usage of the other cast copper-based alloys, but relative to their use in know-how in handling the aluminium bronzes in non-ferrous foundries the use of manganese bronzes has declined.

The author is aware of the use of the alloys in the wrought field in the form of extrusion and forgings, which are touched on in the lecture by S G Temple, Copper 2.

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2 D W Davis and K J Lloyd: The British Foundryman, March 1966.

3 D W Davis, The British Foundryman, April 1967.

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Footnote:

The author recalls his embarrassment on an occasion when he made a remark to this effect to an owner's representative as together they approached a broken propeller. The representative, a much older man, drew himself to his full height, turned, and not without a tone of scorn in his voice replied 'Young man, you clearly have not been properly informed of the relevant facts: the vessel was unavoidably delayed in Boston for more than three weeks; the propeller broke the day after she sailed. Fatigue?'.

Albert H R French MIBF FIM has worked with Manganese Brass and Bronze and then Stone-Manganese for most of his life, mainly at the Birkenhead factory where very many of the world's ship propellers have been cast and finished.

Copper 4: Steam condensers and condenser tubes in the UK 1769-1950

Peter Gilbert

Synopsis

The paper briefly reviews the early history of steam condensers from the time of the James Watt patent in 1769. Surface condensers were rarely used until about 1860, but from then on units fundamentally similar to those in present-day use were put into service in increasing numbers. After briefly reviewing tube manufacture and the fixing of tubes into tubeplates, the paper describes investigations into early condenser tube corrosion problems, the Institute of Metals work carried out between 1911 and 1928 being of particular importance. The development of the various condenser tube alloys is then summarised and the paper concludes with some comments on the changing commercial scene.

Introduction: The Development of Condensers

Steam engines originated with the ideas of Denis Papin (1690), Thomas Savery (1698), and Thomas Newcomen (1705). In Newcomen engines, work was obtained by atmospheric pressure on the piston when steam that had been admitted to the cylinder was condensed. Engines of this basic type, often used for pumping water, were manufactured for some 70 years, but the alternate heating and cooling of the cylinder involved a great waste of energy. This was recognised by James Watt, who, in 1769, obtained a patent for an improved steam engine incorporating a separate condenser. An Act of Parliament in 1775 extended this patent for a further 25 years. With this major step forward in the development of the steam engine begins a story of condensers, though some time was to elapse before condenser tubes became important.

The separate condenser may be either a direct contact, jet condenser, or a surface condenser. Watt first experimented with plate surface condensers, but had trouble with soldered joints and soon changed to direct contact jets. This latter method became accepted practice and was used predominantly in condensing engines for 80 years or more. Nevertheless, there were several engineers during this period who advocated the surface condenser, particularly for marine steam engines. In 1820 David Napier installed a condenser consisting of tubes in a box fixed to the bottom of a ship. The motion of the ship caused flow of seawater through the box condensing steam inside the tubes. Napier subsequently fitted bilge condensers to a number of ships, but the system was not adopted by others. Hall in the UK and Ericsson and Pirsson in the USA were other early advocates of surface condensers. Samuel Hall's condensers covered by an 1836 patent, incorporated vertical tubes with steam condensing inside.

Several difficulties contributed to the unpopularity of surface condensers during this period including fouling problems and splitting of the brazed copper tubes used, solid drawn tubing being then not available. The cheaper and lighter jet condensers were preferred and they performed satisfactorily so long as boiler pressures were relatively low. However, from about 1860 onwards marine compound engines were introduced, steam pressures rose progressively, salt water boiler feed was no longer acceptable and the use of surface condensers rapidly increased. Such condensers were also essential for the next major development, that of the steam turbine. Although commercial steam turbines were built in the USA by William Avery as early as 1831, the really significant developments did not occur until towards the end of the 19th century. The most prominent inventors were Sir Charles Parsons, whose original steam turbine was built in England in 1884, and Carl De Laval in Sweden.

A short digression may be permitted on the development of the high pressure non-condensing steam engine. This was pioneered by Richard Trevithick at the end of the 18th century and patented in 1802. Given a high enough steam pressure, heat rejection can be achieved by the exhausting steam, a supply of suitable feed water being, of course, necessary. This principle was used in the first steam locomotive, constructed by Trevithick and successfully tested in 1804, and has remained in use throughout the history of the steam locomotive. A few condensing locomotives saw service (for instance, in South Africa), but the standard non-condensing engines were used all over the world and still are in many countries, being, indeed, still under construction in China.

To return to the surface condenser, it was in 1857 that a design emerged close to the tubular steam condenser of modern times. J F Spencer obtained a patent for a three-pass horizontal condenser with steam condensing on the outside of the tubes. From then until the end of the century there were modifications to design and construction, but no fundamental changes. Understanding of the theoretical aspects of heat transfer in condensers gradually developed through workers such as Joule, Thomson (Lord Kelvin), Rankine, Nichol, Reynolds, Stanton and Nusselt. One of the points to emerge was the importance of air removal. In Watt's early condensers a single pump removed air as well as condensate and jet water. Thomson suggested separate air and condensate pumps in 1856, but the idea was not fully developed until G & J Weir's patent of 1879. This specified a bottom steam inlet and air extraction, with a separate pump, from the top of the condenser. The patent indicated that the point of air extraction should be as far as practicable from the steam inlet, that baffles should be provided to elongate the path of steam flow and that extra cooling could be provided at the air extraction if necessary. Condensers of Weir design became well established though as steam turbines became increasingly important, redesign was necessary to permit steam entry at the top rather than the bottom.

The G & J Weir Company was one of several British firms that became major designers and builders of condensers in the present century, others included C A Parsons, Hick Hargreaves, Metropolitan Vickers and Richardson Westgarth. This is not the place to dwell further on theories of condenser operation, or the intricacies of design and construction, except insofar as they bear on the questions of tube materials and performance.

Tube Manufacture

Copper is one of the oldest metals in marine engineering, having good corrosion resistance and also being resistant to marine fouling. With its high thermal conductivity it was a natural choice for the tubes in early condensers. As previously mentioned, the early tubes were seam-brazed, but by the 1860s a process for making solid drawn tubes was patented by Charles Green and subsequently developed commercially by the Elliots Metal Co of Selly Oak, Birmingham.

For many years seamless tubes were produced from cast hollows. Improved surfaces were obtained when the castings were bored inside and turned outside and some customers, such as the Admiralty, insisted on this. Production of seamless tube from cast shells continued to be used as late as the 1930s, even though hot-working processes for making copper and copper alloy hollows, viz hot extrusion and rotary piercing, began to be developed in the 1920s.

Hollows are reduced to the required dimensions by cold drawing (with intermediate anneals as necessary) or by tube reducing (Pilger process). In cold drawing the tube is pulled through a die with no internal support ('hollow sinking'), or whilst supported on a mandrel ('bar drawing'), or with an internal plug in the throat of the die ('plug drawing'). The plug may be supported on the end of a rod (ie 'fixed') or may be 'floating'. If a floating plug is used the tubes can be drawn on drums ('bull blocks'), permitting longer lengths to be processed than on straight benches and also allowing much higher drawing speeds. In more recent times seamless tubes have in some cases given way to tubes rolled up from strip and autogenously seam-welded. The wheel seems to have turned full circle.

Tube Fixing

In tubular condensers the tubes have to be fixed into the tubeplates in such a way as to give leakproof joints. It is necessary to allow for the effects of expansion and contraction with changes in temperature and the classical method was to insert suitable packing material between the tubes and tubeplate holes, with screwed ferrules to keep the tubes in place. It is interesting to note that this method was used as long ago as 1836 in the Hall surface condensers. The tubing has to be strong enough not to collapse during packing and is therefore hard-drawn (originally mandrel drawn).

As condensers increased in size the quicker and more economical method of expanding the tubes into the tubeplate holes was developed. 'Rolling-in' is performed using suitable rotary tools or 'expanders'. At first, provision for expansion and contraction was maintained by rolling in the tubes at one end, whilst still packing at the other, usually the water outlet end. This required the use of hard temper tubes with one end locally annealed. In some cases there was advantage in using tubes of a uniform intermediate temper throughout that were strong enough for packing and also ductile enough to permit expanding. The next development was to fix tubes by rolling in at both ends, expansion and contraction being allowed for by means of bellows in the condenser shell, though suitable construction methods are necessary to avoid excessive stressing of local groups of tubes. Another method, developed by the Brown Boveri Company, was to prebend the tubes into slightly wavy form so that when temperature changes occurred the tubes merely bent a little more or a little less. More recently, in applications calling for the highest degree of assurance against leakage, methods have been developed for fixing tubes by fusion welding, explosive expansion or explosive welding.

Investigation of Condenser Tube Problems

The relatively low strength of pure copper can be increased by adding arsenic, and arsenical copper (0.4% As) has been used to some extent for condenser tubes. However, copper was largely replaced by brass, early tubes being of Muntz Metal, a 60% copper 40% zinc two-phase alloy originally introduced in 1832. This was superseded by the single phase 70% copper 30% zinc alloy.

Sporadic corrosion failures became a serious problem and condensers were very unreliable. Not all condensers and not all tubes in a condenser were affected, but failures occurred by thinning, pitting or selective attack (dezincification). Failures occurred in fresh waters as well as seawaters (usually by dezincification). Season cracking of brasses was another problem, giving longitudinal splits due to residual circumferential tensile stresses in the tubes as supplied. Tube manufacturers had to learn how to avoid such stresses by appropriate drawing techniques/heat treatments. Some manufacturers learnt these lessons more quickly than others, but the problem was largely eliminated by the 1950s, though isolated occurrences thereafter were not unknown.

The first part of the 20th century, and particularly the period between the two World Wars, was a time of great progress in the general understanding of corrosion processes and the development of ideas of the underlying theories of corrosion mechanisms. Condenser tube corrosion was given attention from the beginning of the century because of the acute problems in ships and coastal electricity generating stations powered by steam turbines. Failures in naval ships caused much concern and were of such magnitude as to reduce seriously the capabilities of the navies in the first World War. Even the Admiralty's improved brass alloy containing 1% tin (70/29/1), which was widely adopted for naval use, was no solution to the problem.

The seriousness of the situation led the Institute of Metals, soon after its formation in 1908, to set up a Corrosion Committee to investigate condenser tube corrosion. At the outset the work was financially supported by the Brass and Copper Tube Association and by individual companies. The Committee received eight reports from the main investigator, G D Bengough and his collaborators, during the period 1911-1928 and these form the basis for much of the subsequent progress that was made in dealing with the problem.

The First Report to the Corrosion Committee by G D Bengough (J Inst Metals 1911, No 1, Vol v, pp 28-114) gave a comprehensive review of relevant published papers, which revealed a wide diversity of views. Reference was made to experiments carried out in 1902 on the possibility of protecting 70/30 brass tubes by tinning, nickel plating or applying organic coatings. The emphasis in the subsequent investigational work was to be on the behaviour of 70/30 brass in seawater, though it was recognised that failures also occurred in inland situations. A plea for the inclusion of Admiralty brass was made during the discussion of the report.

A Second Report (G D Bengough and R M Jones, J Inst Metals 1913, No 2, Vol X, pp 13-118) described a questionnaire sent to operators. The results were rather inconclusive, but confirmed that lives were very variable. The most common cause of failure seemed to be dezincification and in some land installations tube lives were even shorter than in seawater. Laboratory corrosion tests were carried out in seawater and in concentrated and diluted seawaters at ambient temperature, 40°C and 50°C and an experimental condenser was set up. Four alloys were tested and tubes were supplied by the Muntz Metal

Company, Birmingham, in 70/30 brass, 61/39 brass ('Muntz Metal') and 70% copper, 28% zinc, 2% lead (sold under the trade name 'Nergandin') and by the Broughton Copper Company, Manchester, in 70/30 brass and 70/29/1 Admiralty brass. Two types of corrosion were observed, 'complete' (general) corrosion and 'selective' corrosion (dezincification). The 71/28/1 and 70/28/2 alloys were least attacked by dezincification but suffered more severe complete corrosion than the plain brasses. Complete corrosion was more prevalent in ordinary or concentrated seawater at ordinary temperatures and dezincification was encouraged by diluting the seawater, raising the temperature and aerating the solution. Reference was made in the report to the availability in the USA, of a copper-nickel (sic) alloy known as 'Monel' and to the possible merits of using copper-aluminium alloy tubes.

Subsequent work was disrupted during the 1914-18 War, but the Third Report appeared in 1916 (W E Gibbs, R H Smith and G D Bengough, J Inst Metals, 1916, No 1, Vol XV, p 127). Experiments with Muntz metal were discontinued, in view of its previous poor behaviour, and two additional alloys were included, copper-3.5% tin (phosphor bronze) and copper-8% aluminium. Corrosion tests were carried out on hard drawn and on annealed samples in ordinary, diluted and concentrated seawaters at temperatures up to 60°C. Other matters investigated were the effects of aeration, of contact with coke and of irregularities in the tube surfaces. No very consistent results emerged and none of the alloys was satisfactory in all conditions. Contact with coke was detrimental. Recommentations were made to clean the tubes regularly, to keep the water temperature as low as possible and to make the flow as smooth as possible in order to minimise erosion at the inlet ends.

In the Fourth Report (G C Bengough and O F Hudson, J Inst Metals, 1919, No 1, Vol XXI, pp 37-252) some basic work on the corrosion of aluminium, copper and zinc, and then on 70/30 brass, was reported. In a section on practical problems, the authors stress the compexity of corrosion and state that it is not a single problem with a general solution, but rather a large group of different problems each of which should be dealt with by appropriate measures. The view is expressed that 70/30 brass tubes should normally last 15-20 years, providing that the cooling water is (a) free of acidity and neutral or very slightly alkaline, (b) free of ammonia, (c) free of suspended matter, bubbles and super saturation with air and providing also that the rate of flow is 5-6 ft/sec and that there is proper steam distribution in the condenser.

Five different types of corrosion of 70/30 brass tubes were described in the Fifth Report (G D Bengough, R M Jones and Ruth Pirret, J Inst Metals, 1920, No 1, Vol XXII, pp 65-158) viz general thinning, deposit attack, layer-type dezincification, plug-type dezincification and water-line attack. The occurrence of these and methods of combatting them were discussed. In both the fourth and fifth reports there was a good deal of speculation about the effects of variation of composition and metallurgical structure in the surface layers of condenser tubes. There was a return to fundamental considerations in the Sixth Report (G D Bengough and J M Stuart, J Inst Metals, 1922, No 2, Vol XXVIII, pp 31-135) at a time when the electrochemical nature of corrosion processes was being recognised and the concept of protective films was gaining ground.

Contributors to the discussion of the theoretical aspects of the report included Ulick R Evans and W H J Vernon.

The voluminous Seventh Report by G D Bengough and R May (J Inst Metals, 1924, No 2, Vol XXXII, pp 81-269) was of the greatest importance. The investigators were now clearly coming to grips with the problems and the way forward was emerging. The report gives both laboratory test results and detailed discussions of practical experience. It was shown that an impinging water stream, particularly if containing air bubbles, could cause breakdown of a protective film, leading to local corrosion. The effect was studied by carrying out jet tests on specimens of alloys cut from tubes and by observing flow conditions in glass tubes in a model condenser. Secondly, in investigating the effects of making various additions to 70/30 brass it was discovered that a small quantity of arsenic (as little as 0.01%) would prevent dezincification in seawater. Clearly this was a major breakthrough. Analysis of samples from service confirmed that those containing arsenic were not dezincified, whereas those showing dezincification contained no arsenic. It was observed that in 1913, 75% of the failures investigated were due to dezincification, whilst in 1922-23, the figure was only 10%. This was ascribed to the greater prevalence of arsenic-bearing tubes, presumably resulting from the use of increasing amounts of arsenical copper scrap, and also from copper ores rich in arsenic.

Other notable points in the Seventh Report were:

1. A quick nitric acid test to determine the amount of arsenic in 70/30 brass was described.
2. Deposits can cause attack, probably due to differences in oxygen distribution.
3. Local corrosion does not develop at superficial tube flaws.
4. The effect of variation in crystal size is small.
5. Protective films pre-formed in warm seawater give improved resistance to turbulent aerated water streams.
6. Addition of iron ore to the cooling water at Carville Power Station was beneficial.
7. Presence of hydrogen sulphide produced non-protective films and caused increased corrosion.

Sixty years later these points would still be undisputed.

In 1924 the Department of Scientific and Industrial Research (DSIR) took over the investigation of the scientific aspects of the corrosion of metals under its own Research Committee and there were further publications by Bengough and his co-workers under its aegis. The Institute of Metals Corrosion Committee continued to sponsor work on condenser tube corrosion until the appearance of the Eighth Report on 'Impingement Attack' by R May (J Inst Metals, 1928, No 2, Vol XL, pp 141-185). This final report was another significant document. The major contributions by May were:

1. The development of the technique of studying the formation, breakdown and re-formation of protective films using potential measurements,
2. The development of a laboratory jet-impingement test. The subsequent widespread use of this May jet test, still regularly used in a number of laboratories, has probably been the single most important factor in the development of improved condenser-tube alloys,

3. The demonstration of the high resistance to film breakdown under impingement conditions, and the ability of the film to reform rapidly, with a new brass alloy containing 2% aluminium.

R May joined the British Non-Ferrous Metals Research Association when they subsequently took over the condenser-tube research from the Institute of Metals. Amongst the many aspects investigated at the BNFMRA were:

1. Evaluation of the effects of iron and manganese on corrosion resistance of copper-nickel alloys over a range of nickel contents.

2. Relating the corrosive action of natural seawater to its composition, including the effects of hydrogen sulphide and organic sulphur compounds.

3. Further refinement of the jet impingement test and development of other corrosion testing techniques.

Development of Condenser Tube Alloys

Copper-Nickels

Whilst the Institute of Metals work was in progress, tube manufacturers were making strenuous efforts to develop improved alloys. The most promising alloys were the copper-nickels, in which corrosion resistance improved (but difficulty of manufacture, and cost, increased) as the nickel content increased. The nickel was increased in stages from 15% to 20% and then 30% and even, experimentally, to 40%. Many firms found difficulties with the 70/30 copper-nickel, but by 1930 Allen Everitts had supplied their 'A E Supernickel' throughout the world and Yorkshire Copper Works Ltd were able to report that they had supplied many thousands of tubes with no reported failures. Allen Everitts' successful production process was based on the use of wear-resistant tools and pickling to remove hot-formed oxide.

The Admiralty became convinced that this type of alloy was superior to Admiralty brass and in due course adopted 70/30 copper-nickel as their standard, which it has remained throughout the period of use of steam turbines in warships.

Being the Admiralty, they specified material of the highest purity and in so doing unwittingly ensured they received an inferior product. It gradually came to be realised about 1933, probably by the Yorkshire Copper Works before anyone else, that it was beneficial to incorporate iron in the copper-nickel alloys as this gave greatly improved resistance to impingement attack. Iron had previously been present as an impurity. Manganese also had a secondary beneficial effect. The British Standard for 70/30 copper-nickel condenser tubes was eventually amended to require instead of excluding iron. Other countries followed suit, but not in many cases, until many years later. Most warships, other than British ones, used iron-free 70/30 copper-nickel condenser tubes during the Second World War.

During the early 1930s condenser tubes were failing with great rapidity at two power stations, Portishead and Clarence Dock, where considerable quantities of sand were carried in suspension in the cooling water passing through the condensers, removing protective films quickly from all existing alloys. Having recognised the powerful beneficial effects of iron and manganese in copper-nickels, the Yorkshire Copper Works in about 1935 made a 30% nickel alloy with 2% each of iron and manganese (under the trade name 'Yorcoron'). This alloy proved highly resistant to sand erosion and subsequently has been used successfully in a wide range of seawater heat exchanger applications.

Another copper-nickel alloy, which found more limited use for condenser tubes in the UK (though widely used in the USA), is the 10% nickel alloy with about 1.5% iron (originally sold as 'Kunifer 10' by ICI Metals Division and 'Yorcunic' by Yorkshire Copper Works). Moves towards the use of this alloy were influenced by shortage of nickel at the end of World War II and further restrictions during the Korean conflict.

Brasses

The 70/30 and 70/29/1 Admiralty brasses (incorporating arsenic, of course, since the discovery in the Seventh Report that this inhibits dezincification) have continued in widespread use in installations using fresh water cooling, but are insufficiently resistant to impingement attack to give reliable service in seawater.

An early proprietary brass alloy was 'Barronia' supplied by the Barronia Metal Co, Putney, in various wrought and cast forms. Tubes were made by Earle, Bourne and Company, Birmingham, and were first put into service in condensers in about 1924. The composition varied somewhat, around 84% copper, 4% tin, 0.2% iron, balance zinc. Lead, sometimes present up to as much as 0.8% was apparently not considered to be an essential ingredient. Great claims were made for the high corrosion resistance of this alloy and the firm's literature claimed highly successful results, which were attributed largely to the structure of the metal. Statements were made such as 'Barronia is practically devoid of crystal structure'; 'The finer the grain or crystal structure of the tube metal the greater the resistance to corrosion', 'The pitting and holing of condenser tubes are well known to originate at points of crystal weakness'; 'Compared with other metals, Barronia has no crystalline structure at all'. The alloy had some merit, particularly, perhaps in polluted estuarine waters and there was a period when other manufacturers made their own version ('Kingston Bronze' by ICI Metals Division, 'Yorconia' by Yorkshire Copper Works).

The real break-through came with the development of aluminium brass. The alloy tested by May (Eighth Report had 75% copper, 23% zinc and 2% aluminium and originated from researches on other matters carried out for the BNFMRA at Research Department, Woolwich. The original material had no arsenic and it suffered slight dezincification. The BNFMRA took out a patent to protect their members and there was legal action (eventually settled out of court) against a non-member infringing the patent. The Yorkshire Copper Works incorporated arsenic from the outset in their 'Yorcalbro' alloy, first sold in December 1928 and others followed suit in due course. ('Alumbro' – ICI Metals Division, 'Batalbra' – Birmingham Battery & Metals Co, etc). Various attempts to improve its properties further by modifying the composition met with no success.

Aluminium brass has been widely used in most parts of the world and it remains an important seawater condenser tube alloy to the present day, and was for many years used in most mercantile marine ships, before diesel engines became the norm because it was cheaper than cupro metal.

Aluminium Bronzes and Tin Bronzes

Single-phase aluminium bronze tubes were available from about 1930 onwards from several manufacturers. These alloys usually contained about 7% aluminium and one or more of the elements, iron, nickel and manganese. For instance, ICI Metals Division made 'Broternal', containing 1.5%–2% manganese (Broughton Copper Co) and 'Resisco', containing 2% nickel. The Yorkshire Copper Works '

'Yorcalnic' was originally similar to 'Resisco', but was later modified to contain 1% iron, 0.75% nickel and 0.75% manganese. Aluminium bronze condenser tubes never achieved widespread use, presumably because aluminium brass or copper-nickel alloys offered more economic and/or reliable alternatives. Inconsistencies in hydrogen pick-up led to variations in yield.

Phosphor bronze was tested as early as 1916 (Third Report) and several efforts were made subsequently to introduce tin bronzes for condenser tubes. The alloys did not, however, become commercially very significant because the tin content needed to be fairly high to give good corrosion resistance, making the tubes difficult to manufacture and expensive.

The bronzes have, however, seen limited use as they have advantages over other alloys in some special conditions, notably when cooling waters that are mildly acid have to be used.

Commercial Aspects

Condenser tube manufacturers grew up in the Birmingham area, the centre of the non-ferrous metals industry, and also in other places such as Manchester and Leeds. In many cases tubes were made as part of a wide range of products, but there were some specialist tube makers. Mergers and take-overs have steadily reduced the numbers from the peak and today but two remain in the UK.

ICI Metals Division (incorporating Geo Kynoch and Co and Nobel Industries, with metal manufacturing facilities at Witton and Kings Norton in the Birmingham area) became an important condenser tube manufacturer when in 1928 Allen Everitts and Elliots Metal Co were acquired and in 1934 the Broughton Copper Co joined the group. The Yorkshire Copper Works had been in operation on their Leeds site since the early part of the 20th century (being formerly the Leeds Copper Co) and became a large specialist copper and copper alloy tube manufacturer. These two firms each had about 40% of the UK condenser tube market (as well as large export activities) when they merged in 1958 to form Yorkshire Imperial Metals, which in due course became a subsidiary of Imperial Metals Industries (now IMI). Most of the smaller condenser tube manufacturers were progressively bought out or otherwise ceased trading, eg Charles Clifford & Son, Earle, Bourne & Co, Hudson and Wright, P H Muntz & Co, John Wilkes, Sons and Mapplebeck. The two remaining UK condenser tube makers are IMI's Yorkshire Imperial Alloys (who operate the Allen Everitts factory at Smethwick and the Yorkshire Copper Works factory at Leeds) and Birmingham Battery and Metal Co, Selly Oak.

Before, and for a time after, the nationalisation of the UK electricity supply industry, tube manufacturers had incentives to find improved alloys and many modifications were tested and subjected to field trials. Additions tried included aluminium and/or chromium in copper-nickels and iron or chromium in aluminium brass. However, no condenser-tube alloys of commercial significance emerged, though similar lines of development have, in more recent times, had some degree of success.

Conclusion

The main development in the understanding of condenser tube corrosion problems and the evolution of corrosion-resistant copper alloys occurred in the 34 year period from 1916 to 1950. By contrast, the next 34 years from 1950 to the present has been a period of consolidation and relatively minor change. However, towards the end of this latter period, the position of copper alloys has been challenged by titanium and special stainless steels. It remains to be seen whether the last word has yet been said on copper-alloy condenser tubes.

P T Gilbert's Paper Contribution to Discussion by Professor W O Alexander –

The state of knowledge about corrosion and failure of condenser tubes in the first decade of the 20th century is well exemplified in a case which was heard in the House of Lords in about 1908. This case had been fought through the Law Courts between Broughton Copper Co as defendants vs a marine storehouse and a Steamship Company which operated excursion steamers along the R Clyde. The argument was over a bundle of 70/30 brass tubes which had been used to retube a condenser prior to the Easter excursion season and which failed after five weeks. Because the failures revealed dezincification in plugs across the wall of the tubes, it was argued the copper and zinc had not been properly mixed in casting and making the tubes. Broughton Copper won the final appeal by arguing that if the copper and zinc had not been properly mixed it would have been extended by x660 in making the tube. This might have given long threads of copper and zinc, but plug dezincification was across the wall. Therefore the plaintiffs finally lost their case. Corrosion theory had yet to emerge to explain the phenomenon.

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Copper 5: Other copper alloys

Bill Alexander

Synopsis

Reference is made to alloys which have not been mentioned in other parts of the copper papers, these are:

Copper beryllium bronzes, the wide range of temper hardenable alloys that were examined in the inter-war years, particularly copper nickel aluminium. Other alloys developed during World War I I were copper manganese aluminium, copper lead silver, copper chromium and copper tellurium. Some reference is made to copper cadmium, its origins need study, and to copper nickel manganese alloys which were never developed commercially.

Introduction

Copper, as one of the most alloyable of all metals, has been widely exploited by mankind for thousands of years. In particular, during the last 200 years, certain well defined and specified alloys have emerged and been standardised throughout the world. During the period under review, 1900-1950, further intensive research work led to new alloys being developed and establishing themselves in the market place. These are the specific objective of this contribution with the exception of condenser and other tube alloys, although I am well aware that there are several gaps in the record.

Copper Aluminium or Aluminium Bronzes

Aluminium Bronzes

Aluminium bronzes and a range of copper base alloys containing up to about 14% of aluminium. They are noted for their exceptional strength and corrosion resistance to a wide variety of aqueous solutions and in particular sea water. Certain of these bronzes have been available for ninety years but it has only been since the equilibrium diagram and properties were methodically studied early in this century that a range of complex alloys containing additions of iron, nickel and manganese have also been produced.

In the early period difficulties were experienced due to hydrogen pickup on melting, oxide entrapment on pouring, the excessive contraction on solidification and in the higher aluminium alloys a self-annealing effect which caused brittleness.

More widespread manufacture of aluminium bronzes began in the mid twenties with the tilting table non turbulent pouring technique of PHG Durville in France. Since the early 1930s aluminium bronzes have become increasingly popular as engineers have recognised their ideal suitability for sea water service. All the conventional casting processes are used for components weighing 5 gms to 50,000 Kgms. Gravity diecastings are frequently competitive with steel forgings of complex shape. The selection fork in motor car gearboxes has been made in aluminium bronze for many years and is nominally 10% aluminium 2.5% iron. Alloys D & E containing respectively 7.5% aluminium 2.5% iron and 9.5% aluminium 2.5% iron 5% nickel and 1.5% iron are widely used as end plates in heat exchangers in the petrochemical industry and were developed in the USA as ASTM specifications. But their true origins need recording.

One interesting wrought aluminium bronze was developed for the periscope tubes of submarines for the Royal Navy in both World Wars. This alloy was Broternal, a 7% aluminium 2% manganese alloy cast in 1 tonne ingots hot pierced by back extrusion to a tube shell. It was subsequently cold drawn and annealed to a tube some 6 metres long and 20 to 28 cms diameter. Two such tubes were scarfed together to form the normal 10 metre tube. To illustrate the strength and ductility of such alloys in the wrought form the submarine 'Thetis' was lifted by its two periscope tubes. Another submarine, partly submerged, was rammed by a trawler and the periscope tube bent through a right angle without fracture.

Copper Beryllium Bronzes

The development of beryllium and beryllium alloys was due largely to work carried out by the Siemens Halske Company in the mid 1920s. Publication of their findings by Masing, Dahl, Holm and Hasse followed in 1928 and '29[1]. From this work copper beryllium bronzes emerged as having unique properties of high strength after temper hardening treatment and retaining a relatively high conductivity 17 to 23% IACS. They were from these early days used for all manner of high duty and delicate springs, particularly for electrical applications. They were also used for non-sparking tools, though very expensive. It was also somewhat idly claimed that this alloy was the long lost method of hardening bronze.

A list of additions to copper which produce some 37 temper hardenable alloys was published by M Cook in 1934[2] and

Of these only about six ever attained any industrial or commercial significance, and probably only copper beryllium and copper beryllium cobalt and copper chromium are manufactured today.

Copper Silicon or Corson Alloy

One of the other early workers in this field was M G Corson[3] (publications 1926, '27 and '30) who appears to have been the first to record the temper hardening of copper containing silicon providing nickel, cobalt, iron or chromium were present to precipitate the corresponding silicides. Some commercial alloys were marketed in the USA, but no significant production occurred in the UK, although in Germany a heat treatable alloy called Kuprodur, Cu 0.75% Ni, 0.5% Si, was developed for locomotive firebox plates, but manufacture in the UK proved difficult due to hydrogen pickup, although up to 1940 over 10,000 side plates had been made and installed in Germany.

Copper Nickel Aluminium

Temper hardenable copper alloys must not be allowed to pass without mention of the copper nickel aluminium alloys, brand named Kunial, which were discovered and researched here in Birmingham by ICI Metals Division, now IMI[4]. These alloys well exemplify the tedious and often erratic nature of metallurgical work in the middle of the period being reviewed.

Temper hardenable alloys of copper were 'in the air' and in further exploration of possibilities ICI Metals, and specifically H J Miller and F King, made a series of copper nickel aluminium alloys. These were hot worked and given elementary temper hardening treatment. By this sorting of composition and temper hardening heat treatment the alloy containing 5% nickel and 1.5% aluminium was developed as the optimum. No significant change in microstructure was evident after treatment apart from some slight recrystallisation of grain boundaries and a dullness of the surface on etching. The optimum heat treatment was half-an-hour at 900 degrees C water quenching, followed by 2 hours at 600 degrees C. This new hardenable copper alloy was exhibited at the British Industries Fair.

While there it was suggested in a discussion with Brownsden and Cook that the same hardening process might occur in a 70/30 brass with the same proportion of nickel and aluminium. Low and behold it did, but the optimum temper hardening temperature was now 2 hours at 500 degrees C. Applications for both alloys were from then on being sought without knowledge of the phase changes involved.

As a result of two years' work at Birmingham University, still without X-rays, it was found that the constituent of phase Ni Al was responsible for hardening the quarternary alloy Cu Zn Ni Al, and a completely new phase Ni_3 Al, hitherto unknown, was responsible for precipitation hardening in the ternary alloy Cu Ni Al[5,6,7,8]. Hence the difference in optimum temper hardening temperatures. As an aftermath, it should be noted for the story books that this phase Ni_3Al was one of the main hardening and creep improving constituents in Nimonic, which alloys were further improved with addition of Titanium which formed Ni_3 Ti and Ni_3 (Ti Al).

The interesting uses of Kunial Brass during World War II were initially in the locking nuts for all propeller bosses on the Bristol Hercules engine. Then later as the need for parachute harness buckles became greater for all the requirements of the Parachute Regiment and this coincided with shortages of nickel, Kunial Brass buckles were substituted for Monel metal which had been used hitherto. It was also widely used in cast and heat treated form for non-sparking tools in explosive and petrochemical factories.

Strategic Supply Problems in War Time

After the Japanese bombed Pearl Harbour and the USA entered World War II, strategic supplies to the UK of both nickel and tin, amongst other metals, was very severely restricted. This was a severe blow to British armaments effort, and intensive research work was necessary to find substitute alloys, particularly for the cupro nickels for condenser tubes, the electric resistance alloys such as Constantan and also several of the tin bronzes for non bearing applications. The condenser tubes were taken care of by reducing the nickel content and raising the iron and manganese, or switching to copper zinc aluminium brasses.

The replacement of Constantan was a trickier operation since in addition to requiring a constant temperature coefficient of resistance, it had to have a certain specific resistivity, and finally had to withstand 24 hours at 300 degrees C without change of resistance. After about five months of intensive research and type testing, production of a new alloy Kumanal was started in this city at about 1 ton/week[9]. After the War this alloy was used for under floor heating, but was found to suffer from stress corrosion cracking induced by the pvc plastic coating which was used as an insulation.

Finally, some of the tin bronzes were substituted by copper silicon alloys, which had not hitherto been exploited in the UK as castings.

Copper Cadmium

With the development of electric traction, both on railways and tramways, the use of pure copper for overhead conductors was unsatisfactory in that it was too soft and sagged in use. By the addition of 0.9% cadmium a suitable long life trolley wire was developed without lowering the conductivity to less than 80% IACS. The final strengthening was accomplished by finish rolling the rod at a low temperature about 500°C thus ensuring a very fine grained structure and enhancing the tensile strength and wear.

Copper-Lead-Silver Alloys

The use of additions of lead to base metals to improve their machineability and lubricity, in particular to bronzes and brasses, was well known and exploited before 1900. It was, and continues to be, a somewhat difficult production feat because of the high density of lead and the need to get fine particulate form of the lead phase in the matrix alloy. Furthermore, higher temperatures and greater loadings on bearings were required, particularly on the multi cylindered and highly powered aero engines used in World War II. One type of bearing developed for that period was a copper 1-2% silver 30% lead which was melted in a high frequency furnace and then poured into a flux filled steel shell canister and was rapidly solidified by water cooling inside and out. Such an alloy was used in the Bristol Hercules series engines,[10].

Copper chromium alloys have already been mentioned but it is not widely known that in the 1930s their use for cylinder heads of air cooled automobile engines was suggested and tried in the USA. Although this never matured, Bristol Aeroplane Company followed up this idea and developed a finned copper chromium cylinder head with a nickel plated face which was used on all the Hercules 14 cylinder radial engines[9], and on the subsequent Centaurus engines. The nickel plating was necessary to prevent corrosive attack by the lead tetra ethyl that was used in the fuel. Use of copper chromium instead of aluminium 'Y' alloy was an obvious weight penalty, but the much higher compression which could be obtained because of the greater cooling effect of copper resulted in the HP per cylinder being doubled from about 110 HP to 220 without altering the cylinder dimensions. Examples of such cylinder heads can be seen at RAF Cosford on a Hercules engine from a Handley Page Hermes 4. This alloy is temper hardenable, has a fine grain size, a high softening temperature and a relatively high thermal and electrical conductivity. For these reasons it is widely used as contact electrodes for spot welding.

Copper-Tellurium

The magnetron valve which was developed for radar detection of aircraft during World War II has as its base a very intricately shaped chanelling and structural support device. It had to be made of copper to give it high electrical and thermal conductivity. But copper is not an easy metal to machine and give smooth and accurate surfaces. Addition of 0.3% tellurium gave a free machining copper producing an excellent surface without unduly affecting the conductivity. Later selenium additives have been used and, more recently, sulphur[10].

Copper Nickel Manganese Alloys

These are cited to exemplify that not all research work on alloys was successful, despite apparently obtaining technical objectives. These alloys, containing anything between 10 and 20% each of nickel and manganese, remainder copper, were easy to melt cast and fabricate into strip and wire. Ideally they were made using pure nickel and electrolytic manganese which at the time was being produced in the USA. R S Dean and his colleagues[11] published the first results, and later in UK[12] additional data was published showing that greater hardnesses and higher strengths than copper beryllium could be obtained, of the order of 110 tons/sq in. Further work was also conducted in France, but so far as I know there has been no commercial exploitation.

Copper Silver Alloys

Designers of power generators became familiar with failures of the winding due to shortening in the late 1930s. This was at a time when the demand for electric power was increasing at such a rate that a large number of machines of 300MW output were being constructed. The failures were shown to be due to the copper turns being unable to expand freely as the rotor windings warmed up when the machine was put under load. This restriction caused the copper to creep under the compressed forces and the turn 'shortened', repeated cycles led to fracture. By using a 0.1% silver addition to the copper the creep strength was raised and also the softening temperature above the operating temperature and such failures were eliminated.[13]

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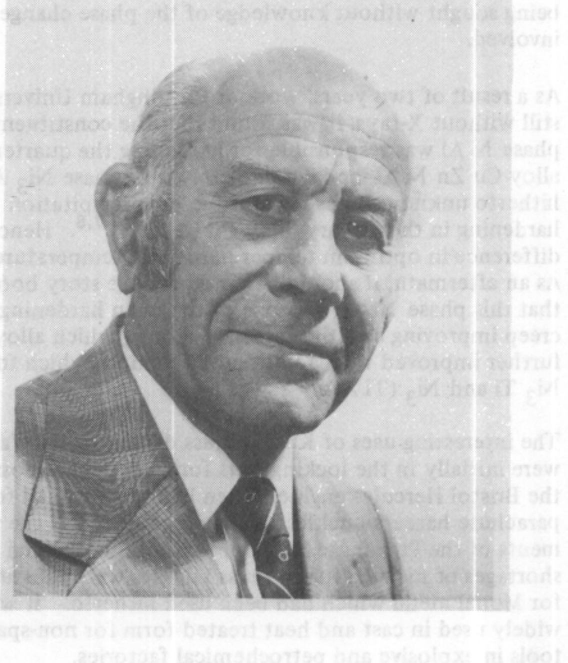

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Zinc: Zinc alloys 1900-1950

Arthur Street

Zinc is not an easy metal to produce. It occurs principally as zinc sulphide; the ore is concentrated by flotation and the zinc sulphide converted to zinc oxide. In parts of the world where electric power is cheap, the zinc oxide is dissolved in sulphuric acid and the solution of zinc sulphate so formed is electrolysed to form metallic zinc. In countries such as Britain, where electrical energy is costly, the zinc is produced from zinc oxide by smelting.

William Champion's process, invented in 1738, involved condensing the gaseous zinc in a water-container under the smelting crucible. The method was laborious and as late as 1850 it required 24 tons of coal to yield one ton of zinc. Then a more economical process was developed in Belgium, using horizontal retorts and by 1950 about half the world's zinc was produced in that way. During the 1930s the New Jersey Zinc Company in USA developed a vertical retort furnace which continued to be used till it was replaced by the invention of the blast furnace process. Works experiments had begun during the 1940s at Avonmouth but the process was not perfected till after 1950. A complex zinc – lead ore is smelted, zinc leaves the blast furnace shaft as a vapour with the furnace gases, carbon monoxide and dioxide and is shock-cooled in a lead splash container. The molten lead, containing zinc in solution, is pumped out of the condenser and cooled, so that the zinc is rejected from the solution and floats on the lead. The zinc layer is poured off the lead, which is recycled. Although this development did not come to fruition till after 1950, it has to be mentioned because, as will be seen later, the essential feature of the zinc-aluminium alloys is the need for impeccable purity; even one-thousandth of one percent of lead will contaminate this widely used alloy, yet the metal now begins its metallurgical life in the closest contact with its enemy.

During the eighteenth and the beginning of the nineteenth centuries most of the zinc produced was required for making brass and it remained the major outlet for the metal till early in the present century. Brass, however, is being discussed in another paper.

In 1742 a French chemist, Dr P J Malouin, described how a protective zinc coating could be applied to iron by dipping it in molten zinc. The process was patented in France and England in 1837 and given the name 'Galvanizing'. This Conference is considering alloys and so galvanizing can only receive a brief mention. The zinc forms an iron-zinc alloy at the interface and from 1911 onwards a small alloying addition of about 0.15% aluminium has been made to limit the formation of the iron-zinc layer to a controlled amount. This made it possible to adjust the thickness of the zinc coating more accurately than before and the zinc coating could be added without cracking or flaking.

By the time of the 1914-1918 war the world output of galvanized sheet was over 1,500,000 tons, Britain producing 800,000 and the USA about 700,000. After the war, Britain's production was reduced and did not recover to over 800,000 till 1925, a level which has not been approached in any subsequent year, owing to the development of galvanizing in other countries.

Although the standard galvanized steel sheet has a zinc coating only 0.025 mm thick, the amount of galvanized material is so enormous that the process surpasses all other uses as the greatest market for zinc.

The zinc-aluminium alloys, which are the main topic of this paper, began to be used in a small way before, during and after the First World War, and then developed very considerably before, during and after the Second World War, though even today the tonnage required for zinc alloy remains less than that required for galvanizing. These zinc alloys are used almost entirely by the diecasting industry.

Statistics on the amounts of zinc used for brass, galvanising and alloys were not produced in the early part of the 20th century but the following Table shows the amounts of zinc used in 1945 and 1950 in USA and UK.

	1945 tons	%	1950 tons	%
USA				
Total zinc used	773,000		877,000	
Galvanizing	306,000	(40)	401,000	(46)
Brass	235,000	(31)	126,000	(14)
Diecast Alloys	119,000	(15)	263,000	(30)
Other uses	113,000		87,000,	
UK				
Total zinc used	254,000		335,000	
Galvanizing	49,000	(19)	101,000	(30)
Brass	108,000	(42)	102,000	(30)
Diecast Alloys	18,000	(7)	34,000	(11)
Other uses	79,000		98,000	

The other uses include rolled zinc sheet, zinc oxide and zinc dust, including sherardizing.

It can be seen from the American figures that during the period 1945-1950 there was a considerable move to use diecast zinc alloy in place of brass castings. Also during the late 1940s there was a vast production of such parts as radiator grilles in USA and this led to the doubling of the diecast tonnage in USA from 1945 to 1950. The spectacular electro-plated grilles and other large decorative components of automobiles started to go out of favour during the 1960s and nowadays the world diecasting industry accounts for about 17% of the total zinc consumption, while brass is about 19% and galvanizing about 45%.

The zinc-aluminium alloys reach their optimum strength when rapidly chill cast so it is the pressure diecasting process as distinct from gravity diecasting (permanent moulding) that uses the major tonnage.

In the early part of this paper reference was made to lead – the enemy of zinc alloy; and it is therefore surprising that the zinc diecasting industry owed its inception to the manufacture of lead alloy printers' type-metal; several of the world's largest diecasting companies began as manufacturers of the lead-antimony-tin alloy that was used by printers until the recent coming of computerized photo-typesetting.

From Johann Gutenberg's invention of a method of producing accurate type in 1439 up till about 1820 each piece of printers' type was produced individually in hand-operated moulds. Then the increased demand for printed matter led to the design of mechanized type-casting machines; for example in 1832 William Church introduced a machine capable of operating at 20,000 letters a day. The experience with such machines encouraged enterprising manufacturers to cast simple components in alloys of lead forced into permanent metal moulds with mechanisms copied from those of the type-casting machines. In 1866 Charles Babbage used diecast lead alloy gears, cams and levers in his early computer, which can be seen at the Science Museum in South Kensington. Early in the twentieth century the automobile industry began to use diecast components, at first in lead alloys for connecting-rod bearings, but in about 1907 some diecasters, particularly in USA, began to use zinc alloys. The pure metal is not suitable for diecasting, because it dissolves ferrous metals, so it attacks steel dies and it causes a zinc-iron sludge to be formed in the melting pots. Additions of 0.5% aluminium inhibited this tendency, so that element has been present in all zinc diecasting alloys. During the 1910 decade alloys containing from 4-8% tin were cast, and later up to 3% of copper was included to increase the strength and hardness, so until the late 1920s these zinc-tin-copper-aluminium alloys were diecast in many parts of the world. They were stronger than the lead-antimony alloys, they were easy to diecast and they could be soldered, either to repair defective castings or to attach the diecastings to other components. These alloys showed no signs of deterioration in use and they were employed to make parts of washing machines, vacuum cleaners, gramophones and cash registers, as well as for an ever-increasing number of components for the rapidly growing automobile industry. During the 1914-1918 war, diecastings were used for grenade fuses and plugs. Some 'old soldiers' recall that these parts could be retrieved and melted down in tin hats, and cast, in loam moulds, to make finger rings, using a carbide barrel as the core.

Diecasters were very much concerned with fluidity and the practice of 'dosing' the molten alloy with pellets of tin or lead to make the metal run better was almost universal and accentuated the traumatic problems which occurred in the late 1920s when a zinc alloy containing 4% aluminium and 3% copper began to be used.

In spite of the primitive conditions and the scarcity of metallurgical supervision, the output of the diecasting industry included some remarkable achievements. The pioneer Herman Doehler in the USA had previously worked in the printing industry and in 1905 created a company whose name is still famous in die casting history. Fig 1 shows the design on one of his earliest machines.

Fig 2 shows the zinc alloy gear case for the pre-war model of the Hotpoint washing machine. This diecasting which weighed 13 pounds, was made by Fry's Diecastings in 1937. It will be seen that the design was quite complicated and two steel pieces to hold the electric motor were placed in the die before casting so that they became secured in the solidified metal. The casting was made on a Polak vertically operating hydraulic machine. Such machines required a great deal of maintenance – water leaks being one problem – but they provided enough pressure on the metal to ensure solidity even in such a large component.

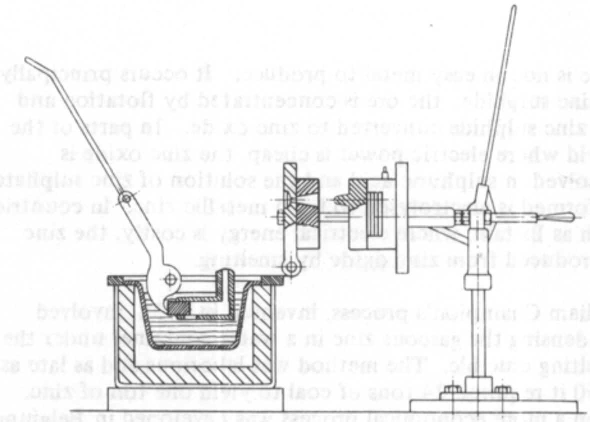

Fig 1 Early design of pressure diecasting machine made by Herman H Doehler in 1905.

The use of zinc alloy for the motor trade was a prominent feature of that period. During the late 1920s Mr C W Parkes of Josiah Parkes of Willenhall made a world tour to investigate companies supplying the rapidly growing motor trade. Eventually he contacted the Birmingham company Wilmot Breeden, who were interested in working with a lock manufacturer in the development of their motor trade business. By 1930 they had jointly developed the disc tumbler lock barrel, and they were advised to place the diecasting business with the Wolverhampton Die Casting Company. The partnership of these three Midlands firms continued for many years. During the 1930s all car manufacturers changed their internal and external door handles to zinc alloy, with the external handle including a square section steel insert that connected the internal and external handles with the door lock mechanism. During this period the lock barrel design was developed between Josiah Parkes and Wilmot Breeden, with Wolverhampton making the diecastings and soon producing many thousands of intricate lock barrels each week.

In order to improve the strength of zinc alloys still further, several compositions with up to 12% aluminium and 3% copper were tested and some of these proved suitable for casting in metal dies, producing components much stronger than those which had been made with the zinc-tin-copper-aluminium alloys. World-wide developments in the zinc alloys took place and the zinc-aluminium series was studied in detail. It was found that alloys with less than 3.8% of

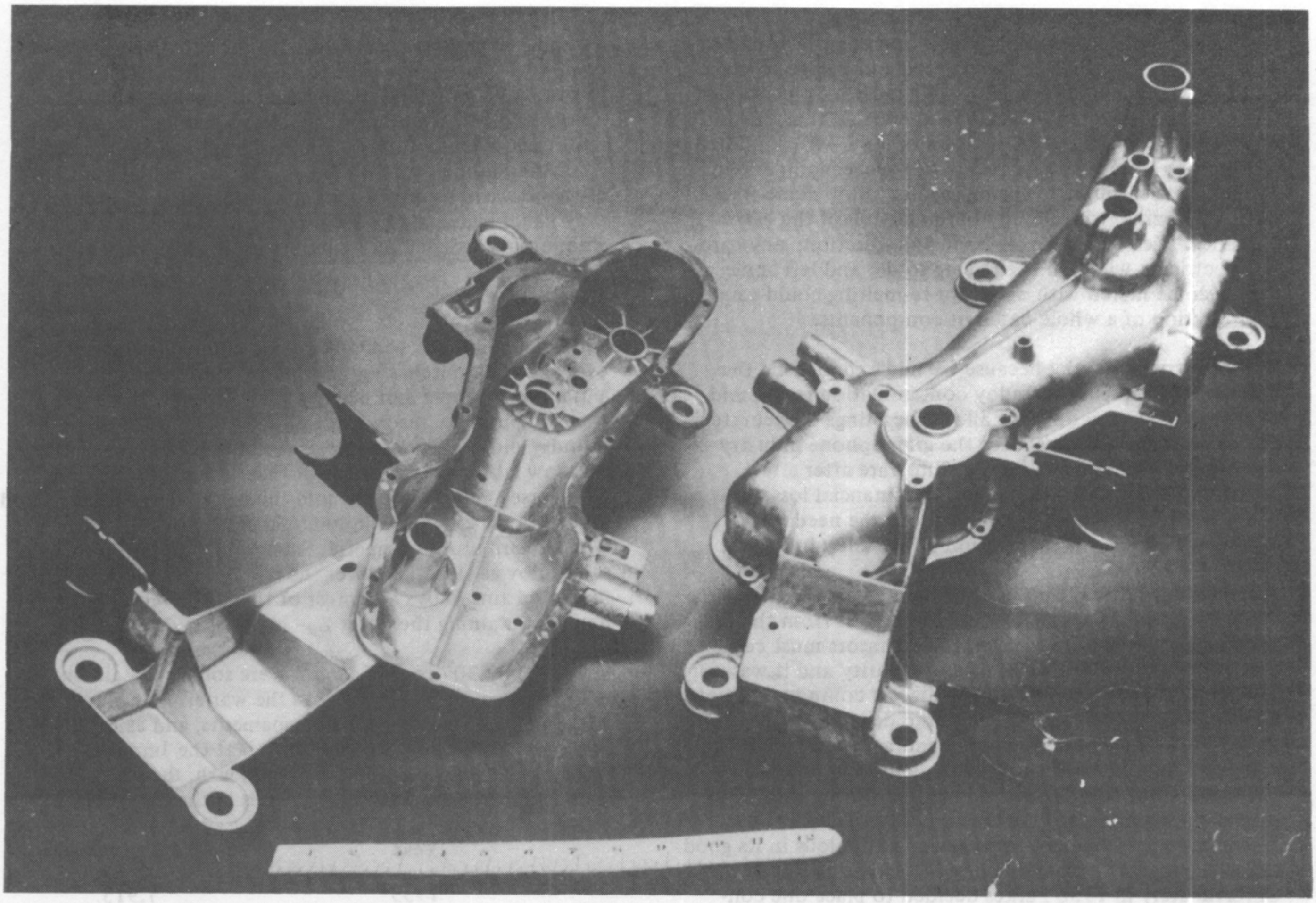

Fig 2 Gear case for Hotpoint washing-machine, produced by Fry's Diecastings Limited in 1937 as a zinc alloy pressure diecasting.

aluminium had poor castability and inferior tensile strength, while above 4.5% aluminium the impact strength of the alloy was reduced. Consequently an aluminium content of 4.0% was accepted to give optimum properties and this has continued to the present day. During the late 1920s and early 1930s additions of about 3% copper were also made. The results of using this new alloy were catastrophic.

The early thermal methods of smelting zinc yielded a metal of only about 98% purity; lead and cadmium, whose compounds occur with zinc ores, were bound to be included in the smelting of zinc. At the same time the zinc-tin alloy was being diecast satisfactorily but rather weak, diecastings in alloys of tin and lead were produced in the same premises, molten metal was being dosed with tin and lead – and the new zinc-aluminium alloy was being used, with apparently good results.

A few months after these new alloys had been made into components such as parts of gramophones, some of them began to crack and disintegrate. This was quite unexpected. Other casting alloys – iron, brass, aluminium were not unduly sensitivee to the presence of impurities and the zinc-tin alloys that had been used before, had not been detrimentally attacked.

Even in those days there was a suspicion that something unusual would occur in the zinc-aluminium alloys. In America Herman Doehler had done some experiments with zinc-aluminium compositions and guessed that they might be susceptible to the presence of lead. He had separated the production of lead castings from that of zinc in his premises and as early as 1907 one of his consultants had made the prophetic remark – 'Some day zinc producers will find a way to produce pure zinc'.

The breakthrough came in the early 1920s when H E Brauer and W M Pierce, of the New Jersey Zinc Company, began a research which culminated in a paper given to the American Institute of Mining and Metallurgy in 1923, entitled 'The effect of impurities on the oxidation and swelling of zinc-aluminium alloys'. To quote from their paper 'It is the belief of the writers that zinc-aluminium-copper alloys free from appreciable amounts of impurities will withstand long exposure to any atmosphere without appreciable loss of strength'.

Brauer and Pierce's work was followed by world-wide research. It was discovered that an addition of magnesium, up to 0.1% helped to inhibit intercrystalline corrosion but, most important, new refining processes were yielding a zinc of greater than 99.99% purity, thus removing the causes of the deterioration. When that was achieved, it became possible to reduce the magnesium content to 0.04%, thus lessening a tendency to hot-shortness that was evident with a magnesium content of 0.1%. The present zinc-aluminium alloys are still required to include 0.04% magnesium.

From the mid 1920s to mid 1930s the zinc diecasting industry gradually came to terms with the fact that if they wished to use the high strength zinc-aluminium alloys they must avoid tin and lead as if they were cholera germs. At first this was done by strict housekeeping, but many diecasting companies still had lead or tin somewhere on the premises. I can remember that in 1933 Fry's Diecasting Ltd were producing some tin alloy grids and covers for gas meters, some diecastings in the zinc-tin-copper-aluminium alloy for parts that had to be soldered and a large tonnage in the new zinc-aluminium alloy. We must have persuaded the (probably reluctant) foundry supervision that the old practise of dosing the alloy with tin or lead was prohibited and by such primitive regulations we succeeded in making parts such as carburettors using the new alloy made from 'four nines' zinc, without any deterioration of the castings in service. Yet this was a cliff-hanging situation; any careless electrician who had been using solder and left some of it to become mixed with metal for re-melting could cause deterioration of a whole batch of components.

The industry was lucky because we had experienced the dreadful consequences of alloy contamination in the mid 1920s when we saw our zinc alloy diecastings – accurate and of good surface finish, for the gramophone industry – develop cracks and sometimes disintegrate after a few months. The shock of this – and the financial losses incurred – made us hyper-sensitive about the need for scrupulous care in the segregation of the alloy in future.

It can be understood that it took many years for the whole diecasting industry to realise that, to benefit from the growing market for diecastings, the operators must come to terms with the requirements of metal purity and it was not till the 1939 war, when zinc alloy diecast components were used for armaments, that the required discipline was totally accepted. The well-known lock manufacturers Josiah Parkes & Sons Ltd, who have been helpful in providing information for this paper, told me that during the 1930s they obtained most of their zinc diecastings from the Wolverhampton company, which was scrupulous in its good housekeeping and whose components gave no trouble. Unfortunately in 1938 Parkes decided to place one contract with another company who, they realised later, had not been so disciplined. Parts of a mortice lock were made but when the war began the parts were put in store, ready for marketing after the war. To everyone's surprise the castings were found to have fallen to pieces.

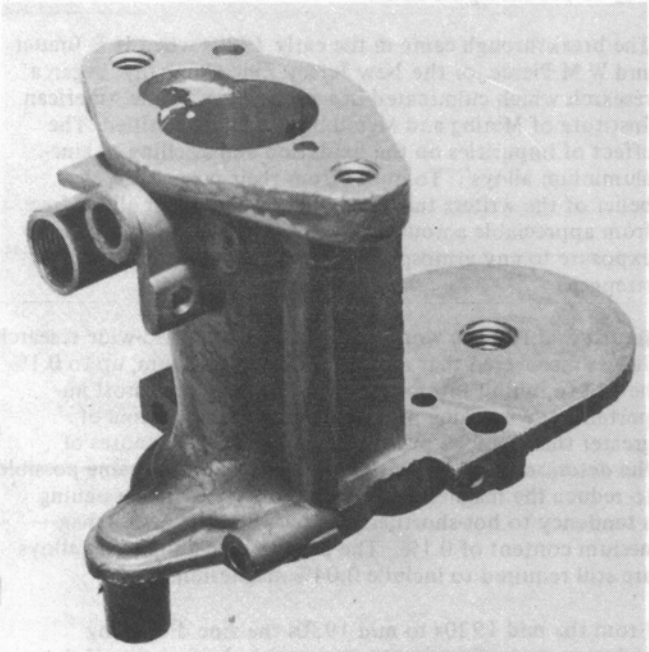

Fig 3 Diecast part of carburettor body showing the base plate and induction throat. Note the smooth surface finish, dimensional accuracy, large number of holes, intricate re-entrant angles and thin wall structures.

A similar experience occurred with the S U Carburettor company. During the 1930s zinc alloy diecast carburettors had replaced gunmetal castings and companies such as Zenith and S U were supplying Morris and Austin and other motor car manufacturers. S U had begun to use the new zinc-aluminium alloy and, like Josiah Parkes, they put some of the diecastings into stock for a long period and found they had disintegrated. Their reaction was to change to aluminium alloy diecast carburettors – which they still use.

Mazak and Zamak

Until the 1939 war, some diecasting companies made their own alloy, by purchasing 'four nines' zinc and adding aluminium, copper and magnesium. However there was a trend to purchase ready-made alloy which meant that a foundry did not have to undertake chemical analyses, using the slow laboratory methods of those days. In the USA the New Jersey Zinc Company sold the material as Zamak (based on the words zinc, aluminium, magnesium and 'Kopper'), while in Britain the Imperial Smelting Corporation sold the same alloy as 'Mazak'. After the war other manufacturers marketed zinc alloys and most of them were given brand names containing the letter Z – Norzak, Ezda, Zama etc.

In 1933 only 307 tons of Mazak were sold in Britain but by 1939 the tonnage was 7,915. As the war effort called for vastly increased production of armaments, and as Britain's zinc alloy production became centred at the Imperial Smelting Corporation plant at Avonmouth, the following years saw further substantial increases in the use of Mazak.

Year	Mazak tonnages
1939	7,915
1940	26,150
1941	38,558
1942	49,128
1943	32,614

As the war came to a close the amount of diecast components was reduced but then the post-war requirements of washing machines, domestic hardware, the motor trade and many other civilian uses caused increased consumption, so that by 1950 the tonnage of Mazak had reached the 1943 level.

Year	Mazak tonnages
1944	7,539
1945	19,073
1946	18,756
1947	32,884
1948	25,676
1949	23,997
1950	32,783

The Effect of Copper Additions

During the late 1920s and early 1930s the alloy with about 3% of copper was favoured. When this alloy was made with 'four-nines' zinc it did not suffer from intercrystalline corrosion but it was subject to a small dimensional change over a long period and when precise instrument components were required this slight shrinkage was detrimental. It was found that if the copper content was lowered or eliminated the tendency to shrinkage was much reduced and during the war years the UK and America began to use the alloy with 3.9% aluminium, 0.04% magnesium and no copper. On the Continent the favoured alloy was that with about 1.0% copper (in more recent years the copper content has been reduced to 0.75%). The alloy with 3% copper was Zamak or Mazak 2, the copper-free alloy No 3 and the alloy with 1% copper Zamak or Mazak 5. Later when British Standards were introduced in 1942, No 3 was B S1004A, and the alloy with 1% copper BS1004B.

It was found that the zinc alloy diecastings could be stabilized by a low temperature annealing treatment, either for 3-8 hours at 100°C or for 10-12 hours at 70°C. Without such treatment the copper-free alloy would have a shrinkage of the order of only 0.8mm per metre (0.0008 per inch) and that with 1% copper about 1.4mm per metre (0.0014 per inch) after 8 years. During the low temperature stabilizing treatment both alloys shrink by about 0.0002 per inch and then the dimensions remain constant.

Zinc Alloys in the 1939-1945 War

During 1937 and 1938 the War Office became interested in the possibilities of using zinc alloy diecastings for percussion fuses and other munitions. Extensive tests were conducted, principally at the Wolverhampton Die Casting Company Ltd, and it was decided to use the copper-free alloy, then entitled Mazak 3.

Early in the war, the Ministry of Supply recommended that companies purchased their alloy from the Imperial Smelting Corporation at Avonmouth. This had the advantage that supplies could be regulated and it ensured that all zinc alloy used for munitions would be based on metal of more than 99.99% purity. The supply of zinc was organised by the Non-Ferrous Metals Control. It became clear that an association was needed to link diecasting companies in order to discuss metal supply and the technical standards that were vital for the production of satisfactory munition components. Mr David Kirkwood (later Lord Kirkwood) who had been seconded from the Imperial Smelting Corporation, took the initiative and encouraged the formation of the Zinc Die Casters Association with Mr Robert Whitehead of Wolverhampton Die Casting Company as Chairman, and Mr. R L Stubbs of the Zinc Development Association as Secretary. ZADCA was formed in February 1942. Nineteen diecasting companies joined at the start and the number had increased to 30 by the end of 1942. It is still a very active association.

At first the utilization of zinc alloy diecast capacity did not go smoothly but in 1942 a delegation from ZADCA, led by Robert Whitehead, visited the Ministry of Supply. In the course of the meeting there was a general review of the properties of zinc alloy and the scope for producing munitions. Henceforth very many zinc alloy armament components were manufactured throughout Britain. Among items produced in great quantity were the 151 fuse for trench mortar bombs, a percussion fuse, the fuse and two plugs for hand grenades, the No 68 rifle grenade for anti-tank operations, the Bofors gun foresight, a large chassis for radar, several carburettors, components of periscopes and Jeep shock absorbers.

So far as I can recollect the British zinc diecasting industry was remarkably free from the effects of enemy bombing and although there were severe restrictions on the use of Mazak for commercial production the required supplies of zinc came through, mainly from Canada.

The use of zinc alloy diecastings saved many man hours and much material. For example when the percussion fuse had been made from brass, it required a great amount of machining, much of which was eliminated when zinc alloy replaced it, as will be seen from the following figures.

Component	Brass Stamping Requiring Machining	Zinc Alloy Diecasting, Requiring Little Machining
Fuse Body	2.70 lb	1.75 lb
Magazine	1.045 lb	0.188 lb
Bottom Cap	0.313 lb	0.032 lb
Total Weight	4.118 lb	1.970 lb

The radar chassis, previously made from sheet metal, required eight forming operations, twice the tool cost of the diecasting and four times as many man hours for manufacture.

Looking back on the war-time co-ordination of zinc alloy diecasters, the main efforts were concentrated on the design of components and dies and mutual assistance in overcoming production problems such as porosity. All the machines were operated manually, there was no instrumentation, very little effort to economise in the use of energy in the oil or gas-fired melting furnaces, no automation in the diecasting process, though a great deal was done in mechanization of the machining of castings. Compared with modern standards there was little attention given to operator safety, fume extraction and noise reduction. The lubrication of dies was almost entirely done by oil-based graphitic materials, applied on various parts of the die with a brush and a simple hand spray by the operator. Yet in spite of the somewhat primitive conditions the rate of output achieved by men and women operators was high and was not surpassed till the early 'seventies when automation was developed.

It will be gathered from my early remarks that the need for scrupulous care in avoiding alloy contamination took the zinc diecasting industry by surprise and probably one of the benefits – hardly realised at the time – of the co-operation through the Zinc Alloy Die Casters Association, was the emphasis on alloy purity, so that even those companies who were making components that did not require a great deal of accuracy, were made to understand that metallurgical control before and during the manufacture of castings, was essential, and must be continued after the war.

British Standard Specification BS1004 'Zinc alloys for diecasting and zinc alloy diecastings' was issued in 1942 and later a Code of Practice defined methods of production and supervision. One of the most important developments that ensured complete freedom from contaminated material was the routine for daily inspection and analysis of zinc alloy diecast production. Each day a representative sample is taken by an outside authority, and until that has been analysed and approved the total production is quarantined and cannot be released.

Plating Problems

When zinc alloy became used as a substitute for brass, it was at first electro-plated by existing methods, without taking into account the different electrochemical properties of zinc. In the early 1930s many zinc alloy diecastings were plated in the same vats that had been used for brass, without any copper undercoat, and often with only a very thin nickel deposit, sometimes only 0.0001"

(2.5 microns); when that proved unsatisfactory, the thickness was increased, but only to 0.0005" (7.5 microns). Nowadays the thickness is up to about 25 microns.

Owing to the unsatisfactory coatings thus produced, it began to be realised that special methods and solutions must be employed. At first two types of process were tried. In one, nickel was deposited from a bath of special composition with addition agents but this caused problems, because zinc accumulated in the solution, producing streaky nickel deposits. This process was soon abandoned.

Then the zinc alloy articles were given a preliminary deposit of copper from a cyanide bath, followed by a normal deposit of nickel. At first the plating was done at low current density, but the deposit tended to form blisters. With such disadvantages, zinc came to be regarded as a very special and difficult material. Some users who had purchased zinc alloy components and plated them either in their brass solutions or with one of the new methods, became quite pessimistic about the possibilities of zinc alloy. This followed the traumatic experiences which had been caused by alloy contamination. It says a great deal for the persistence of zinc alloy enthusiasts that in spite of all the early problems, zinc alloy eventually came to be accepted and widely used. Much credit for this is due to the Zinc Development Association in Britain and research departments of the various international zinc producers and to the efforts of the Birmingham plating firm W Canning.

By about 1933 it had been established that zinc alloys could be plated satisfactorily and that the way was opening towards the operation of automatic plating plants. Fig 4 shows one of the first such plants, installed by Cannings for the motor accessory company Wilmot Breeden in 1938.

There were many other obstacles to be overcome. For example it was found that when articles had been de-greased they must proceed to the next operation in a perfectly dry condition such as was obtained by the use of trichlorethylene vapour. The technique of forming the copper undercoat was an essential feature of successful plating of zinc alloy. A solution of cuprous cyanide, sodium cyanide, sodium carbonate and sodium thiosulphate was recommended. The current density was 50 amps per sq foot and the vat temperature was not less than 65°C.

The efforts to develop a satisfactory nickel plating solution continued and are well documented in papers by N R Laban, S Wernick, L Wright, F Taylor and many others from the plating industry, while research workers from the zinc manufacturers contributed. Without concluding the paper with a long catalogue of ever-improved solutions I will quote from a paper by L White and F Taylor, given to the Electrodepositors Technical Society in Birmingham on 22nd February 1933. In the course of the paper they traced the gradual changes in the plating solution in five states, the final composition being that which gave the best results.

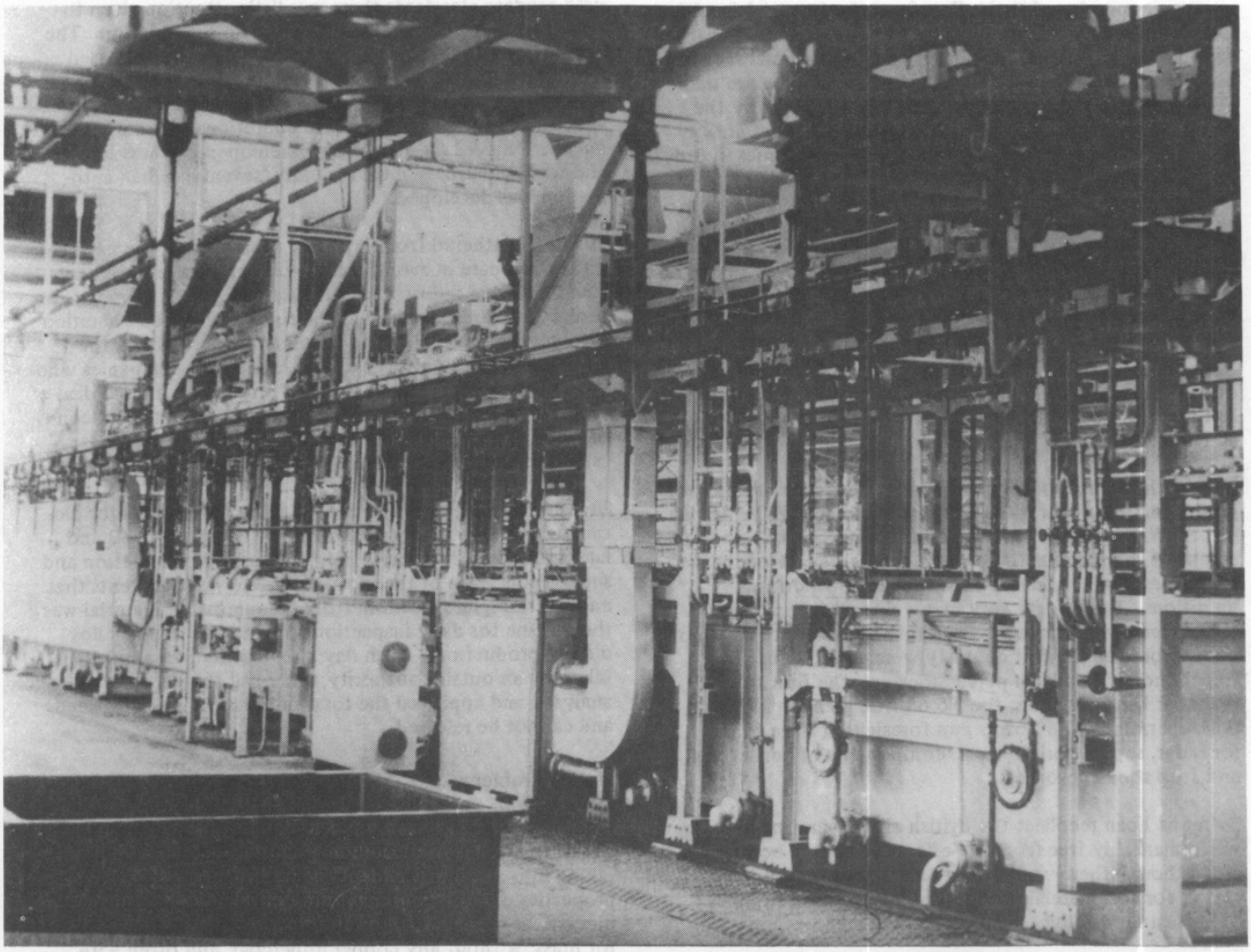

Fig 4 Automatic zinc diecastings plating plant, developed by Cannings Limited for Wilmot Breeden Limited in 1938.

	grams per litre				
Nickel sulphate $NiSO_4\ H_2O$	75	50	30	75	75
Ammonium chloride $NH_4Cl\ 6\ H_2O$	15	16	32	12	12
Sodium sulphate $NaSO_4\ 10\ H_2O$	225	250	290	200	200
Boric acid H_3BO_3	15	15	15	10	10

To provide extra hardness, a final coating of chromium was given and of course is still given. The late Sir Ernest Canning was responsible for the introduction of chromium plate to the treatment of zinc alloy diecastings.

Acknowledgments

I am grateful to Dr A Wall and Miss S Purchase of the Zinc Development Association, Mr. G Welch of Wolverhampton Die Casting Company Ltd, Mr G Johnson of Canning Materials Ltd, several members of Josiah Parkes Ltd, and Mazak Ltd, Mr J Dovey of Joseph Ash Ltd, and several friends from Fry's Diecastings Ltd.

Arthur C Street BSc PhD (B'ham) Consultant. Has been associated with Fry's Diecasting all his working life, becoming Managing Director. Co-author, with Bill Alexander, of *'Metals in the service of man'*, and a Dochler Award winner of the American Die Casting Institution.

Disintegration of Zinc die-castings

Martha Goodway

The pressure die casting of zinc is the outgrowth of several earlier developments, from the permanent mold to the Mergenthaler linotype machine. The first commercial die castings were produced from tin-base and lead-base alloys. These castings were limited in their application by their low melting points and especially their poor mechanical qualities. Zinc is stronger and has a higher melting point, and was tried next.

Zinc-alloy die castings were first produced about 1907[1]. These alloys were made up of the zinc that was available, without regard to purity. They contained from 4 to 8% tin and 3% copper. The molten zinc alloy scavenged iron in the machine, producing a zinc-iron precipitate. This could be prevented by adding about a half a percent of aluminum to the zinc alloy, but the addition of aluminum led to additional problems. The most persistent problem was swelling so severe that these die castings would warp, crack and eventually disintegrate.

A number of different alloys were developed and put into service (see Table 1) in an attempt to overcome dimensional instability, swelling and disintegration as well as hot-shortness, loss of ductility on aging, and to improve castability.

By 1914 the highest grade of zinc available was 99.0% pure, so called high grade zinc (Table 2). By 1916 the highest grade zinc was 99.4% pure. At this time alloys with aluminium contents as high as 12% were being produced, but those with about 5% aluminum were the most satisfactory. Yet these alloys were still susceptible to dimensional changes and to intergranular corrosion.

Williams[2] in 1917, was the first to shed some light on this problem. He noted that heat and humidity were necessary to produce this kind of failure and his observation became the basis for testing aluminum-zinc alloys for stability. In 1923 Brauer and Peirce[3] showed that the intergranular corrosion associated with the aluminum in zinc was stimulated by small amounts of impurities. The most powerful of these corrosion stimulators were lead, tin and cadmium. The present limits on these elements are 0.002% lead, 0.001% tin, and 0.002% cadmium. Zinc of this degree of purity was not available until special high grade zinc, 99.990% pure, came on the market at the end of 1928.

The elements which caused the problem tended to segregate at the grain boundaries where the corrosion was observed to occur. Why aluminum-zinc alloys should be so extremely susceptible to these impurities has not been explained. Apelian, Paliwal and Herrschaft[4] state that 'the governing mechanism and the interplay of various alloying elements in promoting or retarding the intergranular corrosion are not understood.'

Although additions of copper had been found somewhat helpful in controlling intergranular corrosion, it was not eliminated even with the use of special high grade zinc. However, starting in 1926 small amounts of magnesium, 0.1% or less, were being added. When magnesium was used in combination with special high grade (99.990%) zinc intergranular corrosion was eliminated. Thus, by 1929 an aluminum-zinc die casting alloy had been developed which in humid conditions was not subject to disintegration by intergranular corrosion.

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4 D Apelian, M Paliwal and D C Herrschaft, Casting with Zinc Alloys, **Journal of Metals, 33** (1981) 12-20.

5 (Table 1). Historical information supplied by the New Jersey Zinc Company, Palmerton, PA 18071, USA.

Table 1

Zinc Die Casting Alloys: Dates of Introduction[5]

Nominal Composition:

Weight % alloying elements

Date	Zinc Purity	Sn	Cu	Designation	Remarks
ca 1907	98.0	6	3	6% tin alloy	First zinc alloy for commercial die casting. Stable but weak. Castable only in simple shapes.

The addition of **aluminum** to improve castability led to intergranular (subsurface) corrosion:

Date	Zinc Purity	Sn	Al	Cu	Designation	Remarks
obsolete by 1939	98.0	6	0.4	3	ASTM Test XVIII	
"	99.90	6	0.4	3	ASTM Test XXII	
"	99.90		12	3		The 2nd commercial die-casting alloy. The high-strength alloy of its time. Service-life as low as one year. Audible cracking.
1922-1933	99.90		5	3	'5-3' alloy	3rd commercially available alloy. Cast easily. In wide commercial use.
about 1922-1933	99.90		4	3	'4-3' alloy ASTM Test XIV	4th commercially available alloy, in wide use until 1933.
ca 1930	99.99		4	3	Zamak 4	Supplied for less than a year, for use in obsolete machines.
Origin uncertain, also 1942 - 1945	99.90		0.25	5	ASTM Test XIII	Low strength, difficult to cast. Used in World War II because of aluminum shortage.

Magnesium was introduced into zinc die casting alloys to retard 'growth', the dimensional changes after casting, beginning in 1926.

Date	Zinc Purity	Al	Cu	Mg	Designation	Remarks
1926 - 1929	99.90	4	3	0.1	ASTM Test XV ZN 898 Zamak, later Zamak 1 Mazak in England	The original 'Zamak' alloy, trademark of the New Jersey Zinc Company. Lead limit 0.05%.
Obsolete by 1939	99.94	4	3	0.1	ASTM Test XVI	Tendency to hot-shortness.
Obsolete	99.90	3	3	0.3	ASTM Test XVII	Too hot short for practical use.
?	99.94	4	2	0.1 + 0.2Ni	ASTM Test XIX	Never used commercially. The anti corrosive properties of nickel useful only in the absence of copper.

Special High Grade zinc of 99.990% purity became commercially available in 1929. Marketed under the trademark 'Horse Head Special' by the New Jersey Zinc Company.

Date	Zinc Purity	Al	Cu	Mg	Designation	Remarks
1929	99.99	4	3	0.1	ASTM Test XXI Zamak 2	
1929 - 1948 (production ceased)	99.99	4	3	0.02	ASTM Test XXIa ASTM AC43A deleted 1957. New Zamak 2	Corrosion free but embrittled with age. More castable, because of less magnesium required when using purer zinc.
1929-1932	99.99	4	0	0.03	ASTM Test XXIII Original Zamak 3	Stable. Copper, which causes growth on aging, omitted. Not as easy to cast as 0.02% magnesium alloys; required new casting machines.
1930 to the present	99.99	4	0	0.02	ASTM AG 40A SAE 903 Zamak 3	The best known and most widely used zinc die casting alloy
1927-1932	99.99	4	0	0.03+ 0.2Ni	ASTM Test XXV Zamak 3N	Never marketed.
1932 to the present	99.99	4	1	0.03	ASTM Test XXV ASTM AC41A SAE 925 Zamak 5	Stable. Copper at 1% or lower causes no aging changes.
1932 - discontinued 1936	99.99	4	1.25	0	Not in ASTM Zamak 6	Expensive, but good creep resistance. Not dimensionally stable. Large tonnages cast. Suitable to certain obsolete low pressure casting machines.
1960 to the present	99.99	4	1	0.005+ 0.02 Ni	Zamak 7	Patented 1935. Castable. For thin-walled castings. Impurity limits for lead and cadmium 0.002%; for tin 0.001%.

Table 2 Grades of Slab Zinc

Primary or virgin zinc is supplied by the smelter in slabs of 40 to 60 pounds, hence it is commonly referred to as 'slab zinc'. The purity of the various grades of slab zinc that have been used in die casting is given below:

Grade	Zinc	Remarks
Prime Western	98.0	Up to 1.6% lead.
High Grade	99.0	In use by 1914.
Horse Head Zinc	99.4	Trade mark of New Jersey Zinc. In use by 1916.
Special High Grade	99.990	Commercially available 1929.

ASTM Standard B6, Standard Specification for Zinc Metal (Slab Zinc) sets the limits on lead and cadmium at 0.003/ and tin 0.001% for Special High Grade Zinc. The other grades are no longer considered suitable to aluminum-zinc die castings because the limits on these elements are not low enough. These standards do not apply to zinc produced by the 'sweating' or remelting of secondary zinc.

Aluminium 1:1900-1950

Frank King

Synopsis

The period 1900-1950 saw the aluminium industry expand production from tens of thousands of tons per annum to several millions of tons per annum.

In the early days of the industry the problem was to find outlets for the increasing output of metal from the reduction plants. Numerous alloys were developed to widen the scope of application for aluminium. In this paper the development of wrought alloys receives special attention, each of the main alloy groups being dealt with separately.

The earliest wrought products were in the form of sheet and strip, rod and tube. Extrusions assumed increasing importance, particularly in the late thirties and onwards, when there was a demand for heavy extruded aircraft spar sections in heat treatable alloys having high mechanical properties.

During and immediately after the Second World War large tonnages of wrecked aircraft material had to be reclaimed. An outlet was found by developing a series of alloys which were used for the construction of the AIROH prefabricated temporary house.

In the late forties with the contraction of the aircraft industry there was an urgent need to develop new markets. The demand was mainly for non heat treatable alloys in the form of rolled products and medium strength alloys of the Al-Mg-Si type for extruded products.

Introduction

The period covered by this paper may be termed childhood and youth of the aluminium industry. The commercial exploitation of the metal began when Hall in America and Hérault in France developed the electrolytic reduction of alumina in a fused cryolite bath in the early 1880s.

Early aluminium reduction cells were operated using prebaked carbon anodes which were suspended from steel bars connected to the bus bars supplying the electric current.

The purity of the metal tapped from the reduction cells depended not only upon the purity of the alumina and cryolite and that of the carbon anodes and pot lining but also, to an even greater extent, upon the skill and attention of the pot line operators. The anodes had to be changed before they were eroded to such an extent that the cast iron, used to join the steel bars, became exposed to the molten cryolite-alumina mixture and cause serious contamination of the aluminium.

The purity of the metal from each individual cell in a pot line would differ from that of others in the same line. By selection and blending of the hot metal from a number of cells metal having composition within fairly narrow limits was produced.

Iron and silicon are the two major natural impurities present in unalloyed aluminium. For the lower grades of purity the silicon content may be expected to be the range 0.15 to 0.35% with the iron content roughly twice that of silicon.

The importance of small amounts of silicon on the response of certain aluminium alloys to solution heat treatment and precipitation treatment was not understood until about ten years after the discovery by Wilm[1] of this phenomena reported in 1911, a subject which will be dealt with later.

In its unalloyed form the main characteristics of aluminium are its low specific gravity, good thermal and electrical conductivity, good ductility and malleability. Commercially pure aluminium has relatively low mechanical properties even after cold rolling, drawing or pressing.

To increase the demand for the metal aluminium was alloyed with other metals such as copper, zinc, magnesium, silicon, manganese and nickel.

By 1909 the output of aluminium was about 30,000 tons/yr at £50 to £100 sterling per ton. Echavari[2] writing on the subject of aluminium and some of its uses stated that on its first appearance aluminium was proposed for every imaginable purpose from armour plate to chemical chambers – adding that it was this exaggerated idea of the scope of its usefulness which in the end mitigated against its employment for the purposes for which it is most suited.

At this time aluminium alloyed with copper, zinc or nickel was employed for castings such as crank cases, gearboxes and carburettors and sheet was used for panels for cars, trams and electric trains. Other applications were as wallpaper or thin embossed sheet for ceiling panels.

Early sheet alloys were of aluminium with copper but, due to corrosion problems, only pure unalloyed aluminium was used by naval constructors for partitions for deck and chart houses.

Aluminium was, and still is used as foil for wrapping purposes, for cooking utensils, closures, screw caps and small boxes.

Aluminium-copper alloys

In a report on aluminium-copper manganese alloys containing more than 95% aluminium Rosenhain and Lansbury[3] stated that the ternary alloys were little better than aluminium copper but that the presence of manganese appeared to protect these alloys from corrosion. For castings Anderson[4] reported 92% aluminium 8% copper was the most successful alloy.

It was in 1911 that Wilm[1] announced his discovery that an alloy with up to 4% copper and up to 1% magnesium may have its properties materially changed by heat treatment.

Some ten years elapsed before an explanation of this hardening was forthcoming from the work of Marie L Gayler[5,6] who demonstrated the role of silicon and of the precipitation of the compounds Mg_2Si and $CuAl_2$.

It is of interest to note that, shortly before Wilm published his results, attention was drawn at the Research Department Woolwich[7], to age hardening in a light aluminium alloy containing about 10% zinc, a little copper and a small amount of magnesium. The discovery was accidental. The accuracy of some hardness tests was doubted: they were repeated, and it was found that the hardness was increasing with lapse of time. Further investigations showed that whilst the binary alloys of aluminium with copper, zinc or magnesium showed no appreciable age hardening, the ternary alloys, aluminium copper magnesium; and aluminium zinc magnesium, showed rapid and intense age hardening. In some cases, the hardness doubled in a comparatively short time after suitable quenching. No explanation was offered as to why the discovery was not exploited.

Aluminium — Copper — Manganese — Magnesium Alloys

In a 1918 review of industrial aluminium alloys it was stated that the heat treatable 3.5 - 5.5% copper, 0.5% magnesium, 0.5% manganese, exceeded in strength all other aluminium alloys.

The increase in copper content, compared with that of up to 4% quoted by Wilm, was one of the stages in the development of a series of alloys over the next twenty-five years which would give even higher mechanical properties. Increasing the copper content to 4.5% and the magnesium to 1.5%, manganese 0.75% with low iron and silicon gave an alloy which after heat treatment, quenching and natural ageing had an appreciably higher yield strength than that of other naturally ageing alloys.

Another series of alloys was developed which after solution treatment at temperatures such as 510 degrees plus or minus 5 degrees C followed by quenching responded to ageing at ambient temperature but developed optimum tensile properties on ageing at temperatures of 160-200 degrees C. An early version of this type had a composition 3.65% copper, 0.8% manganese, 0.8% silicon, 0.4% magnesium, 0.8% iron. A stronger alloy was obtained by increasing the copper content to 4.2%. Yet another alloy giving similar properties had a composition of 3.8% copper, 0.85% manganese, 1.3% silicon, 0.65% magnesium, 0.3% iron.

By way of contrast a 2.3% copper 0.35% magnesium alloy was developed as having medium strength and good ductility in the heat treated and naturally aged condition. This combination of properties rendered it suitable for the manufacture of rivets which could be supplied ready for use without the need for further treatment. Rivets of heat treatable alloys of higher strength require to be stored under refrigerated conditions immediately after heat treatment to inhibit natural ageing until the completion of closure of the rivets.

Aluminium — Manganese Alloy

The binary aluminium 1.5% manganese was being used mainly for sheet rolling and die castings in 1919[8]. A slightly more dilute version, 1.25% manganese has continued to be used as a sheet alloy right up to the present day. Having very good formability it is used for cooking utensils, for panels and for corrugated sheet.

Up until the early 1940s the normal method for casting sheet mill ingots of this alloy was by pouring into large cast iron tilt moulds. With the introduction of the Direct Chill or Semi-Continuous method of casting the higher cooling rates resulted in more manganese being retained in solid solution. Using the same heating, hot and cold rolling and annealing practices as those used for tilt mould ingots gave rise to coarse grain problems which were solved by the adoption of special homogenisation treatments at high temperatures.

Aluminium Nickel Alloys

In discussion of a paper on the binary alloys of aluminium with copper and nickel[9] it was stated that the nett result of the investigation was to show that alloys of aluminium and nickel were of no practical use and might be dismissed absolutely and entirely for most practical purposes. In reply one of the authors suggested that interesting results, similar to those obtained by the addition of magnesium to aluminium copper alloys might be obtained by the same addition to aluminium nickel alloys. Whilst this idea did not prove to be quite correct investigation of nickel additions was not abandoned.

As a result of a search by the National Physical Laboratory for a light alloy which would retain its strength at comparatively high temperatures 'Y' alloy[10], composed of 4% copper 2% nickel 1.5% magnesium, the balance being aluminium, was developed. The alloy develops high mechanical properties after solution heat treatment at temperatures of 500-520 degrees C followed by quenching in boiling water. In the cast form the alloy was used mainly for pistons. Forged 'Y' alloy connecting rods have been used, working directly on hardened steel gudgeon pins and crank pins without the use of special bearing metal linings.

Aluminium — Silicon Alloys

Aluminium alloys having silicon contents in the range 5% and up to 12%, as in the cast and wrought forms, have low tensile properties of the same order as those of commercially pure aluminium.

In binary alloys silicon has the desirable effect of improving the fluidity of the molten metal, enhancing castability and at the same time reducing the melting point. Small amounts of sodium, residual from the reduction process, or introduced via a suitable salt flux or as metallic sodium has the effect of modifying the eutectic structure of 12% silicon alloy giving a structure free from coarse crystallites of primary silicon.

The silicon series of alloys have found useful application for castings where thin sections of large area or abrupt changes in section rather than high strength is of prime importance.

In the 30s a limited amount of 5% and 12% silicon alloy sheet was used for panelling by the Admirality on account of good corrosion resistance. The alloys can be jointed by welding but it is only in the period since the Second World War that the low melting point of the 12% silicon alloy has been exploited as the cladding on an alloy of higher melting point for the production of brazing quality composite sheet used as intercoolers in the aircraft industry and as large heat exchangers in liquid gas manufacture.

Aluminium - Silicon — Copper — Nickel — Magnesium Alloy

For the Bristol Hercules aero engine, used in large numbers during the Second World War, an alloy was required which was light, capable of being forged, having good mechanical properties at elevated temperatures, and having good wearing properties and a low coefficient of linear expansion.

Furthermore it was essential that the alloy should have good machining characteristics.

The alloy selected had a nominal composition of 12% silicon, 1% copper, 1% nickel, 1% magnesium and less than 1% iron. To meet the machining requirements it was essential that the alloy should be free from large platelets of primary silicon which would rapidly damage cutting tools.

All went well so long as the ingots for extrusion and forgings were made from remelt ingot pre-alloyed from pot room metal at the reduction plant. With the imminent threat of war this supply of material was cut off. The first attempts to make the alloy from commercially pure aluminium, with the addition of the silicon in the form of a 20% aluminium silicon alloy, resulted in failure, even though additions of metallic sodium were made in an attempt to modify the silicon distribution.

Casting of 11 inch diameter hollow ingots for extrusion was by the newly introduced Direct Chill casting process. As casting proceeded large amounts of primary silicon separated out in the molten head of the solidifying ingot and floated to the surface to form a thick crust which broke periodically to form deep folds in the skin of the ingot. Many of these defects were too deep to be removed by machining and the ingots were rejected.

The problem was serious and had to be solved within a matter of weeks in order to maintain deliveries. The solution lay in changing from metallic sodium to salt fluxes and by making the silicon addition in the form of a modified 12% silicon hardener, which was available, together with the minimum amount of 20% silicon hardener required to make adjustments for the copper, nickel and magnesium additions.

Aluminium Magnesium Alloys

The oldest established alloy of the aluminium-magnesium series was Birmabright having a nominal composition of 3.6% magnesium 0.5% manganese. This alloy was used both for castings and wrought products such as sheet and extrusions. It was used for the construction of sea going vessels, hull plates, frames as well as for deck and interior fittings. An alloy having a higher magnesium content of 4.5% and manganese 0.3% is now employed to meet Lloyds Requirements for marine applications.

Alloys having magnesium contents of up to 7.5% have been developed for wrought products. These alloys depend upon cold working for the development of medium to high tensile strength. Strain hardened aluminium magnesium alloys containing 4.5% or more magnesium are susceptible to stress corrosion after prolonged ageing at ambient temperature. For a given high magnesium level it is better to increase the manganese content than to strain harden to increase mechanical strength.

The binary alloys of aluminium magnesium contents in excess of 2% tend to be unstable, additions of manganese or chromium or a combination of these two elements are used to improve stability and improve stress corrosion resistance. Additions of up to about 1% zinc has also been claimed to promote precipitation within grains and reduce grain boundary precipitation.

Noncoralium having 1.35% magnesium 1.1% zinc 0.45% bismuth was developed as having good corrosion resistance and medium strength. The difficulty in disposing of process scrap containing bismuth and zinc must have been contributory to the failure of this alloy to be accepted.

The casting alloy 10% magnesium was used for heavy castings for the undercarriage of the Lancaster aeroplane and gave good service in this application. Tests on this cast alloy showed it to have considerably less resistance to stress corrosion. Material solution heat treated and quenched in hot oil and then subject to a low temperature treatment, to simulate tropical conditions, gave the lowest resistance to stress corrosion.

The addition of manganese and chromium to the alloy did not retard the progress of ageing and over a period of several years the tensile properties increased whilst elongation values and Izod values fell. Thus it was found that an alloy and treatment which had been found adequate for the short term service anticipated in wartime was not satisfactory for peacetime requirements.

The 10% magnesium casting alloy provides an example of the way in which developments in the composition of one product can have side effects on others.

In order to reduce the amount of oxidation during melting and casting and to improve the surface finish of castings it was found advantageous to make additions of a few hundredths to a few thousandths of one per cent of beryllium to the 10% magnesium alloy. From time to time quantities of the 10% magnesium were used in melts for wrought products such as sheet, extrusions and wire. Even when diluted in this way the presence of beryllium was effective in improving ingot surfaces. However, when it became known that beryllium presents a health hazard, particularly if fumes are inhaled, steps were taken to limit the use of this addition and for products such as welding wire the specification limit is set at 0.008% maximum.

Aluminium – Magnesium – Silicon Alloys

For applications where medium strength was required heat treatable alloys of aluminium-magnesium-silicon were developed. In general these can be solution heat treated at higher temperatures than the copper bearing alloys, and they develop optimum mechanical properties after precipitation treatment at temperatures of 160-180 degrees C. These alloys have found particular application for extruded sections since they can be extruded at higher speeds than the high copper alloys and can be treated to give higher mechanical properties than the binary alloys aluminium manganese, aluminium silicon, or even aluminium 2% magnesium.

Three main types of this series of alloys existed during the 30s – these were a) 0.5% magnesium 0.5% silicon, b) 0.6% magnesium 1% silicon, c) 0.3% copper 0.6% silicon 0.9% magnesium.

By a combination of extrusion or bar mill rolling followed by solution heat treatment, cold drawing and precipitation treatment the 0.5% magnesium 0.5% silicon type alloy gives good mechanical properties combined with electrical conductivity values of about 10% lower than that of pure aluminium and has been used for electric power lines.

The composition of the 0.5% magnesium 0.5% silicon type alloy can be modified by minor adjustments to the magnesium and silicon contents to alter the level of tensile properties attainable and to improve the extrusion characteristics.

The 0.5% magnesium 1% silicon alloy yields higher mechanical properties than the lower silicon alloy (a). However it was found that under certain fabricating conditions the alloy could be rendered notch sensitive. The basic alloy was modified by the addition of 0.75% manganese which improved the notch toughness of the alloy which is used for engineering purposes requiring medium strength.

The third group of aluminium-magnesium silicon alloys has properties in the medium strength range and has good corrosion resistance. The alloy has been used for marine applications in the form of plate, sheet and extruded sections.

Aluminium – Zinc Alloys

Rosenhain and Archbutt[11] in 1912 claimed that an alloy of aluminium containing 25% zinc, 3% copper, gave hot rolled bar having properties of 30 tons/sq in and 17% elongation. No application was quoted for this rod but some seven years later Anderson[4] stated that the alloy was well known for casting purposes, adding that binary alloys of aluminium zinc and aluminium nickel were being replaced by ternary alloys containing copper.

The Germans[12] used pressed pistons of aluminium-zinc alloy for aeronautical engines during the 1914-18 war. The choice of alloy was governed by the fact that it avoided the use of copper which was commandeered for other applications.

Aluminium – Zinc – Magnesium – Copper Alloys

In spite of the fact that the age hardening properties of the aluminium-zinc-magnesium-copper alloys were disclosed by Moore[7] during discussion of Gayler's paper in 1921 very little appears to have been made of this series of alloys until the late 30s. With the entry of the Japanese into the Second World War it was learned alloys of this type were being used for the construction of fighter aircraft.

Initially two alloys were introduced in this country, one having a nominal 5.5% zinc content, the other having 7% zinc, both having additions of magnesium, copper, manganese, titanium and/or chromium. These alloys were used primarily for extruded sections for aircraft construction. The 5.5% zinc alloy was also used in small quantities for the production of clad sheet.

For a given zinc content the level of tensile properties depends upon the magnesium content, the higher the magnesium the stronger the alloy. A range of 2 to 2.5% was adopted as a nominal for both the 5.5% and 7% alloys. It was observed that if the total of zinc plus magnesium exceeded 10% the elongation values were adversely affected.. Silicon contents were kept as low as possible because in excess of 0.35% this element reduces the tensile properties attainable. To improve forgeability copper contents of the order of 0.5% were employed, but for the extruded structural sections higher copper contents of 1.35% and 1.75% were typical for the 5.5% and 7% zinc alloys respectively improving tensile properties but decreasing extrudability. Chromium additions were of the order of 0.15% and titanium 0.05% whilst manganese contents were either in the range 0.15 to 0.25% or 0.35 to 0.50%.

In Germany[13], where there were restrictions on the use of copper, alloys having 4.2 to 4.8% zinc, 2.9 to 3.5% magnesium, 0.3 to 0.7% manganese, up to 0.5% copper, 0.1 to 0.2% chromium. One variant of the alloy having a vanadium addition of 0.05 to 0.1% was used for tapered spars forged direct from as cast ingots.

In the form of heat treated and precipitation treated wire the 7% zinc alloy was used for the manufacture of small mandrels for the expansion of Schobert tubular rivets. To ensure that the mandrels snapped off at the pre-formed notch, after having expanded the rivet, the tensile properties were controlled within plus minus 1.5 tons/sq in of a nominal value.

Free-machining Alloys

Aluminium alloy rolled rod is reported to have been used before 1917 for fuse cones for shrapnel shells but, because of the amount of swarf produced this was abandoned in favour of castings by a compression method.

Most heat treated high strength alloys may be machined to give a fine machined surface. However, the swarf produced tends to be in the form of long spiral turnings which cause problems on automatic machines.

A good machining alloy is one which gives a good machined surface and whose swarf breaks into short chips making for ease of removal. For chip breaking characteristics the alloy requires coarse constituents of intermetallic compounds. These may be of low melting such as produced by alloying with lead and bismuth having a composition 5% copper 0.5% each of manganese, magnesium, lead and bismuth. An example of an alloy having hard brittle constituents would be 3% copper 0.6% magnesium 0.15% tin 0.6% antimony. Both types were used extensively during the Second World War.

Reclaimed Aircraft Scrap

The reclamation of metal from aircraft wrecked during the 1939-1945 war reached such proportions that special factories were built to deal with this material.

Obviously it was not possible to strip the wreckage down and segregate it according to alloy group. A rough sorting into wrought and cast material was relatively simple. The sorting of ferrous and non-ferrous components was not quite so simple, particularly when nuts and bolts and stainless steel was involved.

Furnaces were designed with large ledges onto which the wreckage was charged. As the aluminium melted it ran down into the bath of the furnace whilst the iron components remained on the ledge until raked out before charging the next batch of wreckage.

Some batches of sheet ingots made from melts including an appreciable amount of the reclaimed metal cracked badly on hot rolling. This was traced to lead contamination. It is understood that lead was used for balancing light alloy airscrews and this was a source of contamination. It should be remembered that it was not until the later years of the war that spectrographic methods for the quantitative analysis of aluminium alloys were adopted as routine simplifying the detection of impurities.

Before the end of hostilities the aluminium industry and the aircraft industry looked around for an outlet for the metal and production facilities which would no longer be required for aircraft construction. They came up with the idea of the AIROH prefabricated house which was to provide a temporary replacement for the property destroyed during the blitz.

The alloy to be used for the construction of the framework and cladding of the house was based on that of the reclaimed aircraft scrap. Alclad sheet used for cladding the house had a nominal composition of 4% copper 0.7% iron 0.7% silicon 0.7% manganese 0.5% magnesium. For the extruded sections a more dilute alloy was obtained by the addition of between 20 and 30% aluminium pig ingot to give a copper content of about 3%. By this means the through-put of the extrusion presses was increased by about 20%. At the time it was stated that this increase did not offset the extra cost of the pig ingot but it did increase turnover and provided many economic and attractive residences for long after the ten years life for which they were designed. In fact some exist forty years after they were erected.

Conclusions

Aluminium, in its commercially pure form, has a number of desirable properties such as low specific gravity, good thermal and electrical conductivity and good corrosion resistance but has low mechanical properties. To widen the scope of useful application for this metal it is necessary to alloy it with other metals such as copper, manganese and magnesium. In the early days of the period 1900-1950 claims made for some binary and ternary alloys were thought to be very extravagant.

The development of alloys which respond to solution heat treatment yielded material having enhanced tensile properties coupled with good ductility and opened up the possibility of being able to use aluminium alloys for structural applications, duralumin type alloys being used for airships before being used for aeroplanes.

The production of rolled rod has been limited to a comparatively narrow range of alloys for machining bar and for drawing down to wire for the production of rivets. By far the greatest tonnage of bar mill stock has been Electrical Grade Conductor rod for drawing to wire and stranding to make cables for electrical power distribution.

In the form of foil, sheet and plate, alloys have been developed for such diverse applications as packaging, bottle closures, canning, panels for buildings and for transport, corrugated sheeting and for superstructures for ocean going vessels.

Alloys developed for extrusion purposes cover the range from commercially pure aluminium for simple mouldings, through the medium strength aluminium-magnesium-silicon alloys for applications such as window frames to high strength alloys of the Al-Cu-Mg-Mn-Si and Al-Zn-Mg-Cu types for heavy aircraft spar sections.

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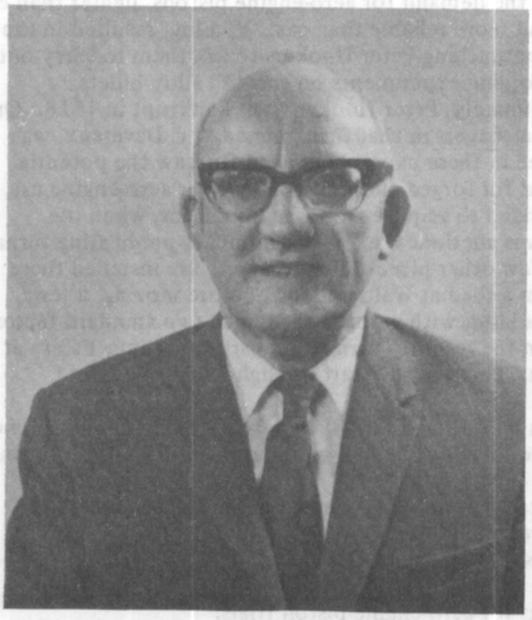

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Aluminium 2: Hiduminium and RR Aluminium alloys up to 1950

William Doyle

Synopsis

With some exceptions the wrought, as distinct from the cast, Hiduminium – RR alloys owe their origin to the classical research work on aluminium alloys at the NPL during the First World War. The founding of High Duty Alloys Ltd in 1928 led to a technical liaison between this firm and the major aero-engine and aircraft companies, which resulted in the development of a series of wrought and cast aluminium alloys designed to meet the specific requirements of designers and manufacturers in these particular fields.

Introduction

The interest in the development of the strong alloys of aluminium commenced with the discovery in 1909 by Wilm in Germany of the age-hardenable alloy known as Duralumin. This led to the classical research and development work on aluminium alloys during the First World War at the NPL under Dr Rosenhain, who designated the more promising of his alloys by letters of the alphabet. We are particularly concerned with the alloys designated 'Y' and 'E'.

Duralumin, in the cast condition, was not very useful as an alloy suitable for elevated temperature service, such as in aero-engine pistons, but 'Y' alloy showed much better potential for this kind of application.. An important manufacturer of aero-engines in the First World War was a firm called Peter Hooker at Walthamstow and this company built Hispano- Suiza engines under licence. In the mid-1920s, the demand for aero-engine pistons, lighter than cast iron and more reliable than cast 'Y' alloy, resulted in the NPL approaching Peter Hookers to ask them to carry out some forging experiments on cast 'Y' alloy billets. Unfortunately, Peter Hooker went bankrupt in 1928. One of the managers in that firm, named W C Devereux, was involved in these experiments and foresaw the potential demand for forged aluminium alloys for aero-engine use. He decided to acquire from the liquidator, when the plant was auctioned, a 5 cwt hammer, a pre-heating furnace and a few other pieces of equipment. He installed these items in a shed at Walthamstow, before moving, a few months later, with a dozen men, into two standard factory bays on the recently formed industrial Trading Estate at Slough. This was the start of High Duty Alloys Ltd.

Dev, as he was familiarly called, was a brilliant entrepreneur and salesman, but he had considerable difficulty in raising capital for his infant firm. He eventually acquired two separate amounts of money from Sir John Siddeley of Armstrong Siddeley, Coventry, on the collateral strength of the share capital of HDA Ltd. Rolls Royce did not supply any money but promised to use his experimental forgings for aero-engine piston trials.

All the development of forged alloys was carried out by HDA and by means of a special commercial agreement, Devereux acquired the very valuable privilege, from a sales angle, of using the 'RR' trade mark as a suffix to his own trade mark 'Hiduminium'. I propose to deal only with the alloys developed for aero-engine and aircraft applications. HDA organised regular technical liaison meetings with the major firms in these fields and, as a result of the full and frank discussion of their requirements, the advances in the higher strength aluminium alloys during the years 1930 to 1950 were outstanding and the aero-engine and air-frame industries took full advantage of these materials.

Wrought Alloys for Aero-Engines

'Y' alloy was not only difficult to cast by the technique available at that time, but it was also difficult to forge. By somewhat empirical methods, such as reducing the copper and nickel contents of 'Y' alloy by 50 per cent and the magnesium content by 30 per cent, a composition was arrived at, which enabled sound billets to be produced by the chill casting procedure and the resulting alloy was very much easier to forge than 'Y' alloy. This alloy was designated Hiduminium – RR 56 and before the last war, it was extensively used for forged aero-engine pistons. Its good forgeability also enabled it to be used for complicated drop-stampings and pressings. One particular application was in the manufacture of connecting rods in, for example, De Havilland Gypsy aero-engines and engines in Scammell Guy and Leyland heavy vehicles. Great care was needed in the machining to avoid sharp notches and prevent trouble arising from fatigue failure.

In the mid-1930s, in order to increase his international prestige, Mussolini, the Fascist Dictator, decided to send a flight of Italian fighter planes by stages across the Atlantic to America. The flight commander was Marshal Balbo and when he landed in England, the story is told that he was met by Mr Devereux, who persuaded Balbo that he could not possibly fly safely across the Atlantic with cast engine pistons. In a few days, HDA forged and machined a complete set of replacement pistons in Hiduminium – RR56, which were presented to the Marshal, who happily continued on his flight.

The alloy development programme virtually became one of refining the composition to develop specific properties. The demand for improved mechanical properties at temperatures up to 250°C led to the development and introduction of Hiduminium – RR 59, which had very much better elevated temperature properties than Hiduminium – RR 56. Very many millions of forged aero-engine pistons were made in Hiduminium – RR 59 during the Second World War.

Whittle Engine Impellers

The need to develop a creep resistant aluminium base forging alloy, capable of operating in the range 200 – 250°C received its impetus from the development of the gas-turbine engine in the late 1930s and early 1940s. The first stage of the work involved extensive research into the isolation of the compositional and other factors responsible for good creep resistance in a forged alloy and which had the other very necessary mechanical properties for service under the operating conditions. The second stage necessitated research into and the development of the detailed process control and heat-treatment variables to ensure the optimum useful balance in all the important properties.

The forgings for the very early designs of compressor units for the Whittle gas-turbine engine were made in the best alloys available at that time, namely, Hiduminium – RR 56 or Hiduminium – RR 59. These were not entirely satisfactory and it soon became apparent that increased power, efficiency and service life required an improved wrought aluminium alloy which was capable of retaining good tensile, creep-resisting and fatigue properties at temperatures of the order of 200 – 250°C. The early impellers were made from chill cast ingots. This technique involved the metal being poured into a thin steel chill mould, which was cooled from the bottom upwards by a carefully calibrated flow of water. Considerable experience had been obtained in the production of these ingots and the product set a standard as regards fineness of grain size and distribution of constituents on which it was very difficult to improve by methods available at that time.

A preliminary alloy development programme had given some indication that an alloy broadly based on the Al-Cu-Mg-Fe-Ni-Si alloy Hiduminium – RR 59, but with a much lower and controlled silicon content, possessed attractive elevated temperature tensile and creep resistant properties.

Semi-Continuous Casting

It was not possible, however, to cast consistently sound billets under production conditions in this type of alloy by the old chill casting technique, or in book-mould dies. At the same time, we were successfully developing the semi-continuous casting process and this new technique enabled the production of sound large diameter ingots in a low-silicon type of Hiduminium – RR 59 alloy to be made. A very extensive alloy development programme was, therefore, initiated to determine the optimum composition, heat-treatment and processing details for this alloy, which was finally designated Hiduminium – RR 58. Under the conditions existing at that time, all research connected with gas-turbine engines was classified by the Ministry of Aircraft Production as 'Secret'. The first forged impellers made in this alloy were fitted to the Whittle engine in the Gloster Meteor Mark 1, which first flew in 1943.

This extensive programme of investigations took several years to complete. Thousands of tons of the alloy have since given highly satisfactory service in the form of forged gas-turbine engine impellers, spacer rings, compressor blades, pistons and structural forgings. Subsequent to 1950, the alloy in the form of forgings, extrusions, sheet and plate was chosen, quite independently of one another, by both the British and French Air Ministries, as the structural material for the supersonic transport aircraft 'Concorde'.

Some mention must be made of the profound effects of the development and introduction of the semi-continuous or direct chill casting process which, in our case, was in the early 1940s, on the quality of aluminium alloy billets and rolling slabs. This casting process set entirely new and higher standards of quality and soundness and the technique had far-reaching effects on improving the service and dependability of highly stressed and vital aircraft and other important parts in aluminium base alloys.

Alloys for Radial Aero-Engines

During the last war, many hundreds of thousands of forged cylinder barrels for Bristol air cooled radial engines were made in Hiduminium S12 (subsequently designated 08). This 11.0% silicon alloy, containing in addition 1.0% each of copper, magnesium and nickel, was developed specifically for this purpose to take advantage of its low coefficient of thermal expansion in order to provide the necessary dimensional stability. Due to the sharp edges left at the base of the cooling fins after machining, there was a tendency for some of these barrels to fail in fatigue near the exhaust port-holes. I remember the Managing Director of Bristol Engines, the late Sir Roy Fedden, telling me that if we did not improve the fatigue resistance, we would be responsible for losing the war. This heavy responsibility caused us to initiate a high priority alloy development programme which resulted in a much improved alloy, at least under laboratory test conditions, and which was designated Hiduminium S103.

We subsequently learned, however, that no advantage could be taken of this development because of the effect on wartime economy of having to write off the thousands of tons of Hiduminium S12 which were under manufacturing processes in the various HDA factories, in the Bristol Engine factories, shadow factories and in sub-contractors' premises. Bristol eventually solved the problem by improving their machining technique, which had been tentatively suggested in the first place.

Hiduminium – RR 57 is a higher purity Al-Cu-Mn alloy, which was developed for service in the range 250 – 350°C. The pistons in the air cooled radial type Bristol aero-engines ran very hot in the centre of the crown and in the immediate post-war period, Hiduminium – RR 57 was used extensively for forged Bristol engine pistons and for some compressor blades. This alloy has a low proof stress to ultimate ratio of approximately 60%, after quenching in water from 532°C and ageing at 215°C. In this condition of heat-treatment, the alloy is free from both stress-corrosion and intercrystalline corrosion susceptibility and it possesses very low levels of residual stress, even in thick sections. This allows full machining to be carried out in the fully heat-treated condition. Advantage is taken of this property in the manufacture of windscreen frames, where the limitation in tensile strength at ordinary temperatures is outweighed by the stability on machining.

Structural Alloys

The original 'E' alloy, developed at the NPL during the pioneer work under Dr Rosenhain in the First World War was an Al-Zn-Mg-Cu alloy containing approximately 20% Zn and having an ultimate tensile strength of about 40 tons per sq in in the forged and heat-treated condition. This alloy gave promise of a light alloy for structural purposes having a strength greater than that of the Duralumin type alloys, except that it suffered from a great susceptibility to stress-corrosion, even under normal atmospheric conditions. A joint investigation by High Duty Alloys and Rolls Royce resulted in the first version of Hiduminium – RR 77 being marketed in 1937. The alloy had a typical 0.1% proof stress of 28 to 33 tons per sq in and an ultimate tensile strength of 33 to 38 tons per sq in and 7 to 12% elongation. This level of mechanical properties gave rise to great optimism for the future use of aluminium alloys for structural purposes. The early version of the alloy contained a small nickel addition, which was later found to be not at all helpful in improving resistance to stress-cracking. A systematic examination of the factors affecting the stress-corrosion resistance was not undertaken until the early years of the Second World War when the need for a high strength structural light alloy assumed great importance. The development work proceeded in the newly-built Research Laboratories of HDA in Slough and by 1943 the nominal composition of this alloy was fixed at 5.5% Zn, 2.8% Mg, 0.5% Mn and 0.4% Cu, which composition has remained virtually unaltered to the present day. Since its introduction, many thousands of tons of this alloy in the form of small and large forged structural components as well as sheet, strip extruded bars and sections have given excellent service in both military and civil aircraft.

Contemporary development work in the United States[1] resulted in the introduction, in late 1943, of the alloy known as 75 S which contained similar amounts of zinc and magnesium to Hiduminium – RR77 but the nominal copper content was 1.6% and a proportion of the manganese was replaced by chromium. The claim was made that the presence of chromium improved the stress-corrosion resistance. The alloy designated Hiduminium 78 contained alloying elements in the same amounts as those in Hiduminium – RR77, except that the manganese content was reduced to 0.15% and a similar amount of chromium added. The necessity to minimise internal stress in large forgings caused a very extensive programme of investigation into quenching conditions following solution heat-treatment. These two versions of high strength forging alloys require different procedures in heat-treatment and machining to develop optimum properties. The chromium bearing alloy is quench-sensitive in thick-section components and, therefore, pre-machining is required to reduce the section thickness in order to obtain adequate quenching in cold water from the solution treatment temperature. This treatment, in turn, gives rise to high levels of residual stress On the other hand, the chromium-free alloy, Hiduminium – RR77, can be quenched in boiling water, which results in lower thermal gradients and consequent reduction in residual-stress levels. By 1950, boiling water quenching was standard procedure for large forgings in Hiduminium – RR77 which was, and is, used extensively for aircraft structural parts, where the high strength/weight ratio may be utilised, such as main frame members, spar-forgings and under-carriage components.

Considerable research was undertaken to investigate and improve the stress-corrosion susceptibility of these high strength alloys. Specific heat-treatments were developed, involving for example, a step-quench into molten salt, which is only applicable to the chromium-free alloy, but I am tending to stray across into a time zone later than 1950 which is the cut-off date of this conference.

SAP

Although we cannot claim the original invention leading to Hiduminium 100 (SAP) – sintered aluminium powder, at least we were the cause of initiating a considerable interest and research into dispersion strengthened powder products in other metals. SAP was a most interesting development by Alusuisse in the field of powder metallurgy in the late 1940s. The excellent corrosion resistance and remarkable properties of this material at elevated temperatures, including stability and recovery of original full properties after prolonged soaking and return to normal temperatures, resulted in High Duty Alloys acquiring the sole licence for the manufacture and development of SAP in the British Commonwealth. Despite considerable development work by HDA and great hopes for it as a compressor blade material, Hiduminium 100 was not used extensively primarily, I suggest, because it appeared on the scene at the same time as the post-war introduction of titanium and its alloys.

In the 1947 reorganisation of the production facilities of HDA, the forging and stamping activities were concentrated at the Redditch factory which had been designed and built in 1939.

Cast Alloys

This paper would not be complete without some consideration of the particular Hiduminium casting alloys which were developed for sand and die-cast engine components. The most popular general purpose casting alloy for service up to 200°C in the 1930s and 40s was undoubtedly Hiduminium – RR50 which was originally developed by Rolls Royce and High Duty Alloys for the cylinder blocks and crankcases for the Schneider Trophy engines, after repeated failures with other types of alloy. Incidentally, about 290 lbs weight of machined Hiduminium – RR50 castings were used on components in the Rolls Royce Phantom III car chassis.

The Alloy contained a nominal 1.1% Cu, 2.4% Si, 1.0% Fe, 0.9% Ni and a controlled magnesium content of about 0.13%. It was used for complicated stressed castings such as water-cooled cylinder heads, cylinder blocks, sumps, etc. The standard heat-treatment for this alloy was a single low temperature ageing and stabilizing treatment at 170°C which obviated any internal stress and risk of cracking or distortion as a result of heat-treatment.

The casting alloy Hiduminium – RR53b was developed for use at elevated temperatures, but it had no ductility. It was used in the 1930s for some pistons and in the aero-engine industry for air-cooled cylinder heads. Hiduminium – RR53c was a modified form of this alloy for general castings, where high strength was required at temperatures up to about 150°C and where the design allowed for a double heat-treatment at 530°C, quenching in water and ageing at 170°C.

In the late 1940s, an extensive alloy development programme, based in the Al – 5% Cu system, resulted in the eventual introduction of Hiduminium – RR350 for sand castings for use in engines up to about 350°C. This alloy, which was a very complex one, containing additions of 1.5% Ni and controlled small amounts of Mn, Sb, Co and Zr eventually supplanted the 53b alloy because of its exceptional elevated temperature properties. We were very anxious that all our customers for the 53b alloy should be fully aware of the superior hot-strength of the new Hiduminium – RR350. We had one customer, however, who persisted in ordering regularly small quantities of a component in Hiduminium – RR53b, despite visits by sales representatives and letters extolling the virtues of the newer alloy. Eventually we sent the Sand Foundry Manager to persuade the customer to appreciate the benefits accruing from the higher elevated temperature properties of Hiduminium – RR350. On his return, we were surprised to learn that the customer was not in the slightest bit interested in the elevated temperature properties. He required the 53b alloy in his components because of its excellent machinability on automatic lathes.

Concluding Remarks

The technical literature rarely mentions the long and arduous time consuming work involved in the development of an alloy for a particular sophisticated requirement, plus the time necessary for mechanical and other testing to accumulate the design data and knowledge of properties, that must be determined, before the alloy is accepted by the design engineer in all its wrought forms.

The spectacular engineering achievements in the aero-engine and aircraft industries, which took place in the twenty years prior to 1950, have tended to over-shadow the less obviously outstanding, but important developments, in aluminium alloys which enabled them to be realised. The designers and manufacturers made very stringent demands on our range of Hiduminium – RR alloys, the use of which undoubtedly contributed a great deal to their success.

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William M Doyle BSc (Liverpool) PhD retired as Technical Director of High Duty Alloys Limited after a lifetime in the aluminium and magnesium casting and forging industry.

Aluminium 3: The early history of alloys

Mac Young

Industrial progress throughout the world has always been identified with man's increasing knowledge about metals, their chracteristics, and how these may be improved or altered to meet more demanding engineering requirements.

Aluminium is a relative newcomer among the structural metals, being only 130 years old. However, it came of age quickly during the last 55 years in a period when many metallurgical tools – the optical and later the electron microscopes, X-rays, and the diffraction camera – were being developed, and when a scientific approach was being applied to alloy designing in contrast to the empirical methods used at the beginning. From many of these early studies made on aluminium, there came discoveries which opened the door to an even broader metallurgical understanding of the principles of alloying, thermal treatments, and their effects on corrosion resistance, which findings, when applied to other metal systems contributed to their further improvement. And so it is with all scientific investigations – one discovery leads to another, and man moves a step further towards a fuller understanding of the marvels of this universe.

One is apt to look with particular pride on the scientific accomplishments of our present generation and to forget the men who laid the foundations, doing so without the benefit of the scientific instruments and text books which we have today.

The history of aluminium began in 1825 when Oerstead, the Danish physicist and chemist, reduced aluminium chloride with potassium amalgam and 'obtained a lump of metal the lustre and colour of tin'. Commercial production, however, did not begin until after 1854 when Sainte-Claire Deville, the noted French scientist, produced several hundred pounds of the metal using as a reducing agent the much cheaper metal sodium.

Accounts of early uses first mention a jewelry article, a baby rattle fashioned in 1856 for the infant Prince Imperial of France; then refer to the important military applications – helmets, spurs, sword handles and sabre sheaths – for it was the Emperor Napoleon III who was the industry's first financial backer. An application less well-known was the fine wire used to replace the silver which was worked into lace and embroidered banners. Surgeons of the day used aluminium suture wire, and one M Charriere in 1857 fitted a patient with a small aluminium tube following a tracheotomy operation. The result was most successful; the tube did not blacken or corrode as a silver one would have done. Optical instruments of all types – field glasses, sextants, surveyors' and portable astronomical instruments – were all being made from this new metal, an indication of its rapid adoption by craftsmen of those days attracted by aluminium's light weight, pleasing colour and corrosion resistance. One very farsighted observation made at this time was that if the problem of aerial flight were ever to be solved, aluminium would be the chief agent in its solution. This was said at least 40 years before Orville Wright's successful trip in the first heavier than air machine, the 'Kittyhawk'.

The analysis of several museum pieces of these early aluminium products show the metal to be what we would today call a 'low purity' aluminium, about 97% to 98%, the principle impurities being iron and silicon in substantial and varying quantities. These articles were undoubtedly produced from the sodium reduced aluminium chloride process of Sainte-Claire Deville, and were made between 1854 and 1886 – the period of the chemical aluminium industry.

The first published account of the attempts to alloy aluminium with other metals, to improve strength, is given in Henry Sainte-Claire Deville's book 'Aluminium – Its Properties, Fabrication and Applications' which was published in 1859 – 27 years before the present electrolytic method of reduction had been discovered and put into commercial use. Although it was even then regarded as a jewelry material, all of the metal made during this period was not cast or formed in the purity as produced, for investigations had started to determine the properties of alloys, and the studies begun in Deville's laboratory mark the real beginning of aluminium metallurgical research.

The earliest record of a commercial aluminium alloy is described by Deville. It was produced by the goldsmith Christophle and contained 2% copper, for casting into artistic articles of large size which required engraving.

If salt fluxes were used when remelting in clay or glass crucibles, silica was reduced and contaminated the aluminium and there were thus 'born by chance' a series of aluminium-silicon alloys which were found to be very brittle – especially those with very high amounts. It was in a 10% alloy that crystallized silicon was first observed by Deville.

Other metals which were added to aluminium and their behaviour noted were: boron, which was found to reduce ductility; lead, which could be alloyed only with difficulty; zinc and tin, which affected properties adversely, as did silver which destroyed malleability although this was not too serious at 2 - 5% silver and was accompanied by appreciable hardening. With cadmium there resulted a series of very malleable compositions. (In the light of future experience these observations especially that relating to zinc, are of particular interest.)

Before leaving the work of these early investigators, it is of interest to find recorded by Deville another significant experiment in which probably the first aluminium clad product was made by Savard and described by him as a veneer. Sheets of aluminium with a copper or brass core were tightly clamped between two iron plates, heated, and then heavily squeezed at that temperature. Adhesion of the plates was so complete that the composite pack could be rolled down into sheet. While such a product does not appear to have received any significant commercial attention except as a means of making non-tarnishing ornamental ware, the method was of interest as a means of extending the use of this costly yet attractive new metal and did demonstrate the possibilities of making other clad products. This was in the year 1854 – about 74 years before the first aluminium alloy clad product was marketed.

The real commercial beginning for aluminium – the start of the present electro-chemical industry – was in 1886, when Hall in America and Herault in France made their simultaneous discovery of the present electrolytic process for the commercial production of aluminium. The price, dropping from $17.00 to $2.00 a pound provided a real incentive to finding new uses for this light metal, and to developing alloys with improved mechanical properties and better casting or working characteristics.

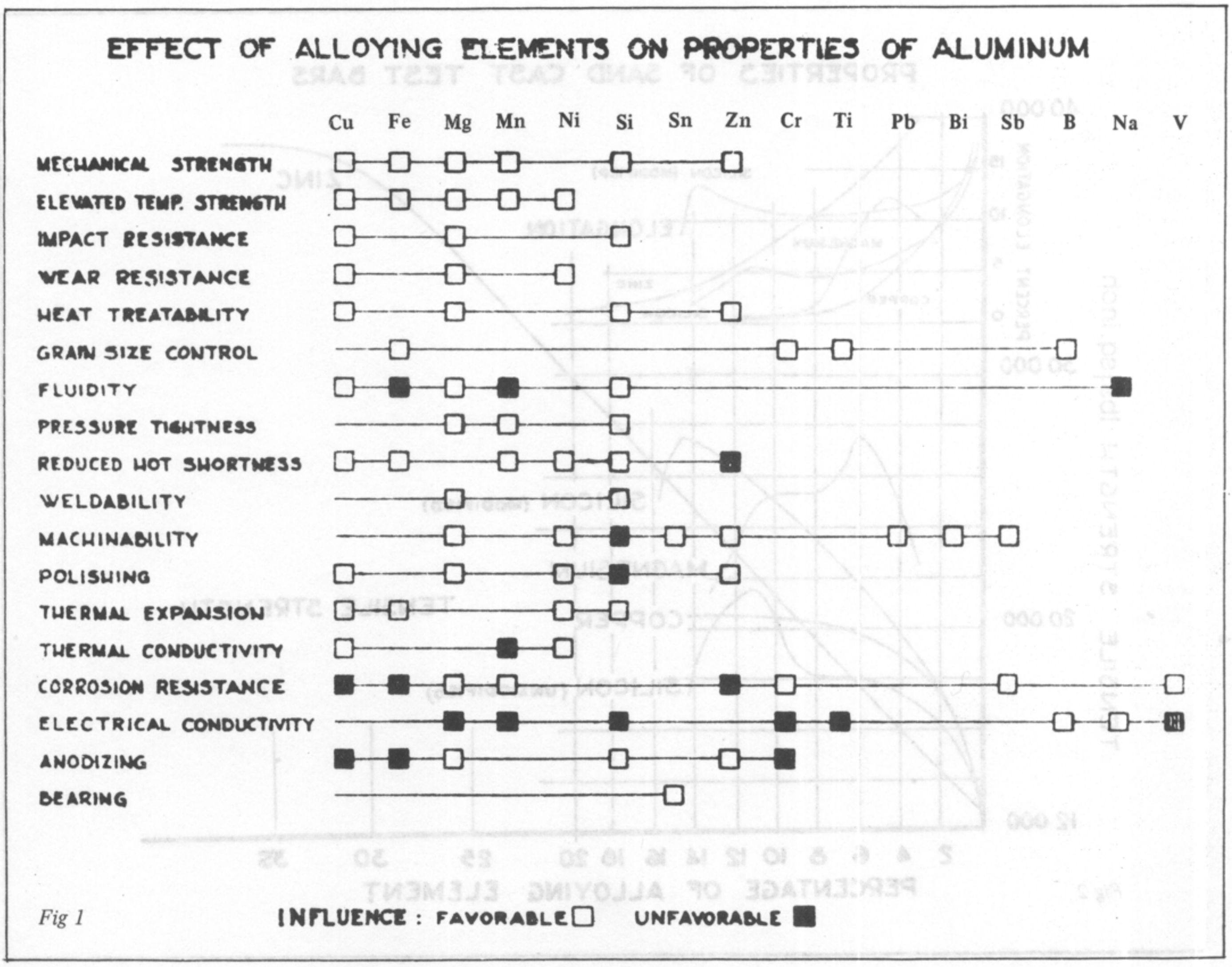
Historically, it would be of interest to retrace the footsteps of progress and, in all parts of the world, to follow the work of hundreds of investigators, for many nationalities have made their individual contributions to our present knowledge about alloying. Such retrospect is of course not possible, and even metallurgical records are not readily available, but some of the story can be pieced together from a review of the earliest patents, manufacturers' literature, and by noting the type of alloys offered for sale in various countries.

Since aluminium alloys readily with most of the common metals, it is quite understandable why numerous and varied were the combinations tried, and marketed too, with many exaggerated claims. In this period, just before and after 1900, 'cut and try' was the method of approach and practical performance the means of assessing the results.

Let us first summarize our present day knowledge of alloying element effects, then as we consider the history of commercial alloy development we may better understand the metallurgical reasons for the many, at first empirically evolved, and later scientifically developed, alloy compositions.

In Figure 1 are shown the principal alloying elements and their influence on the chemical, mechanical and physical properties which are of particular interest when evaluating the usefulness of an alloy. It is difficult to generalize in such a table for, while one element may enhance certain properties if alone, in the presence of others with their complex formation of constituents these properties may be somewhat altered.

From this tabulation we see that copper, magnesium, silicon and zinc all contribute to improved mechanical properties with or without heat treatment. Those elements such as iron, manganese and particularly nickel, which form highly insoluble constituents, are of great value in compositions for elevated temperature applications. Grain refiners are those elements which form high melting point, insoluble constituents in the molten aluminium to provide nucleii during solidification. Copper, magnesium and silicon improve fluidity, and hot shortness on freezing is considerably reduced by additions of copper, iron, manganese, nickel and silicon. It should be noted that zinc adversely affects this property. The coefficient of thermal expansion,



EFFECT OF ALLOYING ELEMENTS ON PROPERTIES OF ALUMINUM

	Cu	Fe	Mg	Mn	Ni	Si	Sn	Zn	Cr	Ti	Pb	Bi	Sb	B	Na	V
MECHANICAL STRENGTH	□	□	□	□		□		□								
ELEVATED TEMP. STRENGTH	□	□	□	□	□											
IMPACT RESISTANCE	□		□			□										
WEAR RESISTANCE	□		□		□											
HEAT TREATABILITY	□		□			□		□								
GRAIN SIZE CONTROL		□							□	□				□		
FLUIDITY	□	■	□	■		□									■	
PRESSURE TIGHTNESS			□	□		□										
REDUCED HOT SHORTNESS	□	□		□	□	□		■								
WELDABILITY			□			□										
MACHINABILITY			□		□	■	□	□			□	□	□			
POLISHING	□		□		□	■		□								
THERMAL EXPANSION	□	□			□	□										
THERMAL CONDUCTIVITY	□			■	□											
CORROSION RESISTANCE	■	■	□	□				■	□				□			□
ELECTRICAL CONDUCTIVITY			■	■		■			■	■				□	□	■
ANODIZING	■	■	□			□		□	■							
BEARING							□									

Fig 1 INFLUENCE : FAVORABLE □ UNFAVORABLE ■

which is an important property in alloys for internal combustion engines, may be reduced with copper, iron, nickel and, particularly, silicon.

It is difficult to deal chronologically with alloy development, but, since casting alloys were the first to come into commercial use, let us consider their introduction, remembering that throughout most of this same period fabrication of the alloys into sheet, extrusions, wire and forgings was also paralleling foundry work. Thus, wrought alloy compositions begin to appear in the tabulations of the alloy families; often they differ only slightly from casting compositions, the changes being necessary to make them amenable to hot and cold working.

To the foundryman of the 1900s who was experienced in casting brass and bronze, the use of tin, zinc and copper as alloying additions for aluminium was a natural choice. Tin was not used extensively, although there is recorded the use of a 15% tin alloy for horseshoes sometime prior to 1894. The results from recent work of the effects on mechanical properties with additions of zinc, copper, silicon and magnesium are shown in Figure 2 for non heat treated alloys. At once it becomes apparent why compositions up to 35% zinc were of such commercial interest. One such alloy, Alzinc, containing 33% of this element, was used extensively by Zeiss for binoculars and camera cases. Such alloys were, of course, much heavier than aluminium, were difficult to cast, being hot short, and many of the products distorted and even cracked on standing. France learned about the instability of these alloys when coins sent to their colonies began to deteriorate, through self annealing and stress corrosion failure. In Germany and England, particularly, we find that alloys of 8 to 10% zinc soon become the standard. The British later improved castibility of these zinc alloys with copper additions, and their L5 alloy became the general purpose aluminium casting alloy in England, used many years for aircraft and vehicle components. Even today there is recognized and used a General Engineering Specification based on 13.5% zinc and 3.5% copper.

Some binary aluminium-zinc compositions were cast in the United States, but to a very limited extent, for the aluminium-copper alloys which also made their debut in this same period showed greater promise of possessing a combination of favourable foundry characteristics coupled with good mechanical strength and greater stability. A systematic study showed that, with increasing copper additions, mechanical strength improved though accompanied by the usual loss in ductility, with a logical compromise being at 8%. This alloy, later to be known as No 12, became the real cornerstone of the aluminium casting industry in America. Variations in composition followed, see Figure 3, when it was found that the addition of zinc aided machinability and silicon improved fluidity. Thus there came into

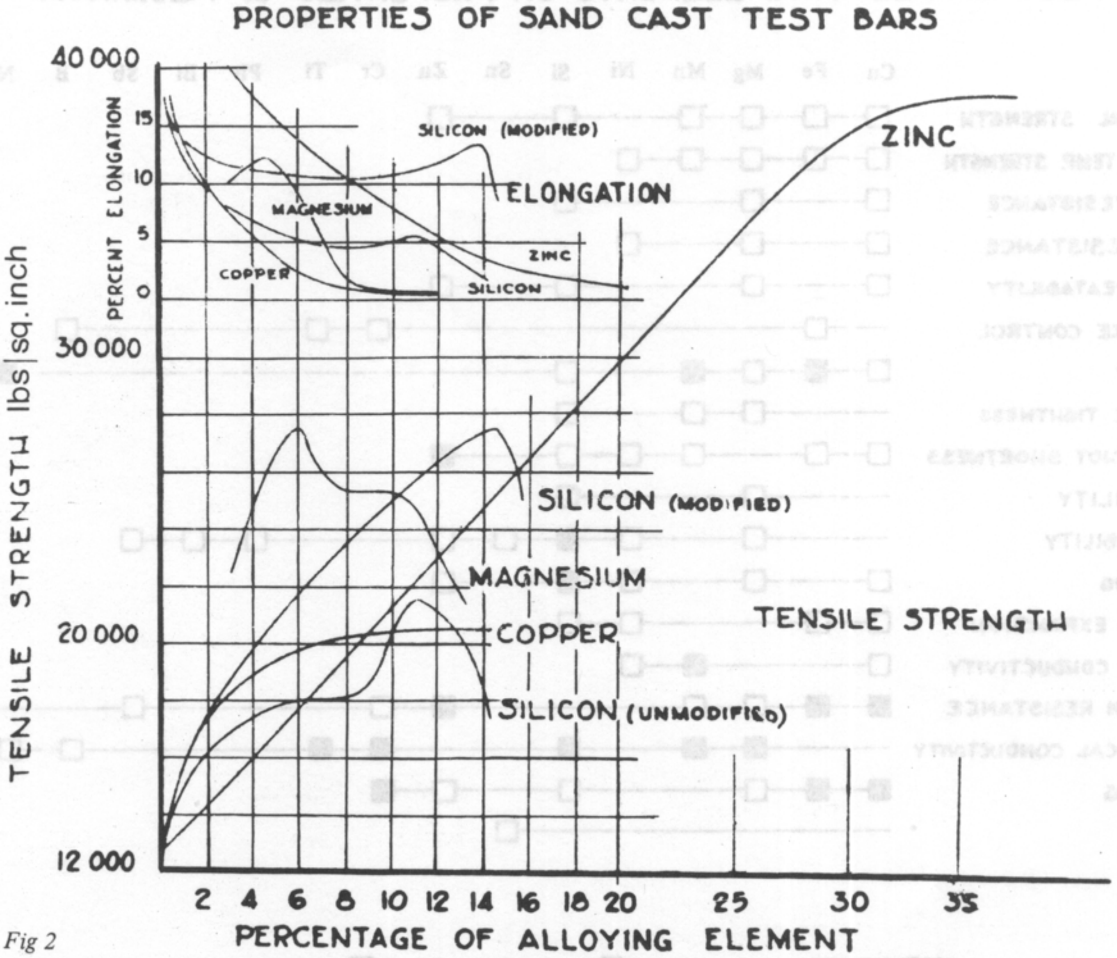


Fig 2

being alloys 112 and 113, and, still later, 212, when iron was observed as minimising hot short cracking if present in an amount less than 1.5%. The British too, began to employ two copper alloys, one at 7%, the other at 12% copper. The latter was used principally for pistons where the somewhat lower ductility is of lesser consequence and the benefit was additional strength but more particularly better wearing characteristics due to an abundance of hard $CuAl_2$ distributed throughout the soft aluminium matrix. These alloys were not heat treated, nor was the similar American alloy 122 for the very good reason that, in those days, hardening by thermal treatments was an unknown metallurgical process for aluminium.

It was in 1909, while investigating for the Prussian Government the use of rolled aluminium for cartridge cases, that Alfred Wilm discovered that an alloy containing 4.5% copper with 0.5% each of magnesium and manganese would harden after an ageing period of several days at room temperature following a quench from an elevated temperature. This alloy 'Duralumin' (named after his company, Durener Metallwerke, and the metal aluminium) opened a new era in aluminium technology.

From Duralumin came a variety of similar alloys in all parts of the world, represented first in America by 17 S. Variations made to this composition by reducing the amount of copper produced A17S (Alcan 16 S), a softer alloy, more suitable for driven rivets. Still later an increase in magnesium content was tried, resulting in 24 S the principal aircraft sheet alloy of the last war.

It was more than seven years later that Giulini, in Germany, the first to work with magnesium silicide as the hardening constituent, observed following solution heat treatment and quenching, that still further hardening could be induced by an elevated temperature or artificial ageing process.

Following this discovery of two stage heat treatment, 25S alloy was introduced in America. Without magnesium, it depended entirely on $CuAl_2$ for hardening. As it could be forged more readily than 17S it was used extensively for propeller blades. A further controlled composition, also of this type, was developed still later – the high strength alloy 14S (Alcan 26S), also employed for forging, and from which most aircraft framing has been extruded.

In our lifetime we have seen it proven many times over – that wars bring about unprecedented scientific discoveries. This is particularly true of aluminium alloys which have been so vital to the progress of the aircraft industry, as was predicted years before, but the many strong alloys born of two World Wars have, nevertheless, greatly benefited man in a multitude of peacetime uses.

The year 1920 marked another important date in casting

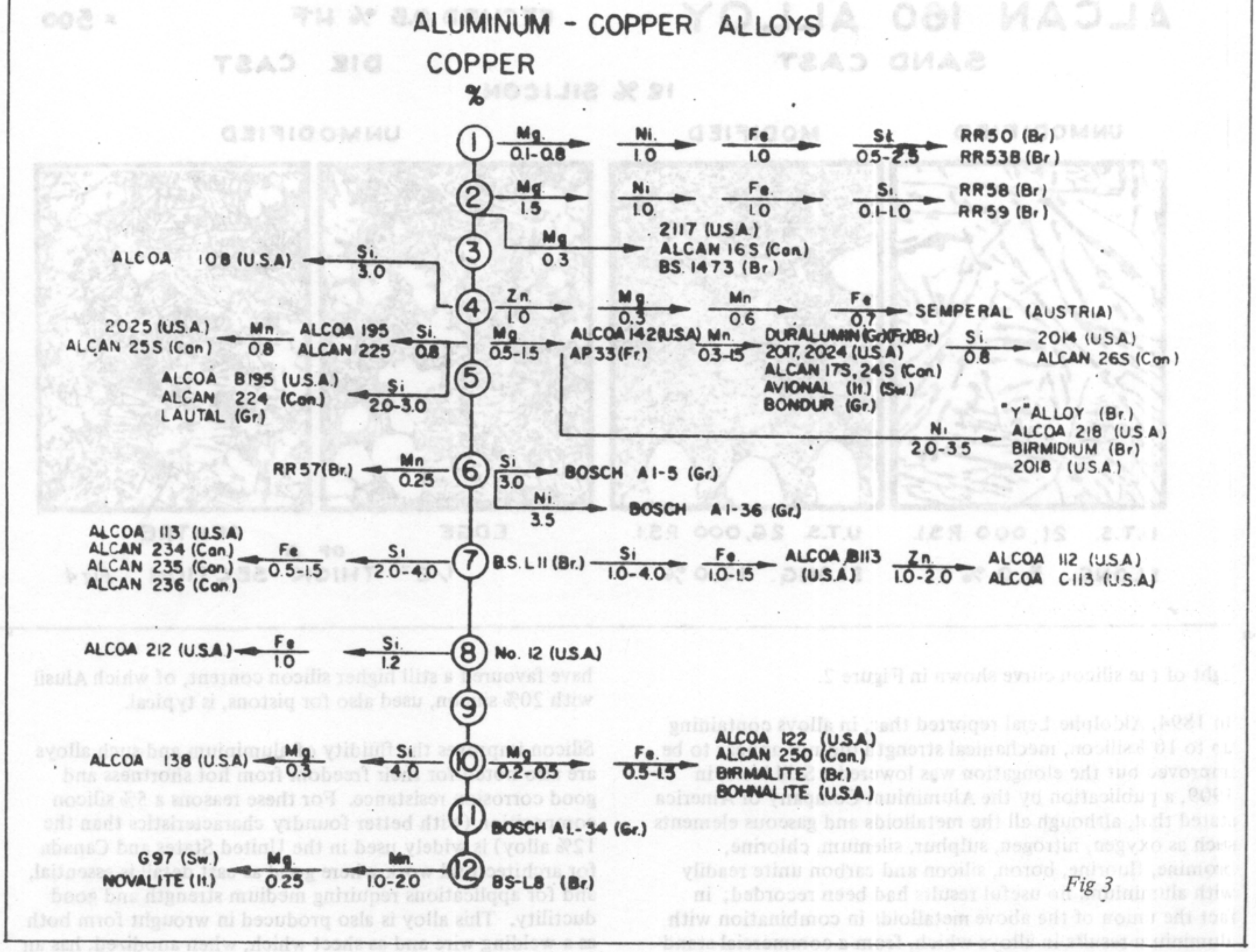


Fig 3

alloy development when Alcoa announced their alloy 195, a heat treatable composition. They had learned that the reason for failure of earlier attempts to realize high properties by thermally treating a sand cast Duralumin type alloy was because of the coarse particle size of the soluble constituents, which did not dissolve as rapidly into the coarser grains of a cast structure as did the finer and more highly dispersed particles in a wrought structure. When given a sufficiently long solution heat treatment period, properties greatly in excess of as cast values were obtained.

About this same time, an intensive investigation at the National Physics Laboratory in England was undertaken to find an alloy for engine castings which would have better elevated temperature properties. By replacing some of the copper in the 3L11 alloy with nickel and adding magnesium there was introduced 'Y alloy' which has since provided the basis of a number of special alloys of the Rolls Royce series – RR50, 53B, 58, 59. These alloys are now being used for castings and forgings of British and Canadian built jet engines. The most recently introduced alloy, RR57 is used for compressor blade forgings in these same engines.

The contradiction existing in investigational data in the early days and the lack of comprehensive knowledge of what work was being done in various parts of the world is shown by the following historical records considered in the light of the silicon curve shown in Figure 2.

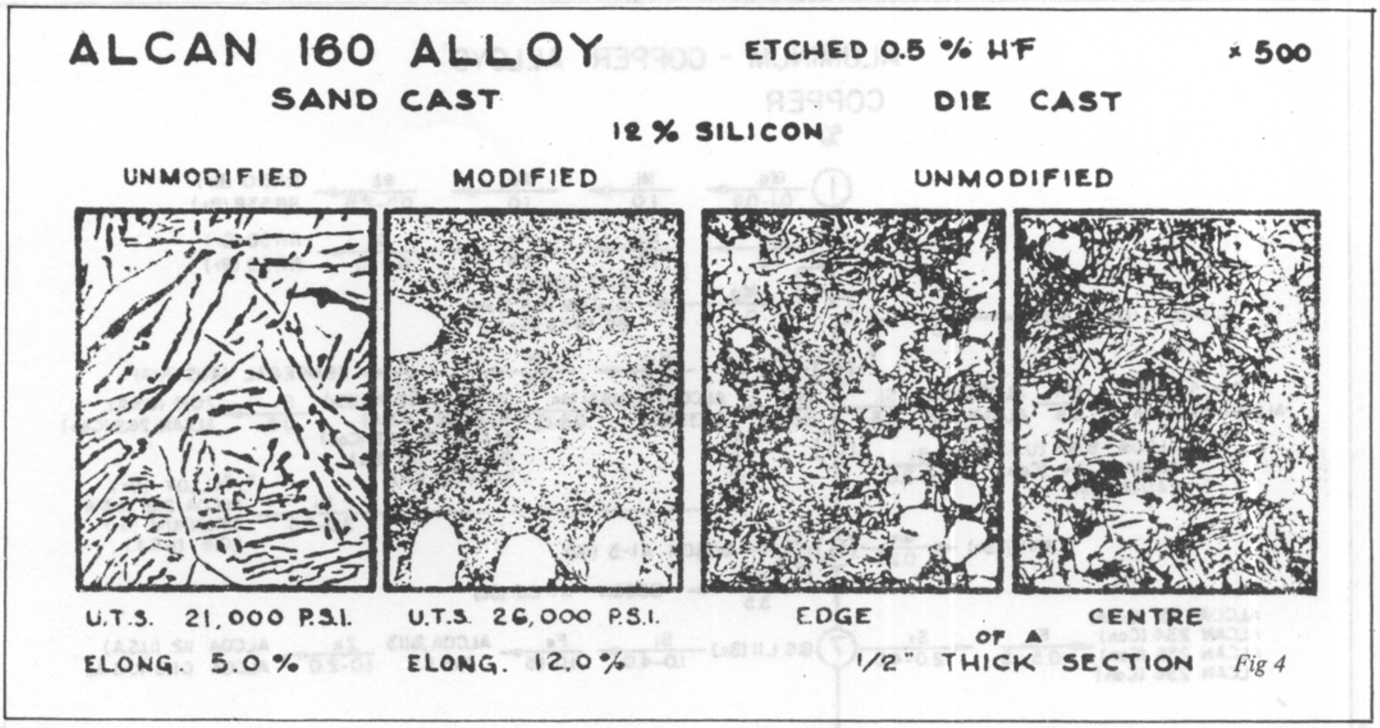


Fig 4

In 1894, Aldolphe Lejal reported that, in alloys containing up to 10% silicon, mechanical strength did not appear to be improved but the elongation was lowered. Still later, in 1909, a publication by the Aluminium Company of America stated that, although all the metalloids and gaseous elements such as oxygen, nitrogen, sulphur, silenium, chlorine, bromine, fluorine, boron, silicon and carbon unite readily with aluminium, no useful results had been recorded; in fact the union of the above metalloids in combination with aluminium results in alloys which, from a commercial standpoint, are undesirable in every way. However, in his book 'De l'Aluminium', published in 1897, Minet reports that when aluminium alloys containing silicon up to 10% are chill cast to develop a fine crystalline texture, they exhibit superior mechanical properties, Figure 4. Dr Aladar Pacz, an American citizen of Hungarian birth, made a further discovery in 1920 when he found that a fine structure could be obtained even when casting in sand moulds, if an alloy of about 12% silicon was 'modified' before pouring. Originally, his patent was practiced by adding sodium and potassium fluoride salts to the molten metal. Later Frary showed that metallic sodium was equally effective and more controllable in influencing the mode of silicon crystallisation, so that, instead of the silicon freezing in large, thin, fragile plates, the structure produced was typically dendritic in appearance, with small, comma-like particles of silicon in the dendrite arms and having greatly improved strength and ductility. Other effective modifying elements are calcium, antimony and bismuth. This alloy, known most widely in Britain as L33, is still greatly favoured by English foundrymen. Unmodified, it is still used in this country for pressure die casting. Its popularity in Europe is shown in Figure 5 by the long list of trade alloys and the numerous variations that have been derived from the basic composition. One very important outgrowth in America was Lo-Ex, a piston alloy with copper and nickel added to improve elevated temperature properties coupled with a low coefficient of expansion imparted principally by the silicon. The Germans have favoured a still higher silicon content, of which Alusil with 20% silicon, used also for pistons, is typical.

Silicon improves the fluidity of aluminium and such alloys are also noted for their freedom from hot shortness and good corrosion resistance. For these reasons a 5% silicon composition (with better foundry characteristics than the 12% alloy) is widely used in the United States and Canada for architectural work where good as cast detail is essential, and for applications requiring medium strength and good ductility. This alloy is also produced in wrought form both as a welding wire and as sheet which, when anodized, has an attractive dark grey colour due to metallic silicon remaining exposed in the oxide layer.

The general purpose casting alloy in England is one developed during the last war from aircraft scrap. It contains 4% silicon, 3% copper, and is known generally as DTD 424.

The early use of magnesium-silicide as a hardening constituent led to development in the United States about 1930 of two heat treatable silicon alloys, 355 and 356, with controlled additions of magnesium, one with and one without a further addition of copper. The excellent casting characteristics of these alloys, combined with high mechanical properties, resulted in their very extensive use throughout the United States and Canada; similar compositions are also to be found in the specifications of several European countries.

As early as 1899 a series of aluminium-magnesium alloys with up to 30% magnesium was being offered in Germany by Mach under the trade name of 'Magnalium'. They had most attractive mechanical properties and for a time were widely used, but after some ten years were gradually discarded due to poor corrosion resistance – an understandable fate in the light of our present knowledge relating to certain critical metallurgical conditions for some of the alloys in this series. Part of the trouble was undoubtedly caused by the low purity of the aluminium and magnesium used, coupled with poor remelting practices. Since the days of Mach's alloys this system has received a great deal of careful scientific study, especially by the I G Farben group in Germany. It still is receiving much attention throughout the world, and from the work has come a long list of very useful and satisfactory compositions.

Looking at Figure 6, you will notice that at the top of the chart there is an extensive list of alloys – not binary compositions but a group that depends on Mg_2Si as the principal hardening constituent. Reference has previously been made to the discovery by Giulini of artificial ageing which was carried out on his alloy, 'Aldur', the first composition of this type which was brought out in Germany for aluminium transmission cables. It was followed in Switzerland with Anticorodal and Aldrey; all of these alloys have been used to string thousands of miles of power lines throughout Europe. Giulini's discovery marked another technological advance in the art of aluminium metallurgical development. The American alloy 6063, and the Canadian 50 S, used so extensively today for window and moulding extrusions, are almost identical in composition to Aldrey. American 51 S gave much higher mechanical properties than Aldrey, but was found to have poor stress corrosion properties due to excess silicon; however, from it Alcoa produced 6151 (Alcan 61S), the corrosion resistance being improved with chromium. Later, 6061 (Alcan 65S) was developed and has found wide application as an intermediate

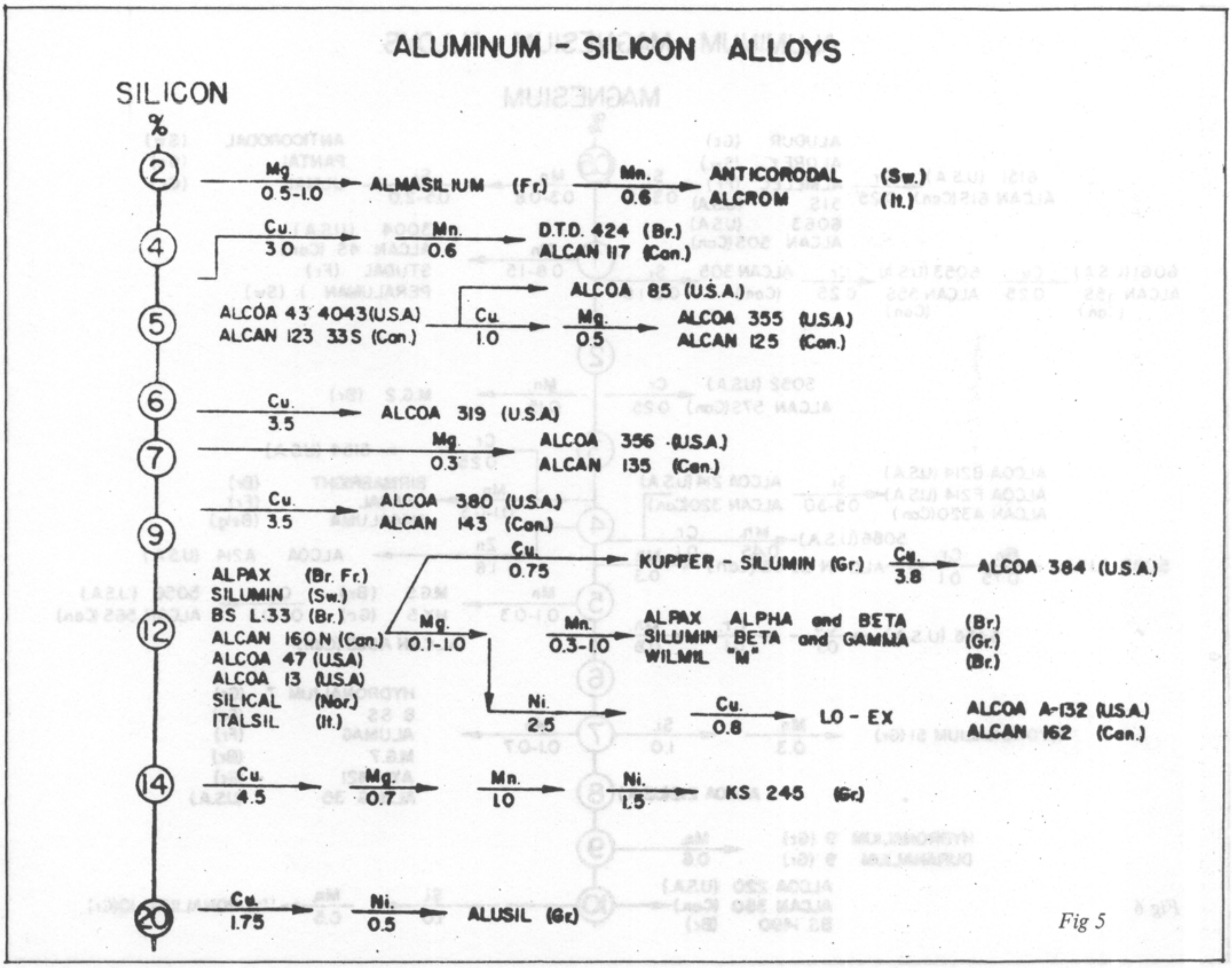


Fig 5

strength alloy. Because of the very high extrusion rates possible with the 51S type alloy, it is still used extensively in England with or without manganese additions which may be added to increase yield strength and corrosion resistance.

The binary aluminium-magnesium alloys offer a wide range of mechanical properties in the commercially used limits for wrought compositions of 2 to 7% magnesium. These become increasingly harder to cold form as the magnesium is increased, and work harden at a much more rapid rate than alloys of other systems. Since these alloys are not amenable to heat treatment, an increase in tensile properties may be introduced only by cold working, and critical amounts of this internal stressing contribute to stress corrosion susceptibility. Another characteristic of the cold worked magnesium alloys is the change in mechanical properties with time – a phenomenon that takes place at room temperature due to precipitation. Whereas precipitates have heretofore been considered as an indication of lattice hardening in this case 'age softening' takes place, because of large particle size instead of a fine dispersion of the precipitate. There is no long transition period between a solid solution and what might be called a coalesced, precipitated phase accompanying this considerable recovery, or stress relief; the net effect is a loss in tensile and yield strength with corresponding increase of ductility. In commercial fabrication such alloys are stabilized following fabrication; this consists of a low temperature thermal treatment to accelerate this reaction without removing all internal stress or bringing about recrystallisation. At the higher magnesium contents these alloys are susceptible to stress corrosion cracking unless great care is exercised in selecting alloying additives which act as grain boundary stabilisers and by a judicious control over the degree of cold rolling and annealing.

In United States the early binary aluminium-magnesium alloy 5052 (Alcan 57S) contained chromium as the grain refining and stress corrosion controlling element. The Germans and the British however, in their Hydronaliums and Birmabright, have favoured manganese. Both elements are effective in controlling grain boundary potential, with the further consideration of their effect on mechanical properties (especially ductility), also a factor in determining selection preference. It was in 1900 that the Austrian, Mach, was granted the first U S patent for binary aluminium-magnesium alloys; since then, production and chemical characteristic have been so improved that today their importance is becoming increasingly greater, with several compositions being offered throughout the world as ideally suited for transportation applications, especially in shipbuilding.

We have already made mention of the early high zinc casting alloys used on the continent, see Figure 7. A few of these remain still in commercial use, though altered in composi-

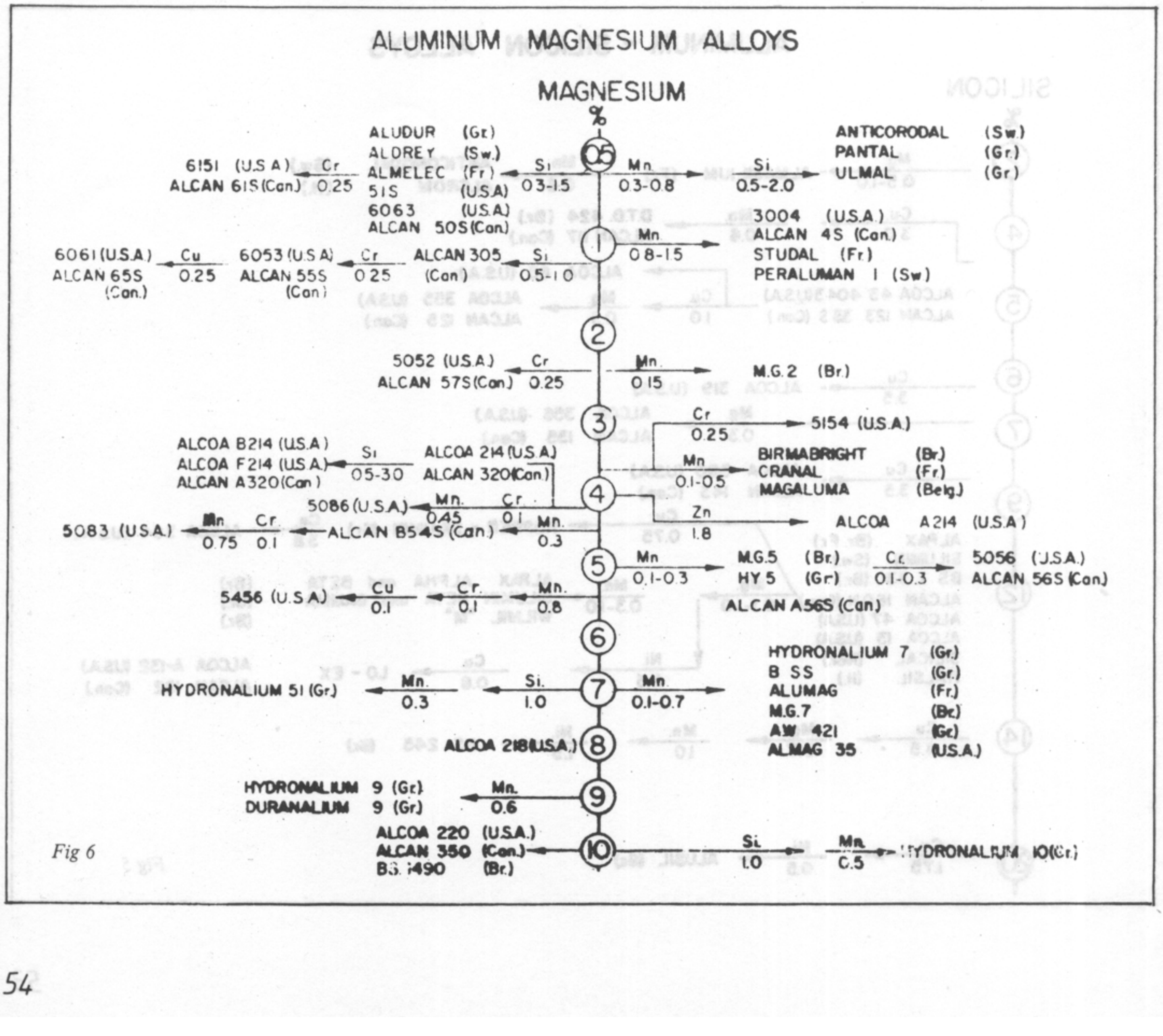


Fig 6

tion, principally by copper additions. The real international interest lies in some very high-strength ternary compositions of zinc, copper and magnesium. In the casting field the outstanding alloys of this group are the American alloys 40-E, Ternalloy 7 and 8, and Alcoa A-612. The alloys are more hot short than those of the silicon or copper series, and require high purity aluminium as a base in order to develop their excellent mechanical properties without heat treatment; they also braze readily, giving good mechanical properties, and anodize to an excellent finish.

Of possibly greater interest, however, are the several zinc containing wrought compositions that have been developed. The word 'developed' is used here in the fullest sense of its meaning, for these are possibly the most complex alloys ever offered by aluminium alloy producers. Mechanical strengths exceeding 100,000 psi have been obtained; yet, in accomplishing this, special problems of notch sensitivity and stress corrosion suceptibility may be introduced.

The first of these high strength alloys was offered in Germany about 1926 under the trade name 'Constructal', but, owing to its unsatisfactory stress corrosion resistance, did not attain technical importance. Many other commercial attempts were made to offer a satisfactory composition and the Rolls Royce alloy RR77, as originally produced and tested, looked promising. It contained zinc 5.3%, magnesium 2.0%, copper 2.0% and nickel 0.5%, and in laboratory tests proved reasonably stress corrosion resistant. However, formed extrusions failed due to stress corrosion and the alloy had to be modified by substituting manganese for the nickel. The result has been good performance. At this time X76S was introduced in America; by employing a hot water quench, internal stress was minimised and a stable structure produced. Now the alloys 7075, Alcan 75S, RR77 and RR78, and the German Constructal 87, all contain additions of chromium or manganese to control the mode of the precipitated phases and the nature of the grain boundary structure.

In 1937 there was published a valuable contribution by the Japanese, Igarashi and Kitahara, who pointed out that a combination of stress and a corrosive environment were necessary for intercrystalline failure to occur, that it varied with the degree and direction of working in an alloy and was dependent on composition. Their time-to-failure curve of ternary aluminium-magnesium-zinc alloys – establishes certain magnesium and zinc ratios to give stable compositions. Their work also points out the beneficial effect of additives, notably manganese and chromium. The Japanese alloy ESD, found in the Zeros of the last war, is an outcome of this work.

Research, coupled with the practical use of these many alloys, has now provided a wealth of knowledge on the mechanics of alloying and the manner in which the basic alloying elements,

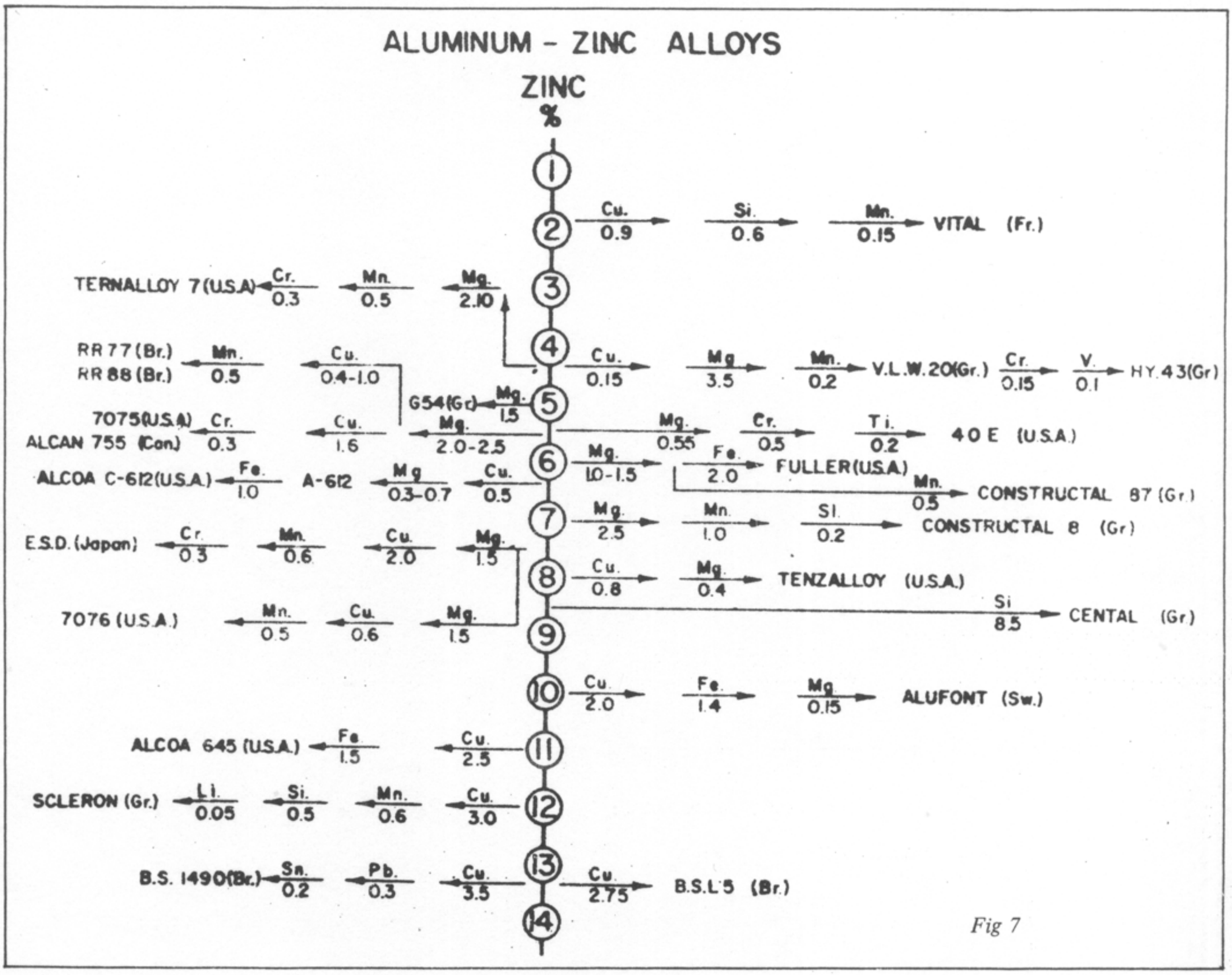


Fig 7

along with many others, act on the characteristics of commercial and superpurity grades of aluminium. Such information is the key to the work of the research metallurgist, and from this knowledge will undoubtedly come new and better aluminium alloys.

Reference was made earlier to the memoirs of Saint-Claire Deville. One most interesting sentence stands out: 'I have tried in this book to demonstrate that it should be possible for aluminium to become a common metal'. His vision has come true. Production in 1859 was 2 tons at an average price of $17.00 a pound; in 1956 world production has been estimated as 3.5 million tons at a market price of about $ 23 per pound.

Aluminium has come a long way in just 100 years of commercial production, and still world capacity to produce more and more aluminium continues to grow, reflecting the increasing and varied use of this metal in our everyday life.

G MacDonald Young BSc. 'Mac' Young was educated at University of Sashatchewan and McGill from whence, on graduation, he went to the Toronto Works of Alcan. In 1940 he was appointed chief metallurgist at the new Kingston Works where he played a major role in developing fabricating practices for the many new alloys and products required in the years of World War II and subsequently. In 1946 he was appointed Technical Director of Alcan in Montreal and finally as Vice President in charge of Alcan R and D. In 1957 he was the first Canadian to be President of the American Society of Metals.

Magnesium: With an Appendix describing production problems

Francis Fox and Gordon Lewis

Introduction *by F A Fox*

As a young fellow having recently joined Magnesium Elektron I was amused and affronted at being announced by a large commissionaire at the Dunlop Wheel Company in Coventry as being from 'Manganese Electricars'. I didn't then know that in truth I should feel only half as insulted. For a time after its isolation by Humphrey Davy, magnesium was called 'magnium' and 'magnesium' meant manganese. A commissionaire of serendipity.

In 1808 Davy used what was essentially an electrolytic route to the metal, producing an amalgam, which, on distillation, yielded the metal. In 1828, the Frenchman Bussy produced a sample of the metal by using a chemical reduction method, reducing anhydrous magnesium chloride with potassium. These two ways underlie the present commercial processes for the extraction of the metal – electrolytic and thermal reduction.

Although some of the basic chemistry and electrochemistry was understood by the end of last century, magnesium in its full scale extraction and engineering use is a creation of this century in a way that few other tonnage metallic materials are – with the obvious exception of titanium.

Utility

As we shall see in a moment, the solution of the technological problems were particularly severe. So one should start by asking – why all the effort? What are the prizes?

In the early days, some of the virtues of magnesium alloys were not apparent, but of course the most obvious was that of the promise of superior strength to weight ratios. The density of magnesium is about 1.74×10^3 Kg/m^3, while that of aluminium is about 2.70×10^3 Kg/m^3. By the twenties of this century, aluminium alloys had shown great value and promised more, especially in the important field of aircraft use. Could not magnesium do better, with such an advantage in density? An accompanying benefit would also clearly be that of low inertial forces in rotating or reciprocating parts; good machinability might have been guessed at (actually it is outstanding) by experience in methods of making magnesium powder. More advantages became clear as the technology progressed; amongst these are:

1 Good stiffness to weight ratio in wrought alloys.

2 Ease of founding large and complex castings (once certain techniques are mastered).

3 Good hot forming properties (again, given the right techniques).

4 Low notch-sensitivity in fatigue, and a high fatigue/ultimate strength ratio.

5 Good thermal diffusivity and low thermal stress modulus (ie non-uniform heating of a component induces only low thermal stresses).

6 Good damping capacity.

Of course the fact that magnesium has a low thermal neutron capture cross section, which makes it valuable in the operation of some nuclear power stations, was impossible to foresee at the beginning of the century. However, wide and ready availability of magnesium-containing natural materials, from dolomite to Epsom salts to sea water was another encouragement, while large deposits of magnesites already being used for refractories in the steel industry were ready-made sources.

The existence too of magnesium in the special form of carnallite ($MgCl_2.KC1.6H_2 0$) in the extensive salt beds of Stassfurt was a strong stimulus to the Germans to become early pioneers in the extraction and engineering technology of the metal.

So much for a glance at some of the prizes. What of obstacles and limitations?

First, obviously, the high chemical reactivity of the metal, leading to extractional difficulties, fire risks, and corrosion problems. Then, a low elastic modulus (about 44.1×10^3 MNm^{-2} – or 6.4×10^6 psi), though it was noted that a low modulus is not, in all engineering uses, a disadvantage. Further, low hardness and limited cold formability were observed early on.

This is a formidable list, but the difficulties were attacked with great energy and perseverance in Germany, Britain, France, Austria and USA. Many technological advances were made, and although we in UK wrote not a few papers, much of what we did went into the form of restricted reports or patents, which of course, are as dull as ditch-water and highly unquotable.

Electrolytic Extraction – Commercial Development

All kinds of attempts to produce magnesium from aqueous or organic media by electrolysis have been quite unsuccessful though such work of great ingenuity continued in Germany till as late as 1983. However, the preferred choice of fused chloride salt baths presents problems because of the harmful effect of water in the electrolyte, and because of the difficulty of producing fully dehydrated magnesium chloride on a production scale. Attempts to imitate the successful aluminium extraction route by solution of Mg0 in fused fluorides and electrolysing, also proved failures, though work continued on these lines till the 1920s in Germany.

An important key to early German success in the electrolytic route was therefore production-scale making of anhydrous $MgCl_2$, and this was achieved by what became the major German pioneer organisation – the IG Farben Industrie. Their developments in extraction and in engineering uses made them the world leaders by the 1930s. Using the name 'Elektron' for their metal and alloys, they were able to license to others internationally their processes, compositions and 'know-how' (a new term then).

Entry of Britain

In the 1930s a British merchanting company, F A Hughes, was led by Charles Ball who, at the end of World War I, an army major, had worked in the Allied Control Commission in Germany. He retained his German contacts in the 1920s and 1930s having dealings with I G Farben on behalf of F A Hughes. He became familiar with their advances in magnesium, and saw a need and an opportunity in Britain. He was able, using his considerable charm, contacts and acumen to interest various organisations in Britain, including the yet relatively young ICI (still, of course, distinctly 'Imperial'), and also the British Government, so that support was forthcoming to build a magnesium extraction plant in Britain, and to use equipment and 'know-how' supplied by I G Farben under licence. The new company was called 'Magnesium Elektron' (MEL), and a location was chosen such that it was close to ICI's supplies of liquid chlorine, and where large electrical consumption was possible at lowest cost and greatest stability of supply. The chosen site was at Clifton Junction in the near neighbourhood of Manchester; and pretty dismal it was too; in 1938 when I went there for interview, I could easily have got lost among the old coal 'slag heaps' lining the approach road – misnamed a lane.

My own contacts with I G Farben were confined to three visits before the war (the June 1939 visit seemed like fighting through a haze of swastikas), wading through convoluted, and often it seemed deliberately vague or opaque technical reports – the opacity seemed to increase rapidly as September 1939 approached, dealing with a few junior German technicians at Clifton Junction, and, rather embarrassingly later, interrogating senior I G Farben personnel in Germany after the war, put into uniform as I was (RAF) for the purpose. Just prior to my post-war visit some unknown piping voice on the telephone from Whitehall demanded without preamble to know if my salary was in excess of £1000 pa. It was, so I was forthwith a Wing Commander for a time. I never discovered what would have awaited me at £900 or at £2000.

The arrangements with I G Farben entitled MEL to receive their data and 'know-how' and to transmit it to MEL sub-licensees in UK, which produced the finished castings and wrought products. After September 1939 I found myself expected to be the metallurgical oracle in place of I G Farben in which I was pretty inadequate, no doubt, particularly at first. We set up joint technical committees to operate with the British sub-licensees to pool knowledge and experience; we had of course the Ministry of Supply making many demands, but also making R & D grants. Very fortunately I was lucky in recruiting a good R & D team at Clifton Junction, which later included Edward Emley, who in 1966 wrote such an excellent tome on magnesium technology.

We had begun at Clifton Junction to use magnesia from sea water as a raw material, and in March 1939 production ingots of magnesium were made from this source – very probably the first time that any metal had been obtained from sea water on a tonnage basis. This struck visitors as all the more remarkable because of the great reactivity and inflammability of magnesium.

Magnesium Elektron and Basic Magnesium Inc.

When the USA was brought into the war by Pearl Harbour, there was a great rush by them to expand their magnesium production. MEL, the British and the US authorities arranged for a 50,000 tons/an. plant, using MEL/IG Farben methods, to be built in Nevada, near Las Vegas and the Hoover Dam – a source of low-cost power. Several of the MEL staff spent many months there during construction and commissioning. The plant needed 4,000 tons of copper bus-bars for the cell-room; in 1942 in USA such large amounts of HC copper were not available; the US treasury supplied instead 4,000 tons of pure silver bus-bars. An armed FBI agent was sent to guard Federal property, but, as reports to us stated, joined with otherwise under-employed crooks from Las Vegas in using his gun to relieve construction workers of their money on pay-days. A special 'pound' had to be built so that drunks wearing the construction company's badge could sober up in safety. Xenophobia combined with the old spirit of NIH started a campaign from interested parties to the effect that the plant would never make metal. The MEL staff people fell into bed on the last day of the agreed construction and commissioning period, good magnesium having been produced at a about 11.30 p.m. They woke the next day, so I was told, to find in each letter-box of the area a printed leaflet saying that any magnesium purporting to have been made at the plant had not been so made, but had been bought and smuggled in to 'salt' the cells so as to give the appearance of success. Fortunately the 'appearance' continued in the shape of large tonnages for a number of years.

Thermal Reduction

Various reducing agents were tried, a requirement of the reduction reactions usually being operated at very high temperatures with continuous removal of magnesium as vapour. Reduction with silicon in the shape of ferrosilicon has proved the most effective, and various plants have functioned with more or less commercial success, depending critically – as does the electrolytic process – on the cost of electricity, or on the cost of the 'canned' electricity represented by silicon, calcium carbide, etc.

L M Pidgeon in Canada pioneered a ferrosilicon reduction plant in 1940-44; this operated at the relatively low temperature of 1150°C, and a pressure of about 0.1 mmHg.

A carbothermic reduction process was the subject of great efforts in Austria, Germany, UK and USA, all complicated by severe conditions of operation. A plant at Swansea operated during the war with a planned capacity of 1000 tons/an. but produced little metal and had a high accident rate. The reduction furnace operated at about 2000°C, and the emergent magnesium vapour was shock cooled by recirculating hydrogen (or natural gas). The solid magnesium was so fine as to be pyrophoric, and had to be pelleted under nitrogen and then later sublimed. Not the easiest of processes.

Many plants were shut down after the war, leaving fused salt electrolysis and the ferrosilicon processes the sole survivors.

Fire and Oxidation Risks

British industry has from time to time been criticised for not caring what country it supplies in peace-time with what material of defence importance. A curious reversal of this might have been seen at Clifton Junction, where in September 1939 there was a store-house containing 5000 tons of magnesium – 5% aluminium alloy, supplied by Germany. This was specifically the incendiary bomb alloy – euphemistically then called 'alloy for pyrotechnic purposes'. Much of it did later return to Germany, dropped as incendiaries.

The presence of this quantity of bomb alloy in one building gave rise to fears as to what might happen if it itself were hit by German incendiaries. I was called on to conduct an experiment/demonstration for various officials. The ingots weighed 2 kg each; would a stack of say forty be ignitable by a standard incendiary? The short answer was 'no', since massive magnesium must melt before it burns, and such a stack of ingots has too high a heat capacity to be melted by an incendiary. A smaller group of ingots, suitably intensely heated made quite a blaze, and when attacked by a water spray burnt more fiercely; large quantities of sand dumped on burning ingots extinguished them (air deprivation), but small amounts of sand burned with great intensity (sand was being reduced to silicon).

At Clifton Junction we were at the receiving end of 'pyrotechnic devices' during the war, but they did negligible damage. High explosives were another matter and might have caused a disaster. Before the war an evaporation station to gasify liquid chlorine from tank weapons each containing 13 tons of liquid chlorine, was right in the middle of the plant. At the outbreak arrangements were made to shift the evaporation station a mile away and place it well into a railway tunnel (with the chlorine tank wagons), and to pipe the gaseous chlorine back to the plant. The tunnel was called 'Black Harry', and well merited its name, and we of the Works Home Guard barked miles of shin stumbling about over its coal-encrusted sleepers (no torches of course) – guarding a 'key point'. One of the HE bombs to fall in the plant happened to land right on the site of the original evaporation station removing a hastily erected 'bomb-proof' shelter, killing an unfortunate ARP man, but otherwise causing minor harm. There was great self-congratulation the next day among the management – the locality is densely populated, and 13 or more tons of chlorine would have made a black day.

Handling of the Molten Metal

To overcome the tendency to burn in the molten state must be a concern of anyone who has to handle the metal; it was also very early apparent that contact of the molten metal with moisture in, say, sand moulds presented problems and demanded inhibitors or use of non-aqueous moistening media. It was discovered in the late 20s that synthetic foundry sands could be usefully mixed with inhibitors like flowers of sulphur, boric acid and diethylene glycol. Considerable effort early in the war went into establishing good sand-foundry 'housekeeping' since only slight contamination with different types of sand produced rapidly rising proportions of scrap castings. It was learnt the hard way that sand preparation systems had to be maintained to a very high standard, and that it was not possible on the sand foundry floor to keep switching between casting magnesium alloys and aluminium alloys. Dusting the molten metal while pouring with flowers of sulphur from a muslin bag became a wide-spread technique.

Chloride Inclusions and Fluxes

Parallel with the problem of burning and oxidation was that of eliminating chloride inclusions which early experience showed caused rapid corrosion of the solidified metal (the inclusions are deliquescent). This had in fact proved to be a total obstacle in the early days to any use of the metal for engineering purposes. The solution developed by the Germans and announced in 1923 was the use of a flux to remove the inclusions, this flux having the property of thickening and collecting them on stirring. Such a flux was known as 'inspissating'; it might also be used as a layer on the surface of the molten metal, giving a protective cover, which could be drawn gently from the crucible lip at pouring. The specifically inspissating agents in the fluxes were usually magnesium fluoride and various oxides.

The inspissating fluxes were originally supplied (to most if not all of the British magnesium industry) by IG Farben, before 1939. In the early days of the war an urgent programme had to be put in hand to find ways of locally producing the fluxes at an economic price, and if possible to improve on them. An effective all-purpose flux was developed at Clifton Junction for both refining (ie inspissating) and covering the metal – for which a separate flux had sometimes been used. This flux became standard for all alloys not containing zirconium: the latter alloys presented problems of their own.

Alloys of Magnesium

The earlier alloys of magnesium contained aluminium (5-9%) as their principal strengthening addition, and this range, with a few percent of zinc, which conferred some additional strength, and with a few tenths percent of manganese which aided corrosion resistance, constituted the backbone of both the casting and forging alloys. Another alloy of magnesium with manganese alone (about 2%) was used for sheet; it had good corrosion resistance, but not remarkable strength.

These alloys were primarily German in origin, evolved since about 1925. Similar compositions could be found in other countries.

In 1939 in Britain there was no real understanding of the effects of metallic impurities, particularly iron on corrosion resistance, and further, though the magnesium-aluminium diagram was well established by work at the NPL and elsewhere, the implied potential for heat-treatment on a production scale was not in a developed state.

So these were two early fields of importance for exploration.

On corrosion problems the pre-1939 approach had, in Britain, been to put it mildly, unsophisticated. I remember a discussion in Birmingham with a sub-licensee's corrosion pundit; he had salt-water immersion tests going, with no temperature control, no exact control of the bath composition, and above all, no analysis for minor elements. – 'Our lab can't test for unusual impurities; why should they? I got the samples from your last lot of ingots'. Routine control tests on production at MEL needed rapid improvement and a paper on spectrographic control was one of the first to appear bearing my name from MEL.

Corrosion

Our work on corrosion was stimulated by the results of a large-scale experiment by the Americans in 1942, led by J D Hanawalt on exposure to the marine environment (immersion-emersion), from which clear limits for the presence of nickel (.005% max) as well as iron could be laid down. Incidentally, we soon latched onto the fact that it could be quite properly stated that unprotected magnesium is more resistant than is mild steel to atmospheric or even to marine-atmospheric exposure.

The work at Clifton Junction was later spear-headed by C J Bushrod, who of course also found himself involved with methods of protection of finished products, and these by 1950 had become very reliable. In the protection field, the RAE labs made valuable contributions; – H G Cole was active here.

After the war the electro-chemical properties of magnesium were applied for cathodic protection of steel structures like ships' hulls, pipe-lines, piers – or even in hot-water tanks – all this was a slightly disturbing reversal of role for those earlier devoted to stopping the corrosion of magnesium.

Heat Treatment

On heat-treatment possibilities we had first to make sure of metallographic techniques, and this was not always simple, since spurious structures easily appeared and had even been shown in publications. A German monograph on the metallography of the alloys, by W Bulian and E Farhrenhorst in 1942 did not come our way till 1944; but by then we had become proficient in the techniques and in interpretation of structures of the alloys not containing zirconium, and were on the way to understanding something of the latter. All this of course was using the ordinary light microscope. Late in the war I was agitating for an electron microscope, but at first met no other response than to be rather stiffly reminded by Head Office how to spell 'Elektron'!

We found that with the aluminium containing alloys, solution and precipitation treatments were quite readily possible and that proof and ultimate stresses could be raised usefully – in fact by up to 50%. The metallographic structures were not unlike those of steel, and we used terms like 'pearlite' to describe them. These heat-treatment procedures were put into production use quite satisfactorily and usefully.

Production of Aircraft Quality Castings and Wrought Products

The work to translate research findings into quantiy production under high-pressure war-time conditions was arduous and demanding, and perhaps the most successful team was that of Sterling Metals in Coventry. Here highly complex sand castings were made to exacting standards in the older, and later in the zirconium containing alloys, as a result of skilful analysis of solidification processes in the casting, and a thorough understanding of techniques that were relevant. A bugbear of the alloys, if everything was not just right, was the production of castings showing microporosity; I watched many large magnesium-alloy aircraft landing wheels compressed to failure under a press as a sampling check for fracture examination. Microporosity showed as areas of a golden sheen, often in layered forms. John Sully and Humphrey Millward of Sterling Metals ensured that this problem was kept at a low level. Other manufacturing developments in the wrought alloy field came principally from James Booth and Birmetals, Birmingham, where extrusions and large forgings were made, the latter in very heavy presses using 'squeezing' techniques. Magnesium alloy aircraft propellers were important products of this effort.

Effects of Grain Size

For casting alloys (the larger proportion), a very important feature was grain size. A coarse grain size led to reduced mechanical properties, even more so with magnesium than with other metals. Furthermore, with the aluminium containing alloys particularly, there seemed to be a 'memory' effect – coarse grained ingot tended to produce coarse-grained finished castings. The original procedure for ensuring fine grained ingot, emanating from I G Farben, was to superheat the alloy (the standard melting pots were – and are – made of mild steel), to about 900-925°C and cool quickly to casting temperature. Slow cooling from superheat caused the beneficial grain-refinement to vanish. The Germans maintained a superstitious aura about the mechanism of the process, however a little thought suggested some kind of nucleation process was probably operating. Experimental work we did at Clifton Junction during the war, using anhydrous ferric chloride as a nucleant proved to have been paralleled by I G Farben who took out patents on their ferric chloride process. Iron as an impurity in the final alloy had of course to be carefully controlled because of corrosion problems, so the process was delicate and problematic. Later work showed that some form of carbon inoculation was thought also useful, and using hexachlorethane was thought to produce a de-gassing effect as well (chlorine). It was noted that the mild steel melting pots were always decarburised on the inner surfaces; it seemed probable that Al_4C_3 nuclei played an important part in the process, and this still I believe holds the field as the principal nucleating agent in the aluminium containing alloys.

The Search for Stronger Alloys

Any alloying agent which could directly cause grain refinement of the final alloy without superheating would be valuable, particularly if the alloy had reasonable ductility so that further strengthening was in prospect. Early work before 1939 had suggested that practical alloys other than those containing aluminium, zinc and manganese were hard to visualise, though mention was made by the Germans of zirconium as a grain refiner, and also of cerium (more properly – as it was then called, 'mischmetall' – rare earth metals not clearly differentiated). I must differ from my old friend Edward Emley where he says in his book that zirconium containing alloys were based on a 1947 discovery by F Sauerwald. We were working at Clifton Junction on the alloys well before this, and in fact I added zirconium 'metal' powder as an alloying agent in experimental melts as early as, I believe, 1940. The fact that the metal was heavily contaminated with hydride didn't help, though grain refinement did occur.

However, we persisted, and did see indications of strength improvement. The complexities of the later methods of zirconium addition, with the appropriate fluxing procedure, were developments of the period 1942-50, in which the successful fluoride-based alloying process was evolved, largely as a result of Edward Emley's own efforts. There is now a valuable range of these zirconium-containing alloys, both cast and wrought, some with further additions of silver and of 'cerium'.

Independently, at first of zirconium, another possible alloying element presented itself – thorium. I recall one night on sentry-go – in the rain of course – in the MEL home guard, deciding that thorium must be given a try; it was a group IV element, and it had an 'in-thing' going for it – it was within the favourable 14% range of inter-atomic distances (vis a vis magnesium), making alloying favourable.

Edwin Lardner and I did some exploratory work as early as possible, using thorium chloride as the alloying medium. Thorium was readily introduced into magnesium and magnesium-zinc alloys, but where aluminium was present it formed insoluble intermetallic compounds. Although of no value with the aluminium containing alloys, it might, I thought, be useful with differently alloyed magnesium-base materials. So it later proved to be, particularly in amounts of 0.75 – 2.5% in conjunction with zirconium and zinc, conferring improved ductility and creep resistance. It is now a standard addition for many alloys.

Canning Uranium

The choice of magnesium as a canning material for natural uranium was just presenting itself by 1949, and the detailed technology came outside our period; nevertheless, the early days were in some ways the hardest, since the engineers were sceptical as to the absence of fire hazard in uses up to 450°C. Once they were convinced, the other properties were so clearly appropriate that the metal (with minor alloying elements), practically chose itself for gas-cooled reactors using CO_2 and temperatures up to 500°C.

Welding

This is a large field. I shall content myself by noting that we made contributions to the technology in the shape of fluoride-based non-corrosive fluxes, and spent much time using an experimental workshop demonstrating that effective fabrications could be made by welding. Self-sealing magnesium alloy petrol tanks was one interesting and valuable field, and tubular welded aircraft seats another.

Envoi

Since 1950, magnesium, like all other metallic materials, has had to compete against an ever improving range of non-metals for engineering use. Nevertheless it has reached a world production figure today which considerably exceeds its wartime maximum; this is now about 300,000 tons annually, to be contrasted with about 20,000 in 1937 and 239,000 in 1943 (note the eleven-fold increase due to wartime needs of the aircraft industries – all in six years).

Today the major field is in the automotive industry, of which the V W 'Beetle' was the pioneer; here were the Germans using their old skills and initiative.

The technology has continued to progress even to the point of heat-treatment of the rare-earth metal-containing alloys in hydrogen – to the ears of a metallurgist an improbable enough procedure.

These are the disjointed jottings of an old hand of the business, and if much has been omitted I hope I may stand excused – much has happened since 1950.

I remember with the keenest pleasure the comradeship of our war-time team and the considerable qualities of many of my metallurgical colleagues – particularly Edward Emley whose untimely death in a mountaineering accident in 1980 I sadly recall. Much of the foregoing refers to events during World War II – necessarily so, since this was the period of most rapid change in the technology and scale of activity.

The struggles of the chemists at MEL and elsewhere I have hardly mentioned; Alfred Hock, Gordon Lewis and John Fletcher could (and should?) a tale unfold too.

In the field of lead technology, I remember a Frenchman remarking to me that it had 'une sale métallurgie'. Well, magnesium has – or has had – 'une métallurgie perverse', and, one might add, 'stinky' (what's the French?). I've been glad to have been a part of it.

Presentation by G J Lewis of Dr Francis Fox's Paper on Magnesium

Francis Fox and I were colleagues for ten years during the hectic War days of the expansion of magnesium production in this country and elsewhere and that started a friendship which has endured for well over forty years. So I could scarcely refuse when he asked me to present this paper for him, although I do so with some hesitation because I am not a metallurgist and therefore I am a bit of a maverick in this company!

I am going to assume that you have all read the paper – indeed I hope you have – and if you have not, I commend it to you because there is no-one, certainly no Englishman, who is better qualified to write the history of the first fifty years of this century in terms of magnesium and the development of its alloys. There are other sources I would recommend to you if you wish to fill in the background but perhaps the most comprehensive is the book on *'The Technology of Magnesium and its Alloys'*, by Adolph Beck, which is a very comprehensive review of the development over those years. It was published by F A Hughes & Co, the company of which Magnesium Elektron was the daughter company. Then there is another one on *'The Metallography of Magnesium and its Alloys'* by Bullien & Fahrenhorst. This also is a translation from the German and was also published by F A Hughes. Finally the book *'Thirty Years of Elektron from 1909 to 1939'*. It is in German, published by I G Farbenindustrie, and is a fascinating record of the steps by which this development occurred. The pictures with which it is filled show a great variety of different artifacts which were made from magnesium alloys during that period illustrating the wonderful castability and machinability of this metal which makes it ideal for application in places where light weight combined with rigidity is important.

For my part, I intend to try to fill in some of the gaps which Francis Fox had to leave in his narrative and to expand on some of the aspects with which I am perhaps more familiar than he is because it was my responsibility in the MEL set-up to manage the production and I was concerned, therefore, with all the extraction methods, not only the ones we used but also the ones we might have used. If you want a very full account of these there is an excellent one in *Ullmann's Encyclopaedia* in the 12th volume of the third edition where there is a section written by Drs Moschel and Schmidt of I G Farbenindustrie which covers very comprehensively the different processes that have been either tried or used commercially for the extraction of magnesium from its raw materials.

The extraction processes fall into two clear groups – electrolysis and chemical reduction. The electrolytic route essentially boils down to the electrolysis of the magnesium chloride in a fused bath of sodium, potassium, calcium and magnesium chlorides in such proportions as to comprise virtually an eutectic mixture. The temperature and the density of the melt are such that magnesium floats in liquid form to the surface of the cathode compartment and from there can be scooped off and cast in blocks of so-called 'raw' magnesium. The electrolytic processes differ one from another only in the source from which the magnesium chloride has come and the means by which it has been rendered anhydrous. The naturally-occurring form is Carnalite, which is a double chloride of magnesium and potassium. It occurs as the hexahydrate as also does magnesium chloride crystallized from aqueous solution. This has to be dehydrated which is commonly done in two steps – first by drying down to the dihydrate and then finally rendered anhydrous, sometimes in the cell itself but under special conditions which preclude the formation of magnesium oxychloride.

The source which is most widely used is the one which was the basis of German, British, and later, American manufacture. It is the I G Farbenindustrie process in which the magnesium chloride is obtained directly in anhydrous form by the chlorination of magnesium oxide in the presence of carbon. That sounds simple but in practice it is really quite complicated. The reaction mixture has to be prepared in pelletted form and was originally bound together by peat and then carbonized leaving a porous mass in which the peat had been converted into a reactive form. Then that pelletted reaction mixture is charged into a shaft furnace, heated electrically in the bottom zone and provided with ports through which chlorine is introduced into the mass. The magnesium chloride made by this means accumulates as a liquid in the base of the furnace from which it is tapped off and conveyed, molten, direct to the cells for electrolysis, the chlorine released being recycled.

Something about the chemical reduction processes must be said although, with one possible exception, none of them have really been commercially successful. Various reducing agents have been used, the first one is mentioned in Fox's paper – Bussy used potassium vapour to reduce magnesium chloride. In this country the only pre War manufacturer of magnesium other than MEL was Murex at Rainham where they used calcium carbide. The silicon process has been the one which has been most successful and I will talk a little bit more about that later on. But the interesting one which has always attracted attention is the so-called carbothermic process in which carbon was used as the reducing agent – a fiendishly difficult process, requiring operation in an arc furnace at temperatures in excess of 2,000°C and producing magnesium vapour which had to be shock-cooled with hydrogen or hydrocarbons to recover the metal in the form of a fine dust. Since it was so fine as to be pyrophoric in air, it had to be handled under oil and pelletted in order to be melted down to produce reguline magnesium. Not an easy job and in fact nobody has succeeded in making it work commercially. The Permanente plant in California which Kaiser built during the War produced magnesium in the form of a mixture with oils which later got the rather dreaded name of Napalm. That is about the only use to which the carbothermic process has really been usefully put.

The chemical reduction process is attractive because it potentially offers freedom from contamination of the raw metal with chlorides which is characteristic of all the electrolytic production methods. In the founding of the metal in the preparation of alloys inspissating fluxes have to be used to get rid of chloride inclusions which otherwise could lead to serious corrosion of finished castings. Theoretically, at least, one could avoid this by making the magnesium metal by chemical methods such as the reduction with silicon which has been the most successful of the thermal processes. It was developed by IG in the years before the War under the impetus of Dr Pistor – a great and inspiring leader of the light metal industry in Germany at that time. A reaction mixture of ferro silicon with magnesium oxide and calcium oxide (in the form of calcined dolomite) and a small quantity of calcium fluoride, was pelletted and charged into a vacuum furnace, heated to about 1000°C by a resistance element made of graphite. The magnesium vapour produced was condensed in an adjacent chamber and either melted down and tapped off or taken out as a sort of crown. This process was not only operated in Germany on an experimental scale but a continuously operating shaft furnace producing one ton of magnesium per day was developed. In 1937, I was seconded from ICI to study these thermal reduction processes and in that year, first saw them being operated. On returning to Britain we, at MEL, built and operated a demonstration plant where, for the first time, all-British magnesium was produced from British dolomite and silicon.

So much for the main extraction methods. The story of the commencement and growth of production in the United Kingdom has been sketched by Francis Fox in his paper. It starts with Major Ball – a very dynamic person who liked to say that his first contact with magnesium was when it was shot at him on the battlefields of the Western Front in the First World War! This may be a colourful story but certain it was that he picked up a small pencil of a metal, the lightness of which intrigued him. He put it in his uniform pocket and forgot about it until, after the War, he was appointed to the Allied Commission of Control.

Donning his uniform again he found the little pencil and determined to use his opportunity to seek out the source of it in Germany. He found it in a firm called Griesheim Elektron (the forerunner of the magnesium division of I G Farbenindustrie) in Bitterfield in Saxony and negotiated licensing agreements to import magnesium alloys into the UK for fabrication. Francis Fox tells in his paper how, by his acumen, by the use of his charm and his contacts, Major Ball formed Magnesium Elektron as a subsidiary of F A Hughes & Co with support from ICI, from I G too, and with the backing of the British Government to manufacture magnesium and its alloys in the UK. The plant was built at Clifton Junction near Manchester and the first 5000 ton/year unit was commissioned in 1936 – the foundry got going a few months thereafter, early in 1937.

By this time it was pretty obvious that War, if not inevitable, was very likely and we in the magnesium industry were called upon to start making preparations for it at least two years before it broke out. The three problems we had to tackle can be summed up in a very few words, although their solution meant a lot of work. First, we had to find a new source of the raw material magnesite, which up to that time had been imported from Greece and India along sea-routes which would obviously be vulnerable in time of War. We turned to that inexhaustable source of magnesium – sea water. There was a small plant operating in Britain in 1937 sited at Hartlepool, making dead-burnt magnesium oxide from sea water by the so-called Chesney process for refractory use. We persuaded them to calcine the precipitated magnesium hydroxide a little lighter and thus produce a reactive form of magnesium oxide. The first 1000 tons of that was delivered to us early in 1939 and we used it to make the first magnesium from sea water that was ever made on a commercial scale.

That may contradict what you read in the history of the magnesium since Dow have always laid claim to this achievement. They did it by using calcined oyster shells as the source of lime used to precipitate magnesium hydroxide from the sea water of the Texas Gulf. But that was in 1941 – I am afraid MEL had pre-dated them by at least two years!

Secondly, there were a number of other essential imported materials, notably the fluxes used in the foundries. The Elrasal fluxes were all imported from Germany. We had to match them using constituents which were available in this country and that was successfully done and, as Francis Fox says in his paper, those British-made fluxes have remained the standard for use ever since that time.

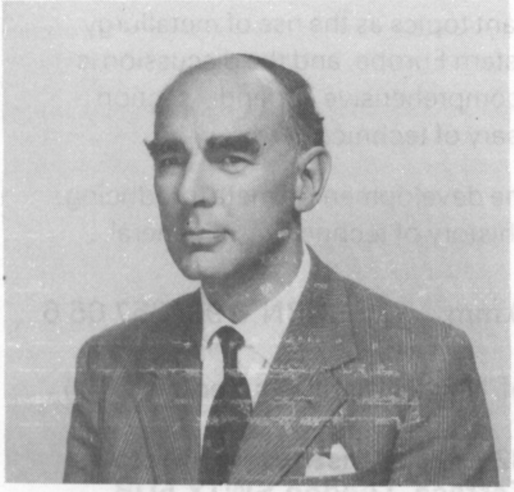
Lastly, and most importantly, we had to expand production. In the United Kingdom we increased production fivefold between 1938 and 1942. We doubled up the original plant at Clifton Junction before the outbreak of War; we commissioned a third plant on the same site in 1941; finally we built, for the Ministry of Aircraft Production, a double plant at Lowerhouse near Burnley. Our capacity then was 25,000 tons a year, but at that time, the Allies needed a great deal more magnesium than we could produce. Beaverbrook, who was in charge of armaments supplies for aircraft production at that time, decided that the Allied supplies of magnesium should be made in North America. This was a very sensible decision on strategic grounds but it rather overlooked the fact that the Americans were far less experienced in both magnesium manufacture and magnesium alloy making and fabrication than we were in this country. So we of MEL were called upon to help the Americans too and we had to devise, design, help construct and then train the key workers and supervisors who were to commission an enormous plant to produce 50,000 tons/year which was built out in the Nevada desert near Boulder Dam. The plant site is now called Henderson, Nevada, the second biggest town in the State, but which started as a trailer park for the accommodation of construction workers! The plant functioned very well. The Americans turned out to be very successful and very ingenious operators and, giving credit where it is due, they produced a number of very significant and helpful improvements in the process.

But also in North America the silicon reduction process was being used and here I must part company with Dr Fox because he says that L M Pidgeon pioneered the ferro silicon reduction process. This is not true. It was IG who developed it, patented it and MEL had the British Empire rights to those patents. All that Lloyd Pidgeon did was to crib the IG process from the IG patents. As evidence for this I can tell you that in 1946 I was sent out to Ottawa with our patent agent to help our attorneys to prepare an infringement action against the Canadian Government which eventually was settled out of Court in our favour!

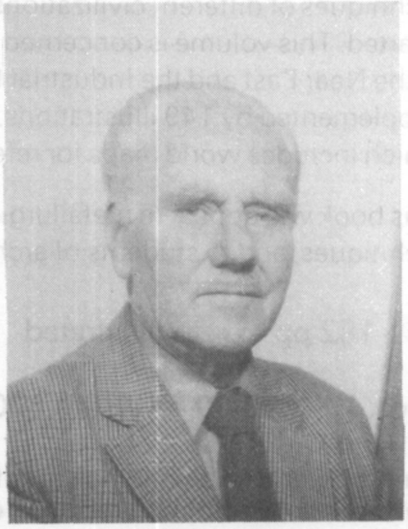
However, Lloyd Pidgeon and the other operators of his process (particularly New Jersey Zinc), succeeded in developing a rather crude and simplified form of the ferrosilicon process, looking a little bit like Belgian zinc furnaces but with provision for a rather higher temperature and rather higher vacuum, too, producing crowns of sublimed magnesium metal. Dominion Magnesium in Canada still use the same process.

So we come to the post-War period. As far as the magnesium industry is concerned, the War finished in about 1944, by which time the Allies had magnesium running out of their ears! MEL's developments then were devoted to the improvement of the alloys and notably amongst these of course the zirconium-containing alloys. The strength of alloys produced by alloying magnesium with zirconium were outstanding and much of this achievement is due to Francis Fox and his colleagues, but it would not have been possible without a convenient and reasonably-priced zirconium salt which could be used for alloying purposes. The Germans, just before the War, had started using zirconium tetrachloride for that purpose – a very nasty material indeed – difficult to make from the available raw materials, involving very high temperature chlorination and then the handling of a material which was both hygroscopic and tended to hydrolyse. Something better, more stable and less costly, was required and research was undertaken by Dr Fred Hock to whom I am indebted for this short description of the way a better zirconium alloying agent was eventually produced.

The first idea was to use, not the chloride, but zirconium fluoride which is a much better alloying agent, not subject to the same objections as zirconium tetrachloride. Unfortunately it needed the use of the zirconium tetrachloride as an intermediate so although it was a better alloying agent, it was certainly no cheaper to make. What Dr Hock and his colleagues evolved was a very elegant process for producing potassium zirconium penta-fluoride (which may be written as either $KF.ZrF_4$ or $KZrF_5$) and which is the preferred



Francis A Fox BSc (Hons) DSc (B'ham) joined Magnesium Electron Limited in 1938 and became Chief Metallurgist in charge of research. Moved to Eindhoven and then to CSIRO Australia where he became Director of Research CSIRO Melbourne.

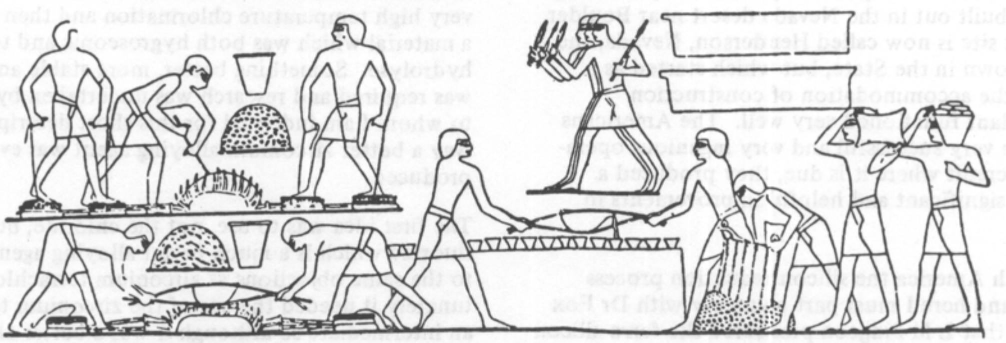


Gordon J Lewis PhD FIChemE CEng originally started working with ICI and was seconded to F A Hughes and Magnesium Electron Limited in 1938. Was involved as Chief Engineer with the vast expansion in magnesium extraction and production in the United Kingdom, USA and Canada.

alloying agent. It is produced quite simply by reacting Baddileyite, (a relatively pure form of zirconium oxide) with concentrated hydrofluoric acid and then treating the resultant solution with KC1 when a highly insoluble form of the potassium-zirconium double fluoride is precipitated – a somewhat unexpected reaction. The success of the zirconium alloys was due in no small measure to the work of the chemists who devised this process.

To conclude, I would like to endorse Francis Fox's remarks about the stimulating experience that we all had at MEL during the War years and being part of its rapid growth and development. We were all very young men at the time. Most of us were either in our late 20s or early 30s when we were required to take on responsibilities beyond our years. Dr Fox has mentioned a few names but I would like to add two or three more to his list. I would like to add, first of all, the late Harry Leech who, as Works Manager and later, Technical Manager, gave inspiring leadership to the whole of the efforts required of us. One must also mention the late Jack Charles, Chief Engineer, who achieved with his team under difficult conditions remarkable speed of construction, not only in this country, but in America too.

Lastly, and perhaps unexpectedly, I would like to mention the names of two Foremen, Tom Rogers and Joe Eaton – the first organising the production workers and the second, the foundrymen. To them fell the job of getting people to work efficiently on very unpleasant and often dangerous processes in appalling conditions imposed by the black-out. We should not have got anywhere without them!



Nickel 1900-1950

James Bradbury

In selecting the first fifty years of the century for the basis of this conference, the Historical Metallurgical Society also chose the period in the course of which two most important developments occurred which led to tremendous leaps in the development of the science and technology of metals. These important developments were, firstly, the almost universal availability of electric power and, secondly, the use of petroleum products for both motive power and chemical production.

Up to the turn of the century construction materials had been restricted largely to those which had been available for centuries – wood, stone, leather, brass, bronze, copper, cast or wrought iron – and they were used almost exclusively for providing mechanical properties. The advent of electricity, and of the internal combustion engine, demanded the availability of materials to meet entirely new property requirements – electrical resistivity, magnetic characteristics, high strength or other advanced mechanical properties, corrosion resistance and so on. Further, engineers now demanded these properties in a wide variety of forms, such as sheet, tube, bar, plate, wire and castings.

In this fifty years alloys, new to engineering designers, physicists and chemists, were developed which enabled them continually to improve the performance of machines, develop new chemical processes and to invent radio, television, the atom bomb, atomic energy and innumerable other highly scientific or technical devices that we now regard as commonplace. In almost all of these, nickel plays its part for it is one of the most ubiquitous of metals which shows not only unique properties itself but, when incorporated with other metals in a wide variety of alloys, enables them to develop special properties demanded by the designer.

The range of the developments in nickel and nickel containing alloys is consequently very wide and space allows for only a cursory mention of many of them. For the purpose of this conference it is intended to deal primarily with those metals containing about forty or more percent of nickel though mention will be made of lower but major nickel content materials when appropriate.

As nickel is one of the more costly of the tonnage metallic elements it is normally only used when it, or alloys containing nickel, show properties not readily obtainable without its use.

The alloys to be discussed fall, therefore, into three main groups, namely, alloys with:-

1. Special Physical Properties.
2. Special Mechanical Properties.
3. Special Corrosion Resisting Properties.

1. Alloys with Special Physical Properties

The three physical properties of nickel-containing alloys which are of particular interest are:

1.1 electrical resistivity;

1.2 magnetic properties;

1.3 thermal expansion.

1.1 Electrical Resistivity

The expansion in the use of electricity led to two requirements by designers – a metal of high electrical resistivity but low temperature coefficient of electrical resistivity to enable accurate control of electrical devices to be achieved irrespective of the ambient temperature or the temperature the resistor reached in service – and a metal of high electrical resistivity that could be used for electric heating applications.

Work by a number of investigators examining the properties of the nickel-copper series of alloys had resulted in data summarised in curves published in 1921 by the US Bureau of Standards and shown in Figure 1.

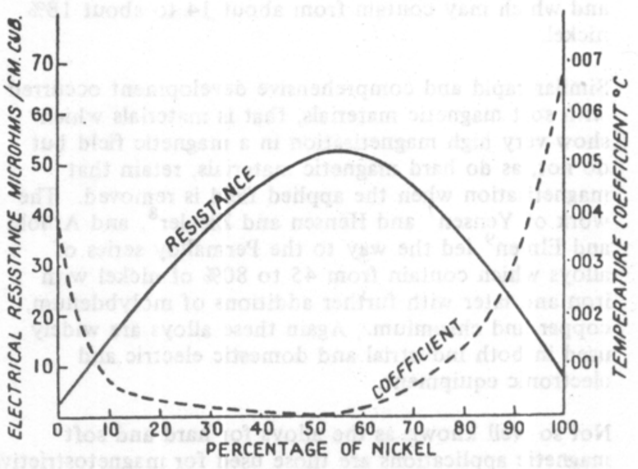


Fig 1 Electrical Resistance and Temperature Coefficient of Nickel-Copper Alloys.

It was the availability of this data which led to the development of the 45Ni55Cu alloy, generally known as Constantan, which satisfied the first requirement for an alloy of high electrical resistivity and low temperature coefficient of resistance. Developed in the first decade of this fifty years, the alloy has remained markedly unchanged and is still used in electrical instruments and for the control of electrical equipment such as electric traction motors.[1]

It is also interesting to note that the alloy is also paired with platinum, copper or iron to provide thermocouples for temperature measurement.[2]

The second requirement for an alloy for electrical resistance heating applications was met as a result of work by A L Marsh[3] who, in 1906 patented alloys of nickel and chromium with and without iron which showed high electrical resistivity (at least twice that of the 45Ni55Cu alloy) with adequate strength at temperature and good resistance to oxidation. Subsequent development of these alloys, by the addition of silicon, the rare-earth metals, manganese or aluminium, improved the performance of the alloys for different applications but little further development of them has been made in the last half of this century. They are still widely used in both industrial and domestic heating equipment.

1.2 Magnetic Properties

One of the fields of alloy development that received the most attention in the fifty years has been that of alloys for magnetic applications. There have been numerous new alloys developed both for hard and soft magnetic applications.

Uses of hard magnetic materials, that is of permanent magnets, is far more widespread than is generally appreciated. Today, there must be few households where there are less than fifty permanent magnets used in domestic equipment, such as refrigerators, washing machines, radios and so on. It was the work of T Mishima[5] in Japan and W E Ruder[6] in the USA in 1934 that led to the development of the whole series of aluminium, nickel-iron alloys, later modified with additions of cobalt, copper and titanium, which are known under such names as Alnico, Cunico, Cunife, and which may contain from about 14 to about 18% nickel.

Similar rapid and comprehensive development occurred with soft magnetic materials, that is materials which show very high magnetisation in a magnetic field but do not, as do hard magnetic materials, retain that magnetisation when the applied field is removed. The work of Yensen[7] and Hensen and Ziegler[8], and Arnold and Elmen[9] led the way to the Permalloy series of alloys which contain from 45 to 80% of nickel with iron and later with further additions of molybdenum, copper and chromium. Again these alloys are widely used in both industrial and domestic electric and electronic equipment.

Not so well known as the alloys for hard and soft magnetic applications are those used for magnetostrictive applications and for magnetic compensation in electrical instruments.

Magnetostriction, the change in dimensions when a material is subjected to a magnetic field (Fig 2), is used for developing sound waves as used for echo depth sounding Asdic equipment [10]. Equipment for dislodging dirt when cleaning instruments, such as watches, or cleaning clothing. Nickel is widely used in such 'sound generating' and 'sound receiving' equipment for nickel, alloys of nickel with iron and with cobalt show strong magnetostrictive effects.

The change in dimensions due to magnetisation is known as the Joule effect and the change in magnetisation due to stress as the Villari effect. The uses of both these phenomena were developed during the years prior to the second world war and have been refined since. Nickel and nickel alloys, remains the predominant material used.

The second little known but important application of magnetic alloys of nickel is that of magnetic compensation in electric meters and the most common design of speedometers. The use of magnetic shunts through their own change in magnetic properties with temperature, adjusts the magnetic field across the moving aluminium disc which is the basic component in these instruments. Thus the change in the electrical resistance of this aluminium disc with change in ambient temperature is compensated otherwise significant errors, up to 10%, in readings of power consumption or speed would result. The alloys used in this application came from the nickel-iron or the nickel-copper series and have changed little since they were first developed in the later half of our fifty years.[11,12]

1.3 Thermal Expansion and Constant Modulus Alloys

Late in the nineteenth century researchers[13] had been studying the nickel-iron series of alloys and had discovered that an alloy containing 36% nickel showed almost a zero coefficient of thermal expansion at room temperature and that with higher nickel contents this minimum of the coefficient of expansion occurred at higher temperatures. This unique property of this series of alloys was rapidly made use of in the nineteenth century, to replace the costly platinum-iridium alloy that had previously been used for the production of standard lengths. In addition they were used to satisfy the demand for metals which would form a seal with glass and provide improved properties over the copper to glass seals which had previously been used. Also as the low expansion component of assemblies used as pendulums in clocks and other equipment demanding that no dimensional change should occur over a range of temperatures. Later the alloys were used in the temperature control switches or thermocouples so common now in electric irons, water heaters and so many other applications in domestic and industrial equipment.[15,16] Fig 3.

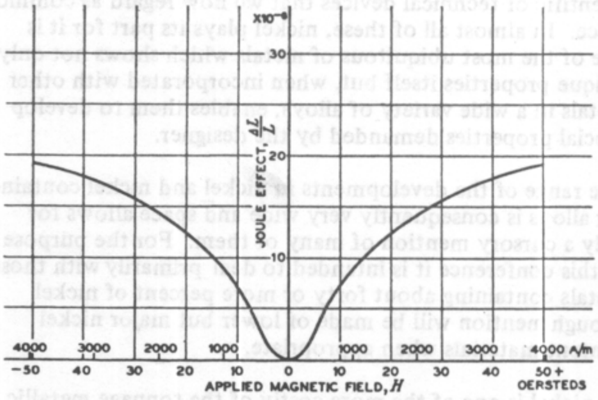


Fig 2 Magnetostrictive Effect in Nickel

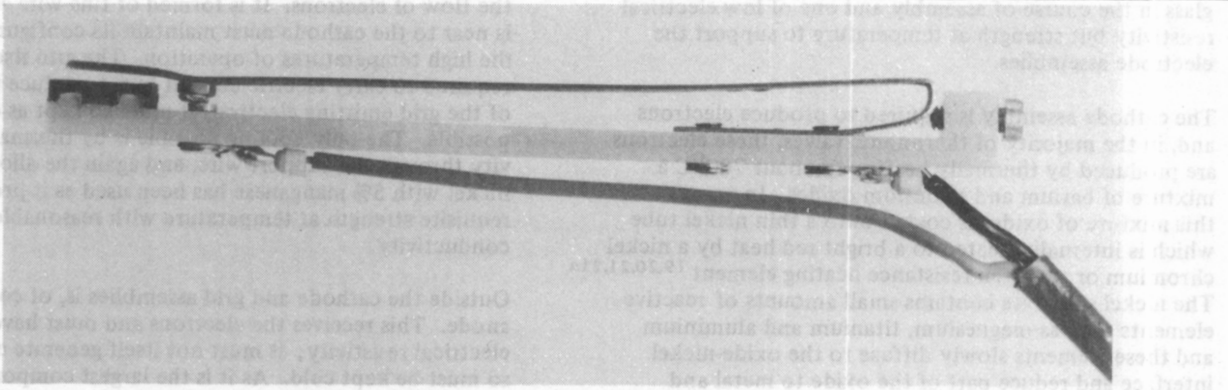


Fig 3 Thermostat, using bimetal strip, for controlling temperature in fish tank.

A further development of this interesting series of nickel-iron alloys was that of age hardening alloys which showed a constant modulus of elasticity over a wide range of temperatures from sub-zero temperatures to about 500°C. These alloys, and there are many of them, may contain up to 42% nickel with cobalt, chromium, manganese, silicon, molybdenum, and are used as spring materials in watches, clocks and other instruments where it is essential that the properties of the spring must not vary over a range of temperatures.[17, 18]

1.4 Thermionic Valve Alloys

This heading may well seem out of place in this section which deals with alloys of special physical properties, but the requirements of the thermionic valve for radio, television and other electronic equipment led to the development of a series of nickel-base materials for specialised applications, certain of which remain in use today in cathode ray tubes. These alloys required both physical and, in certain cases, chemical properties and are, in the majority of cases, unique.

The basic components of a thermionic valve are electric leads to carry the electric current and which must pass through the glass envelope; a cathode assembly which produces the electrons, grid assemblies which control the flow of the electron and an anode assembly at which the electrons are collected (Fig 4).

The electric leads which must seal into the glass envelope in order that the vacuum in the valve can be maintained demand the use of the nickel iron alloys of controlled thermal expansion referred to earlier. These alloys then need to be joined to alloys of low electrical resistance but reasonable strength at above ambient temperature so that they can support the arrays of the cathode, grid and anode assemblies. For this application alloys of nickel with about 5% manganese were developed. However where the lead leaves the glass an intermediate material has been used which is a short piece of nickel wire with the special property that, when sealed into the glass envelope it produces bubbles in the glass. These bubbles fracture readily if the nickel-manganese alloy wire support for the electrode assemblies has to be bent during assembly. The bubbles act as a buffer to prevent a crack spreading right through the glass section and destroying the seal. Thus, the leads into the glass envelope required three different nickel alloys – one to form the seal with the glass, one to prevent cracking of the

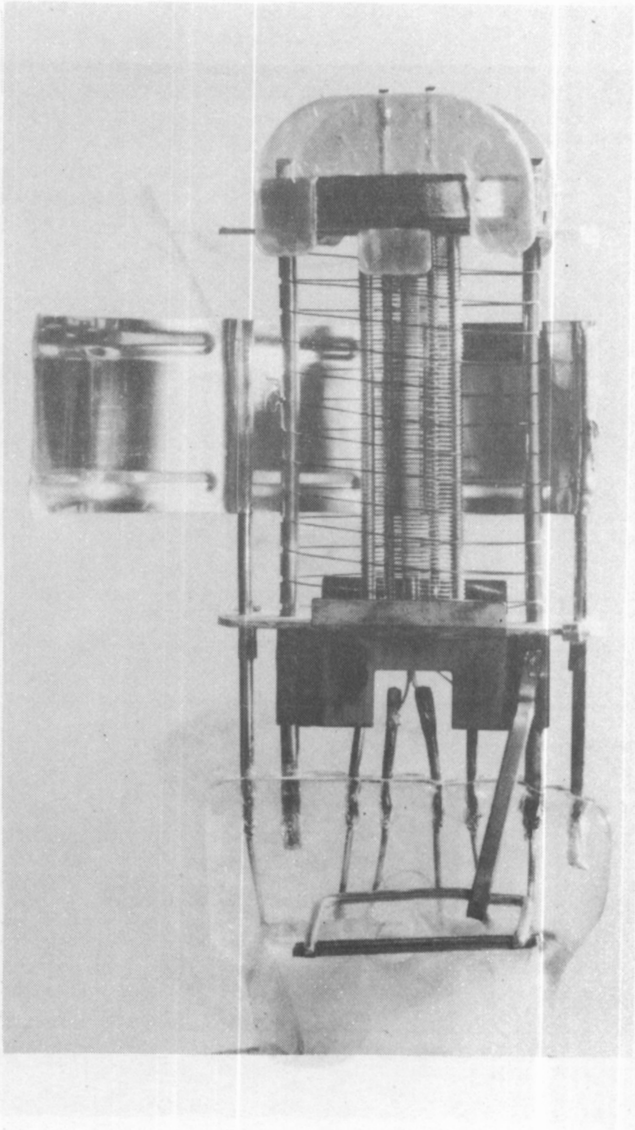


Fig 4 Radio valve showing glass to metal seals and cathode, grid and anode assemblies with support wires.

glass in the course of assembly and one of low electrical resistivity but strength at temperature to support the electrode assemblies.

The cathode assembly is required to produce electrons and, in the majority of thermionic valves, these electrons are produced by thermally heating to about 700°C a mixture of barium and strontium oxides. In many valves this mixture of oxides is coated onto a thin nickel tube which is internally heated to a bright red heat by a nickel chromium or tungsten resistance heating element ^{19,20,21,21a}. The nickel substrate contains small amounts of reactive elements such as magnesium, titanium and aluminium and these elements slowly diffuse to the oxide-nickel interface and reduce part of the oxide to metal and improve the electron emission characteristics of the cathode.

The grid assembly surrounds the cathode and controls the flow of electrons. It is formed of fine wire and as it is near to the cathode must maintain its configuration at the high temperatures of operation. The grid itself is not required to carry electric current but, to reduce the chance of the grid emitting electrons it must be kept as cold as possible. The only cooling possible is by thermal conductivity through the support wire, and again the alloy of nickel with 5% manganese has been used as it provides the requisite strength at temperature with reasonable thermal conductivity.

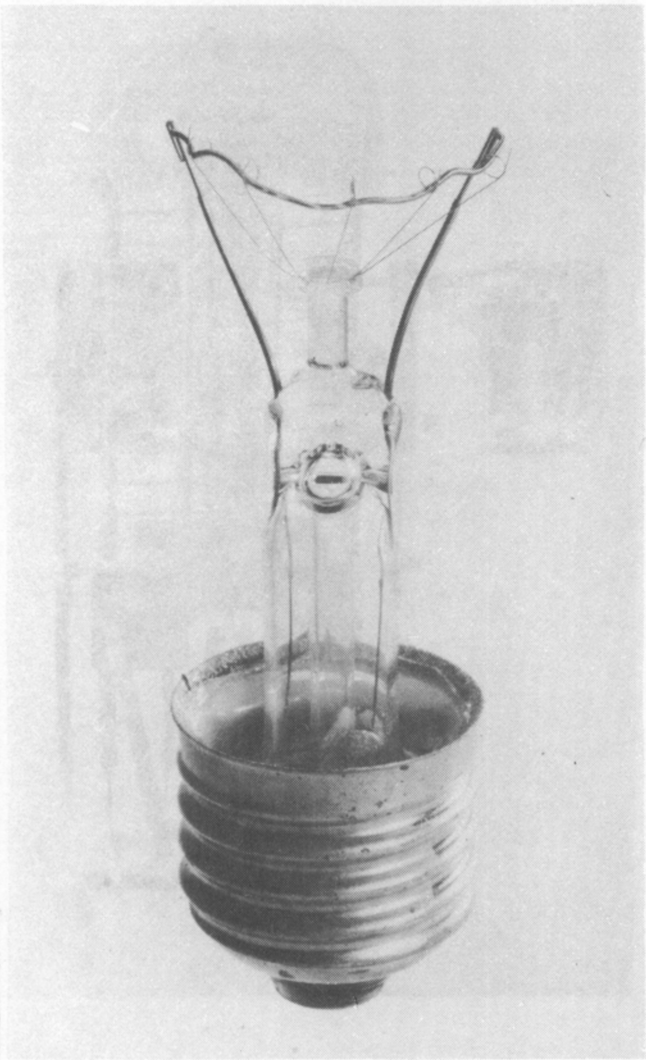


Fig 5 Domestic lamp bulb showing glass to metal seals and filament support wires.

Outside the cathode and grid assemblies is, of course, the anode. This receives the electrons and must have a low electrical resistivity; it must not itself generate electrons, so must be kept cold. As it is the largest component in the whole valve assembly it must also not contain gas which will diffuse out and destroy the vacuum. Nickel itself has proved one of the most effective anode materials. It has low electrical resistivity, it is malleable and weldable for production purposes and, with regard to thermal emission, essential to keep it cool, can readily be coated with a thin film of carbon to provide the black surface required for good thermal radiation.

Thus, in the thermionic valve, some six different nickel alloys provide the special physical and chemical properties required for the various components.

It is interesting to note that the alloys used for the glass to metal seals and lead in and support wires in the thermionic valves are also used in the same applications in the common electric lamp (Fig 5).

2. Alloys of Special Mechanical Properties

The second group of nickel alloys that were developed in these fifty years and which have helped to change our way of life are those which are used because of the special mechanical properties they offer to the design engineers. These properties are primarily those which provide strength at high temperature in many cases along with corrosion resistance at those temperatures. Certain of the alloys are also used at sub-zero temperatures.

The most widely known application for these alloys for use at high temperatures is, the gas turbine but, as will be mentioned later, they have applications in other fields of technology.

The basis for the development of the alloys for high temperature use was the series of nickel-chromium and nickel-chromium-iron alloys which had proved effective as electrical resistance heating materials and which have been referred to earlier. One of the earliest applications of the nickel-chromium alloy was as a coating to the seats of the exhaust valves in petrol engines using fuel with a high content of lead.

With the invention of the gas turbine came the requirement for two main types of metal to operate at the very high temperatures required in the operation of the gas turbines. The two principal applications in the period we are discussing were for the combustion chambers, in which the liquid fuel was burnt to provide the hot gas to drive the turbines, and for the stator and moving blades of the turbine itself.

Clearly the nickel-chromium alloys would provide the oxidation resistance required at the service temperature but in the form developed as an electrical resistance material, though they showed workability required for producing the sheet material for combustion chambers or bar material from which blades could be forged and machined, they did not provide the strength that was essential at the operating temperature.

This strength was initially developed in these alloys by carefully controlling the addition of small percentages of titanium, aluminium and carbon. These additions coupled with special heat treatments hardened the basic 80% Ni, 20% Cr composition by a precipitation hardening mechanism whilst the basic formability of the alloys remained adequate for production purposes. It was alloys of basically this type which formed the early 'Nimonic' series of alloys which included Nimonic 75, 80 and 80A. Later the strength was further improved with major additions of cobalt and molybdenum which increased the strength of the matrix[22,23,24].

At the same time these wrought alloys were being developed alloys which could be cast to the final blade shape required for the stator and moving blades were also being developed.

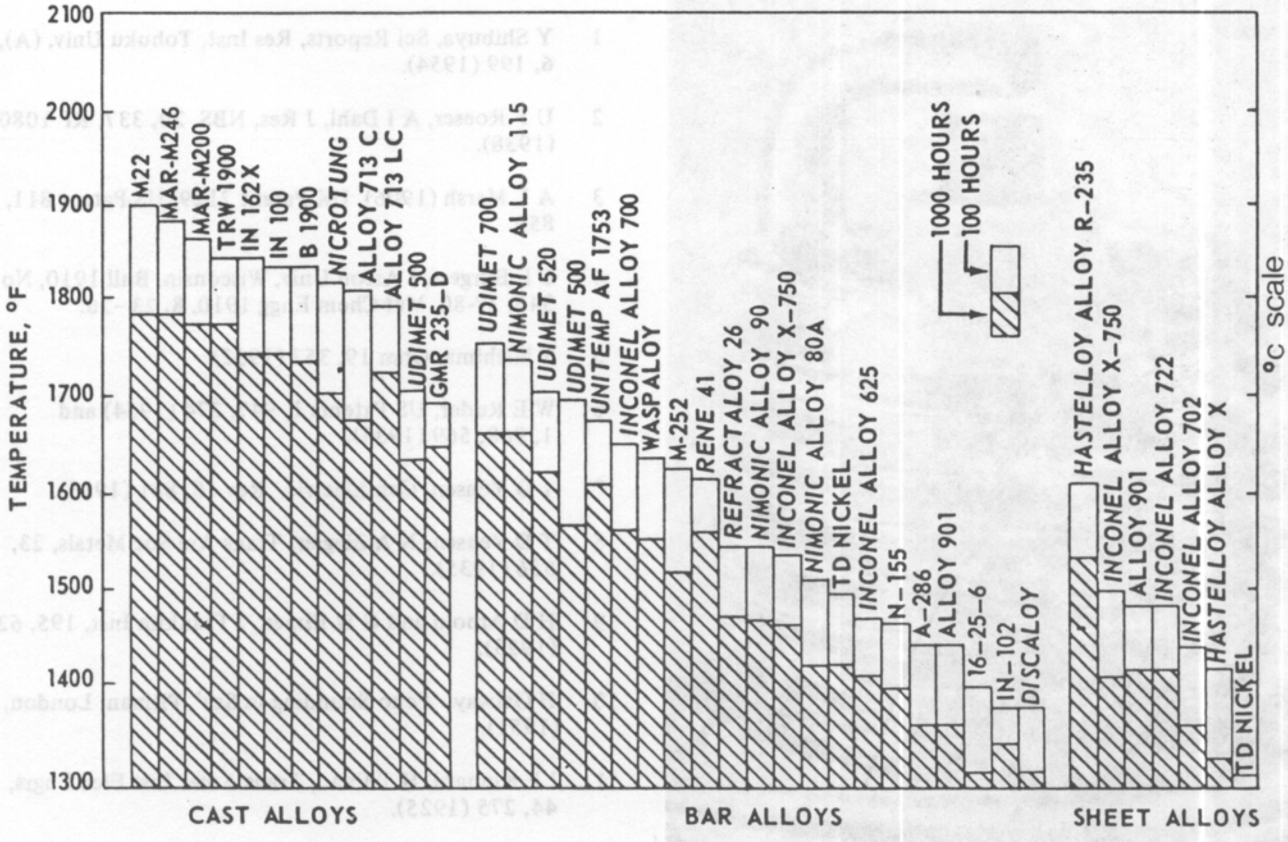


Fig 6 Temperature to Produce Rupture in Various High Temperature Alloys in 100 and 1000 hr, at a Stress of 20,000 psi.

These cast alloys tend to be highly complex, some containing as many as nine elements, including lanthanum, chromium, aluminium, tungsten, molybdenum, vanadium, zirconium, carbon and, of course, nickel[25].

The range of alloys is illustrated in Figure 6 which gives the temperature at which rupture will occur in 100 and 1,000 hour of stress at 20,000 psi.

In other fields of technology alloys of nickel with minor additions of silicon and up to 55% chromium were developed as casting alloys for use in plant for cracking of petroleum products and in high temperature boilers where a material with strength at high operating temperatures is required to resist the products of combustion of fuel oils[26].

3. Alloys with Special Corrosion Resistance

Nickel itself shows valuable corrosion resistance to a wide range of media. These include potable waters, mineral acids, alkalis, salts and organic acids. It is widely used in the construction of water meters for the production of caustic soda and caustic potash, for the handling of phosphoric acid, hydrochloric acid and fluoric acid but it is not resistant to corrosion when the conditions are oxidising as with ferric chloride or with hypochlorates[27].

It is the resistance to corrosion by fluorides that resulted in the use of nickel powder for the production of the diffusion membranes used in the separation of Uranium 235 as the hexafluoride.

One interesting application is for sparking plug electrodes where, nickel with minor additions of silicon, manganese chromium, resists wear under the conditions to which such electrodes are subjected in an internal combustion engine. Fig 7.

An alloy of nickel with 30% of copper 'Monel'[28] has a useful resistance to many of the media to which nickel is corrosion resistant and also higher mechanical properties at a lower cost. Modifications of this alloy with additions of silicon provide an alloy that can be cast for valve and pump parts. If modified by additions of aluminium and given appropriate heat treatment an alloy showing high mechanical strength with little loss of the corrosion resistance as compared with the parent alloy is provided.

Alloys of nickel with about 28% molybdenum and with 17% molybdenum and 15% chromium display high resistance to corrosion by all concentrations of hydrochloric acid at temperatures up to boiling, and the latter alloy shows an unusual degree of resistance to oxidising substances – again, especially those containing chlorides[29,30].

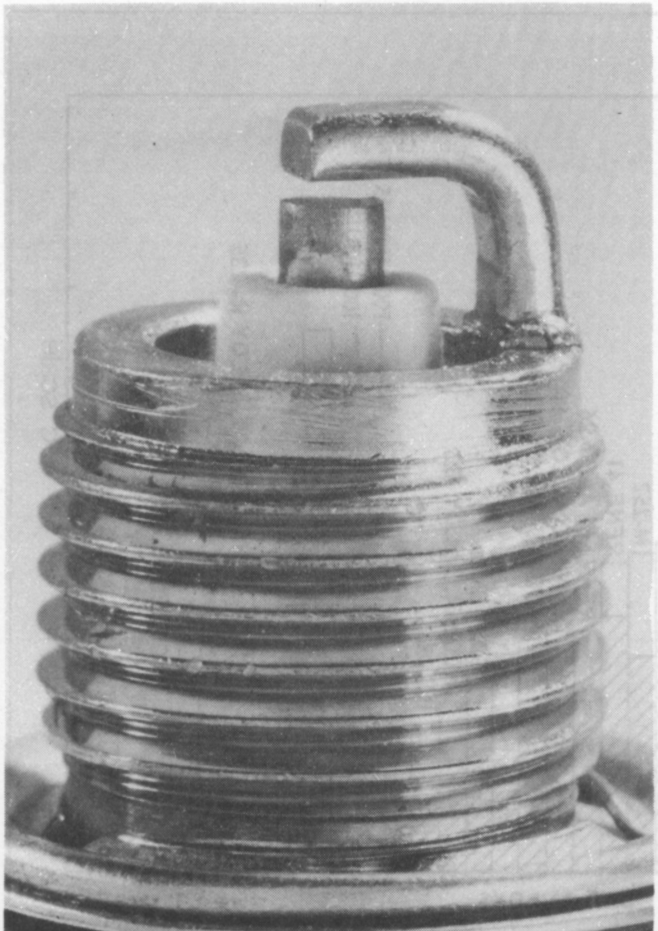


Fig 7 Nickel alloy electrodes in sparking plug.

4. **Conclusions**

As was explained at the beginning of this paper, the fifty years that we are concerned with saw developments in nickel and nickel-based materials for use throughout all branches of engineering. Certain scientific work had already prepared the way for these developments, notably that of the investigation of the physical properties of nickel and the nickel-iron series of alloys, but it was the first fifty years of this century which saw the commercial development of the production and use of those alloys. New nickel-based alloys were devised during this period to meet the ever increasing demands of all engineering disciplines and along with the scientific work involved to identify the alloys which showed the required properties went the development of the production techniques to make them available for use.

Since 1950 development of new materials has slowed and in certain cases alloys developed for specific applications as in radio valves have fallen almost into disuse as the component itself has been replaced by new devices, in the transistor.

Nickel is an ubiquitous metal and undoubtedly cannot be substituted for in many of the applications. Its uses are varied and highly technical and interesting, but it is hoped that this somewhat cursory account has described adequately its history in the first fifty years of this century.

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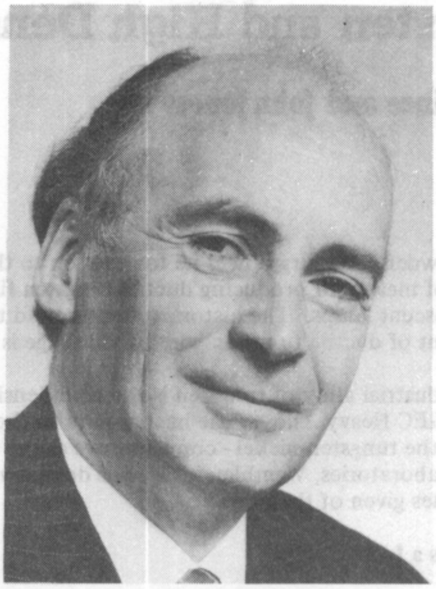

Ernest J Bradbury M Eng MIMechE CEng FIM graduated at Liverpool University and joined Mond Nickel Research in 1938. From 1940 until 1945 he served in the Royal Air Force being seconded to the Ministry of Defence for Defence Procurement. Returning to industry he became Research Manager at INCO Research and Development and later, Director of INCO Europe London. During the last few years he has been Director at British Nuclear Fuels, Metal Technology Centre.

Tungsten and **High Density alloys**

Alan Prince and John Jones

Synopsis

Modern powder metallurgy owes its foundation to the discovery of means for producing ductile tungsten filaments for incandescent lamps. The historical background to the development of ductile tungsten wire by Coolidge is traced.

A major industrial alloy of tungsten is the high-density alloy known as GEC Heavy Alloy. The background to the invention of the tungsten-nickel - copper alloys at the GEC Research Laboratories, Wembley in 1935 is documented and examples given of their use.

Tungsten as a Light Source

Just over 100 years ago, in October 1881, the first commercial supply of electricity became available from a central power station in Godalming[1]. Power was generated by a Siemens dynamo driven by a water wheel. Some 200 years ago Alexandro Volta invented the 'Voltaic pile' consisting of discs of copper separated from discs of zinc by flannel soaked in brine. On connecting the two metals by a wire bubbles formed on the copper and the wire became hot. Volta had discovered a means of producing and transmitting a relatively constant supply of low voltage electricity. He was led to his discovery by the prior work of Galvani who showed that contact between metals and animal tissues produced muscular contractions – the frog's leg experiment beloved of all school-children. One of the consequences of Volta's work was the stimulation it gave to work in England. Using Voltaic cells Nicholson and Carlisle electrolysed water and Davy (1807) separated potassium and sodium from potash and soda respectively. More significantly Davy demonstrated the carbon arc lamp before an audience at the Royal Institution in 1808. He brought together two carbon electrodes fed from a massive set of batteries and, on moving the poles a short distance apart, he pulled an intense arc between them. In the early 19th century there were available the two ingredients for an electrical lighting system – a source of power and an illumination system.

A practical lighting system did not emerge for another 70 years. On the one hand a cheaper and more reliable power source was required and on the other a more practicable illumination source had to be developed. The carbon arc was an intense source of light but it needed a great deal of power and it emitted noxious fumes as the carbon electrodes and insulation were consumed. Faraday's discovery in 1831 of electromagnetic induction, the production of an electric current by moving a magnet through a coil of wire, ultimately led to the development of the electrical generator. With the advent of an effective power source what was needed was a practicable source of illumination – an incandescent lamp.

The lightning conductor had been invented in 1752 by Benjamin Franklin so it was well known that a metal conducting electrical current became hot enough to glow red. As an aside Franklin supervised the installation of conductors on British buildings in the 1760s and became embroiled in an argument in the Royal Society as to whether lightning conductors should have sharp or blunt ends. To raise the conductor to a high enough temperature for it to become incandescent and provide a light source requires some means to protect the conductor from oxidation. In terms of the development of an incandescent filament lamp progress became critically dependent on the production of a good vacuum in which the conductor could operate at high temperature without fear of oxidation. It was not until Sprengel invented the mercury vacuum pump in 1865 that the vacuum problem was solved. All that then remained was to search for a conductor. The story of the development of the carbon filament by both Edison and Swan has been told many times. Each introduced a carbon filament lamp in 1879, the filament being made by carbonising naturally-occurring fibres such as bamboo or cotton thread. By 1890 artificial fibres were in use; they were produced by dissolving cotton wool in a solution of zinc chloride to extract the cellulose as a gelatinuous fluid. When squirted through a die into alcohol the gelatinous thread loses any remaining moisture and hardens into a thread that can be wound on to a drum for final air drying. Carbonising of the thread, to drive off the hydrogen and oxygen of the cellulose without consuming the carbon, was done in sealed plumbago (carbon) pots to exclude ingress of air. In this way carbon filaments were made. That one can extract light from cotton wool is a fact; it should be compared with the vain attempts by the academician of Lugado, in 'Gulliver's Travels', who spent eight years trying to extract 'sunbeams from cucumbers'. Incidentally the process for producing carbon filaments briefly described above was that used in Robertson Electric Lamps Ltd, later to be known as the Osram-GEC Lamp Works. The Robertson Lamp was first produced on a commercial scale in 1893 in Hammersmith, London, Figure 1.

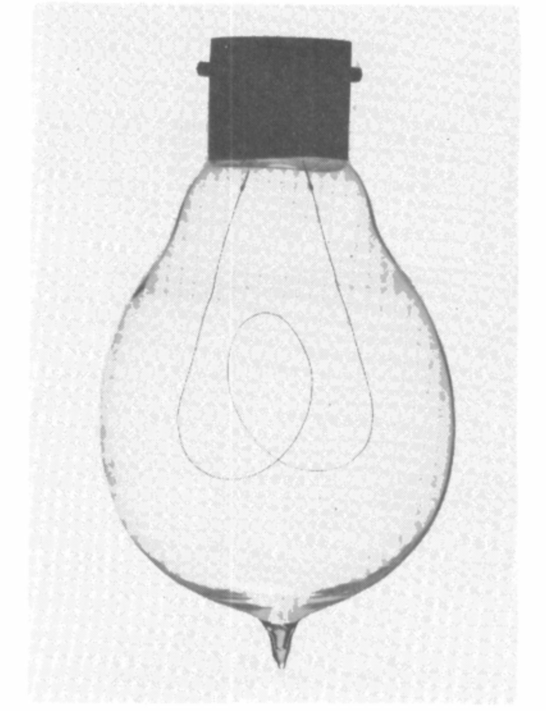

Figure 1 A Robertson lamp with carbon filament, 1893.

Carbon as a filament material has a limit to its operating temperature. As the temperature is increased the rate of evaporation of the carbon filament increases and the carbon lost from the filament is deposited on the glass bulb. The blackening of the bulb drastically reduces the light obtained from the lamp. For carbon filaments an operating temperature of not more than 1600°C is dictated by this factor. A cautionary warning from the Robertson Electric Lamp Company to its customers is worth quoting:

> **To Electric Light Consumers**
>
> **Don't** believe that the lamp which costs the least is the most economical.
>
> **Remember** current costs more than lamps, and cheap lamps are 'wasters'.
>
> **Don't** believe that the lamp which lasts the longest is invariably the best or the cheapest.
>
> Directly a lamp blackens it should be cast aside.
>
> **Remember** again, current costs more than lamps.
>
> **Don't** burn lamps until the filaments are fractured.
>
> **Remember** yet again, a new lamp will cost you far less than the current you will waste.

This advice still holds good today when lamps are produced under stringent quality control for a 1000 hour standard life.

Any further progress had to depend on the development of metal filaments that would operate at higher temperatures and increase the available illumination. Attention focussed on the refractory metals, those with high melting points. Osmium filaments, melting at 3033°C, were used in the first commercial metal filament lamps. Auer von Welsbach produced filaments of osmium salts, mixing the powder with sugar syrup and squirting through fine dies. The thread was then heated as for carbon threads to drive off the organic binder and sinter the osmium into a rudimentary metal filament. The osmium filament lamp was produced commercially from 1898 to 1900. Osmium was expensive and scarce and the osmium lamp was soon superseded by the tantalum lamp, a development of von Bolton of Siemens and Halske. By purifying the tantalum it became sufficiently ductile to be drawn into wire. The tantalum filament lamp was marketed in the first decade of this century but it in turn was displaced by the superior tungsten filament lamp and this remains the standard filament material to this date.

The story of the development of the tungsten filament is a strange one. Tungsten has the highest melting point of the metals at 3422°C. It has a relatively low evaporation rate and good strength at high temperatures. It is easily oxidised and must be protected for high temperature operation by enclosing it in a good vacuum or an inert/reducing atmosphere. The trouble with tungsten is that it is a brittle metal and cannot be worked in the conventional way. The first tungsten filaments were produced in 1904 by Just and Hanamann of the Royal School of Technology, Vienna. They mixed very fine black tungsten powder with dextrin or starch to form a paste which was forced through a fine diamond die. The thread was subsequently heated to a red heat to drive out moisture and light hydrocarbons and then raised to incandescence by passing electric current through it whilst surrounded by hydrogen. This treatment removed the binder and allowed the tungsten to sinter into a solid metallic filament. These first tungsten filaments were an appreciable advance on the carbon filament in that they provided a brighter light but these tungsten filaments were brittle. In a foreword to an article[2] by S L Hoyt on the development of ductile tungsten H W Gillett says:

'We will remember the early filaments of 1907 in a few lamps we had in the Cornell laboratories, how gingerly we screwed them into the sockets lest they break and what a contrast they were to the feeble carbon lamps at the boarding house. (In fact the landlady couldn't afford to use enough carbon lamps to make it possible to study, so she provided an oil 'student lamp').'

Lamps with these squirted tungsten filaments were made from about 1908 in our Hammersmith factory.

The breakthrough came in the period 1906-1910 when W D Coolidge of the U S General Electric Company mastered the brittleness of tungsten and developed a method for drawing it into fine wire for filaments. Coolidge was not a metallurgist and in his paper to the Sorby Centenary Conference of the AIME[3] he started by answering the question why the discovery and development of ductile tungsten were made by the US General Electric Company and how he, rather than a metallurgist, happened to have a leading role in this.

'As I see it now, fifty-odd years after the event, it was due, among others, to the following circumstances:

1. Dr Willis R Whitney had recently established for the Company a pioneer industrial laboratory for fundamental research.
2. The Company had a large incandescent lamp business.
3. One of the early contributions of the Laboratory was Dr Whitney's substantial improvement in the carbon filament of that lamp, which emphasised the possible fruitfulness of research in the incandescent lamp field.
4. German work on metal filaments of osmium and, especially, tantalum, had threatened the competitive position of the carbon filament, thus justifying much research in the metal filament field'.

The story of Coolidge's work has been described by S L Hoyt. It can be divided into three stages. The first stage, occupying 1906 and the early part of 1907, initiated the amalgam process for tungsten filaments. In Coolidge's words:

' In the course of these experiments with impregnated rods, we had become acquainted with cadmium amalgams, and the long temperature range through which they are plastic. We found, for example, that a 50% cadmium amalgam could be extruded under pressure, from a heated mold, through a die, into nice smooth wire. We also found that if this amalgam were heated up to its plastic temperature range in a mortar, we could, with a pestle, rub tungsten powder into it, and that even after getting in more than 50% by weight of tungsten, we could, at a lower temperature, squirt it through a die into a pliable, strong, smooth wire. It also developed that, by passing current through a loop of this wire in a vacuum, the mercury would vaporize out first, and then, with rising temperature, the cadmium, to be followed by further temperature rise, with complete sintering of the tungsten into a smooth shiny filament. With minor modifications, such as the addition of a little bismuth to the amalgam, this became the so-called Amalgam Process, and was used in our first commercial production of tungsten lamps, US Patent No 1, 026, 343, granted May 14 1912. It yielded filaments free from carbon and also free from mechanical defects. Such filaments not only made good lamps, but they also served as the starting material for our first drawn tungsten wire.'

The second stage, undertaken by C G Fink under the supervision of Coolidge who was busy introducing the amalgam tungsten process into factory production, took as starting material the 10-25 thou diameter amalgam process filament. The idea was to draw this filament to finer diameters. Conflicting views were held on how best to do this. It was argued that if one annealed the starting material the tungsten would be in a ductile condition such that it could be drawn like other metals. Coolidge though it futile to attempt to induce initial ductility into tungsten. He believed that tungsten might be drawn hot since it should have some plasticity under these conditions. Work started in 1908 and by October Fink drew the first length of tungsten wire through heated diamond dies. On checking the wire Fink found that it was ductile; it could be permanently deformed at room temperature.

The third stage in the development of ductile tungsten was concerned with scaling up the process for commercial production. A larger starting size than the 10-25 thou diameter amalgam filament was needed. Coolidge decided to follow the powder metallurgy route, pressing dry tungsten powder with no binding agent. Industrial powder metallurgy was about to be born. Not only was painstaking research done to prepare tungstic acid, fire it to tungsten oxide and reduce the oxide to metal powder with the requisite particle size, particle size distribution and purity; also the design of the moulds and methods of filling with tungsten powder had to be worked out. The fragile pressed compact was partly sintered in a hydrogen furnace to give it enough strength to be handled. Full sintering was achieved by passing current through the rod until it was brought almost to its melting point. By such means ¼ inch square tungsten bars were produced. This represented a 125 times increase in cross sectional area compared with the 25 thou alamgam process tungsten wire used for hot drawing. Modern practice uses bars up to 1 inch square.

Means had to be devised to produce fine wire from the sintered ¼ inch bars. In Coolidge's words 'we tried hot-hammering such rods, first by hand, and then with a small power-hammer. Some blows could be struck without cracking, but others not. A skilled blacksmith from the Works was even less successful than we were, for the reason that his first blow chilled the work locally and, from force of habit, he couldn't refrain from striking other blows in that same area, thus producing cracks. In November of 1908 we tried hot rolling, by passing 400 to 500 amperes from roll to roll through the rod – this with a small mill, having rolls only about 1.5 inches in diameter. This was not very successful.

Hammering looked better; but it was now clear that it must be under close control, both as to location of the blows struck and as to the amount of deformation produced by each'. Coolidge finally decided to try swaging to take advantage of the circular shape of the swaging dies. Ductile metals were swaged cold using long bearing dies; tungsten could not be hot swaged with the customary equipment. Short bearing dies had to be developed so as to limit the hammer blow to only a small part of the length of the sintered bar and the speed of feeding the bar through the swaging die had to be such that the part which had been hammered once would not receive a second blow.

Working schedules, relating the reduction in cross sectional area and the temperature of swaging, had to be devised. Swaging was continued through a series of dies until the bars were reduced to 30 thou diameter. Thereafter the tungsten was hot drawn through diamond dies to finished diameter. The history of diamond die development is not part of this essay but could make a fascinating study.

At the end of 1909 Coolidge visited Europe taking with him some of his ductile tungsten wire. His first visit was to the laboratories of AEG in Berlin, a company with a large production of tungsten lamps based on the Just and Hanamann process. Coolidge appears to have had some difficulty in arranging to see the director of laboratories in AEG, but when he did so on November 8, he showed a small spool of fine tungsten wire.

'What is it?' he said. I told him that it was tungsten wire. 'But', he said, 'What is it?' I repeated my answer. He grabbed the spool of wire and rushed from the room. I assume of course, that he went somewhere to test it. When he returned, he seemed almost crazy, so much so, that I worried lest he should do harm to himself. His behaviour left no question in my mind as to whether our secret had, until then, been well kept from the entire European tungsten-lamp industry, with which he was in contact'.

An assessment of the part Coolidge played in the development of the incandescent tungsten filament lamp should touch upon the mastery of the brittleness of tungsten and consider the wider implications of this success.

Coolidge characteristically hit the nail on the head with the final paragraph of his Sorby Centenary paper. 'The successful outcome of our ductile tungsten work was due to the production of the right microstructure. I must, however, say that we were guided in the main, by the experiment itself, rather than by metallurgical knowledge'. In metallurgical terms the behaviour of tungsten cannot be equated to that of the normal metals. Copper, for example, is soft and ductile when it has a fine uniform grain structure. Tungsten is also soft but very brittle when it has the same microstructure. Cold working copper increases its hardness and lowers its ductility. Extreme cold working elongates the individual grains in the direction of working and produces a fibrous structure. In the ultimate ductility is exhausted and the copper splits. Cold working is a relative term. It refers to the plastic deformation of a metal at a temperature below its recrystallisation temperature. When a heavily cold worked metal is heated the elongated grain structure is replaced by a fine uniform equiaxed grain structure at the so-called recrystallisation temperature. With low melting point metals, such as lead, heavy deformation at room temperature is hot working since the lead recrystallises as it is deformed. Working copper at room temperature is cold working and working such a high melting point metal as tungsten at 1500°C is also cold working in that the tungsten is even then below its recrystallisation temperature. (Tungsten specially purified by zone refining has a much lower recrystallisation temperature). Whereas copper loses ductility when cold worked or drawn to an elongated fibrous structure tungsten acquires ductility when cold worked at 1500°C to form a fibrous grain structure, Figure 2. Cold worked copper regains its ductility when equiaxed grains are formed by heating it above its recrystallisation temperature. Tungsten is embrittled if the fibrous structure is replaced by an equiaxed grain structure by a recrystallisation anneal.

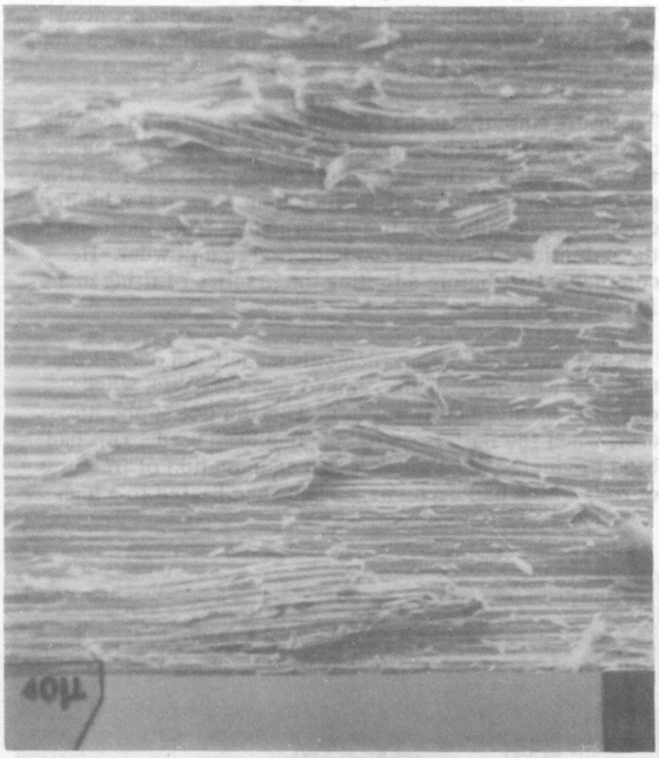

Figure 2 Fibrous structure of cold worked tungsten (fracture surface of a wire split along its length).

Coolidge recognised that the key to successful working of tungsten was the production of a fibrous structure. In litigation against infringement of Coolidge's patent the fibering principle was upheld:

> 'The process which brings out the ductility of tungsten destroys ductility in other metals. The condition in which tungsten is most ductile is the condition in which other metals are least ductile; the condition in which other metals are most ductile is the condition in which tungsten is least ductile.'

By experimentation Coolidge found that a small amount of cold working at high temperature induces ductility at a lower temperature at which the tungsten had been brittle before being worked. In swaging the sintered ¼ inch bar it was initially heated to 1500° – 1600°C. By the time the heated bar was inserted into the swaging machine its temperature would be closer to 1300°C. As swaging continues through smaller dies the temperature was dropped. The ductile range of tungsten is extended to lower temperatures as the degree of working is increased. Each working stage is carried out at progressively lower temperatures until finally, during the later stages of wire drawing the tungsten is drawn at temperatures around 550°C. If the temperature of working is too high no fibrous structure will develop and if too low the tungsten will break. As an aside it is perhaps surprising that the US General Electric Company published very little on tungsten except in the patent literature. It was left to C J Smithelles, one of the founder members of our General Electric Company's research laboratories, to produce a text whose first edition was dated 1926 and which was the standard work for close on forty years. Trade catalogues are publications of a different kind. An extract from our Osram* catalogue, dated January 1912, is worth quoting.

> **Osram Lamps with Drawn Wire Filaments**
>
> By the time this catalogue is in the hands of our customers, considerably over a million **Drawn Wire Osram Lamps** will have been in use for a considerable period.
>
> These lamps are manufactured under some original patented processes of ours and we have also acquired the use of patents not owned by us, the two enabling us to make the **best drawn wire lamps in the World.**
>
> The advantages of the Drawn Wire Filaments over those made under the pressed or 'squirted' process will, we think, be obvious; the filaments now being perfectly solid and pliable, are in consequence, able to withstand considerable shock in cleaning and handling, besides which all transit troubles are now eliminated.
>
> We specially wish to make it clear that the electrical characteristics of the Osram Lamp:- Long Life, High Efficiency, ie smaller current consumption than other make of lamp, and high maintenance of Initial Candle Power, are fully maintained, if not excelled, in the Osram Lamp with Drawn Wire Filaments.
>
> A further important advantage is that owing to the filaments being wound in one continuous length it is possible to employ considerably smaller bulbs.
>
> **See the Name OSRAM on Every Lamp**

We must now turn to the wider implications of the development of incandescent filament lamps. The advent of the carbon filament lamp some 100 years ago as a result of the work of Edison and Swan rapidly led to the beginnings of the electrical supply industry. J E Harris[1] has charted the early history, starting with the first central power station at Godalming where electricity was generated by a Siemens dynamo driven by a water wheel (1881). This first station supplied only 27 incandescent lamps and four arc lights. As tungsten filament lamps consumed a third of the energy of carbon filament lamps Coolidge's production of ductile tungsten wire brought the price of electric lighting on to a competitive basis with that of gas lighting using the incandescent mantle. At the outbreak of the First World War the UK had 500 electricity supply stations but these supplied only 75% of the power that four units run by Commonwealth Edison did for the city of Chicago. Nevertheless the initial reason for building central stations was to provide a public source of electricity for lighting homes and buildings. The incandescent tungsten filament has been quoted as the most beneficient gift that metallurgy has given to mankind. It only needs an interruption of supply in winter to bring home to us how much our daily lives depend on tungsten.

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* A combination of osmium and wolfram, the name originating in Germany.

The incandescent filament lamp also led to the thermionic radio valve and the birth of the radio industry. This originated with the discovery of electron emission from heated carbon and tungsten filaments in the vacuum lamps made in the 1890s. The presence of an established lamp industry with its accumulated manufacturing expertise did a great deal to rapidly expand the valve industry. Indeed commercial valves were originally manufactured in lamp works.

Metallurgically modern powder metallurgy owes its foundation to the commercial production of tungsten filaments. No alternative technique to powder metallurgy processing has surfaced in the past 80 years. This is in contrast to Wollaston's original work on the fabrication of platinum by powder metallurgy; the advent of melting processes for platinum rendered the powder approach obsolete.

The use of tungsten as a lamp filament poses many metallurgical problems as, in contrast to the majority of industrial metals and alloys, it is used at temperatures considerably higher than its recrystallisation temperature. The early Coolidge filaments were made from pure tungsten without any additional substances. Such a material is produced as a fine wire with a fibrous grain structure. On heating to operating temperature, over 2000°C, by passing electric current through the filament the fibres break up and are replaced by minute equiaxed grains. The tungsten is said to have recrystallised. The time scale for recrystallisation at 2400°C is under one minute. With continued heating the size of individual grains increases by absorption of neighbouring grains. This process is called grain growth. In pure tungsten filaments grains are produced that span across the wire diameter. The boundaries between these large grains are frequently perpendicular to the axis of the wire and this structure can deform by slipping of one grain over its neighbour, a phenomena called offsetting in the lamp industry, Figure 3. In addition to offsetting grain growth can continue, albeit slowly, during the life of the filament. This continued grain growth can also lead to pronounced distortion, or sagging, of the filament between its mounting posts in the lamp, Figure 4.

To ensure stability of the filament it is essential to exercise close control over the grain structure developed during recrystallisation. The original method was to aim for a fine grained structure in which further grain growth is inhibited. Coolidge originally used fireclay crucibles from Battersea for the reduction of tungstic oxide to tungsten powder. He comments that before adopting the practice of firing in a Battersea crucible –

'We had found that lamp filaments made from our drawn tungsten wire offset badly, and so had short life, when operated on alternating current. This did not apply, however, when the Battersea crucible had been used. This had been preducted from microscopic examination of fractures of rods which had been swaged and then heated to a high

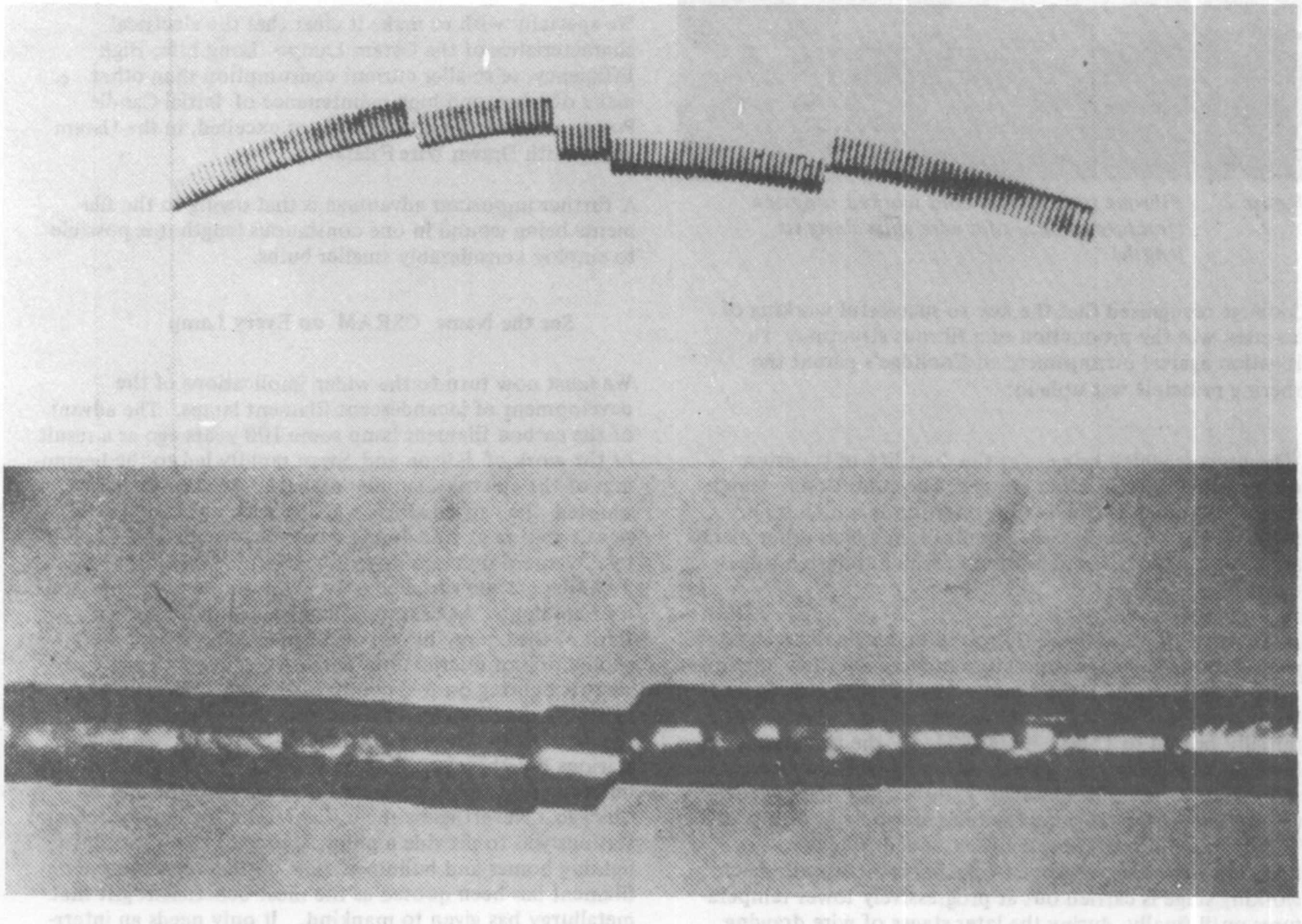

Figure 3 Offsetting in coil and wire.

temperature. Without Battersea-firing, the fracture would often show large crystals, while, with the Battersea, the fracture was relatively fine-grained. Refractory oxides had been introduced by the crucible from its hot walls, and these impurities carried over into the tungsten, where their presence interfered helpfully with crystal growth. We found that rare earth oxides, such as thoria, for example, added to tungsten powder, in whose preparation no Battersea crucible had been used, also prevented offsetting, as did zirconic and ceria.

Powder metallurgy had, then, made possible the control of crystal growth that one would not have had if the starting rod had been a melted ingot.'

The so-called Battersea process is of historical interest. The introduction of 0.1% alumina and 0.1% silica from the crucible walls into the tungstic oxide resulted in a tungsten wire containing a fine dispersion of these oxides. It was probably the first oxide dispersion strengthened metal to be made. Reliance on picking up oxides from a hot crucible wall inevitably gave a product with variable properties and performance. In 1910 Coolidge patented the use of thoria to give a fine grain structure on recrystallisation of the tungsten filament. This gave good life for the type of lamp then produced. These used long straight wires of tungsten mounted under tension in the form of a cage and enclosed in an evacuated glass bulb. As a comment on the secrecy surrounding tungsten wire production the Osram factory at Hammersmith were producing tungsten containing 0.75% thoria in 1919 under the pseudonym of 'gallium'. With the exception of mercury, gallium has the lowest melting point of the elements and the use of its name for one of the highest melting point alloys would appear eccentric.

Up to 1912 the filaments of incandescent lamps operated in a vacuum. Then Langmuir began a series of brilliant researches which showed that a lighted filament of a gas-filled lamp is surrounded by a cylindrical layer of relatively stationery gas in fairly close proximity to the filament. Beyond this 'Langmuir layer' convection causes turbulence in the filling gas. The diameter of the 'Langmuir layer' is largely independent of the diameter of the incandescent filament. Heat loss from the filament is proportional to the surface area of the Langmuir layer and not to that of the filament. If the filament is coiled to reduce its length the heat loss is greatly diminished by the reduction in length of the Langmuir layer. The filament can be run in a gaseous atmosphere while avoiding a prohibitive loss of heat to the gas. Coiling the filament reduced heat losses and raised the luminous efficiency of the lamp. The gas filling also helped to suppress evaporation of the tungsten and allowed the temperature of the filament to be increased without decreasing the life, thereby contributing further to the increase in efficiency. The gas-filled lamp with a coiled tungsten filament, patented in 1913 by Langmuir, is the basis of the modern tungsten lamp, Figure 5. The filling

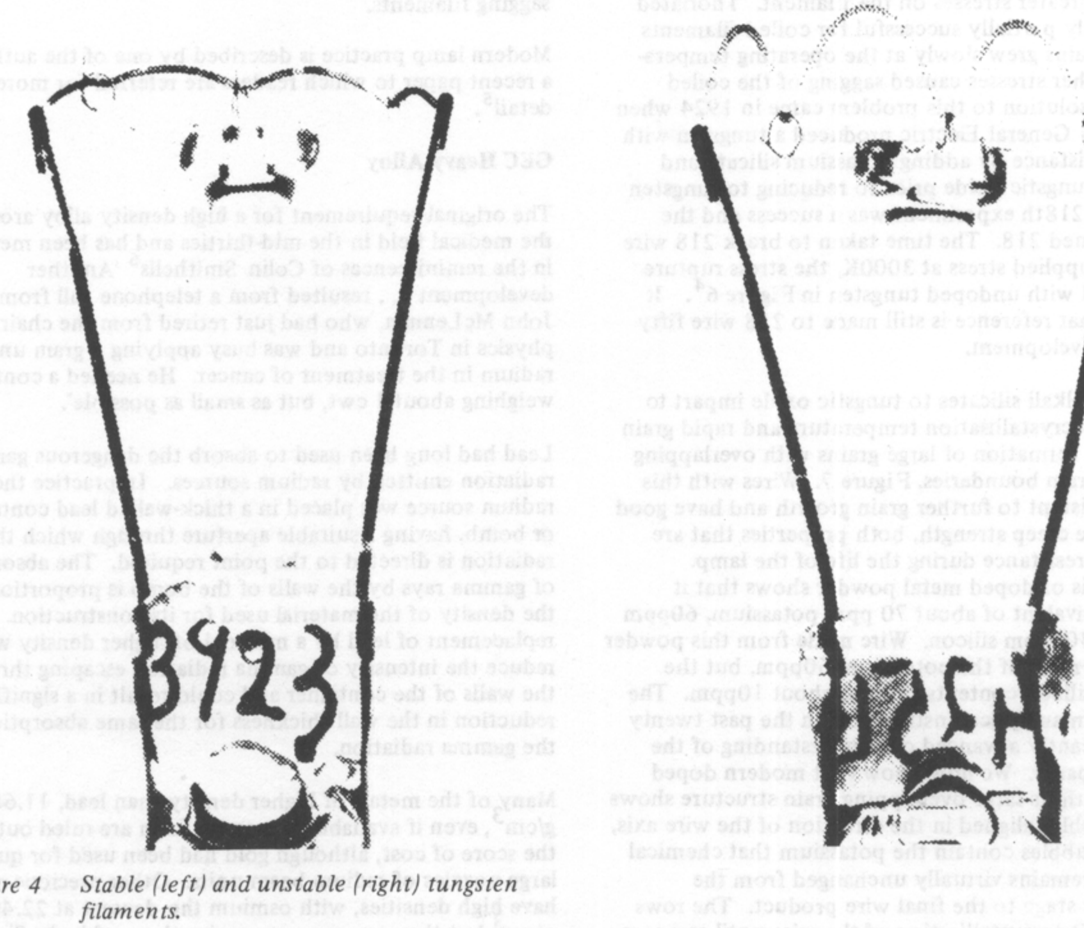

Figure 4 Stable (left) and unstable (right) tungsten filaments.

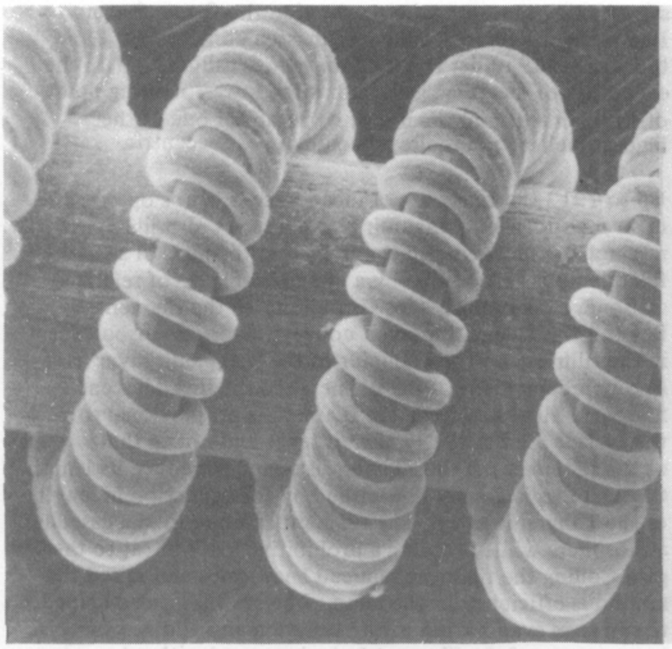

Figure 5 Electron micrograph of a coiled coil filament.

gas is 93% argon and 7% nitrogen.

The introduction of the gas-filled incandescent lamp in 1913 involved coiling the filament into a fine helix, and this introduces greater stresses on the filament. Thoriated tungsten was only partially successful for coiled filaments since the fine grains grew slowly at the operating temperature and the higher stresses caused sagging of the coiled filaments. The solution to this problem came in 1924 when Dr A Pacz of US General Electric produced a tungsten with adequate sag resistance by adding potassium silicate and alumina to the tungstic oxide prior to reducing to tungsten powder. Pacz's 218th experiment was a success and the wire was christened 218. The time taken to break 218 wire with increasing applied stress at 3000K, the stress rupture life, is compared with undoped tungsten in Figure 6[4]. It is noteworthy that reference is still made to 218 wire fifty years after its development.

The addition of alkali silicates to tungstic oxide impart to the wire a high recrystallisation temperature and rapid grain growth with the formation of large grains with overlapping axially aligned grain boundaries, Figure 7. Wires with this structure are resistant to further grain growth and have good high temperature creep strength, both properties that are essential for sag-resistance during the life of the lamp. Chemical analysis of doped metal powder shows that it contains the equivalent of about 70 ppm potassium, 60ppm aluminium and 300ppm silicon. Wire made from this powder will still contain most of the potassium, 60ppm, but the aluminium and silicon contents drop to about 10ppm. The advent of modern analytical instruments in the past twenty years has significantly advanced our understanding of the behaviour of dopants. We now know that modern doped tungsten wire with its large overlapping grain structure shows rows of tiny bubbles aligned in the direction of the wire axis, Figure 8. The bubbles contain the potassium that chemical analysis tells us remains virtually unchanged from the tungsten powder stage to the final wire product. The rows of bubbles inhibit recrystallisation of the wire until temperatures over 2000°C are reached. When recrystallisation occurs it is accompanied by a sudden exaggerated grain growth of a few grains in the wire cross section. The presence of the rows of bubbles produces the overlapping elongated grain structure that is characteristic of non-sagging filaments.

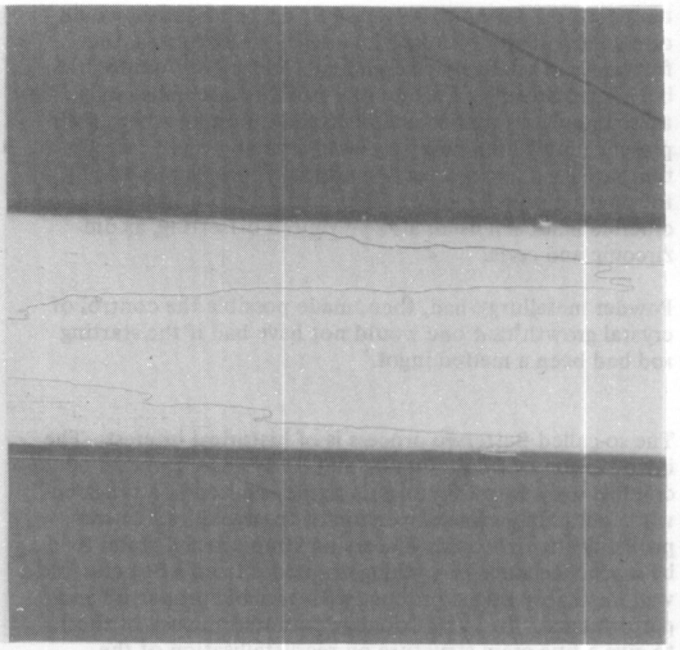

Figure 7 Microstructure of doped tungsten wire after heat treatment at 2400°C (magnification, X100).

Modern lamp practice is described by one of the authors in a recent paper to which readers are referred for more detail[5].

GEC Heavy Alloy

The original requirement for a high density alloy arose in the medical field in the mid-thirties and has been mentioned in the reminiscences of Colin Smithells[6] 'Another development . . . resulted from a telephone call from Sir John McLennan, who had just retired from the chair of physics in Toronto and was busy applying 5 gram units of radium in the treatment of cancer. He needed a container weighing about 1 cwt, but as small as possible'.

Lead had long been used to absorb the dangerous gamma radiation emitted by radium sources. In practice the radium source was placed in a thick-walled lead container, or bomb, having a suitable aperture through which the radiation is directed to the point required. The absorption of gamma rays by the walls of the bomb is proportional to the density of the material used for its construction. The replacement of lead by a material of higher density would reduce the intensity of gamma radiation escaping through the walls of the container and could result in a significant reduction in the wall thickness for the same absorption of the gamma radiation.

Many of the metals of higher density than lead, 11.68 g/cm^3, even if available in massive form are ruled out on the score of cost, although gold had been used for quite large nozzles of radium beam units. Other precious metals have high densities, with osmium the densest at 22.48 g/cm^3 but they are more expensive than gold. As Sir John McLennan originally suggested, a tungsten alloy

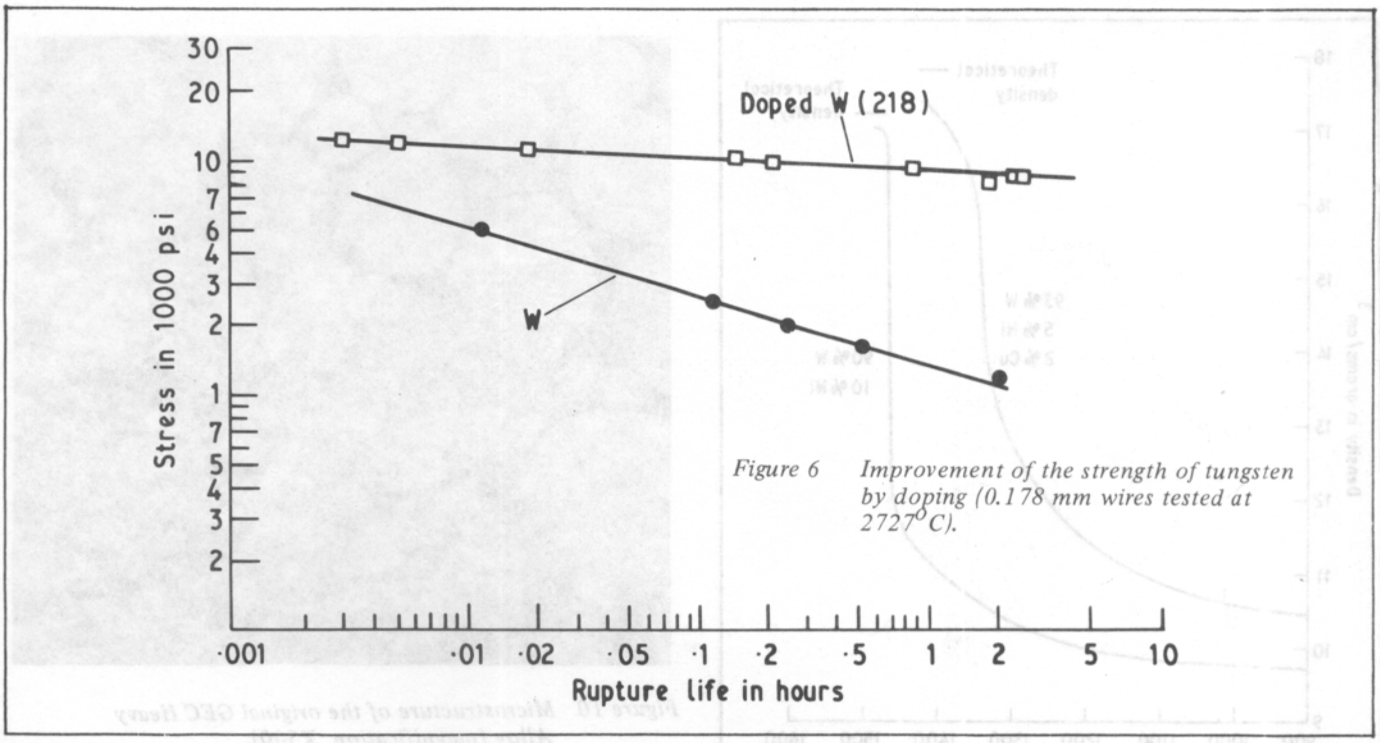

Figure 6 Improvement of the strength of tungsten by doping (0.178 mm wires tested at 2727°C).

that could be fabricated in reasonable dimensions and that was machinable would be a very useful engineering material. Tungsten itself had serious limitations owing to the high sintering temperature required and it is exceedingly difficult to machine.

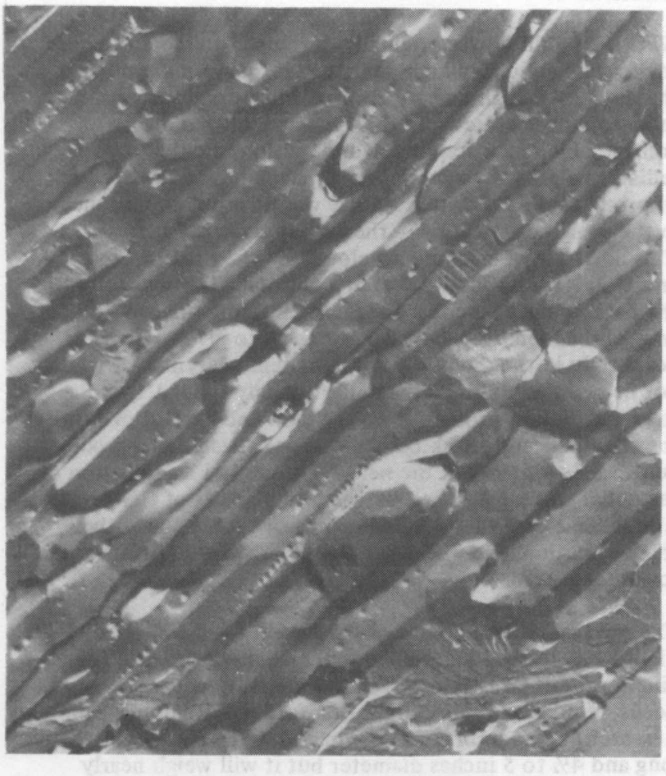

Figure 8 Rows of fine bubbles in the fracture surface of doped tungsten wire after heat treatment at 1100°C for 30 mins (magnification X2000).

The first experiment of Smithells and his colleagues at the GEC Research Laboratories, Wembley was to mix and press tungsten powder with a sufficient quantity of lead powder to fill the interstices between the tungsten particles, when the mixture was heated. The idea was that the lead would melt and fill the voids between the tungsten particles so that on cooling the density would be the mean of the lead and tungsten constituents. It was found, however, that molden lead would not wet tungsten and consequently it was not possible to make pore-free homogeneous masses. It is essential to have the liquid metal wet the tungsten so that shrinkage can occur on heating and densities approaching the theoretical obtained.

Trials with nickel additions to tungsten were successful in producing high density alloys provided the powder mixtures are heated above the melting point of the nickel. This is shown in Figure 9 which plots the effect of sintering temperature on the density achieved for a 90% tungsten, 10% nickel alloy. Rapid changes in density occur between 1450° and 1500°C, corresponding to the melting of nickel at 1455°C. Copper additions to tungsten do not give any densification; the only effect of sintering is that the molten copper wets the tungsten particles and cements them together.

The addition of copper to nickel brings a progressive lowering of the melting point of the nickel and it was logical to see whether additions of copper and nickel to tungsten would produce a high density alloy that would sinter at lower temperatures than 1500°C. This proved to be the case. In what has become a classic paper in the metallurgical literature Price, Smithells and Williams described the development of copper-nickel-tungsten alloys produced by liquid phase sintering[7]. The alloys became known as GEC Heavy Alloys. The maximum density was found with a nickel-copper ratio of about 2:1 and with a tungsten content around 90%. The work reported in 1937 was based on a 5% nickel, 2% copper alloy sintered in hydrogen for one hour, Figure 9, although the

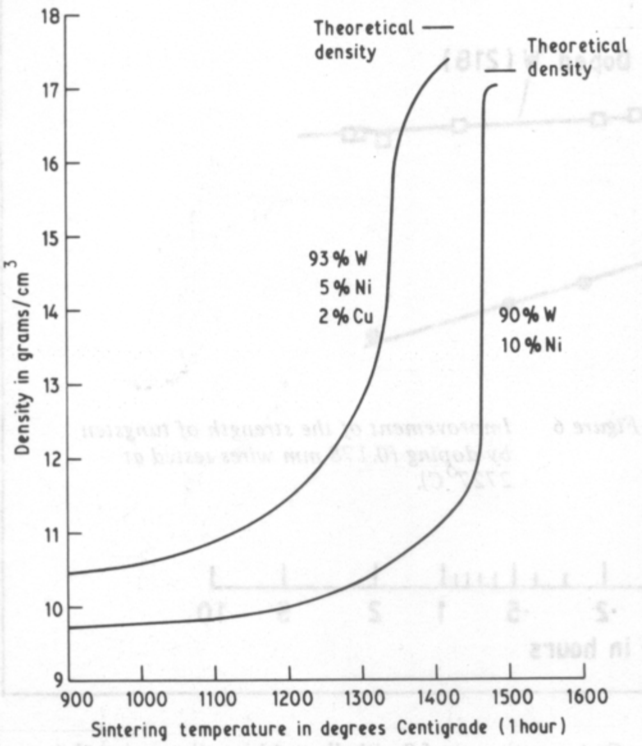

Figure 9 *Effect of sintering temperature on the density of a 90% tungsten, 10% nickel alloy and of the original GEC Heavy Alloy.*

original radium bombs were produced from an alloy with 5% nickel, 5% copper having a density of about 16.5 g/cm^3. This is some fifty percent greater than that of lead. Subsequent developments resulted in tungsten base alloys of improved densities $>$ 18g/cm^3.

The structure developed in heavy alloys is one of large rounded tungsten grains in a matrix of a opper-nickel-tungsten solid solution, containing upwards of 17% tungsten. The original size of the tungsten powder before sintering, about 5 microns, is not reflected in the size of the final liquid-phase sintered alloy. Tungsten grains some 50 microns in size are present, Figure 10. There has been much discussion on the mechanism of densification in heavy alloys but it is accepted that there are two stages to the process. On initial melting of the copper-nickel alloy some reaction with the tungsten particles will occur but the initial shrinkage will be brought about by a rearrangement of the tungsten particles in terms of them sliding over one another when lubricated by the molten alloy matrix. In the second stage, when shrinkage and hence densification really occurs, particles of tungsten are dissolved by the molten copper-nickel matrix and reprecipitated on other particles to allow overall growth of large tungsten grains.

The copper-nickel-tungsten high density alloy has a strength approaching 50 tons/sq in with an elongation of 1 to 6% when quickly cooled after liquid phase sintering. It is machinable, in contrast to tungsten, resistant to atmospheric corrosion and it may be electroplated with the standard finishes (for example, nickel and chromium).

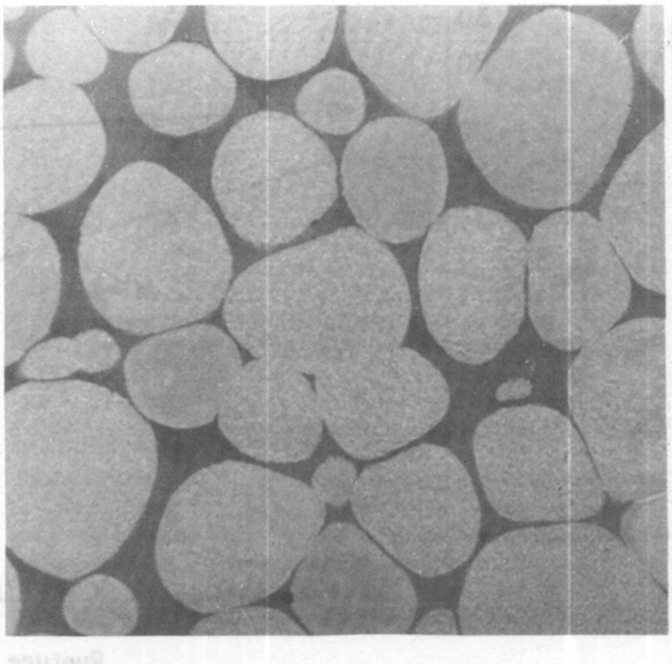

Figure 10 *Microstructure of the original GEC Heavy Alloy (magnification, X500).*

Developments outside the timescale of the period 1900-1950 have continued and a new series of heavy alloys of the tungsten-nickel-iron type introduced[8].

Industrial Uses

GEC Heavy Alloy was originally developed to meet the need for a relatively cheap high-density material in radium beam therapy[9]. Its high density and its ability to absorb gamma radiation more effectively than lead meant that a very considerable reduction in size and section thickness of radiation shields was possible without reducing the degree of protection. This latter feature was of prime importance in the design of telecurie – therapy apparatus, Figure 11. This illustrates a machine developed by the Christie Hospital and Holt Radium Institute at Manchester. It brings round the patient's neck a collar in which 28 gamma-ray sources were embedded. The collar is cut away to give a radiation beam only in the direction of the patient's larynx. It would not be possible to make the collar entirely of lead, in order to give radiation protection to the chin and head above and the shoulders and trunk below, because a lead collar would be too tall to fit round the neck. The central lead portion of the collar was sandwiched between two pieces of GEC Heavy Alloy. This gave the required degree of protection with a thinner section, and at the same time provided a firm support for the soft lead.

The original radium containers or bombs are featured in Figure 12. By 1937 eleven containers had been made for nine hospitals (Westminster, Birmingham, Cancer, Aberdeen, Leeds, Middlesex, Edinburgh, Bradford and Radium Beam Research). A radium container may only be 6 to 8 inches long and 4½ to 5 inches diameter but it will weigh nearly one hundredweight. Other applications of the alloy as a protection against radiation have been found in gamma radiography, where there is a requirement to have available containers in which radioisotopes can be safely transported, parts for remote-control handling equipment and beam collimators for linear accelerators.

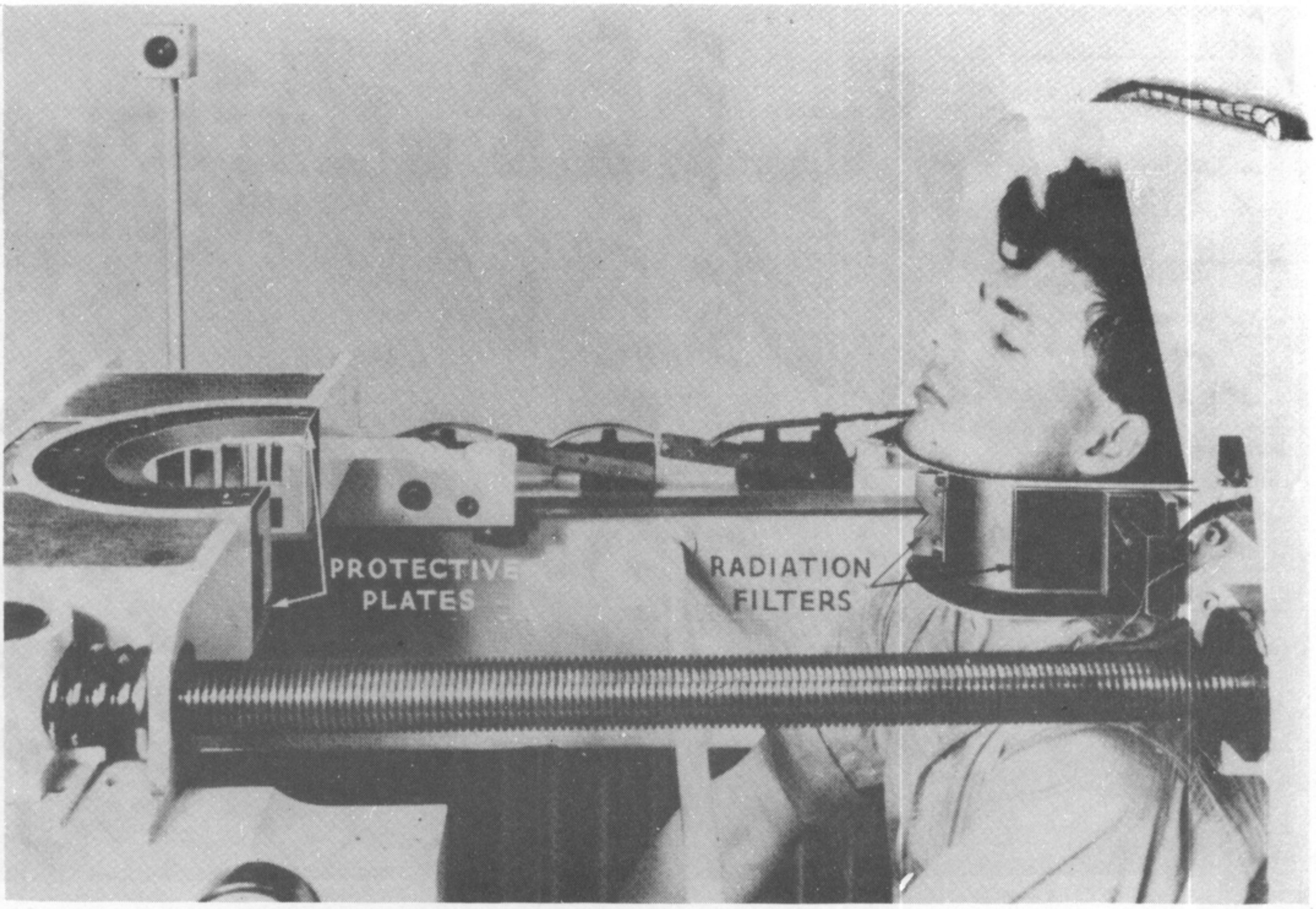

Figure 11 *Apparatus for treatment of cancer of the larynx by radium gamma rays. Components of GEC Heavy Alloy are indicated by arrows.*

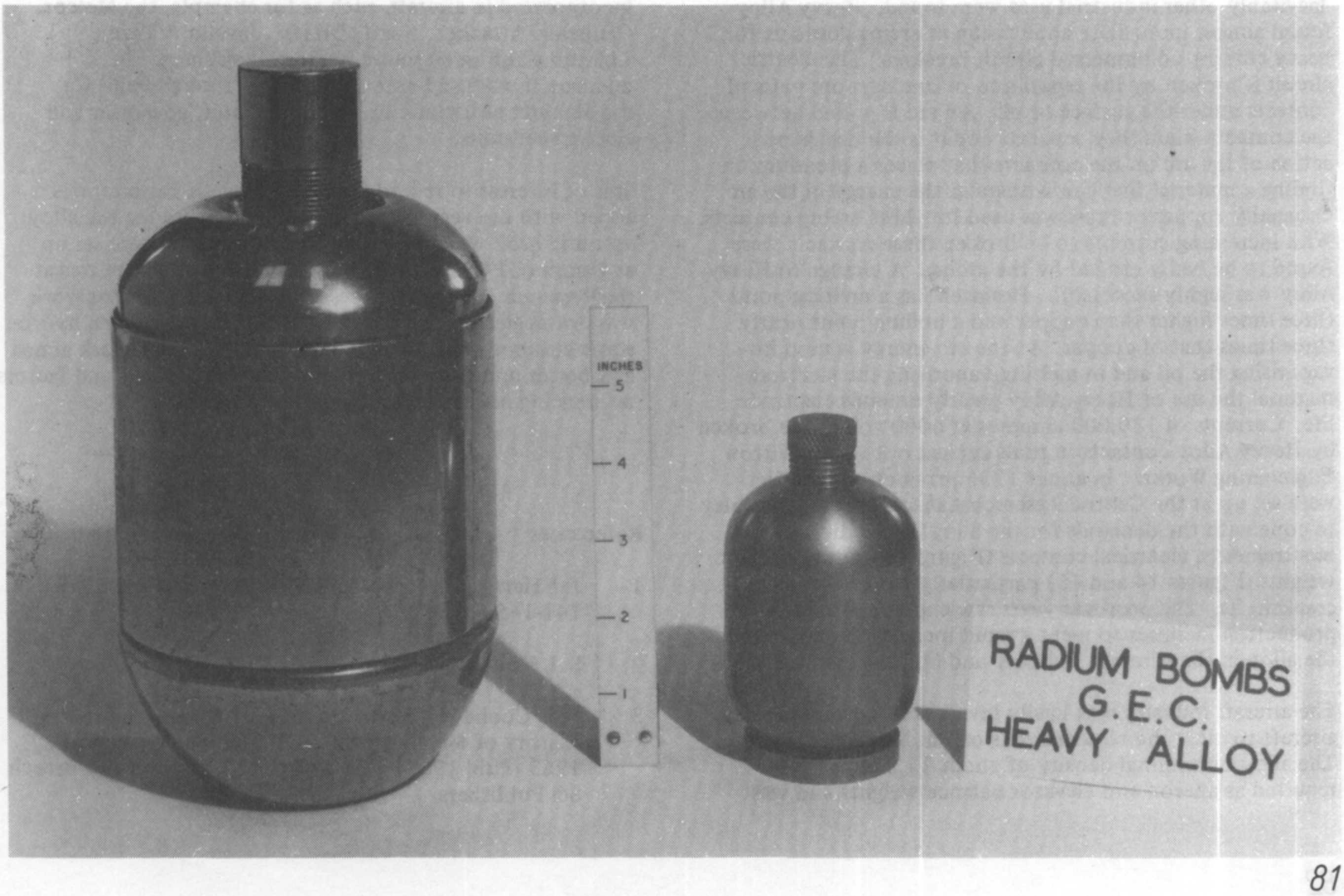

Figure 12 *Radium containers.*

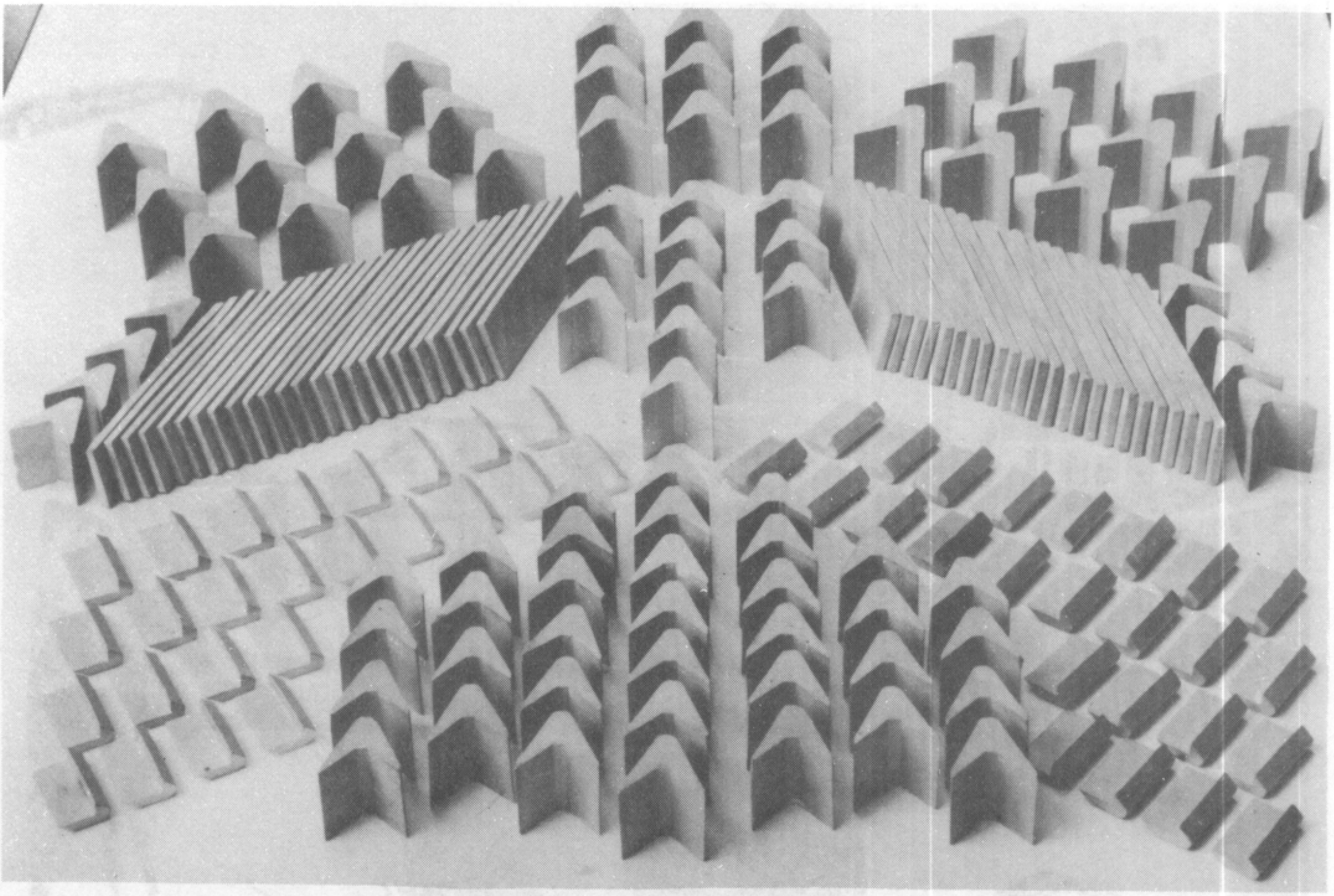

Figure 13 Group of Heavy Alloy contacts for circuit breakers.

Inevitably other industrial uses were found. Heavy Alloy found almost immediate application as arcing contacts for heavy current oil-immersed circuit breakers. The electric circuit is broken by the separation of one or more pairs of contacts under the surface of oil. An arc is pulled between the contacts when they separate and it is the destructive action of the arc on the contacts that places a premium on finding a material that can withstand the energy in the arc. Originally copper or brass was used for these arcing contacts. With increasing currents to be broken these contacts were found to be badly eroded by the arcing. A change to Heavy Alloy was highly successful. Tungsten has a melting point three times higher than copper and a boiling point nearly three times that of copper. As the arc energy is used in vaporising the oil and in melting/vaporising the electrode material the use of Heavy Alloy greatly extends electrode life. Currents of 130,000 amperes at 6000 volts were broken by Heavy Alloy contacts in trials carried out at our Witton Engineering Works. In about 1936 production facilities were set up at the Central Research Laboratories at Wembley to cope with the demands for the alloy for medical requirements, electrical contacts (Figure 13) and as balance weights (Figures 14 and 15) particularly for aero-engine crankshafts. The post-war years saw a major expansion in production facilities to meet a rapid increase in demand for the alloy in the Aircraft Industry and Military fields.

The aircraft industry was busily involved in developing new aircraft to meet the requirements of The Royal Air Force. The alloy of nominal density of about 17.2 g/cm^3 was required as aileron and elevator balance weights and was incorporated in aircraft, such as for example, the Meteor, Canberra, Attacker, Swift, DH108, Javelin, Valiant, Lightning and numerous commercial airliners. In addition it was used extensively for gyroscopes and for the Maxeret automatic brake control unit, governors and ejector seat units.

It is of interest to record that the Research Laboratories coped with the very rapid increase in demand for the alloy up until 1952 when new production facilities were set up at Osram (GEC) Ltd, Wembley. Whilst production was at the Research Laboratories research and development work was not neglected and investigations into new alloys, hydrostatic and hot pressing techniques together with work aimed at a better understanding of sintering mechanisms and factors influencing mechanical properties continued.

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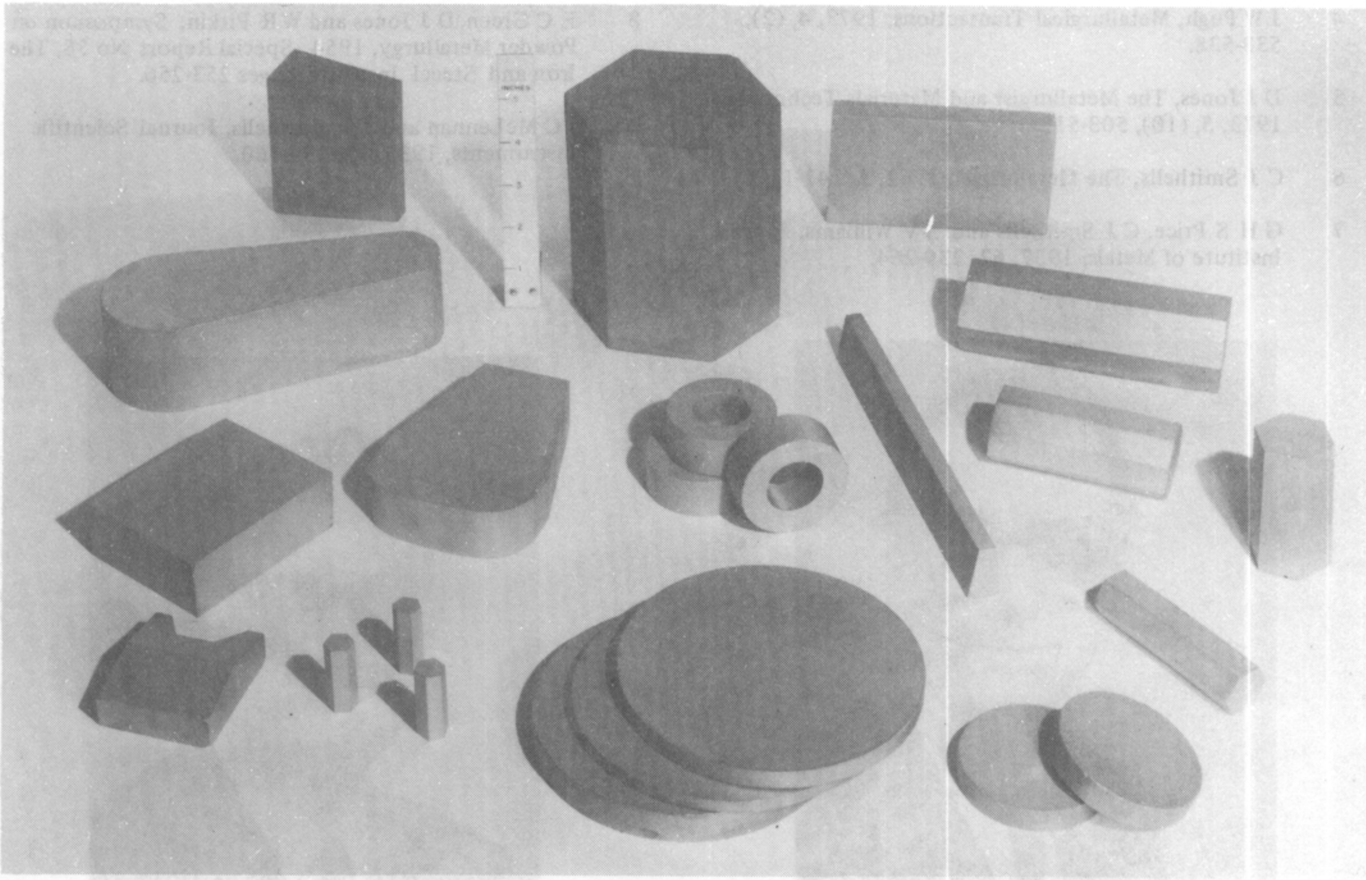

Figure 14 A variety of Heavy Alloy balance weights.

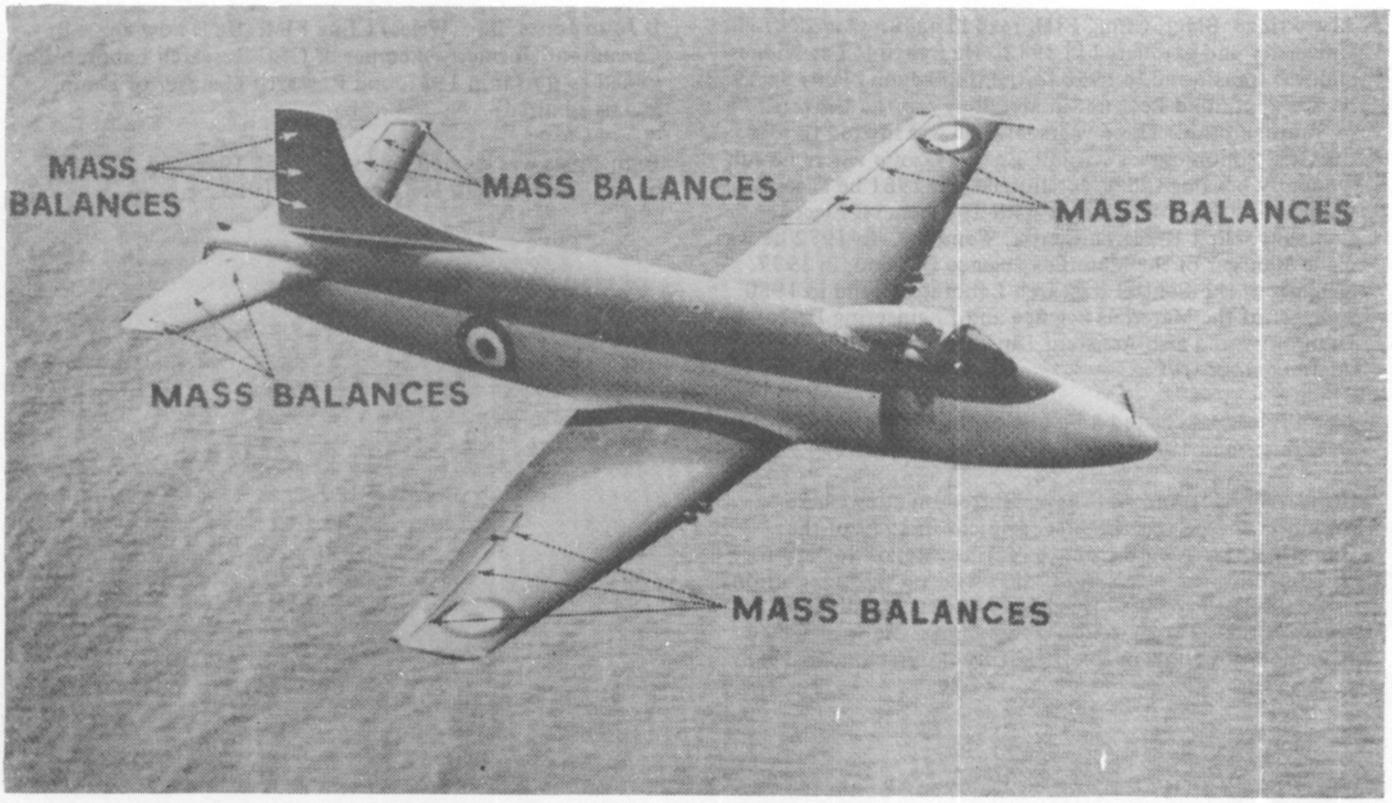

Figure 15 A Vickers-Supermarine 'Attacker' showing positions of aileron and elevator balance weights.

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Alan Prince BMet, CEng, FIM, read metallurgy at Sheffield University and graduated in 1948. He joined ICI at Widnes and was transferred in 1950 to the Billingham plant. In 1953 he was appointed Lecturer in Metallurgy at the University of Southampton. Three years later he was invited to join the GEC-Simon Carves Atomic Energy Group where he subsequently became Chief Metallurgist. In 1961 he accepted the post of Chief Metallurgist with The General Electric Company, Hirst Research Centre, Wembley. In 1972 he was made Manager of the Materials Science Division, in 1977 Manager of the Central Research Laboratory, and in 1980 Manager of the Materials Science and Engineering Research Laboratory and also Assistant Director of Research (Materials) for GEC.

Alan Prince was elected a Fellow of the Institution of Metallurgists in 1965 and President for the year 1972-73.

His metallurgical interests have centred on alloy phase equilibria and he was the first recipient in 1979 of the Hume-Rothery Award from the former Metals Society for his contributions in this field. He serves on the International Council for Alloy Phase Diagrams and acts as Editor-in-Chief for their Ternary Alloy Programme. He was elected an Honorary Fellow of Sheffield City Polytechnic in 1983.

D John Jones BSc (Wales) CEng FIM. He is now a Consultant (formerly member of GEC Research Laboratories, joined as Bursar in 1937, and Research Manager of Lamp Metals Limited).

John Jones was elected an Associate in 1946 and a Fellow of the Institution of Metallurgists in 1955.

Hardmetal: The history to 1950

Jack Sandford

Synopsis

Hardmetal began with the discovery of hard carbides of tungsten at the end of the 19th century. The idea of mixing tungsten carbide with a metal of lower melting point, eg cobalt, and the launching of hardmetals by Krupps in 1927 started the present world-wide industry. New alloys were developed and the field of application widened, but customers and their workers accepted the new material reluctantly because of its price and great hardness. During the last war, the importance of hardmetal for machining much-needed components grew, and its use for armour piercing shot was an important factor in the outcome of the war. After 1945, the expected decrease in demand to pre-war levels did not materialize and processes changed to those of large-scale production.

Introduction

Hardmetal is a sintered alloy of tungsten carbide and cobalt, with or without other hard carbides such as those of titanium, tantalum, niobium, chromium, or vanadium. The term 'hardmetal' is derived from the German 'hardmetall' but the American term 'cemented carbide' is now in common use in many countries.

Early History

Tungsten carbide was discovered by the French chemist Moissan[1,2,3] who melted a mixture of tungstic oxide and carbon in an arc furnace and identified a carbide W_2C which was very hard and scratched corundum easily. Then Williams[4] prepared a new carbide, WC, by heating a mixture of tungstic oxide, iron and carbon in a very hot forge furnace, and removing iron with hot hydrochloric acid, followed by a magnetic separation. He reported that the carbide was very hard. The process of using a 'menstruum' of liquid metal is historically interesting because it later became a commercial process for making the double carbide of tungsten and titanium.

These discoveries remained dormant until the first World War when Voigtlander and Lohmann[5] produced compacts of tungsten carbide (possibly a mixture of WC and W_2C) by recrystallisation at a temperature just below the melting point.

At the same time, the research laboratories of Deutche Gasgluhlicht Gesellschaft (the predecessor of the Osram Group) made dies of cast tungsten carbide. The work was interrupted by the 1914 war but was resumed in 1921 when the price of diamond drawing dies became exorbitant in Germany. The dies, consisting of the eutectic of WC and W_2C were, however, according to Schroter[6] too brittle and quickly fractured.

In 1922, Schroter found that tungsten carbide (WC) powder, mixed with 10% of a metal powder of lower melting point (eg iron, nickel or cobalt) could be pressed and sintered at about 1500°C to produce a substantially pore-free compact. Of the three metals, iron, nickel and cobalt, the last-named gave the greatest toughness for a given hardness.

The scanty evidence available does not suggest that Schroter investigated all the hard carbides, and it is likely that the use of tungsten carbide was inspired by the interest that the Osram group had in tungsten. Nevertheless, whether it was luck or not, Schroter's work was invaluable in laying the foundations of the present industry.

In Germany, the new sintered alloy replaced diamond dies for drawing tungsten wire, and in 1923-24 it was used in the Osram Group under the name 'Osram Hartmetall', not only for wire drawing but also for cutting tools. In order to market it, an agreement was reached in 1925 between Osram and Fried Krupp AG of Essen, whereby the latter was given a licence for its production.

In 1927 Krupp introduced the first commercially successful tools under the name Widia ('wie diamant'). The first alloy comprised tungsten carbide with 6% cobalt, and had a hardness around 1500 HV. Over 50 years later, hardmetals of this composition, with slight variations of hardness, are still produced by more than 80 companies world-wide.

Soon after this date, the Fansteel Corporation[7,8] in the USA produced hardmetals based on tantalum carbide bonded with nickel, and in Germany, Deutsche Edelstahlwerke developed an alloy of the carbides of titanium and molybdenum also bonded with nickel. Both attempts, probably to circumvent the Krupp patents, failed because the mechanical properties and especially the toughness were inferior.

The Beginning of the Industry

In 1927, Fried Krupp exhibited at the Leipzig Fair; part of the display was of the new hardmetal, Widia, machining cast iron at hitherto unheard of speeds.

A young Englishman, Axel C Wickman, was at the Fair and when he saw the Krupp demonstration he realized that, if it was not a 'conjuring trick', Widia was the cutting tool of the future. He managed surreptitiously to pocket a Widia tool

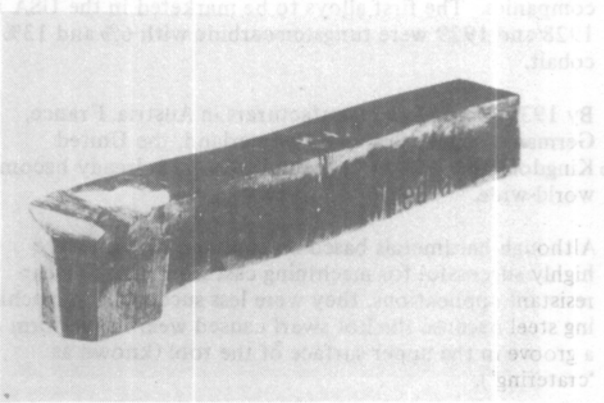

Fig 1 One of the first hardmetal tipped tools made in England from imported Widia, c 1928.

and the tests he did in Coventry confirmed all that was claimed. Within a few days, he was in Essen, knocking on the gates of the great Krupp empire. Although he was unknown to anyone, his forceful personality and fluent German admitted him and he was given selling rights for the United Kingdom; moreover he was allowed to import tips, not finished tools, to braze them to shanks and grind them, thereby giving employment during a time of depression. See Fig 1.

In 1931, Wickman persuaded Krupp to start manufacturing in England, and Tool Metal Manufacturing Co Ltd was formed, with Krupp as the major shareholder. Krupp however kept a stranglehold on the British company, in that all mixed powders were supplied by them at prices they set. Technicians in England knew little of the composition and processes for producing them; they were trained only to press, shape and sinter.

From 1928 onwards, Krupp granted licences or sub-licences to several companies in this country and in the USA, although precise dates cannot be determined. According to Brookes[9]. by the end of 1929, that is only 2 years after the launching of Widia, similar hardmetal was being made by Carboloy (USA), Metallwerk Plansee GmbH (Austria), Sumito Electric Industries Ltd (Japan), Teledyne Firth Sterling (USA) and Wallram Hartmetall GmbH (Germany).

In this country, Metropolitan Vickers started to manufacture hardmetal which was probably the first to be produced in England. Other companies, some licensed by Krupp, were the British Thomson Houston Co (before 1934) but now defunct: Firth Brown Tools Ltd (formed by Firth Brown Steels Co Ltd in 1935): Tungsten Electric Co (in 1936); now a subsidiary of Richard Lloyd Ltd: Murex Ltd (in 1938). Higher Speed Metals Ltd was formed in 1939 from an earlier small company, Alteg. Anglardia Ltd also commenced in 1939, and there may have been other small companies who have disappeared. By 1939, the main producers were the 'big five', namely Tool Metal Manufacturing Co Ltd, and its licencees BTH Co Ltd, Metro-Cutanit Ltd, Firth Brown Tools Ltd and Murex Ltd.

In the USA, the General Electric Co and Firth Sterling Steel Co had conducted independent research into tungsten carbide and its alloys. However, Krupp was awarded the master patents in the USA and gave General Electric Co an exclusive licence. Its subsidiary, Carboloy, licensed Firth Sterling, Fansteel Co, Callite Tungsten Co and North American Cutting Alloys Co. (The last named went out of business in 1938). Some had a technical link with British companies. The first alloys to be marketed in the USA in 1928 and 1929 were tungsten carbide with 6% and 13% cobalt.

By 1935 there were manufacturers in Austria, France, Germany, Japan, Sweden, Switzerland, the United Kingdom and USA, and the industry had already become world-wide.

Although hardmetals based on tungsten carbide were highly successful for machining cast iron and for wear-resistant applications, they were less successful in machining steel because the hot swarf caused wear in the form of a groove in the upper surface of the tool (known as 'cratering').

In 1930, Schroter[10] found that the addition of about 10% of tantalum carbide reduced the rate at which cratering occurred and later he and others replaced it by the cheaper titanium carbide which was even more effective.

From then until 1939 there was a proliferation of hardmetal grades, based on tungsten carbide but with additions of titanium carbide and sometimes tantalum and niobium carbides, suited to machining steels of various hardnesses over a wide range of speeds and feeds. In general, only titanium carbide was used in Europe, whereas tantalum and niobium carbides were also used in the USA.

It was difficult to prepare titanium carbide free from oxygen, which produced somewhat porous hardmetal, and the discovery was made that a solid solution of TiC and WC (by carburizing tungsten or tungsten carbide with titanium dioxide and carbon) gave hardmetal with much less porosity. Because, even when starting with a mixture of the two carbides, the solid solution is formed during sintering, the German Patent Office refused to grant patents based on the use of pre-prepared solid solution (the term 'mixed crystals', from the German, is used in the industry), and the earliest recorded patents are apparently those of Wolfram and Molybdan A.G.[11] Mixed crystals of titanium and tungsten carbides are now used throughout the industry.

A novel method of producing solid solutions of carbides was invented by McKenna in the USA in 1938, which echoed the experiments of Williams in 1898. He produced the carbides in a bath of molten nickel (the 'menstruum' process) and dissolved out the nickel with acid. This gave solid solutions of great consistency and freedom from oxygen and the resulting hardmetals were the most reliable for machining steel at that time.

From early days it was recognised that the hardness of alloys of tungsten carbide and cobalt could be varied either by the cobalt content or by the grain size of the tungsten carbide, finer carbide increasing the hardness. For some applications such as machining chilled cast iron, a fine grain size and high hardness were required. Then it was found that the addition of a small amount, usually less than 1%, of certain carbides, such as those of tantalum, chromium or vanadium, prevented grain-growth during sintering, and, in about 1939, this led to new, harder alloys which are still being produced world-wide.

Another invention of importance to the industry was that of hot-pressing, whereby the powders are pressed and sintered simultaneously in graphite moulds. The first patent for this process was granted to Diener[12] in 1928, and it was used extensively for many years to manufacture large pieces of hardmetal. In fact, one British company produced all its hardmetal pieces, large and small, by this method up to recent times.

A review of all important patents up to 1939 was given by Dawihl[13]. Loach[14] has given a more detailed account of the rise of the industry in the USA than is possible here.

A Hardmetal Factory in the 1930s

The output of hardmetal in the 1930s was very small. Dawihl[14] gives figures for German monthly output of 1 tonne in 1930, 4 tonnes in 1936 and 10 tonnes in 1939. The largest British company produced just over 1 tonne in the whole of 1932, a little over 2 tonnes in 1935 and 5.2 tonnes in 1939.

A factory in the 1930s was therefore very different from what it is now. Powder was ball-milled in batches of 5 to 8 kg and when it was necessary to blend two batches, mixing was done by hand in a large bowl with a spoon! Powder was often stored in glass jars intended for bottling fruit, so that a powder factory looked like a hybrid of a laboratory and a kitchen. There were no tabletting presses; individual blocks, called ingots or strips, were pressed on 5-tonne hydraulic presses. After being presintered, they were marked out to the shape of the tips required, cut with a hacksaw blade and shaped by hand on a grinding wheel.

Furnaces were like enlarged laboratory furnaces. Some consisted of a horizontal carbon tube which was also the resistor. Others had an alumina tube wound with molybdenum wire or tape. Hydrogen was fed in at one end and burnt at the other. The mixture to be carburized or hardmetal pieces to be sintered were packed into graphite 'boats' and pushed through at a rate to give the required time at maximum temperature. These furnaces at first had tubes only 2" diameter, but larger ones with 3", 4" and finally 6" diameter tubes were used later. Metro-Cutanit used vacuum furnaces from 1930, and industry adopted them more and more even before 1939.

With the small output, sintering furnaces could not be run continuously for the whole week. One British manufacturer (a large one for those days) would press, presinter and shape from Monday to Thursday. Then one or two sinter furnaces would be brought to temperature and the week's work would be sintered throughout Friday, Friday night and Saturday morning. Three or four workers did everything: pressing, shaping, sintering and inspection. Job Enrichment is thought to be a modern management technique!

Customers' Opinions of Hardmetal

Because of its hardness, there were problems with grinding hardmetal throughout the 1930s and even after 1939 a British manufacturer still had a warning in his catalogue that special grinding wheels must be used.

Some operators in customers' works thought they knew how to heat-treat tool steels and high-speed steels better than the manufacturers. In spite of warnings about the impossibility of heat-treating hardmetal because its hardness came from the inherent hardness of tungsten carbide, they insisted on applying their 'pet' treatment to it, and when the result was a heap of yellow tungstic oxide, it just proved that this new-fangled stuff was no good. Again, after 1939, the manufacturer referred to above printed a warning that 'the tips are supplied in a hardened condition and will not respond to heat-treatment, such as hardening, tempering, annealing or normalizing'.

Another problem was that, whereas tools of steel and high-speed steel had large top rakes, hardmetal tools had to have top rakes of 10° or less. But experienced machinists knew better and insisted on regrinding them to their own ideas. When the cutting edge broke, it was further proof of the uselessness of hardmetal!

There were few machine tools with the necessary speed and rigidity to use hardmetal, but nevertheless it was welcomed for machining cast iron because it would cope with scale and hard spots.

British manufacturers had to contend with a myth that the original Widia tools were best and that nothing had been produced subsequently to equal them. When Tool Metal Manufacturing Co Ltd changed its trade-mark from Widia to Wimet but continued using the same Krupp powder and processes, there was, in the opinion of some customers, an immediate deterioration of quality and complaints were received that 'this new Wimet isn't a patch on Widia'. Even after the last war, there was a worker in a machine shop in Coventry who kept an original Widia tool in his locker and used it whenever he had a difficult job to do.

A further obstacle to the use of hardmetal was its price which was calculated per gram. Initially it was about 1 shilling in this country, reduced to 6d by 1939, and initially $ 1 per gram in the USA. Many customers looked on it as a precious metal and locked it in the safe every night. In about 1955, when the present author was quality manager, he received a complaint from an Irish customer that he (the customer) had bought some tips in 1935. Not wishing to use them at that time he put them away in his safe and on looking for them 20 years later found that they has disintegrated into a heap of powder. Please could he have replacements free of charge? A reply was sent that if he would kindly return the powder, we would be pleased to press and sinter it into whatever tips he wanted!

Hardmetal Between 1939 and 1945

The threat of war in 1938 and its outbreak in 1939 caused the industry to move from peace-time products to those required by a country at war. There was a need for tools suitable for machining shells, guns of all types, torpedo mechanisms, tank parts, air-frames and many other components. It was easier to increase demand than to satisfy it. Manufacturers had to procure new plant at a time when other industries were also attempting to expand, and deliveries were very long. These problems and how they were overcome can be appreciated by looking at the history of one British company.

Because of disagreement Krupp had become the sole owner of Tool Metal Manufacturing Co and when war started the company was without an owner. The custodian of enemy property considered closing the factory until Wickman convinced him that it was of paramount importance to the war effort.

Capital was raised and Wickman took control. Many Krupp patents which had been assigned to Tool Metal Manufacturing Co Ltd had not expired and four of the largest manufacturers had licences, paid royalties and operated under a quota so that their production was limited to a fixed percentage of that of TMMC. Wickman immediately gave them free licences and abolished the quota system so that the maximum possible production could be achieved. He changed the company's name to Hard Metal Tools Ltd to sever all connection with Krupp.

Stocks of powder, which at pre-war demand would have lasted for 6 months, dwindles to a few weeks' supply. Stainless steel for making ball-mills was on 12 to 18 months delivery and the future looked bleak. Whereas today all raw materials for producing hardmetal (carbides, cobalt and ball-milled powders) can be obtained from specialist producers to a very high standard of quality and consistency, this was not so in 1939 and the early 1940s. Wickman was not a man to tolerate problems, nor did he try to solve them by endless committee meetings. He acted.

He first arranged for Firth Brown Tools Ltd of Sheffield to supply carbide powders which had only to be ball-milled with cobalt. This went on for some time and allowed production to continue. He doubled the staff of metallurgists (from one to two!) and they worked up to 18 hours a day to determine processing conditions.

He next succeeded in obtaining from Carboloy in the USA a steady supply of powder ready to be pressed and sintered at Coventry. He bought much-needed plant; a large ball-mill and carburizing and sintering furnaces.

He saw a new method of pressing hardmetal powder in use at Carboloy, using tabletting presses. One of them was shipped to Coventry and soon Hard Metal Tools was in full production, 24 hours a day and 6½ days a week.

Similar problems were experienced by all British hardmetal manufacturers but the production of tools for machining essential war materials increased rapidly, so that by 1942 output was of the order of 10 times what it had been in 1939. New companies sprung up and there are records of 6 more in this country and 9 in other countries.

The importance of hardmetal to the war effort can be shown by two examples. The aluminium alloy spar booms for Lancaster bombers could not be extruded nearly to shape and 75% of the metal had to be machined away. Special tipped cutters were produced and the floor-to-floor time for one operation was cut from 150 to 20 minutes.

By the end of 1941, shells of all types were being machined with hardmetal tools and between 1939 and 1944 one manufacturer alone produced over 2 million tips for this purpose.

Hardmetal for Armaments

From the beginning of the war and possibly before, Germany had the idea of using hardmetal in ammunition. An alloy of tungsten carbide with only 3 or 4% of cobalt or nickel was used, but the shot (or cores) were very brittle and frequently shattered on impact against the armour of tanks. The first ones were small, but as larger sizes were required, surplus small ones were re-used by putting one or two into a graphite die with powder packed round them, and hot pressing the whole. See Fig 2.

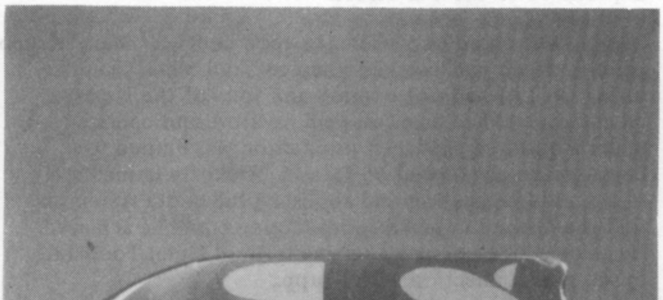

Fig 2 German AP core, 74 mm long, with smaller cores embedded in it, c 1940. (By courtesy of Richard Chadwick).

This use of tungsten carbide in Germany quickly led to an acute shortage of tungsten since wolfram had to be imported. Attempts were made to resolve the conflicting demands of cores and tipped tools by finding tungsten-free alloys for the latter use. A hardmetal comprising titanium and vanadium carbides with nickel was developed and, although it was very inferior as a cutting tool, tungsten-containing alloys were strictly rationed except for ammunition.

It is ironic that, unknown to anyone in Germany, there were large deposits of wolfram in occupied Austria which were not discovered until 1967.

The British soon learnt of the use of hardmetal cores but realised that some toughness was required to penetrate armour plate. An alloy of tungsten carbide with 12% cobalt was chosen and it was so successful and so superior to German cores that it was used throughout the war and even afterwards; it was also adopted by the USA. Fig 3 shows the penetration into armour plate which could be achieved.

Plans were put into action very rapidly to produce AP shot in large quantities. Three factories were set up by the Ministry of Supply, each managed by a large manufacturer; Firth Brown Tools, Hard Metal Tools and Metro-Cutanit; production started in 1941. Murex and Higher Speed Metals produced high tonnages of tungsten metal powder, and the assembly of shot was done in ammunition factories. Production reached about 1500 tonnes a year, levels which in 1939 would have been thought to be impossible. The first cores were for 0.303 ammunition but larger and larger ones were made, eventually reaching a weight of 1.7 kg.

Hardmetal Between 1945 and 1950

When the war ended, there were gloomy forecasts that the demand for hardmetal would fall to what it had been in 1938, but this was not so. The greatly increased use during the war for machining components had dispelled doubts about its value and had shown that it was economical in spite of its cost.

Greater production, larger batch sizes and the use of tabletting presses helped to reduce prices, which had been stable throughout the war. As an example, in 1945, a British manufacturer reduced the prices of standard tips by 45% and tools by 20%. According to Jeffries [15], in the USA the price had fallen from the initial $1/g to 7.5c/g by 1942.

New companies sprung up: at least 5 in this country and 21 world-wide, so that many countries began producing hardmetal for the first time.

Many of the old alloys or grades, such as tungsten carbide with 6 and 13% Co, went on being produced (and still are) but a use was found for cobalt contents of 20, 25 and 30% for bolt-heading dies where greater toughness was necessary. These alloys are also in use today. The effect of grain-size was extended by using coarser carbide with 9 to 11% cobalt for percussive rock drills in quarrying and rock drilling. Sandvik of Sweden, who started production of hardmetal in 1942, did much to develop suitable alloys and were helped, no doubt, by the fact that Stockholm is built on very hard rock!

Hardmetal was used more and more for wear-resistant applications (not only for drawing dies): guides for the textile industry, small circular knives for cutting paper, guides for cigarette packing machines, and many many more.

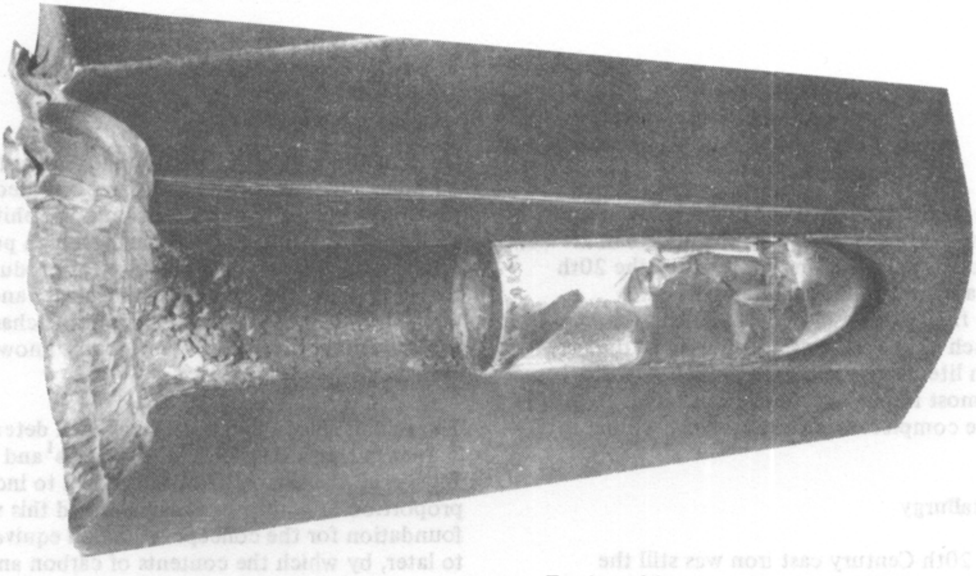

Fig 3 A 20 mm tungsten carbide armour piercing projectile embedded into 11 cm tank armour plate.

The possibility of making larger and larger pieces of hardmetal produced large tube drawing dies and rolls for Sendzimir mills. At the other end of the size range, there was the production of small tips for dental drills: the invention of the now ubiquitous ball-point pen led to the use of hardmetal balls.

The major change in the alloys was the increased use in Europe of additions of tantalum and niobium carbides in conjunction with titanium carbide for machining steels, and customers were supplied with an improved product at even less cost.

Increased production led to the use of larger ball-mills from the old 5 to 8 kg batch: to 50 kg, 100 kg and even up to 500 kg and over. Hydrogen atmosphere sinter furnaces gradually gave way to vacuum furnaces, with increased economy and better control of temperature and carbon content.

So by 1950, hardmetal had changed from being something new and strange, presenting users with innumerable problems, to something commonplace and readily accepted throughout industry.

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Alloy Cast Irons: The development from 1900 to 1950

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Summary

This paper presents a brief record of the major alloy developments in cast irons, together with the approximate dates of their introduction in the first 50 years of the 20th Century. This was a period of immense activity and development in the field of new materials and laid the foundations for much of the alloy cast iron used at the present time. Much literature exists from which a selection from the most important items is included, though this is unlikely to be complete and further study will be rewarding.

Early Cast Iron Metallurgy

At the dawn of the 20th Century cast iron was still the principal material from which the majority of metal articles were made both for engineering and domestic purposes. Melting normally took place in the cupola or, on a small scale, in coke fired crucible furnaces, and the state of technology was such that the use of special alloying elements was hardly contemplated. The types of cast iron were extremely limited. Ordinary grey cast iron, having a structure of flakes of graphite in a ferrous metallic matrix, which was relatively weak and brittle, was used for nearly all engineering purposes and for a wide range of domestic applications such as window frames, building structures, cooking utensils, rainwater goods and pipes for gas, water and waste. Firegrates and cooking stoves burning solid fuel or gas were also normally constructed from this material. Hard white iron in which the carbon was in the form of eutectic iron carbide could also be produced and was used for crushing and grinding machinery and for applications suffering wear such as ploughshares. By controlled rapid cooling local parts only of castings could be made hard in this way. Malleable cast iron was another form available in thin sections, where considerable ductility was achieved through casting with a carbidic structure and subsequently decarburising during a long annealing heat treatment, and such irons were used for a great variety of smaller components, for example in parts of harness, chain fittings and pipe fittings.

Cast iron at that time was produced almost wholely from pig iron, which could be made in a variety of compositions through control of the blast furnace charge and operating conditions, the structure and quality of which was assessed mainly by observing the appearance of the fracture. Ironfounders selected their pig iron by batch, with reference to its manufacturing origin and by fracture and produced the mixes that they required by combining proportions of pig irons from different heats, segregated at the blast furnace stockyard and from different blast furnaces together with their own returned scrap. For practical purposes the important composition of pig iron and cast iron was concerned essentially with the five main elements carbon, silicon, manganese, sulphur and phosphorus, but chemical analysis was only infrequently carried out as a routine control. When it was, the principle concern was the relationship between free carbon, present in the form of soft graphite and combined carbon, present as pearlite or hard eutectic iron carbide. The proportions of these constituents controlled to a large extent the differences in fracture of pig iron, cast iron and the properties of the castings produced. Much of the skill of the ironfounder resided in techniques for adjusting these proportions and included selection of pig irons having a high proportion of graphite to produce soft graphitic irons, or irons having a high proportion of iron carbide with a white fracture for producing hard castings. A number of structure features and properties were known to be transmitted from the charged pig iron to the castings produced – a property known as 'heredity'.

The role of silicon had been fairly well determined by Turner in classical studies in the 1880s[1] and by Hatfield[2]. Increasing the silicon had been shown to increase the proportion of graphite in cast iron and this work laid the foundation for the concept of carbon equivalent, referred to later, by which the contents of carbon and silicon could be combined in a formula according to which the greater the carbon equivalent the greater the amount of graphitic eutectic would be found in the casting.

Fluidity of cast iron was an important property when making thin or intricate castings and it was known that an increase in carbon and silicon improved fluidity. About the turn of the century it was appreciated that phosphorus also improved fluidity. In this respect the work of Stead[3] in 1900 was important. In central Eastern England there were large deposits of iron ore rich in phosphorus and use of these indigenous ores led to a high proportion of British cast iron containing up to 1 per cent or even 1.5 per cent of phosphorus at that time and throughout the period under review.

Although manganese and sulphur were known to have an effect on the structure and properties of cast irons, the true role of these elements was not understood at that time.

The use of nickel as an alloying element had been known for over 100 years because in America it was a constituent of certain ores[4]. There was, however, little appreciation of the behaviour of nickel and discussions of the effects of this element usually only centred on whether it made a dense iron or a strong iron. Chromium was already known as a carbide former and therefore a promoter of hard iron.

Against this background the early part of the 20th Century was a fruitful period for experiment and research in all aspects of the understanding, control and alloying of cast irons, and a great explosion in new knowledge occurred during the first 25 years or so. Many companies discovered how to use alloying elements, but because of the mystique attached to the foundryman's art, little information was made available to the public, and much of the credit for making and recording new inventions went to those companies and organisations which set up professional research teams of metallurgists and others who subsequently were able to publish their work. There is therefore probably much scope still for exploring and recording the contributions made privately in different companies which may not have received the public recognition accorded to professional research workers.

Carbon and Silicon

In addition to carbon, silicon is an essential element in cast iron, ranging from about 0.5 per cent up to 3.5 per cent. The principle source of increased silicon at that time was high silicon pig iron, commonly known as silvery pig iron on account of its fracture appearance. The development of ferrosilicon containing 50 per cent or more of silicon as a source of this element followed much later, although as a material it had been known for some considerable time[5]. Normally within the above range silicon is a graphitising element promoting a soft machinable structure, but in silvery pig iron, containing upwards of 14 per cent of silicon, a very hard brittle silicon-rich series of constituents is formed. In 1903[6] it was recognised that up to 20 per cent of silicon promoted a considerable degree of corrosion resistance, and in subsequent years irons containing about 14 per cent of silicon became widely used for the production of pipes and parts of chemical equipment to resist attack particularly by acids. One such iron took its name from the Durion Casting Company[7] but many other proprietary names were also used[8]. A feature of these castings was their extreme brittleness and difficulty both in production and annealing to avoid the occurrence of cracks.

An important use of cast iron was for elevated temperature applications such as in steam engines, and in parts of furnace doors and fittings. Under repeated heating and cooling grey cast iron expands through a combination of ratcheting and oxidation, and this behaviour, known as growth, was of great importance and widely studied. In 1928 Norbury and Morgan developed Silal[9], a cast iron containing between 4 and 10 per cent of silicon which had considerable resistance to growth, and became popular in a wide range of industrial heat resistant applications. Again, this iron was inclined to be brittle and had to be handled with some care.

The relationship between carbon and silicon was widely studied and the eutectic composition, having minimum melting point and maximum fluidity, was shown to be at a carbon equivalent value of around 4.3 per cent according to formula:

$$\text{Carbon Equivalent} = \text{carbon \%} + 1/3 \text{ silicon \%}$$

In Germany, the relationship of the carbon equivalent content to that of the eutectic temperature was expressed in terms of a degree of saturation, or eutectic content[10] Sc value. A typical formula for degree of saturation is that given by Cook[11] as

$$Sc = \frac{\text{Total Carbon \%}}{4.26 - \dfrac{\text{Silicon \%}}{3.6}}$$

but many variants appear throughout the literature. Maurer[12] produced a diagram illustrating the structures of cast irons with varying carbon and silicon contents, in which composition fields were distinguished ranging from white cast iron to mottled cast iron and grey cast iron with a pearlitic matrix or with a ferritic matrix as the carbon and silicon contents increased. Maurer's diagram has since been criticised for its inaccuracies and many modifications have been proposed by others[13] but it was the first serious attempt to describe the influence of carbon and silicon on structure.

Since graphite is a weak constituent, it had long been known that the lower the carbon content the higher the strength of the iron, although at very low carbon contents hard brittle white cast irons were produced. In the selection of metal charges the use of a proportion of steel scrap or wrought iron to reduce the carbon content and increase strength had been recorded[5] in 1846 and 1876. In the early part of the 20th Century, however, there was a resurgence of interest in the use of low carbon irons to produce higher strengths, and ways in which they could be produced to overcome the tendency for iron carbide formation. Great controversy raged over the merits and means of production of irons in which steel was included in the charge and which were generally known as semisteel. In the 1920s and 1930s in Germany a large number of processes were introduced in which low carbon irons were poured into heated moulds. The slow solidification which resulted led to graphitic structures and to castings with very good strength properties. Many irons were described in the literature[14] having special names which included Lanz, Schuz, Emmel, Corsali Ardelte, Hanemann and Holly. Some of these irons also had small additions of alloying elements such as nickel.

Inoculation

By promoting the formation of graphite, and avoiding formation of iron carbide, it was possible to produce machinable irons with lower carbon and silicon contents, and therefore of higher strength. Traditional art achieved some control of the graphitising characteristics of the iron or, in some cases, the promotion of iron carbide, through manipulation of the melting process and treatment of the molten metal. For example, the proportion of graphite in a casting could be increased by adding to the bath of molten metal graphite powder, of which a common commercial form was known as blacking, or lumps of high carbon graphitic pig iron. The effect of such additions was ephemeral and they were regarded as having some nucleation effect. Conversely the amount of graphite in the iron could be reduced by superheating the liquid metal or by introducing oxygen in the form of haematite iron ore. Melting processes which occurred over a long period of time or at high temperature were clearly understood to cause a greater amount of iron carbide in the castings. These practices were jealously guarded secrets of the ironfounder's art and not surprisingly they are not fully recorded in the literature.

A growth in interest was shown in this topic early in the century and much experimenting took place to find new and reliable additives which could promote the formation of graphite and so enable stronger irons to be produced using low carbon compositions which would otherwise solidify with carbides in their structures. In 1922 Meehan[15] showed that calcium silicide, containing some 60 per cent of silicon was a potent graphitiser when added in small amounts to liquid cast iron shortly before casting. This process became known as inoculation and was quickly followed by the discovery of many other similarly-acting silicon-rich alloys, including ferrosilicon, so that by the 1930s inoculation had become a well-established practice in ironfounding in America and Europe. Iron produced using Meehan's invention became known as Meehanite.

The known effects of superheating and long holding times led to many workers[4,16] theorising on the role of oxidation of cast iron in control of structure. The use of silicon-rich alloys for inoculation was also referred to by many as a deoxidation process, by analogy to the process of adding deoxidants to steels. Certain melting conditions which produced iron of unsatisfactory properties for one reason or another became recognised and such iron was sometimes referred to as oxidised iron[17]. There has never been good evidence that such iron is, indeed of high oxygen content, although subsequent workers have established other changes in chemical composition or metal temperature which can take place which may affect cast iron properties.

Around the 1940s there was widespread speculation and discussion on the role of inoculation and of practices favouring or suppressing graphitisation, and many hypotheses were postulated concerning the nucleation of graphite[18,19]. The nature of the nuclei from which graphite grows in cast iron has remained a matter for speculation to this day. In the early days proposals centred round nuclei which consisted of graphite particles, of oxides and silicates, sulphides and carbides. In modern times an even wider range of theories has developed.

Grey cast iron contains graphite in the form of flakes. The finer the flakes, the higher the strength and the higher the modulus of elasticity of the iron. In 1933 Norbury and Morgan[20] showed that by making a small addition of titanium to the liquid iron and bubbling carbon dioxide gas through it prior to casting it was possible to achieve a very fine graphite structure which they referred to as undercooled graphite. Titanium was already known in cast iron because it was a common element, present in pig irons in small amounts. Some Scandinavian pig irons were made from ores rich in titanium, and others contained both titanium and vanadium. A proportion of such pig irons mixed into the charge could provide the amount of titanium required by Norbury and Morgan. The titanium was shown to be present in small cubic crystals having a pale golden colour or colourless. These consisted of mixed carbide and nitride, referred to as titanium cyanonitride and were a feature of the microstructure of these irons. Titanium is also a scavenger for the sulphur and it later became known that the neutralisation of sulphur and the removal of hydrogen by gas bubbling are the two critical features of the process developed by Norbury and Morgan.

Manganese and Sulphur

Both manganese and sulphur are normal elements occurring in cast iron. Prior to the present century sulphur was known as an element controlling graphite, while manganese was known as an element conferring hardness when present in large quantities, but their effects were not fully recorded nor understood. In 1931 Norbury[21] established clearly the relationship between manganese and sulphur and its effects on the proportion of graphite present in cast iron. He showed that the maximum tendency to form graphite is achieved when the sulphur content is stoichimetrically balanced by the manganese content with some excess of manganese. With a ratio of sulphur to manganese higher than this there is a greater and erratic tendency for iron carbide to form. The formula

$$\text{manganese }\% = 1.7 \times \text{sulphur }\% + .3\%$$

was suggested to indicate the minimum manganese content needed for the reliable production of grey iron castings. This relationship has continued to be accepted as the recommended composition for practical purposes.

Malleable cast iron as traditionally made in Europe prior to the 20th Century contained a manganese : sulphur ratio of less than the stoichimetric value of 1.7 : 1. With a low silicon content this enabled the iron to solidify with a structure free from graphite, and on prolonged heat treatment in an oxidising atmosphere the carbon was removed at a high rate relative to the rate at which iron carbide decomposed to graphite, so that thin sections were completely decarburised, but thicker sections contained compact graphite nodules in a pearlitic matrix. The fracture of this iron in thin sections was completely ductile, but in thicker sections was white and crystalline, leading to the name whiteheart malleable iron. In America in the 18th Century another malleable iron process had been introduced in which the ratio of manganese to sulphur was greater than 1.7, the graphite-free as-cast structure being obtained with a lower silicon content. On heat treatment this iron was not decarburised and produced a less compact graphite nodule structure in a completely ferritic matrix. The iron was ductile in all sections and the fracture had a dark black appearance leading to the name blackheart malleable iron. This material has a number of advantages and disadvantages compared with whiteheart malleable iron, but for heavier section castings has sometimes been preferable and involved less production problems. It was known in Britain[22], but not used commercially until the beginning of the 20th Century, when it began to spread in the UK, where it is now the predominant type of malleable iron.

During the Second World War attention was paid to means for increasing the strength of malleable iron, already widely used in vehicles. By increasing the manganese content of blackheart malleable iron pearlite could be stabilised, in place of ferrite in the matrix, and strength correspondingly increased. However during the later 1940s a much higher quality product, referred to as pearlitic malleable iron was developed which involved heat treating blackheart malleable iron of normal or only slightly increased manganese content in which the matrix could be modified to consist of fine lamellar pearlite, spheroidised pearlite or tempered products of bainite or martensite. These materials not only had better strength but also improved ductility compared with the as-annealed high manganese pearlitic malleable iron. They now constitute an important part of malleable iron production.

Chromium

Chromium, in the form of ferrochromium, was a well-known alloy in the early 1900s, but its use in cast iron was very limited since it was known to promote hard iron carbide structures in grey cast iron. It was sometimes used for this purpose deliberately in small amounts up to 1 or 2 per cent, but by 1924[23] its use in large amounts was accepted and irons containing from 15 to 35 per cent were commercially available. The principal use of the higher contents was to achieve corrosion resistance and heat resistance, for which purposes high chromium irons are still used on a small scale.

Nickel

Prior to 1900 nickel was believed to confer corrosion resistance on cast iron[24], but there is little evidence of its having been used commercially for this purpose. In the early 1900s[25] it was recognised that nickel is a graphitising agent, promoting the formation of graphite rather than iron carbide in a manner similar to, but less strongly, than silicon. However whether or not nickel was beneficial was a subject of considerable discussion in the early years. In the Lanz process for producing hot mould iron, nickel was recommended up to 3 per cent. The International Nickel Company, and in the UK the Mond Nickel Company created a very considerable interest in the use of nickel in cast iron as a result of the work of their research investigators, and in 1928 Merica[26] and Coyle[27] developed a new cast iron of improved strength containing a low carbon content with up to 5 per cent of nickel which they called Nitensyl. For many years to come engineering components requiring improved strength commonly contained between 1 and 2 per cent of nickel as a result of this work, and a very high proportion of automobile engine components[28], for example, were alloyed in this way. Through the 1930s the benefits of nickel in small amounts in cast iron were being widely advertised.

Other types of nickel alloyed cast iron followed in rapid succession. The combination of nickel from 2 to 10 per cent with chromium up to 4 per cent to produce a wear-resistant graphite-free cast iron with a martensitic matrix in the as-cast condition, known as Ni-hard, was announced in 1929[29]. In 1931 Norbury and Morgan developed a cast iron containing from 4 to 20 per cent of nickel, from 4 to 8 per cent of silicon and up to 10 per cent of chromium for heat resistance, which they named Nicrosilal [30] and which was shown to have improved heat resistance and machinability compared with existing cast irons and steels. These workers also developed during the 1930s nickel-manganese and nickel-silicon cast irons of improved strength.

In 1920 Dawson [31] developed Nomag, a cast iron containing 10 per cent of nickel and 5 per cent of manganese which was austenitic as-cast, having very low magnetic susceptibility with good machinability, and which immediately became popular for electrical components , and in particular stator rings for generators. It was known at that time that fully austenitic irons could be produced by adding sufficient nickel, but in 1926 a new austenitic [32] iron containing nickel and copper, replacing some of the nickel, was developed using additions of monel-metal scrap to cast iron and was found to be an excellent material for corrosion resistance in dilute acid solutions, also with some heat resistant properties. This material, initially named Nimol, but later renamed Ni-resist, became standardised at 14 per cent nickel and 7 per cent copper, and widely used in pumps and components in water treatment and sewage plants and for handling saline waters. Modifications of both Nomag and Ni-resist continue to be important alloy cast irons.

Molybdenum

In 1931 it was known [33] that molybdenum increased the strength of cast iron when added in amounts of about 0.5 per cent. It still continues to be used for this purpose. In 1922 [34] Smalley referred to molybdenum as a grain refiner, though this loose terminology was commonly used to refer to anything which increased strength by modifying graphite or matrix structure. In fact molybdenum affects the transformation of austenite to give a finer pearlite structure with greater strength. Austenite transformation characteristics of steels began to be of interest in the 1930s, and in 1940 Flinn, Cohen and Chipman showed that a combination of up to 6 per cent of nickel and up to 1.5 per cent of molybdenum could be used to produce a bainite structure in the as-cast condition in grey cast iron. [35] The resulting material was named acicular cast iron and became popular for certain applications where high strength and fatigue resistance were desirable, crankshafts for diesel engines being an important example. Acicular grey irons continued to be important special irons until about the middle of the century.

Small amounts of molybdenum became quite widely used, together with other elements, mainly nickel, chromium and copper, in the 1940s and 1950s. Such irons had higher strength and responded better to such treatments as surface hardening by chilling, flame or induction. An example of one such iron was that known as Monikrom, used for camshafts from the 1940s [36]. Its composition included 0.15 to 0.25 per cent of nickel, 0.8 to 1.0 per cent chromium and 0.15 to 0.25 per cent molybdenum.

Tungsten was also known to be an element in increasing strength of cast irons in a manner somewhat similar to molybdenum, and this was possibly correctly referred to first in 1917.[37]

Aluminium

Aluminium has never been a very popular element in cast iron because it forms a tenacious oxide on the surface of the metal which can lead to foundry casting defects. However it was studied by Everest[38] in 1925, who confirmed a rather complex series of structures with increasing aluminium content. Shortly before the Second World War[39] Bampfylde developed Cralfer, a cast iron containing 7.5 per cent of aluminium and 0.75 per cent of chromium for heat resistance and showed that it had very superior properties to other types of heat resisting iron at temperatures up to 1000°C. However in order to introduce the aluminium content it was necessary to use a special alloying process in which the aluminium was melted and the liquid iron poured into it. This iron has never achieved widespread use, because of founding difficulties.

Copper

Copper was used in Ni-resist in the 1920s but it was also used during the first quarter of the century[40] in small quantities as an additive to malleable iron to promote the graphitisation process during heat treatment. In the early 1930s the Ford Motor Company[41] announced a low-carbon rapidly-annealing malleable iron containing 1.5 to 2 per cent copper which became very widely used for crankshafts in automobile engines.

Vanadium

It was probably known before 1900 that vanadium hardens cast iron, but in 1909[42] it was recognised clearly that this element promotes the formation of eutectic iron carbide, and at that time it was used in cylinder castings to promote wear resistance. This application has remained important, particularly in large marine diesel engine liners.

Tellurium

Until the 1930s tellurium and many other minor elements in cast iron had been the subject of periodic speculation and discussion. A number of elements had been added in trace amounts and their effects reported variously as graphitisers or hardeners without any real consistency or understanding of these terms. In 1938 it was discovered that when tellurium was added to the liquid metal in very small amounts it caused the formation of hard chill in the more rapidly cooled parts of the casting and at casting surfaces. At the same time it was also discovered that by painting tellurium metal on the surface of the mould local hardening could be achieved, and patents [43, 44, 45] were granted on these topics. Since then the use of tellurium paint locally in a mould has been an exotic feature of foundry practice not only for the purpose of causing local hardening, but also a means of overcoming local unsoundness through a mechanism which has never been fully explained.

Titanium

Titanium is another of the minor elements about which much controversy existed at the beginning of the century. In 1923 Piwowarsky[46] reported that it had the effect of refining the graphite structure and of improving the strength of the iron. His studies revealed the nature of the carbides and nitrides of titanium and paved the way for the work of Norbury and Morgan which has already been mentioned.

Boron

As early as 1920 boron was known to be a hardener of cast iron and to promote the formation of carbides. During the decade the use of less than 0.1 per cent of boron in malleable iron was also shown to improve annealability through creating a higher graphite nodule number, and the practice of using this element as an additive to malleable iron became an established part of the malleable iron process[47]. It was not until 1946[48] that control of the hardening behaviour of boron was exercised for the purpose of producing uniform mottled structures in otherwise grey cast irons.

Bismuth

Bismuth is another minor element promoting carbide formation in cast iron, but until the 1930s this knowledge was not clearly established and conflicting views were held. Work in 1931[49] and 1934[50] established control of the addition of bismuth in very small amounts to malleable cast iron in which it was subsequently used between 0.001 and 0.01 per cent to enable higher silicon contents to be used in the initially white castings, thereby helping to create rapidly annealing malleable irons which became standard products later in the century.

Tin

Although tin was commonly used as a protective coating on cast iron prior to the 20th Century, and its presence in cast iron had been noted as a result in remelting tin plate scrap, no agreement was apparent on the behaviour of this element until 1937[51] when Valenta and Chvorinov showed that it strengthened the matrix of cast iron. Much later it was shown by Rehder[52] that this was a pearlite stabilising effect. This use of the element in amounts of between 0.01 and 0.05 per cent subsequently became of considerable importance as a means of achieving improved wear resistance in automobile engine castings.

Spheroidal Graphite Cast Irons

The crowning achievement of the period was the development of as-cast iron with spheroidal graphite in place of the flake graphite which had previously been a characteristic of grey cast irons. Compact irregular or spherulitic nodules had already been known in malleable cast irons since before the century had begun but no as-cast process had existed for producing them. Two remarkable research efforts characterised this development. Morrogh can perhaps truly be said to have been the inventor of spheroidal graphite iron. He had observed graphite nodules incidentally occurring in various kinds of iron and was convinced that a method could be devised for achieving a completely spherulitic graphite structure in the as-cast condition. By a combination of diligent experimentation, acute observation and logical thinking he succeeded in producing such a structure by the addition of a small amount of cerium to cast iron[53]. Almost simultaneously, research carried out by Millis and others at the International Nickel Company in their Bayonne, NJ, laboratories was attempting to find an alloy substitute for chromium to produce Ni-hard cast iron having a carbide eutectic structure of improved wear resistance. They added many elements, often alloyed with nickel, and discovered that when magnesium was used in this way much tougher structures were obtained which were found to contain spheroidal graphite[54]. A residual content of as little as 0.04 per cent, or even less, of magnesium or cerium was able to achieve this effect in irons which would otherwise have had normal flake graphite structures. These irons, referred to by Morrogh as nodular irons and by Millis and his co-workers as spheroidal graphite, SG iron or ductile iron, had, in the as-cast condition strength at least double that of grey cast iron together with up to 30 per cent of elongation and considerable resistance to impact fracture. The development soon led to many castings for agricultural and automobile applications where improved strength and ductility were required, and eventually these irons became major competitors of malleable irons and largely displaced other higher strength irons such as acicular flake graphite irons.

Today automobile castings such as crankshafts and spun cast iron pipes represent the bulk of the tonnage of this material which is still growing in importance and capturing an ever-increasing share of the cast iron markets, ranging at present from about 10 to 20 per cent in different countries of the world.

Conclusion

This review has shown that during the first half of the 19th Century the principal functions of almost all of the major alloying elements in cast iron became established, and the foundations were laid for most of the types of alloy cast irons used up to the present day. A great range of compositions and structures were explored and evolved, many of which have now ceased to be of interest, but much information was made known which would continue to influence the use of alloyed cast irons. Perhaps the main limitation of the period was the inability to analyse accurately and by routine methods the trace element contents of cast irons, so that the effects of lead, nitrogen and rare earths, now commonly considered, were not appreciated, nor were the complex effects of trace elements in promoting the action of inoculants or in modifying the structures of high duty, irons and, later, spheroidal graphite cast irons.

Nevertheless the period produced knowledge of the principal alloying means for influencing the matrix structure and properties, as well as ways of modifying graphite structure ultimately to produce spheroidal graphite, so that it was inevitable that spheroidal graphite irons with different matrix structures would later be produced by alloying and heat treatment to achieve higher strengths, toughness, hardness, wear resistance and corrosion resistance. It might be said that the developments which have occurred since the 1950s have been comparatively subtle compared with the great advances in cast iron alloying of the early 1900s.

Acknowledgement

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Tool steels and **high speed steels** 1900-1950

Samuel Keown

Synopsis

1900 marked a notable turning point in the history of tool steels with the development of high speed steels by Taylor and White in the USA. These steels were the forerunners of modern high speed steels and by 1906 a steel composition close to the familiar 18W 4Cr 1V steel was well developed alongside the memorable discovery that very high hardening temperatures, close to the melting point, followed by a tempering treatment around 620°C gave tools which enabled cutting speeds to be increased approximately tenfold.

Previously, Mushet's self-hardening steels had provided better cutting performance over traditional carbon steels produced by crucible steelmaking.

Between 1900 and 1950 major developments occurred in tool steels by the introduction of vanadium, cobalt and molybdenum to the existing high carbon tungsten chromium steels. World wars and strategic element supply problems together with cost savings, prompted the trend towards molybdenum high speed steels and by 1951 the 6W 5Mo 2V grade had displaced the 18-4-1 tungsten grade in tonnage production.

Also in this period, thousands of tool steel grades of lower alloy content than high speed steel were developed by hundreds of tool steel companies throughout the world. Very few tool steels have in fact been developed since 1950 and the current tendency is for a reduction in the number of tool steels specified and manufactured rather than for new alloy developments.

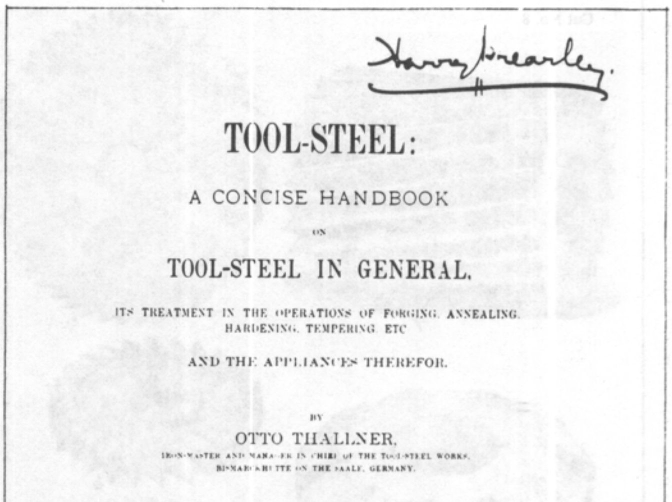
Introduction

From the earliest times iron and steel have been used for hand cutting tools. With the advent of steam power in the 18th century and the development of machine tools, the tool materials available proved to be inadequate and significant developments in steels for tools and other applications occurred throughout the 19th century. By 1900 the available materials were cast iron, wrought iron, cementation steel (blister or shear steel), crucible steel, Bessemer Steel and Open Hearth Steel. Alloy or special steels were just developing under conditions of great secrecy in several parts of the world but particularly in England, America and France[1]. Otto Thallner, in his book 'Tool Steel' published in 1902[2], Figure 1, noted that the special steels available included self-hardened steel, tungsten-steel, chrome-steel, nickel-steel, molybdenum-steel, titanium-steel and vanadium-steel but, to most steel producers and users, alloy steels were shrouded in mystery, Figure 2[3]. Several enlightened metallurgists had, however, started to investigate, understand and develop important alloy steels with very significant success for the future of tool materials. Foremost amongst these were Robert Mushet who developed his high tungsten, self-hardening steel in 1868[4] and Robert Hadfield with his low silicon tool steel and his high manganese work hardening steel developed in 1883 and 1886 respectively[5]. Details of these steels and their discovery are given in a recent paper[1] and will not be repeated in this article which concentrates on the period 1900 – 1950.

Tool Steels – 1900

Barraclough[6] has conveniently defined steel as lying somewhere between wrought iron and cast iron with respect to carbon content. Thallner[2] used the definition that steel is 'iron which is capable of hardening by quenching', 'this property of iron resulting from a content of carbon which may amount to between 0.5 and 2%'.

All the early metallurgists agreed that carbon steels or 'ordinary' steels contained unwanted impurities such as phosphorous, sulphur and copper and useful additions such as silicon or manganese to improve the properties of the steels whilst not yet constituting an alloy steel. Hadfield's definition[5] of an alloy steel covers this point and holds good even to the present day:- 'Steels which owe their properties to the presence of elements other than carbon, even though the carbon still plays a vitally important part in determining the characteristics of the alloy. This definition does not include as alloy steels those to which a small percentage of manganese, silicon, aluminium, titanium or other element is added in order to eliminate objectionable constituents or mechanical defects such as blow-holes, from carbon steels.'



Harry Brearley.

TOOL-STEEL:

A CONCISE HANDBOOK

ON

TOOL-STEEL IN GENERAL.

ITS TREATMENT IN THE OPERATIONS OF FORGING, ANNEALING,
HARDENING, TEMPERING, ETC

AND THE APPLIANCES THEREFOR.

BY

OTTO THALLNER,
IRON-MASTER AND MANAGER IN CHIEF OF THE TOOL-STEEL WORKS,
BISMARCKHÜTTE ON THE SAALE, GERMANY.

AUTHORIZED TRANSLATION FROM THE GERMAN,

BY

WILLIAM T. BRANNT.

ILLUSTRATED BY SIXTY-NINE ENGRAVINGS

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ST. DUNSTAN'S HOUSE, FETTER LANE, FLEET STREET.
1902.

Figure 1 Title page of Otto Thallner's book on Tool Steel published in 1902[2]. Note the signature of Harry Brearley (the discoverer of stainless steel) who owned this copy.

Carbon Steels. The best tool steels at the turn of the century were crucible or cast steel although electric melting was introduced around 1906. Becker[7] in 1910 gave the following range of carbon steels with typical values of residual or added elements:-

Use	C	Mn	Si	S	P
Hammers	0.5 -0.75	0.21	0.21	0.022	0.020
Knives, shears	0.65-0.80	0.20	0.18	0.020	0.015
Drills, reamers	0.85-1.30	0.18	0.21	0.015	0.014
Lathe tools	1.00-1.30	0.26	0.20	0.010	0.010
Razor steel	1.30-1.50	0.22	0.20	0.006	0.009
Graving tools	1.30-1.50	0.16	0.14	0.014	0.012

Whereas these analyses would generally prove acceptable at the present time, Becker[7] went on to indicate the variability of carbon content encountered for three well-known brands of carbon steels in use at that time for lathe tools whose performances were practically identical.

Steel	% C
111 and Z	1.047
11	1.240
S	0.681

Carbon steels were hardened at 700 to 800°C, quenched in water and tempered at temperatures between 200 and 300°C[2].

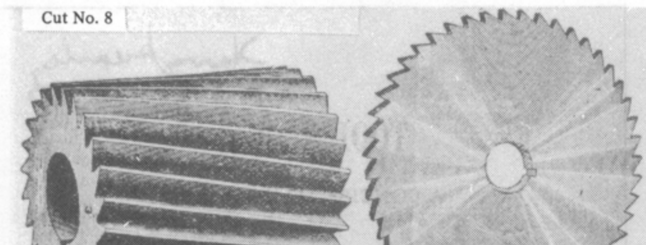
Alloy Steels. With regard to alloy steels, Thallner[2], reviewing the range of alloy additions encountered in 1902 indicated 0.2 to 0.5% manganese in ordinary steels, 8 to 20% in 'actual manganese steel' and up to 10% tungsten, but usually 2 to 4% or occasionally less than 1% in tungsten steels. Chromium was added at less than 1% in 'softer steels' and 2.5% in 'very hard turning tools'. Nickel steels contained 6 to 7% but were not really suitable for tools in the hardened state. Regarding molybdenum, titanium and vanadium, Thallner pointed out that the high cost of these metals and steelmaking difficulties restricted their application in tool steels. He went on to comment 'Nevertheless, varieties of steel – especially of English origin – are brought into commerce under the names of molybdenum-steel, titanium-steel, vanadium-steel, but of course, they do not contain any of the constituents'[2]!

Self-hardening Steels. Becker[7] described the available 'self-hardening' steels and 'high speed' steels available in 1910. The definition of these types of steel is worthy of more detailed consideration.

Robert Mushet's original steel, according to Hadfield[5] contained, 2.3% carbon, 6.62% tungsten, 2.57% manganese, 1.15% silicon and 1.15% chromium. This was the

Figure 2 Figures (cuts) from Alling's book[3] on tool steels published in 1903. The vague, non-technical description of the various tool steels recommended, indicates the generally poor state of knowledge regarding tool steels at the turn of the century. ▼

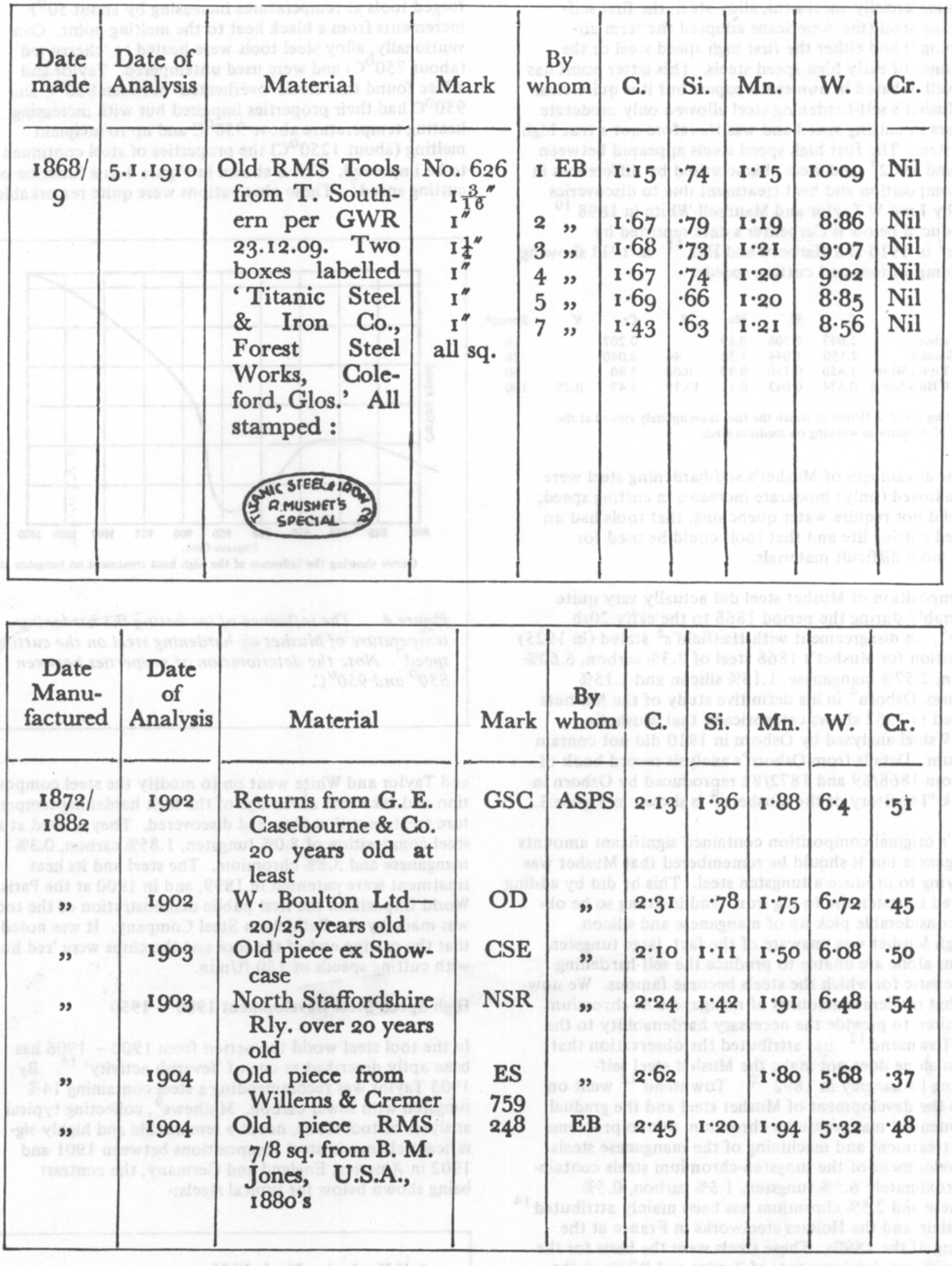
Cut No. 8



Eight different shape milling cutters, which it is economy to make of a steel at least as good as any of the extra and special brands, and which it is still greater economy to make of the best brands obtainable.

Cut No. 17.

Four different styles of chucking reamers, two being solid and two adjustable with inserted teeth. The best material known for these inserted teeth is one of the high grade, water-hardening alloy steels. The stem and body for holding these teeth should be made of a cheap grade of crucible steel hard enough not to batter easily: the solid reamers should at least be made of an extra quality of tool steel, though they could be made of the alloy steel also with good economy.



Date made	Date of Analysis	Material	Mark	By whom	C.	Si.	Mn.	W.	Cr.
1868/9	5.1.1910	Old RMS Tools from T. Southern per GWR 23.12.09. Two boxes labelled 'Titanic Steel & Iron Co., Forest Steel Works, Coleford, Glos.' All stamped :	No. 626 1 3/16"	1 EB	1·15	·74	1·15	10·09	Nil
			1"	2 ,,	1·67	·79	1·19	8·86	Nil
			1¼"	3 ,,	1·68	·73	1·21	9·07	Nil
			1"	4 ,,	1·67	·74	1·20	9·02	Nil
			1"	5 ,,	1·69	·66	1·20	8·85	Nil
			1" all sq.	7 ,,	1·43	·63	1·21	8·56	Nil

Date Manufactured	Date of Analysis	Material	Mark	By whom	C.	Si.	Mn.	W.	Cr.
1872/1882	1902	Returns from G. E. Casebourne & Co. 20 years old at least	GSC	ASPS	2·13	1·36	1·88	6·4	·51
,,	1902	W. Boulton Ltd—20/25 years old	OD	,,	2·31	·78	1·75	6·72	·45
,,	1903	Old piece ex Showcase	CSE	,,	2·10	1·11	1·50	6·08	·50
,,	1903	North Staffordshire Rly. over 20 years old	NSR	,,	2·24	1·42	1·91	6·48	·54
,,	1904	Old piece from Willems & Cremer	ES 759	,,	2·62		1·80	5·68	·37
,,	1904	Old piece RMS 7/8 sq. from B. M. Jones, U.S.A., 1880's	248	EB	2·45	1·20	1·94	5·32	·48

Figure 3 Entries in Fred Osborn's analysis record book[4] showing the composition of Robert Mushet's Special (RMS) in 1868/69 and 1872/82. There was no chromium in the original steel and only about half of one percent in later grades.

first commercially successful, alloy steel, the first self-hardening steel (the Americans adopted the term air-hardening[8]) and either the first high speed steel or the forerunner of early high speed steels. This latter point has been well debated in numerous papers but it is quite clear that Mushet's self-hardening steel allowed only moderate increases in cutting speed and was therefore not a true high speed steel. The first high speed steels appeared between 1901 and 1902[9] and were characterised by differences in steel composition and heat treatment due to discoveries made by Fred W Taylor and Maunsell White in 1898 [10]. Reproduced below is Carpenter's data reported by Becker[7] in 1910 and Harbord and Hall [11] in 1911 showing steel compositions and cutting speeds:-

Steel	C	Si	Mn	W	Cr	V	Speed*
Jessop Carbon	1.047	0.206	0.19		0.207		16
Mushet Special	2.150	1.044	1.58	5.44	0.040		26
Original Taylor-White	1.850	0.150	0.30	8.00	3.80		60
Best 1910 High Speed	0.674	0.043	0.11	13.19	5.47	0.29	100

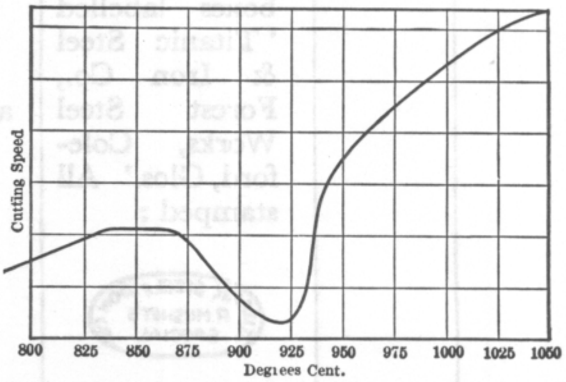
* Cutting speed in ft/min at which the tool is completely ruined at the end of 20 minutes working on medium steel.

Thus the advantages of Mushet's self-hardening steel were that it allowed (only) moderate increases in cutting speed, that it did not require water quenching, that tools had an extended cutting life and that tools could be used for cutting more difficult materials.

The composition of Mushet steel did actually vary quite considerably during the period 1868 to the early 20th century[4]. In disagreement with Hadfield's[5] stated (in 1925) composition for Mushet's 1868 steel of 2.3% carbon, 6.62% tungsten, 2.57% manganese, 1.15% silicon and 1.15% chromium, Osborn[4] in his definitive study of the Mushets published in 1952 shows categorically that Mushet's 1868/69 steel analysed by Osborn in 1910 did not contain chromium. Details from Osborn's analysis record book of tools from 1868/69 and 1872/82 reproduced by Osborn in his book 'The Story of the Mushets'[4] is shown in Figure 3.

Mushet's original composition contained significant amounts of manganese but it should be remembered that Mushet was only trying to produce a tungsten steel. This he did by adding powdered tungsten ore to pig iron[4] and in doing so he obtained considerable pick-up of manganese and silicon. Although Mushet was unaware of the fact, large tungsten additions alone are unable to produce the self-hardening characteristic for which the steels become famous. We now know that moderate amounts of manganese or chromium are required to provide the necessary hardenability to the steels. Townsend [12] has attributed the observation that tungsten alone does not make the Mushet steel self-hardening to Langley in 1892 [13]. Townsend [12] went on to trace the development of Mushet steel and the gradual replacement of manganese by chromium due to problems of heat treatment and machining of the manganese steels. The development of the tungsten-chromium steels containing approximately 6.5% tungsten, 1.5% carbon, 0.5% manganese and 2.5% chromium has been mainly attributed [14] to Brustlein and the Holtzer steelworks in France at the beginning of the 1890s. These steels were the basis for the very significant developments of Taylor and White at the turn of the century and the birth of high speed steels.

High Speed Steels. Bigge[8] pronounced that 'the year 1900 may well be accepted as a milestone in metallurgy' due to the introduction of high speed steel. In 1898, Taylor and White working on a self-hardening American steel containing 7.72% tungsten, 1.14% carbon, 0.18% manganese and 1.83% chromium, planned a series of experiments to heat forged tools at temperatures increasing by about 50°F increments from a black heat to the melting point. Conventionally, alloy steel tools were heated to 'cherry red' (about 750°C) and were used untempered. Taylor and White found that steels 'overheated' between 850°C and 950°C had their properties impaired but with increasing heating temperature above 950°C and up to incipient melting (about 1250°C) the properties of steel continued to be improved. This is shown in Figure 4 as a function of cutting speed[7]. These observations were quite remarkable and Taylor and White went on to modify the steel composition and take best advantage of the high hardening temperature treatment that they had discovered. They arrived at a steel composition of 8.0% tungsten, 1.85% carbon, 0.3% manganese and 3.8% chromium. The steel and its heat treatment were patented in 1899, and in 1900 at the Paris World Exposition the first public demonstration of the tools was made by the Bethlehem Steel Company. It was noted [15] that the cutting end of the tool and the chips were 'red hot' with cutting speeds of 150 ft/min.



Curve showing the influence of the high heat treatment on tungsten steels.

Figure 4 The influence of increasing the hardening temperature of Mushet air-hardening steel on the cutting speed[7]. Note the deterioration of properties between 850° and 950°C.

High Speed Steel Development 1900 – 1950

In the tool steel world the period from 1900 – 1906 has been aptly described as one of 'feverish activity' [16]. By 1903 Taylor was recommending a steel containing 14% tungsten with lower carbon. Mathews[9], collecting typical analyses of tool steels, noted a remarkable and highly significant change in steel compositions between 1901 and 1902 in America, England and Germany, the contrast being shown below for typical steels:-

Self-Hardening Steels 1901

C	Mn	Cr	W
1.69	0.45	3.73	7.63
1.14	0.33	2.00	7.98
1.55	0.24	3.22	7.80

High Speed Steels 1902

C	Mn	Cr	W
0.42	-	4.95	10.75
0.57	0.43	3.30	11.58
0.37	-	5.10	13.83

Despite patent cover (which was challenged and eventually defeated in 1908) it appears that details of the steels and heat treatments were well known to Bethlehem's competitors. By 1906 Taylor had made further significant discoveries, notably a second lower temperature heat treatment (temper or 'high draw' for five minutes at 621°C) and an optimisation of the steel composition to 18.19% tungsten, 0.674% carbon, 5.47% chromium and 0.29% vanadium. Therefore, in the space of eight years, Taylor and White had brought about developments that had radically changed the tool steel industry, replacing the self-hardening Mushet steel by the forerunner of the now standard 18-4-1 high speed steel with a totally new concept in heat treatment involving a high hardening temperature of about 1220°C and a tempering treatment at around 620°C. Taylor and White's monumental achievements can be ranked alongside Mushet's tool steel developments thirty years earlier and the development of sintered carbide materials twenty years later in Germany as the most significant developments in the history of tool materials.

Vanadium Additions. Mathews is generally accredited with the idea of adding vanadium to high speed steels[17]. His notebook of September 14th 1900 shows that he was considering the idea and his own review paper of 1919[9] indicates that he commenced experimentation in 1903 'when vanadium was almost a chemical curiosity' and cost $15 a pound! Mathews was granted a patent for additions up to 1% vanadium in 1905 and, as previously stated, Taylor's best high speed steel of 1906 contained 0.3%. Several years later, according to Roberts[17], a consortium 'led by seven McKenna brothers' established a company solely to undertake the manufacture and sale of 1% vanadium high speed steel. Thus the present-day 18-4-1 steel was 'commercially born' in 1910.

High vanadium, high carbon steels sometimes called 'super' high speed steels were developed in the 1930s[18] to give vastly improved wear resistance. These steels contain 3 to 5% vanadium and their superior wear resistance is due to increasing amounts of large vanadium carbides in the microstructure.

Cobalt Additions. Cobalt was first added to high speed steels at the 3 to 5% level in 1912 in Germany[17,19,20] to improve the hot strength. By 1923 12% additions were being used and it is interesting to note that cobalt additions to modern steels are at the 5, 8 or 12% level showing that little further development has occurred over the past 60 to 70 years (apart from the present tendency to substitute cobalt by other elements due to its strategic nature in the 1980s).

Molybdenum Additions. Molybdenum in self-hardening and high speed steels was noted by Mathews in 1901 and 1902 but the element did not find real commercial application in tool steels until the 1930s[19]. The decline in the use of molybdenum was due to the higher cost of molybdenum over tungsten, which it was able to replace quite successfully, and heat treatment difficulties. However, the discovery of molybdenum ore deposits in Colorado and very significant metallurgical developments in the USA in the 1930s, spurred on by tungsten shortages during the first World War, led to the inception of several new molybdenum grades of high speed steel[19]. These were the 1.5% tungsten, 9% molybdenum steel developed by Emmans of Cleveland Twist Drill, the 0% tungsten, 8% molybdenum, 2% vanadium steel independently developed by Kingsbury of Crucible Steel and Gill of Vanadium Alloy Steel, and finally the world-famous 6% tungsten, 5% molybdenum, 2% vanadium (6-5-2) steel developed by Brealer of Allegheny Ludlum[19]. These molybdenum high speed steels are designated M1, M10 and M2 respectively in the AISI specifications where TI is the 18-4-1 tungsten grade. The growth of the molybdenum grades and the decline of the tungsten grades is shown below:-[20]

Percentage of Production

Year	Total Tonnage	M2	M1	M10	T1	Other T Grades
1945	17,194	24.2	5.3	4.1	57.7	3.8
1948	17,761	31.7	8.4	3.7	44.8	6.0
1950	17,904	34.4	8.7	5.3	38.1	5.7
1951	38,056	50.9	19.7	6.4	15.9	2.4
1952	22,465	52.6	18.6	12.5	7.1	3.6
1953	24,585	46.0	21.5	15.0	9.5	4.7
1954	15,355	42.0	21.0	15.9	12.0	4.6
1955	24,961	42.1	23.6	16.4	9.5	3.9

This trend is mainly accounted for by the Korean war (1950–53) when tungsten supplies from China were jeopardised. In the earlier World Wars there were restrictions on the use of tungsten, the effect of the Second World War on molybdenum steel production being shown in Figure 5[21]. The M2 steel (6-5-2) is now firmly established as the leading high speed steel due to its cost advantage and the strategic supply problem for tungsten but its properties are only marginally better than that of the long established T1 (18-4-1) grade.

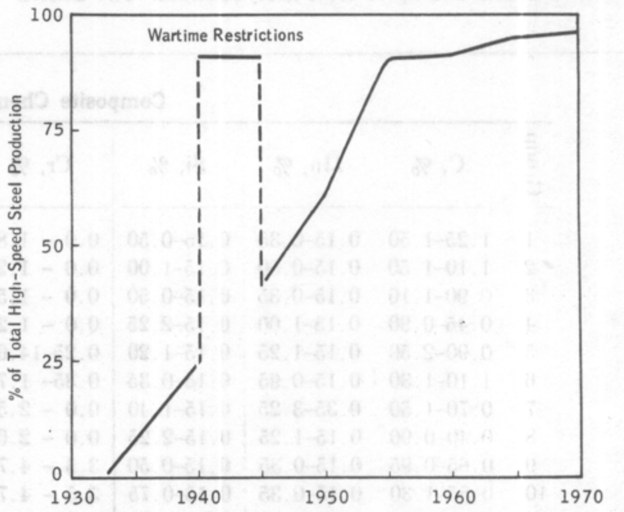


Figure 5 Estimated production of molybdenum and molybdenum-tungsten high speed steel in the USA, 1930-1970 (after Fairhurst[21].)

Other Tool Steels 1900 – 1950

It is virtually impossible to document the changes and developments occurring in tool steels other than high speed tool steels in this period. Earlier in the paper it was shown that carbon steels were well established and that alloy steels were in the early stages of development at the beginning of the century. Between 1900 and 1950 thousands of different steels with varying combinations of carbon and carbide-forming elements were developed (usually commercially) and sold by hundreds of tool steel companies throughout the world.

A convenient record of the position in 1950 is given in the book 'The Selection and Hardening of Tool Steels' by Seabright[22] published in that year. This book gives some indication of the complexity of the tool steel situation and employs the Chambers classification for tool steels issued in 1940, based on the wear-toughness ratio. All steels, including high speed, are divided into four fields of application, linked to carbon content:-

Wear Resistance	1.3 to 2.5% carbon
Cutting Tools	1.1 to 1.3% carbon
Dies	0.75 to 1.1% carbon
Shock Resisting	0.30 to 0.75% carbon

These categories are sub-classified into hardening requirements, water or oil/air hardening and temperature resistance as follows:-

Field of Application	Water Quenched	Oil/Air Hardened	Heat Resisting
Wear Resistance	1	5	9
Cutting Tools	2	6	10
Die Steels	3	7	11
Shock Resisting	4	8	12

These groups of steels 1 to 12, Figure 6[22] are broken down into 45 types according to their analyses. For example, Group 1 are wear-resisting carbon steels with 1.25 to 1.5% carbon, up to 6% tungsten, up to 1.8% chromium, up to 0.3% vanadium and up to 0.5% molybdenum. The United States tool steel producers in 1950 were offering 46 different steels falling into this Group 1 category! with typical compositions and trade names as follows:-

Steel Company	Trade Name	C	Mn	Si	W	Cr	V
Atlas	Atlas XXX	1.35	0.3	0.3	3.75	0.35	
Bethlehem	Finishing	1.33	0.3	0.2	4.23		
Carpenter	KW	1.30	0.3	0.3	3.50		
Latrobe	ESA	1.40	0.25	0.23	4.00	0.15	0.25

All 46 steels are different (only just!) but their properties must have been remarkably similar.

From the 12 groups and 45 types, Seabright listed 967 steel compositions from 65 American companies using combinations of 10 alloying elements!

Obviously many important grades emerged during these developments such as the 5% chromium, 1.5% molybdenum, 0.4% carbon hot work steel, the 12% chromium, 1% molybdenum, 0.5% vanadium, 1% carbon cold work die steels and many more.

In 1950 tool steel production in the USA[20] amounted to almost 100,000 tons sub-divided into:-

20.3%	carbon steel
19.1%	high speed
9.2%	hot work
7.7%	high chromium
43.7%	all other grades

The almost universally accepted AISI classified system for tool steels divides the steels into 6 categories with single letter designations followed by numbers for individual grades:-

Figure 6 The composition ranges of the 12 grades of tool steels in Chambers' classification[22].

Composite Chemical Analysis of Steels in Each Group

Group	C, %	Mn, %	Si, %	Cr, %	W, %	V, %	Mo, %	Co, %	Ni, %
1	1.25–1.50	0.15–0.35	0.15–0.50	0.0 – 1.80	0.0– 6.0	0.0 –0.30	0.0– 0.50	(Al 0.00–0.25)	
2	1.10–1.50	0.15–0.50	0.15–1.00	0.0 – 1.20	0.0– 2.50	0.0 –0.30			
3	0.90–1.10	0.15–0.35	0.15–0.50	0.0 – 1.50	0.0– 2.50	0.0 –0.50			
4	0.45–0.90	0.15–1.00	0.15–2.25	0.0 – 1.20	....	0.0 –0.35	0.0– 0.60	....	0.0–0.50
5	0.90–2.50	0.15–1.25	0.15–1.20	0.25–14.00	0.0– 2.00	0.0 –1.25	0.0– 1.50	0.0– 4.00	0.0–2.00
6	1.10–1.30	0.15–0.95	0.15–0.35	0.35– 1.75	0.0– 2.50	0.0 –0.30	0.0– 0.75		
7	0.70–1.50	0.35–3.25	0.15–1.40	0.0 – 2.50	0.0– 1.10	0.0 –0.50	0.0– 1.75		
8	0.40–0.90	0.15–1.25	0.15–2.25	0.0 – 2.00	0.0– 3.00	0.0 –0.60	0.0– 2.20	....	0.0–2.50
9	0.65–0.95	0.15–0.35	0.15–0.50	3.5 – 4.75	0.0–23.00	0.75–3.00	0.0–10.00	2.0–15.0	
10	0.55–1.30	0.15–0.35	0.15–0.75	3.5 – 4.75	0.0–21.00	0.50–4.25	0.0– 9.50		
11	0.25–0.60	0.15–0.75	0.15–1.75	1.25– 7.50	4.0–19.0	0.0 –1.25	0.0– 9.50	0.0– 2.00	0.0–3.00
12	0.30–1.00	0.15–1.25	0.15–1.10	0.50– 7.50	0.0– 4.25	0.0 –1.00	0.0– 3.00	0.0–0.60	0.0–5.00

1)	Water Hardening	W
2)	Shock Resisting	S
3)	Special Purpose . . .	
	Low Alloy	L
	Carbon-Tungsten	F
	Mould Steels	P
4)	Cold Work . . .	
	Oil Hardening	O
	Med Alloy/Air Hardening	A
	High C/High Cr	D
5)	Hot Work	H
6)	High Speed . . .	
	Tungsten	T
	Molybdenum	M

This system embraces a total of 84 different basic tool steel compositions of which about 40 account for the majority of tool steels used. A more comprehensive AISI system is used to cover a total of about 180 steels.

All this serves to illustrate and hopefully to clarify the vast ranges and complexity of tool steels available. Almost all the existing tool steels were developed in the period 1900 to 1950 and the current tendency is to reduce the number of steel grades rather than to carry out further alloy development.

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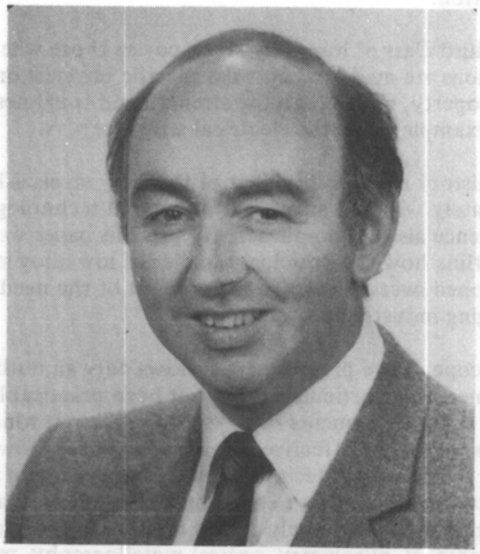

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A history of **alloy steels** 1900-1950

David Dulieu

Introduction

It is first necessary to define alloy steels in the present context. A suitably wide-ranging definition was adopted in the 1930s by the Alloy Steels Research Committee of ISI and BISF, who covered their area of activity in the following way:-

'Carbon steels are regarded as steels containing not more than 1.5% manganese and 0.5% silicon, all other steels being regarded as alloy steels.'[1] In this paper we consider the 'low alloy steels', those containing less than some 6 wt% total alloying additions; a very broad category of compositions which can be roughly subdivided further into three classes:-

The family of high strength structural steels which evolved from compositions which were first used in the 'natural' (ie as-rolled or mill finished) state. Typical products are the structural sections, rails and plates.

The heat treated engineering steels principally are forged or machined to components and alloying additions are used to confrol the properties in the hardened and tempered condition.

The third class of low alloy steels covers those where the additions are made to control a specific physical or electrical property, rather than the strength and toughness, the best example being the electrical strip steels.

The history and development of the alloy steels is linked intimately with the advance of industrial technology, and hence also economic activity. In this paper we attempt to outline how the principal families of low alloy steels developed over 50 years in the context of the need to meet changing industrial requirements.

The scope of the present paper allows only an outline treatment. In particular, it has not been practicable to cover the developments in physical metallurgy which were necessary for the effective use of alloy steels. However, the major experimental techniques used to investigate microstructure and response to thermal treatment have all emerged in comparatively recent times, since about 1860, (dilatometry, pyrometry, optical metallography, resistiometric and magnetic measurements, X-ray diffraction and electron microscopy). For this reason, the original literature is reasonably accessible. Appendix 1 lists some references which cover the experimental developments.

The 19th Century Background

The systematic study of the roles of the new common alloying elements to control the properties of steels, as opposed to investigation of process chemistry and the control of impurities, is generally accepted to have started with the publication of Stodart and Faraday's work in 1820[2]. This initiated the chain of investigations leading to the medium and high carbon chromium steels, which had found limited commercial application for their comparatively high strength by 1870[3]. The 1% carbon, 1.5% chromium steel, still widely used in ball and roller bearings, dates from this period and is thus probably the oldest established standard grade of low alloy steel.

(The commercial use of chromium steel was contemporaneous with the introduction of Mushet's carbon-tungsten-manganese tool steel, the starting point for the air hardening and high speed steels.)

The evolution of the principal families of steel compositions from the 19th into the 20th century is summarised in Table 1. This gives examples of significant commercial utilisation of the alloys, but these are not necessarily the earliest recorded applications. The availability of ferro alloys and steel melting methods for their use is obviously a factor governing the systematic, rather than the fortuitous use of alloying elements. and this aspect is outlined in Table 2. To complete the summary of the 19th century background, Table 3 lists some of the major industrial sectors which would influence the demand for alloy steels in the first half of the 20th century.

1890 — 1914

The best publicised growth of alloy steel use early in this period was associated with the ordnance and naval construction industries. The saga of the development of projectiles and armour requires a separate paper to do it justice. In summary, projectiles evolved from the chilled cast iron shot capable of defeating wrought iron armour to the use of medium carbon chromium, chromium-nickel and chromium-vanadium shot and shell. Shell cases were differentially heat treated by various secret techniques, such as fully quenching into warm oil followed by filling the shell cavity with molten lead.

Following the first adoption of iron armour, various attempts were made to produce laminated high and low carbon steel plate. However, the most rapid advance was made with the discovery of the strengthening effect of nickel. Following earlier French work, the studies of Riley[4] in 1889 were influential in this respect. They led to nickel rivalling chromium as an addition to high strength structural steels and shortly afterwards the synergistic benefits of nickel and chromium were realised. The use of up to about 4% nickel medium carbon steels allowed the production of homogeneous armour plate by quenching and tempering. This was satisfactory for lighter plates, up to some 150mm, but it was quickly realised that the nickel and nickel-chromium steels were sufficiently hardenable to provide a back face of adequate strength and toughness to support a carburised front surface. Plates of 200-500 mm thickness were treated to produce carburised layers up to 40 mm in depth.

Considerable heat treatment expertise was applied, not only to the carburising treatment, but also to the logistical problems of bending, shaping and drilling locating rivet holes prior to the final differential quenching treatment. The two principal processes, of Harvey and Krupp, relied on pack and gas carburising respectively. A typical composition quoted for Krupp armour in 1911 was, 0.3% C, 0.7% Mn, 3.5% Ni, 1.5% Cr[5]. However, there was far less disclosure of armour developments in the literature after about 1900 and actual compositions and heat treatment

TABLE 1

OUTLINE OF THE EVOLUTION OF THE PRINCIPAL FAMILIES OF LOW ALLOY STEELS

Manganese Steels

The only recognised 'manganese alloy steel' was the abrasion resistant 13% Mn – 1% C metastable austenitic composition derived by Hadfield from exploration of the use of high carbon ferromanganese. However, the possibility of using lower levels of manganese for its hardenability effects was recognised and, by 1910, 2.5% had been identified as the practicable upper limit for both air cooling and hardening and tempering. The near equivalence of manganese and chromium was also recognised, together with the advantages of a balanced addition of the two elements up to the same nominal maximum level. Manganese-chromium steels for heat treatment were available commercially by c 1920 and have remained in use since. They were joined by the Manganese-Molybdenum steels by 1930.

A combined manganese and chromium addition was widely used in structural steels, for example, the specification for the high strength weldable steels BS968.1941 recognised two compositions, one with 1.8% Mn and 0.35 Cr max, the other with 0.80% Mn and 0.80% Cr max.

Silicon Steels

The potential strengthening effect of silicon when added up to some 1.0% was recognised at the turn of the century and the element was added to both structural and heat treated steels. However, the major surviving use of the element in low alloy steels, apart from electrical applications, is to confer low temperature tempering resistance in high strength steels, principally the 'silico-manganese' (2% Si, 1% Mn) spring steels.

Chromium Steels

The difficulty of melting low (below c 0.3%) carbon steels limited the early application of the simple chromium steels to the higher strength applications (cutlery, tools, components of security systems such as jail bars and safe and vault laminated plates, from c 1870). The benefit of an addition of vanadium to improve hardening and tempering response was established by 1900 and medium carbon Cr-V steels were in commercial use in both the UK and French automobile industries for forgings and stampings. Although applied to armour as early as 1878, the medium carbon 1.3% Cr steels were overtaken by the Ni-Cr steels.

Nickel Steels

From 1894 to c 1912 the simple nickel compositions rapidly became established as the dominant general purpose low alloy steels. The absence of the carbon contamination of the ferro-alloy, compared with the chromium steels, allowed ready production of the lower carbon contents required for carburising and structural applications. The advantages of additions of up to some 7% Ni to produce air-hardening steels, particularly for carburising, were recognised and used in the French automobile industry by 1905.

Vanadium Steels

Additions of vanadium were considered as deoxidants, but work between about 1884 and 1905 established clearly that small additions (up to about 0.5%) were most effective in enhancing strength and toughness. These investigations are of interest in that they provide the earliest reports of the properties of the microalloyed steels, 0.08-0.4% C Mn-V steels being described in the work of Arnold, Hadfield and Guillet. (Most early references to 'Vanadium Steels' refer to Cr-V compositions).

Nickel-Chromium Steels

It is probable that the first Ni-Cr steels were made as 'natural' alloy steels by using a low phosphorus Cuban iron ore converted in a duplex Bessemer-open hearth process to give a final composition in the range 0.2 - 0.70% Cr with 1.0 - 1.5% Ni. However, 'synthetic' Ni-Cr steel compositions were established in production by 1900. Their use for armour plate has been described in the text.

Molybdenum Steels

Although studied systematically in the period 1894 - 1913, there was little early use of the simple molybdenum steels before the development of the low carbon tube quality for boiler applications from c 1928.

From 1918 molybdenum came into general use, principally added to the Cr and Ni-Cr steels. The major application was to provide hardenability and temper embrittlement resistance for heat treated heavy section products. The low carbon Cr-Mo and Ni-Cr-Mo steels were also used as high strength welded tubes, particularly for air frame construction.

Other Alloying Additions

Tungsten was not seriously considered as a useful strengthening addition for low alloy steels as molybdenum became more generally available, its principal application being in the magnet and tool steels.

Titanium was used as a deoxidant and was not exploited as a microalloying addition within the period under consideration.

Copper had been added to structural steels to improve corrosion resistance from c 1900 and was to continue in limited use, usually combined with nickel and phosphorus additions.

The use of high sulphur contents to improve machinability was known in 1879, but by 1913 only one resulphurised steel appeared in the SAE specifications. With the decline in Bessemer production of special engineering steels, and a consequent reduction in nitrogen and phosphorus levels, specifications were introduced covering both rephosphorised and resulphurised steels. There were no major changes in machining steels practice until the introduction of lead as an additive shortly before the second world war.

Footnote – For a comprehensive survey of early properties data on the low alloy steels, see the Carnegie Memoir of Guillet, reproduced in the JISI, **70** (1906), pp 1-143.

conditions are not widely available. It is probable that additions of both vanadium and tungsten were also used.

Temper embrittlement was for some years so closely associated with the early alloy steels used for the heavy products of the ordnance industry as to become widely known as 'Krupps Krankheit'. Molybdenum was used as an addition to an armour plate steel in 1894; however, it remains to be established when it was first used to offset temper embrittlement. Tungsten was in use as a strengthening addition at the turn of the century, but never became a significant general purpose addition. It was established by 1904 that molybdenum was similar to tungsten in its effects on transformations and the resulting properties, but was twice as effective on a weight percentage basis[6].

Up to 1910 the bulk of both consumer and heavy industrial products required only carbon steels for their manufacture. However, a major influence in the adoption of alloy steels was the general need to transmit greater power and loads in machinery, this often at higher rotational speeds and with greater precision in the location of components. Improved rolling contact bearings were required, over a range of applications from textile and general machinery to the turret rings and thrust bearings of battleships. They were required also in the automobile, a product which has been intimately linked in its history with the growth in the use of low alloy steels over the period under examination.

The car industry evolved from the cycle, agricultural machinery, stationary engines and general engineering sectors, almost all of these making little use of alloy steels. Figure 1 shows the construction of a typical early light car[7]. At its heart lies a three speed sliding mesh gearbox, presenting to its designer problems of lightness, compactness, high local stresses and wear. (These problems to be shared in turn, on differing scales, by the marine engineer seeking to expand the range of application of the Parsons turbine by the development of a viable reduction gearing.)

The value of chromium and chromium-vanadium steels for vehicle parts was recognised early in the century and these steels were preferred by the drop forgers and stampers because of their better surface characteristics and behaviour in hot forming, when compared with the nickel steels[8]. However, the automobile industry appears to have had a strong preference to the nickel and nickel-chromium steels. Debates in the technical literature concerning the consistency of properties, especially heat treatment response and machinability[9] are echoed to this day. This concern was to lead to active measures to standardise steels. The theme of definition of the response to heat treatment has recurred through national standards and the ten steels chosen for assessment in the first major UK low alloy steels collaborative research programme[9,10] reflect the interests of the car industry at this time, Table 4.

Standardisation appears to have started earlier in the US, where initial work was taken over by the Society of Automobile Engineers in 1900, to result in the influential SAE specifications. By 1915 the 23, 31 and 33 hundred nickel steel series of steels were standardised. However, the adoption of alloy steels in volume vehicle production appears to have been somewhat slower in the US than in Europe[11].

The interest shown by the car makers in the strengthening effects of nickel, chromium and vanadium, applied to steels in both the 'natural state' and after hardening and tempering, was shared by the civil engineer. From the first, possibly inaccurate, claims for the use of chromium steels in the St Louis Mississippi Bridge in 1871,[3] there are numerous reports of the application of low alloy steels, mainly in tension members in large scale bridgework and other structures where weight saving was important. A wide range of compositions was explored; including those containing copper for improved corrosion resistance. Enhanced silicon levels were also used for increased strength.

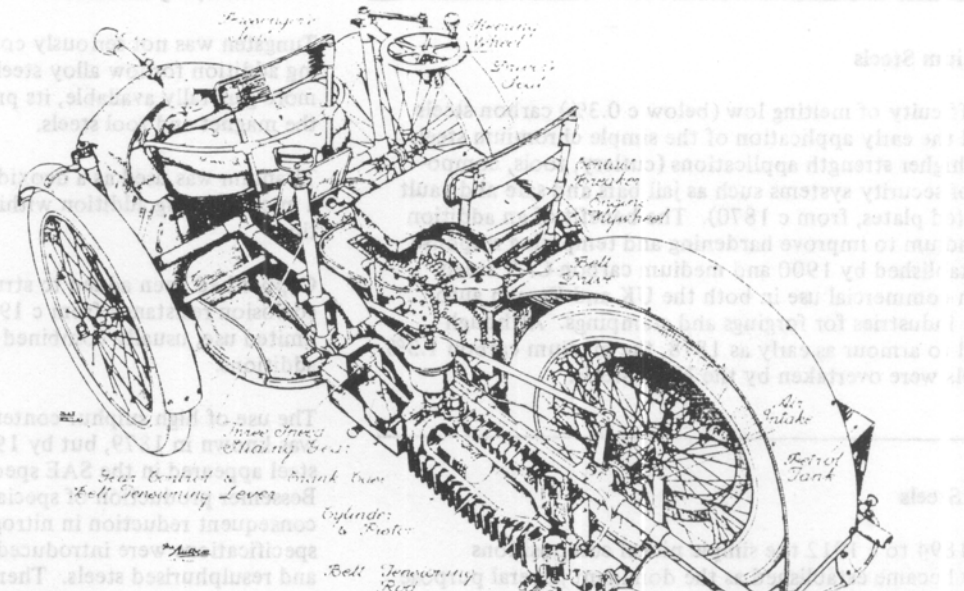

Fig 1 The 2hp Leon Bollee Tricar of 1896[7].
The tubular frame and wheel derive from cycle construction and the single-cylinder engine from gas engine practice.

TABLE 2

The Availability of Ferro-Alloys at the Start of the 20th Century

FeMn. Exploitation of high carbon ferromanganese led to Hadfield's 13% Mn steel, 1875-82. Blast furnace production of ferro-alloy supplemented from 1900 by the availability of the Goldschmidt alumino-thermic and later electrolytic routes.

FeCr. High carbon ferro-manganese-chrome and ferrochrome produced initially in the crucible or blast furnace. Higher chromium contents achievable by the Goldschmidt and Moissan arc reduction methods, 1900-1905.

FeNi. New Caledonian deposits exploited 1874, Mond process developed for high purity nickel 1888, Canadian deposits later to dominate western world supply first exploited 1915.

FeV. Ferrovanadium produced initially by Goldschmidt or arc furnace routes. Peruvian deposits discovered in 1905 and exploited by 1st World War using hydroelectric power.

FeMo. Early investigators used molybdenum powder, often with sulphur contamination. Ferromolybdenum produced initially by carbon and ferrosilicon reduction in crucible processes, later the Goldschmidt process was used. US dominance in supply began with exploitation of Bartlett Mountain Deposits from 1917.

FeTi. Available from electric furnace production c 1910.

TABLE 3

THE INDUSTRIAL SCENE, INTO THE 20TH CENTURY

1900	Successors	Present Time
Mining and Minerals Extraction.	Oil and gas exploration and extraction.	
Civil Engineering, Bridgework, Buildings, Cranes and Hoists.		Off-shore Construction
Mechanical Engineering, Hydraulics, Steam-Raising Plant	Pressure Vessel Industry.	
Textile, General Engineering Plant, Machine Tools.		
Agricultural Machinery, Cycles, Oil & Gas Engines, Steam Traction.	Earthmoving Equipment Automobiles, Industrial Power, Compressors and Turbines.	
Railways	The transition from steam, 1930 onwards.	
Electrical Power Generation and Transmission.		Nuclear Power Industry
Industrial Chemicals and Process Plant.	Coal Conversion and by-products, Petrochemicals.	Biotechnology
Marine Propulsion.		
Ordnance, Artillery, Naval Construction, Small Arms	Armoured Fighting Vehicles Aircraft Industry, Aero-engines, Airframes.	Aerospace.
Precision Bearings.		

However, the nickel steels appear to have been most widely employed, with carbon contents in the range 0.2 - 0.4% and nickel additions of from 0.5 to 4%. Examples of the properties of these steels, in the natural and heat treated conditions, and their applications are given in summary by Hibbard[12] and Cone[13].

For as long as riveted construction was adopted, the users of structural steels were able to make a wide choice of carbon level, alloy content and heat treatment conditions for structural applications. Use was made of convenient tensile strength levels of some 400 - 500 N/mm^2. It follows that the relatively sharp distinction between 'structural' and 'heat treated engineering' steels of the present day was unknown until after the 1930s. In the earlier part of the century one can find reference to a 0.3% C nickel steel being used for applications as diverse as armour plate, gears, shafts and structural members. These were used as-rolled, normalised, annealed, carburised and hardened and tempered.

By the turn of the century electrical power generation and distribution was a major growth industry. At first this brought no major demands for alloy steels in either the steam plant or rotating machinery. However, one class of low alloy steels was to make a major impact. The low hysteresis silicon steels for transformer construction were pioneered by Hadfield in work published in 1899[14], his 'Stalloy' being used from 1903. The silicon ferritic steels typify the low alloy steels in general, in that after the basic recognition of their properties, most remained in production for the next fifty years, subject to refinement in the understanding of factors governing their behaviour. The performance improvement obtained from this understanding has been most probably, greater for the silicon transformer steels than for any other type. Figure 2 is a summary of the improvement obtained to 1930.[14] This reflects the appreciation of purity level and grain size. Ahead lay the realisation in the late 30s of the significance, at Westinghouse and Armco, of the control of grain orientation and the production of 'Hypersil'[15].

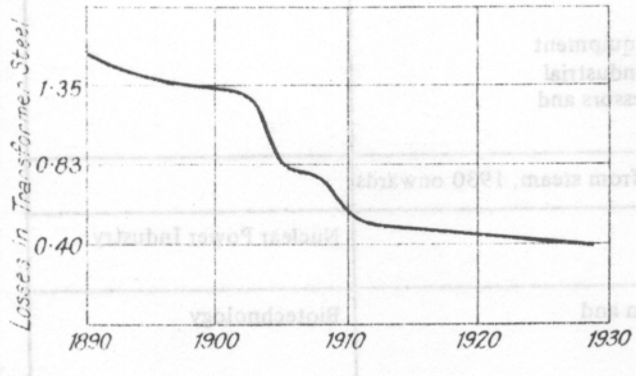

Fig 2 The reduction in energy losses in transformer steels (Watts per lb weight of steel) for the period 1890-1930.[14]

1915 – 1930 – War and its Aftermath

The First World War brought a massive expansion in the output of steel products. The pressures of wartime production required multiple sourcing of steels and their processing and heat treatment. There was an urgent need to solve problems rapidly, and this tended to undermine the pre-war attitudes of secrecy and the promotion of proprietary steels by individual steelmakers. The foundations were laid for post-war formalised collaboration in areas of general interest[1]. Typical of the problems were the difficulties in producing large quantities of forged gun barrels. There were extensive studies of the macro and microstructures in ingots, the evolution of directionality in the forgings and their resultant effects on transverse toughness and ductility. (The importance of these topics[16,17] may be compared with more recent concern with the toughness of gas and oil linepipe steels). The allied heat treatment problems, for example, temper embrittlement also received a high level of attention.[18,19]

The aircraft industry emerged as a significant user of special low alloy steels. The early wooden-framed aircraft were powered largely by rotary engines which were designed within current metallurgical limitations. However, by the end of the war steel tubing was in use in airframes and the larger engines were of the in-line, water cooled type. These were of four times the power of the rotaries and were derived from the more advanced automobile designs of 1914. The principal metallurgical problems with these engines were fatigue, particularly of the crankshafts and valve springs, and the short lives of exhaust valves. The erosion and corrosion of gun barrels by smokeless powders may be linked with the exhaust valve requirements as factors leading to the further exploration of the higher chromium steels, and hence the evolution of the stainless steels.

In a review of aero-engine developments[20] in 1930, there was a major concern at the problems of inspection for defects in critical components of the engine, such as the connecting rods, crankshafts and reduction gearing (Fig 3). Much interest was aroused by the prospect of using the nitriding steels of the Nitralloy type (medium carbon, MnCrMoAl steels)[21] and their successors were to become widely used for high duty crankshafts.

The extended use of molybdenum had its origin in the dependence of the US on imported ferroalloy production at the commencement of the war. Vigorous promotion of the use of indigenous resources led to investment in molybdenum mining[22]. Molybdenum supplies were abundant in the post-war period and there was extensive promotion of their use, drawing on the earlier studies as indicated in Table 1. The 'forty' series of alloy steels, to become perhaps one of the most widely used of all low alloy steel families, were added to the SAE standards by the introduction of the 4100 (1% Cr, 0.25% Mo) series in 1926[23]. However, manufacturers were offering a range of CrMo, NiMo and NiCrMo steels from about 1920 onwards[24].

As an illustration of how the automobile industry was using low alloy steels, Table 5 shows the steels specified by American and European car manufacturers for two classes of component. These are taken from a compilation published in 1930[25] which provides a reasonable summary of practice. For the crankshaft of the relatively basic Model A engine, Ford employed a medium carbon steel. At the other extreme, was the 4.5% nickel-chromium steel employed by Daimler Benz. The other manufacturers employed medium carbon steels of varying alloy content, nickel, nickel-chromium and nickel-chromium-molybdenum steels being represented.

The gear steel specifications again show a spread of practice; Ford and Chevrolet employing medium carbon chromium and chromium-vanadium steels respectively, these used

TABLE 4

AUTOMOBILE STEELS STUDIED BY THE JOINT IAE-SMMT RESEARCH COMMITTEE, 1920 [10]. (NOTE SULPHUR AND PHOSPHORUS RANGES)

Class of Steel	Mark	Composition wt%						
		C	Si	Mn	S	P	Ni	Cr
10 C Case Hardening Steel High Limit	1H	0.17	0.24	0.72	.041	.047	-	-
Low Limit	1L	0.06	0.01	0.25	.010	.050	-	-
15 C Case Hardening Steel	2H	0.20	0.11	0.99	.066	.049	-	-
	2L	0.12	0.05	0.71	.080	.048	-	-
2% Ni Case Hardening Steel	3H	0.15	0.05	0.61	.017	.012	2.60	-
	3L	0.12	0.07	0.32	.025	.014	2.40	0.10
5% Ni Case Hardening Steel	4H	0.17	0.39	0.34	.014	.014	6.00	-
	4L	0.07	0.06	0.18	.020	.008	5.10	-
20 C Steel	5H	0.26	0.30	0.75	.044	.050	0.15	0.04
	5L	0.13	0.06	0.41	.025	.036	0.20	0.08
35 C Steel	6H	0.45	0.32	0.78	.020	.025	-	-
	6L	0.26	0.20	0.50	.060	.065	0.03	-
3% Ni Steel	7H	0.37	0.17	0.65	.020	.030	3.65	-
	7L	0.17	0.05	0.34	.033	.023	2.90	0.20
1½% NiCr Steel	8H	0.38	0.33	0.60	.045	.039	1.72	1.65
	8L	0.28	0.08	0.40	.020	.018	1.52	0.80
3% NiCr Steel	9H	0.31	0.14	0.70	.027	.030	3.27	0.82
	9L	0.17	0.15	0.37	.022	.012	2.95	0.45
Air-Hardening NiCr Steel	10L	0.32	0.12	0.46	.017	.014	3.70	1.42
	10LL	0.27	0.16	0.49	.040	.040	3.45	0.95

TABLE 5

STEELS FOR AUTOMOTIVE COMPONENTS, 1930

+ x = maximum, compare with levels given in Table 4.

Component, Manufacturer and Model	Steel Specn.	%C	%Si	%Mn	%S	%P	%Cr	%Mo	%Ni	Others & Comments
Crankshafts										
Ford US 'Model A'	EE	0.35-0.40	0.07-0.4	0.70-0.90	0.05x	0.03x^{+}	-	-	-	
Renault	-	0.30	0.15	0.25	0.035x	0.025x	0.65	-	2.5	
Daimler-Benz	DINVCN45	0.30	0.35	0.4-0.80	0.04x	0.04x	1.0-1.20	-	4.25-	
Horch 8 cyl.	-	0.36	0.3	0.75	0.01	0.01	1.0	0.4	0.5	
Morris 6 cyl.	-	0.40	0.3x	0.60	0.06x	0.06x	-	-	1.0x	
Transmission Gears										
Ford Main Drive Gear	AA4	0.35-0.38	0.10-0.20	0.65-0.80	0.04x	0.03x	0.90-1.10	-	-	
Cadillac	SAE 2525A	0.12-0.17	0.15-0.30	0.30-0.60	0.04x	0.04x	-	-	4.75-5.25	
FIAT	-	0.14-0.17	0.35	0.70-0.80	0.04	0.04x	0.6-0.8	-	2.0-3.0	
Daimler-Benz	ECN35	0.12-0.16	0.35	0.50	0.04x	0.04x	0.55-0.95	-	3.25-3.75	
Chevrolet-Six (Car)	SAE 6150	0.45-0.44	0.15-0.30	0.50-0.80	0.05x	0.04x	0.80-1.10	-	-	0.15% V
(Truck)				As above, Cadillac						

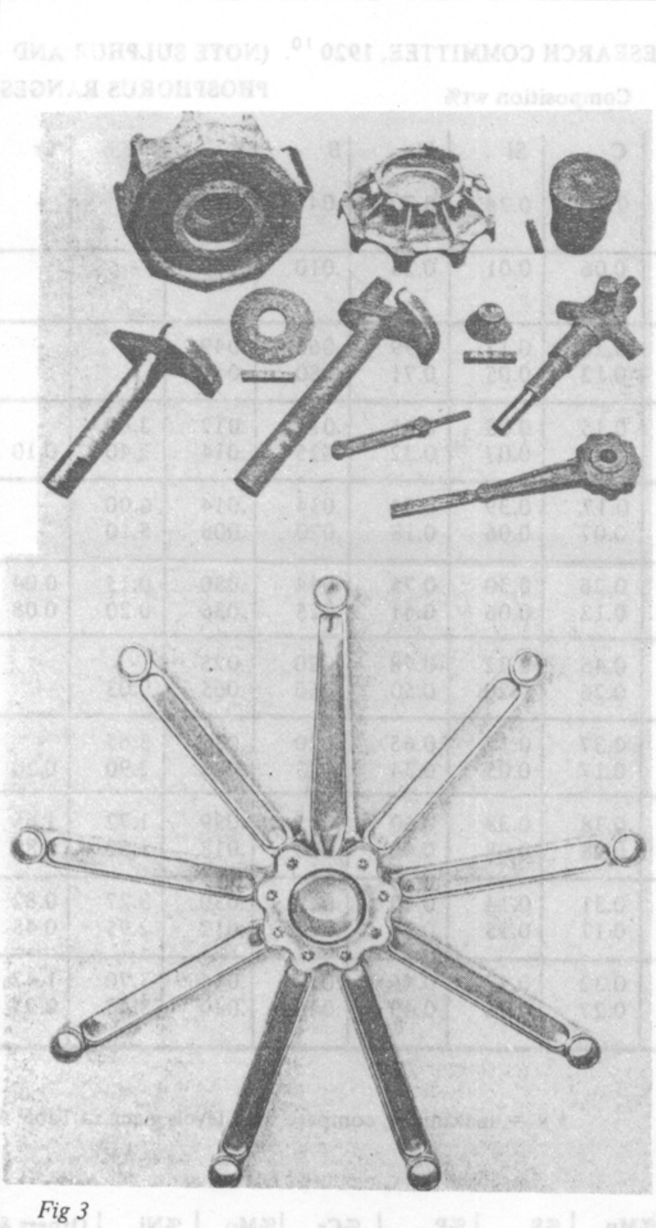

Fig 3

Low Alloy Steel Components in the 500hp Bristol 'Jupiter' air-cooled radial aero engine, upper, rough forgings in '65 ton' NiCr steel with Izod test extensions. The lower Figure shows the finished master (vertical) and articulated connecting rods.[20]

presumably in the hardened and lightly tempered condition. The other manufacturers listed all used nickel-chromium carburising steels of varying alloy content for car gears, Chevrolet retaining a nickel steel, again carburised, for truck gears.

This period saw, in the UK, steam railways approach their zenith in technology. The senior Chief Mechanical Engineers had made significant contributions to the use of improved materials. In 1929, W A Stanier was stressing that nothing but the best was good enough for the Great Western by emphasising the importance of good heat treatment practices[26]. Other railway companies were deriving benefits from the use of low alloy steels to reduce the weight of reciprocating masses in piston and connecting rods[27] Figure 4. In trackwork the value of both the low alloy medium carbon and high manganese steels for wear resistance had been appreciated for some time, as indeed was the potential for the application of heat treatment to rails.

High temperature steels emerged as a recognisable family, consequent upon the need to increase the efficiency of power generation units by raising size, operating temperature and pressure. As steam turbine rotors increased in dimensions, alloy steels were adopted to meet the strength requirements. The addition of molybdenum to the nickel-chromium rotor compositions in 1924[28] laid the foundation for the present-day large rotor compositions. These developments in turn focussed attention upon the problem of hydrogen cracking of large alloy steel sections.

The value of molybdenum for elevated temperature strength was recognised and the low carbon 0.5% molybdenum steel became established for service as steam tubing for temperatures up to 500°C.

1930 - 1950 – Re-armament, Petro-chemicals, Wars and Welding

Metallurgical developments in the immediate pre-war period included the promotion of the manganese-molybdenum medium carbon heat treatable steels as low cost competitors to the established NiCr steels, particularly for the UK automobile industry[29]. There was also more active promotion of the higher strength, quenched and tempered structural low alloy steels, particularly in America[13]. For the high temperature steels, the importance of graphitisation in molybdenum steels, and the role of aluminium in promoting this effect, was recognised. There was some interchange of experience between the petroleum and power generation industries in the use of improved high temperature and moderately corrosion-resistant steels, based on low carbon-molybdenum enriched with chromium[30]. The strong effect of vanadium in conferring high creep strength was exploited.

Considerable effort was devoted to the welding fabrication of both mild and higher tensile strength structural steels. The significance of carbon and alloy content was recognised and some interesting pioneer work in the field of micro-alloyed steels came about as a result of the use of titanium additions to reduce the hardenability effect of carbon[31]. The dramatic problem of brittle fracture in the volume-produced welded ship hulls in the Second World War led to a substantial investigation programme. Apart from the intrinsic interest of this work for an understanding of brittle failure mechanisms[32,33] the overall investigation provided a good example of the integration of engineering and metallurgical approaches to service problems. Although not directly concerned with low alloy steels, the episode was to influence strongly the emergence of the improved toughness, high yield strength microalloyed structural steels in the post-war era.

The new structural steels also had origins in the work on weldable high strength structural steels required in military engineering. Mechanised warfare and the rehabilitation of devastated territories required rapidly assembled bridgework, such as the Bailey system, on a scale far exceeding any earlier field engineering activity. From this experience, came the low carbon, molybdenum-boron structural steel 'Fortiweld'[34] which was in turn the precursor of the family of controlled processed bainitic and acicular ferritic high strength linepipe steels.

The theme of the period for the heat treated steels was reduction in the use of alloying elements. In Germany the foundations of a siege economy were laid in several programmes instituted before the war to recycle strategic materials and optimise the use of indigenous raw materials, such as vanadium-bearing iron ores[35]. The German industry suffered a progressive withdrawal of alloying elements, so that by 1943, critical parts such as aero engine crankshafts were being made from MnCr carburising, rather than NiCr carburising or CrV nitriding steels. The situation worsened, as supplies of tungsten, nickel and chromium ceased. (A study of the considerable efforts made to eliminate alloying elements at this time form an essential starting point for any current programmes for alloy conservation). It is fortunate that the activities are fully documented in the FIAT Reports prepared post-war by the Allies[36,37]. Compositional and heat treatment techniques still of interest include the development of ersatz chromium-reduced bearing steels, Table 6, direct quenching from rolling operations and selective flame hardening for armour plate production.

The UK and US were less pressed for the major alloying additions, but major economies were effected in the use of chromium, molybdenum and nickel. For the heat treated steels, compositional modifications could be made against the background of the systematic study of heat treatment response based on iso-thermal and continuous cooling transformation methods[38,39] and the practical hardenability tests[40].

Although the nickel and nickel-chromium steels were to continue in national standards, their use was to decline as War Emergency balanced, Mn, Ni, Cr, Mo steels became incorporated into post-war revisions[41,42]. This trend was accelerated by the shortage of nickel supplies resulting from the Korean War.

In the US, the 'EX' series of steels represented the first systematic attempt to make available a range of low alloy heat treatable steels in which a given level of hardenability could be obtained by the selection of equivalent options among combinations of the principal strategic alloying additions[43].

The pressures for economy accelerated adoption of boron as an effective hardenability addition. The full exploitation of this element in manganese and lean alloy steels required close control of deoxidants and nitrogen stabilising additions in steelmaking, together with an understanding of the boron distribution during heat treatment which required examination techniques developed outside the period in question.

The post-war period to 1950 was mainly one of consolidation, in which the experiences of the war period were digested, manufacturing industry had embraced the following changes:-

The widepsread adoption of welding fabrication with an associated understanding of the risks and causes of brittle fracture and a realisation of the importance of lower carbon contents in structural steels.

The use of design changes to reduce the machining requirements of items such as small arms, with extensive substitution of pressings and tubulars for bar-derived components.

A drastic reduction in the alloy contents of heat treated steels, allied to closer control of heat treatment practices

Expanded demand for tube and pipe products, albeit mainly in unalloyed steels, for fuel oil distribution and new products such as rocket casings.

In several senses, 1950 is an arbitrary date on which to end this outline history. Ahead lay the massive expansion in the UK fossil power generation capacity, the nuclear power industry, and the rapid expansion in gas and oil exploration, extraction, distribution and conversion. However, as sketched above, the bases for most of the steels in this period have been foreshadowed within the first 50 years of the century.

Some Process Considerations

In 1900 the principal melting methods for alloy steel production were the crucible process and the acid open hearth, both of which allowed ferro-alloy additions to be melted without excessive losses from oxidation or contamination.

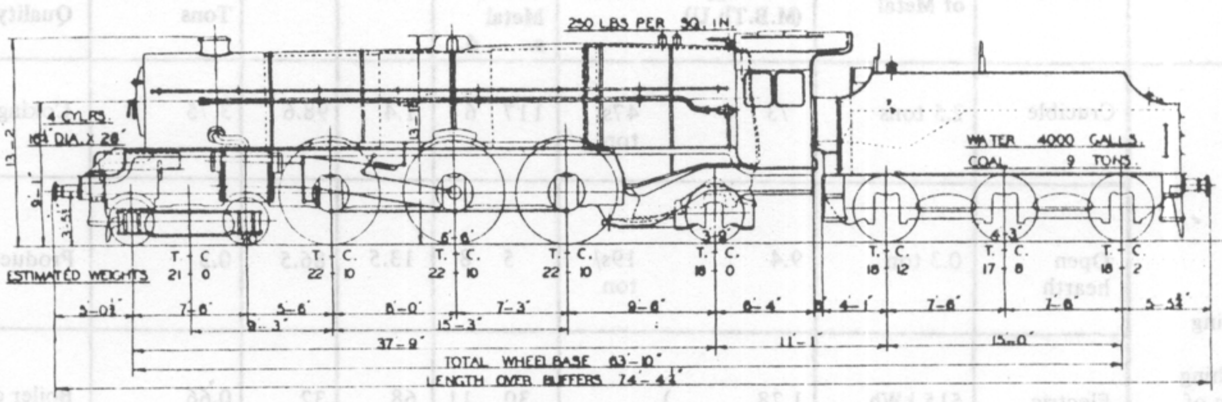

Fig 4 4-6-2 Express Passenger Locomotive 'Princess Royal' of the London, Midland & Scottish Railway. The Armstrong-Whitworth 'Vibrac' medium carbon, 2.5% Ni, 0.5% Cr, 0.5% Mo steel was adopted for coupling and connecting rods.[27]

TABLE 6

ALLOY CONSERVATION, THE REDUCTION IN CHROMIUM CONTENT IN THE STANDARD 1% C, 0.4% Mn, 1.45% Cr THROUGH-HARDENING BEARING STEEL (BS970-535A99, SAE 52100)

Date	Originator	Composition Range or Typical Analysis							Comments
		%C	%Si	%Mn	%Cr	%Ni	%Mo	Ideal Dia. mm	
1939	German Bearing Industry	0.5/ 0.6	1.0	1.0	-	-	-	45	Leanest 'ersatz' bearing steel
		1.0	0.5	0.7	0.85	-	-	55	DEW 1% C - 1½% Cr replacement (1944)
1945		0.95/ 1.15	0.2/ 0.7	0.25/ 1.25	0.30/ 1.65	-		59	Range of chromium bearing steels, 1939-45
1965	Inco (SAE EX-2)	0.7	0.3	0.35	0.25	0.85	0.1	50	Has been used in bearing applications
1971	Timken TBS-9	0.9	0.25	0.7	0.3	-	0.1	51	Claimed to be a close equivalent to SAE 52100
1972	Habrovec	0.70	2.0	2.0	1.0	-	-	-	-

TABLE 7

FUEL COSTS AND THERMAL EFFICIENCIES FOR THE THREE PRINCIPAL STEELMAKING METHODS, BASED ON A SPECIAL AND ALLOY STEEL PLANT, 1917 MUNITIONS PRODUCTION[44]

Operation	Fuel or Method Employed	Fuel or Energy per Ton of Metal	Cost of Fuel or Energy						Coal Used in Producing Fuel or energy	
			Thermal Units in Fuel or Energy (M.B.Th.U)	Unit Cost	Total Cost per Ton of Metal s.	d.	Heat Efficy. %	Lost Heat %	Tons	Quality
Melting and finishing 1 ton of fluid	Crucible	2.5 tons	73	47s/ ton	117	6	1.4	98.6	3.75	Coking coal
	Open hearth	0.3 ton	9.4	19s/ ton	5	8	13.5	86.5	0.3	Producer coal
	Electric to melt	515 kWh	1.78	) 0.72d per unit	30	11	68	32	0.66	Boiler coal
	Electric to melt and refine	780 kWh	2.68	)	46	10	47	53	1.0	Boiler coal

The electric arc melting process was in its infancy in 1900, but was well established by the time of the First World War, having overcome the stigma of having order enquiries stamped 'Electric steelmakers need not apply'.

The arc furnace was to replace crucible melting for the high alloy tool steels and grow in importance for special and low alloy steel production. The metallurgical advantages of scrap melting and good compositional control outweighed the higher fuel costs, which initially were higher than for the open hearth furnaces. The relative costs are indicated in Table 7, based on 1917 data from the Hadfield's Sheffield Works[44].

High Frequency (HF) Furnaces were introduced for small scale melting, but large (3-5t) furnaces of this type did not come into use until the mid-30s.

The development of vacuum treatments for hydrogen control, together with secondary steelmaking vessels and secondary refining technology made a major contribution to the production of alloy steels. However, their introduction lay just outside the perid under study.

The Growth of Alloy Steel Production

It is unfortunate that detailed industry statistics for alloy steels production do not appear to be available for the first half of the century. Figure 5[14] shows the trend for the period 1894 to 1929, but the source is not attributed. Hibbard[12] quotes outputs for individual alloy steel types in 1919, but again the background to the figures is not described.

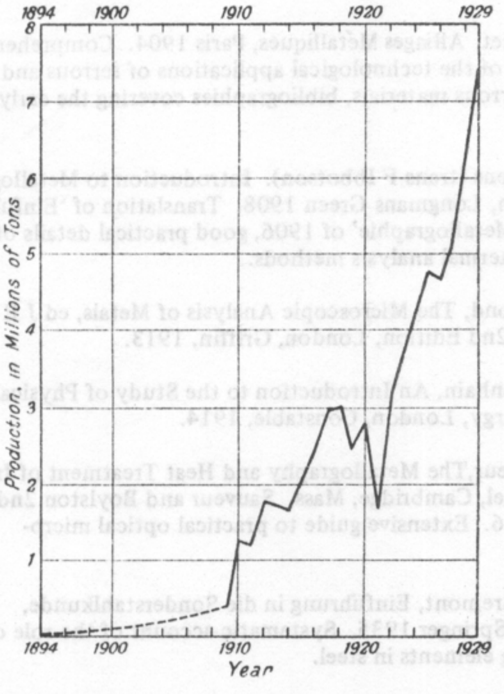

Fig 5 World Production of Alloy Steels, 1894-1929.[14]

The percentage of total World Production of steel ingots and castings made as alloy steels in 1910, 1920 and 1925 was 2.0, 3.85 and 5.3% respectively.

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Appendix 1 — Men and Experimental Methods

The introduction of alloy steels was dominated by the work of a handful of men who set aside empirical examination of steels produced ad hoc from materials and plant to hand, making instead systematic investigations of the effects of varying carbon contents and the levels of alloying additions. Among the outstanding figures were Arnold (vanadium steels), Hadfield (manganese and silicon steels), Guillet (molybdenum steels), Swinden and Bain. These workers used primarily the methods of thermal analysis, optical metallography and mechanical testing after controlled heat treatments. They also used, to an extent perhaps surprising to the modern physical metallurgist, electrical and magnetic methods. Their principal handicap was a lack of means to dermine the distribution of elements between phases in the microstructure on the atomic scale. This deficiency led to the formulation of hypotheses, some prescient, others short-lived, which could only be tested as first X-ray diffraction and then electron-optical and microanalysis techniques became available.

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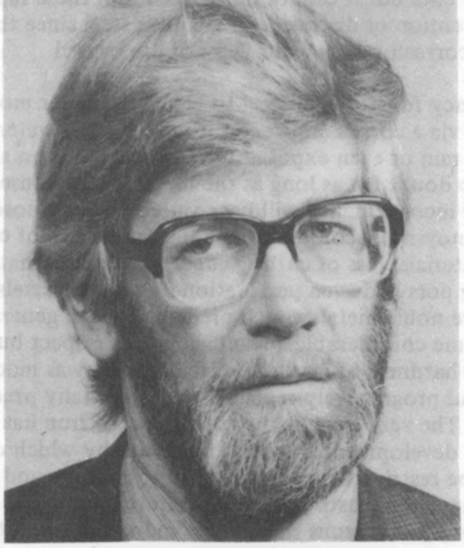

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Stellites

Maurice Riddihough

The discovery and development of the hard, stainless, cobalt chromium alloys was the work of Elwood Haynes who was born in 1857 in Indiana, USA, died 1925. His early experiments were in search of an alloy which 'would resist the oxidising influences of the atmosphere and take a good cutting edge'. The original alloy was a binary of cobalt and chromium (patent 873,745, 1909) which was subsequently improved in hardness by the addition of tungsten or molybdenum. Patents on these ternary and quaternary alloys were obtained in 1913. The alloys were originally intended for the production of forged dental and surgical instruments, table and pocket cutlery. But the addition of tungsten increased the hardness at high temperature so that they were unforgeable but became widely used during the 1914/18 war for shell turning in the USA, UK and Russia. In 1918 up to four tons of the alloys were cast per day.

In 1920 the Haynes Stellite Company was acquired by Union Carbide and work by their combined research departments established a commercial range of compositions from the softer alloys of 25% Cr, 5% W, 0.1% C, bal Co, to the hardest 35% Cr, 15% W, 2.5% C, bal Co. In 1922 the deposition of the alloys by oxy-acetylene welding led to the hard-facing of oil well drill bits and internal combustion engine and steam valves. In the late 1920s the dental and surgical alloy Vitallium was developed with 30% Cr, 6% Mo, 0.2% C bal Co.

These surgical prostheses and denture plates are made by the lost wax or investment casting process and when Rolls Royce planned the production of gas turbines early in the 1940s they decided to use this process for the production of their nozzle guide vanes, complex shapes which would be difficult to produce by machining. The process was already successfully used in the USA for the production of the supercharger blades on the Boeing 'flying fortress' using the surgical alloy Vitallium which had been found to have adequate heat and creep resistance. Similar alloys are still in large scale use in gas turbines for stator blades, machine gun barrel liners and anti-fretting bearings and surfaces.

(Note. This summary is prepared from the publication 'A History of the Haynes Stellite Company' by Ralph D Gray.)

The initiation and growth of high alloy (stainless) steel production

John Truman

Synopsis

Stainless steels, that is steels whose chromium content is sufficiently high to give immunity from corrosion in a range of environments which would cause attack of low alloy or carbon steel, were first used for a commercial purpose in 1914 in Sheffield, England. There had been a quantity of academic work on high chromium steels spread over a substantial time before this but in the main the interests of the investigators had not included corrosion resistance and the stainless steels remained undiscovered. In a few instances however, the improved corrosion behaviour was noted but with no further activity. Following the use of 13% chromium steels as aero engine valves in the 1914-1918 war, there was intensive research and commercial development activity in post-war years, early commercial activity being almost entirely confined to the 13% chromium types. These proved excellent for use as cutlery and in various engineering applications but growth of use for other applications was slow. Growth of the industry was much more rapid following commercial development of the chromium-nickel 'austenitic' types which proved to have a much greater potential for applications in the chemical industry, for domestic use and for architecture. The first commercial alloy was of German origin, but there was early development in England, where the later famous '18/8' originated, followed by activity in many countries.

The flexibility of use of the austenitic types encouraged improvements in production capacity and methods and growth in the 1930s and especially early post-war years was marked.

The writer was invited to outline the discovery and development of that group of steels termed the stainless steels with particular reference to the pioneering areas since the detailed history of these (and other metallurgical development) is rapidly becoming obscure with records disappearing. This latter certainly has proved to be the case with the stainless steels where changes in the structure of the industry have led to the loss of non-technical records while the technical data are often not of such a nature that the original development steps can be dated with accuracy. Thus for the earlier stages in particular there has been heavy reliance on published information which, again is not always adequate for accurate dating, there understandably having been a considerable degree of secrecy. The writer apologises should there seem to be an undue emphasis on Britain and especially with the organisation with which he has been associated for many years although in that period it has changed in both name and form several times. Naturally, there has been more access to data than from other organisations with also association with the traditions of and in some cases actual involvement with individuals who had been engaged in the early development. There is no intention to minimise the activities of others in this field.

A definition for stainless steel is necessary and the one normally used is an iron base alloy with not less than 10% by weight of chromium. This is not intended to be a technical paper but some indication of the role of the chromium is in order. Iron (and some other metals) react with the air to form an invisible thin film of oxide. Under some environmental conditions this can prevent further corrosion but in the case of iron, even mild conditions can destroy it giving rise to the familiar progressive rusting or to corrosion without rust in the case of acids. If the iron is alloyed with sufficient chromium this potentially reactive metal leads to a modification of the invisible film so that it is rich in chromium oxide and will withstand much more aggressive corrodents (the resistant state is known as passivity). Some other elements can interfere with this effect so that the definition must be broadened to exclude compositions not readily developing, passivity such as iron chromium alloys with a very high carbon content. Chromium may be added to steel for other purposes, notably to improve the mechanical properties although this is usually at lower contents than giving rise to 'stainlessness'. This is worth bearing in mind since some metallurgical studies were involved in the production of high chromium steels at a quite early date but it cannot be claimed that these represented the invention or discovery of stainless steel since the improved corrosion behaviour was not discovered.

The tendency for iron and steel to revert to one or more of the oxides via a corrosion process if immersed in water, wetted by rain or even exposed to moist air has been a liability no doubt for as long as the metal has been used. Degrees of inconvenience will have varied with purpose including annoying discolouration of the article and of contacting materials, loss of cutting edges, the contamination of cooking pots and even perforation of storage vessels. Other more noble metals which predated iron in general use had some considerable advantage in this respect but lacked the hardness of iron while latterly iron was much cheaper and progressively replaced these for many practical purposes. The very long history of the use of iron has involved the development of ways and means by which corrosion may be restricted, notably by use of coatings and also an acceptance that rusting 'is in the nature of things'. It is perhaps for these reasons that, as the industrial revolution and associated material developments got under way, there appears to have been less effort at improving the corrosion resistance of iron and steel than one might, in retrospect, have thought probable. As industrial development proceeded the need for improved mechanical properties was progressively met but corrosion prevention in engineering still relied mainly on protection.

The first practical developments in improving corrosion resistance of iron involved the use of large amounts of nickel or silicon. The 25% nickel steel exhibited reduced corrosion rates rather than 'stainlessness'and, while of some use was expensive and of limited strength. The high silicon irons are very brittle and could be used only as castings but their resistance to certain acids is still utilised. Not until 1913 did the high chromium steels emerge practically but since then they have, in effect, taken over the corrosion resisting steel field except for some slow-rusting, low alloy steels.

The full development of stainless steels may be divided into several aspects; the pioneering individuals and organisations were involved in each of these to differing extents.

1 The realisation that suitably high chromium contents can, under favourable conditions, lead to freedom from

corrosion in certain environments.

2 The realisation that attainment of this feature depends on the control of certain composition, metallurgical and physical features and the identification of these.

3 The realisation that this superior corrosion resistance is of practical value and the exploitation of it.

4 The extension of usefulness by improving mechanical properties and ability for fabrication.

The stainless steel story starts with the discovery of a new mineral in Siberia by Lehman (1766) and the identification of a metal, chromium, by Vauquelin. This was extracted as an iron-chromium-carbon alloy (ferrochromium). Bunsen[1], Delville[2], Fremy[3] and Wohler[4] all noted the good corrosion resistance of chromium or ferrochromium and there were in the 19th century a number of investigators who made steels containing chromium. Stodart and Faraday[5,6] were first and were followed by Berther[7] who not only made chromium steels but suggested their use as a cutlery. Mushet patented the production of chromium steels in this country and Baur[8] in his 'Chrome Steel Works' in Brooklyn made steel with 0.6% chromium for the Mississippi bridge at St Louis. John Brown made similar steel in his Sheffield works in 1871 while Brustlein[9] initiated the use of steels with a few percent of chromium in France. The objectives, however, had been the development of mechanical properties and similar steels with up to approximately 3% chromium are still used widely. In 1872, however, Woods and Clark [10] applied for a patent in Britain for a steel with 30 - 35% chromium and 1.5 - 2.0% tungsten for which acid and weather resistance were claimed but it appears that neither was a full patent granted, nor was there any further activity, but as the intention of improved corrosion resistance was declared perhaps they should be acknowledged as the inventors of stainless steel. With this exception the researchers up to this time had done no more than touch upon any of the aspects listed above. This may be due to the fact that carbon in substantial quantity works against the 'stainlessness' of iron-chromium alloys forming chromium carbides in which form chromium is ineffective. Only high carbon ferrochromium was available and thus an increase of chromium content of the steel was accompanied by a concurrent increase in carbon content. Even had the earlier researchers realised this effect, there was little they could have done about it. The removal of carbon from a high chromium melt without associated loss of chromium remained a steelmaking problem for many years being fully solved only after the period covered by this review.

This feature played a part in affecting the extensive and careful work of Hadfield [11] published in 1892. He made a range of steels with chromium contents up to 16.74% but the ferro-chromium used had a chromium/carbon ratio as low as approximately 10 and the higher chromium steels had a correspondingly higher level of damaging carbon. Along with thorough study of metallography, mechanical and physical properties he did give some attention to corrosion resistance but again was unfortunate, this time in choice of test reagent. Passivity is not possible in the 50% sulphuric acid which he used so that his high chromium steels actually corroded faster than the low chromium ones and wrong conclusions were drawn.

The means of avoiding the high carbon difficulty became available when Goldschmidt[12] developed a method of making low carbon ferrochromium by reacting the oxides with aluminium and it could well be that this was the greatest single step in the history of stainless steel development. Guillet[13-17] was the first to take advantage of the feasibility of making chromium steels with controlled carbon contents. He made a large series of alloys and among them were combinations which either conform with or almost conform with currently used stainless steel specifications; 410S21 and 420S45 of BS970, 446 and 440C of the AISI range. He was not looking for corrosion resistance, however, and while he studied the metallography and mechanical properties in great detail he did no corrosion testing. Not until 1914 did he pay any attention to this aspect. Similarly Portevin[18] in 1909 studied a range of compositions some of which would be acceptable as standard grades used today, but he neither sought nor stumbled upon corrosion resistance. It was exactly similar with Geisen [19] in Britain in the same year, whose steels with approximately 0.3% carbon contained 8 - 18% chromium. It was Monartz who identified the vital contribution of chromium in producing resistance to corrosion. With Borchers[20] he had applied for a patent for a high chromium composition in 1910, this being issued in 1913 but in 1911 he published a study of iron chromium alloys indicating passivity to be the reason for their remarkable corrosion resistance and among other remarkable discoveries, pointing out the necessity for high chromium and low carbon contents.

Amazingly these findings appear to have excited no commercial interest at all. For the commercial birth of stainless steel we must turn to H Brearley.

Brearley had worked for Thos Firth & Sons in Sheffield since 1883, some years being spent at their factory in Riga. In 1913 he was head of the Brown-Firth Research Laboratories, this being a collaborative organisation owned jointly by the then otherwise unrelated firms of Firths and John Brown & Co. Firths were involved, among other things, with ordnance and Brearley was concerned with solving a fouling and erosion problem of gun barrels and considered that high chromium steels might provide a solution. He made a series of steels with chromium contents between 6 and 16% using the crucible process but was not satisfied with the resulting mechanical properties and moved to electric melting. His second electric cast contained 12.8% chromium and 0.24% carbon and he found this could be cogged, rolled and machined. He noticed that the steel was difficult to etch in his metallographic studies and that its etching response varied with treatment, also that the steel did not stain in the laboratory atmosphere. Because of this resistance to corrosion he suggested that the steel might be useful for some engineering applications and also for making cutlery. His suggestion apparently excited no great enthusiasm but some steel was processed by two cutlers who discarded it finding it difficult to forge, harden and grind. In mid-1914 there was another attempt this time at Mosley's in Sheffield. Here Brearley met with the difficulties of the kind not unknown to would-be inventors; that advice on production is not welcomed by craftsmen, even when new materials are involved. At first there were forging difficulties, almost certainly because the temperature used was that traditionally utilised for carbon steel while high chromium steels require higher values. A further attempt gave brittle blades this time probably due to overheating! Fortunately there was perseverance and yet another attempt yielded good blades which were corrosion resistant. It is pointless to speculate what course of events would have followed but for the first world war but apparently all the high chromium steel produced during hostilities was used to make aero engine valves, no doubt because of its good heat resistance.

Actually Brearley [22] refers to the existence of a steel FAS in 1914. As this designation continued to be used for many years after the war for a 0.4% carbon, 13% chromium steel and was then an abbreviation for Firths Aeroplane Steel, it might be inferred that the steel was actually used for this purpose in 1914 and this is certainly at variance with the usually accepted sequence of events. Brearley disagreed with Firths about the promotion of the chromium steel and also about the rights to the invention and he joined Brown Bayley's as Works Manager. Later it was agreed that he and Firths' had equal rights and the Firth-Brearley syndicate arose.

No attempt at patenting in England appears to have been made, but in 1915, a Mr John Maddocks suggested that a patent be sought in the USA and with his help patents were obtained first in Canada[23] and then in the USA[24]. While, and even before these actions proceeded, Haynes was working on chromium steels in the USA[25] and actually attempted to patent a stainless steel in 1912. Both his and Brearley's original USA attempts were rejected and both submitted revisions in 1916, this time Brearley's being accepted and Haynes's not. Haynes did not give up however, and rather than undergo the delay and expense of litigation the interests of the two men were merged, the rights being turned over to the American Stainless Steel Company which was made up of the patentees and prominent USA alloy steel manufacturers. There seems to have been justice in this, in that both men had quite independently come to similar conclusions satisfying one to three of the four aspects listed earlier and thus, unlike most predecessors, qualify as the inventors. Perhaps Brearley was successful in his application in that he dwelt on the manufacture of stainless articles and pointed out the need for suitable heat treatment and finishing, albeit with little detail. One must feel regret for Monartz however, who undoubtedly anticipated them but now seems largely forgotten as his ideas were not developed. In 1918, the American Stainless Steel Company did not have the Ludlum Steel Company among its licensees and litigation occurred when the latter began to market a low carbon, chromium steel with silicon. Proceedings were drawn out and at first ruling went against the American Stainless Steel Company but judgment was eventually in their favour on appeal. Strangely the steel which caused the controversy is not in the AISI range but is in BS970 as a valve steel (401S45).

However sluggish the response of industry might have been to the initiation stage of stainless steel there was certainly no lack of enthusiasm in the post war years with aspects three and four being pursued with energy. Only twelve years after Brearley's first melt a comprehensive text book was published[26], the author being J H G Monypenny of Brown-Bayley's. This may even have been anticipated by a publication of Firths'[27] but priority is not clear as the latter was not dated, this being a failing which was to prove common. The Firth book was a manual of manipulation and a collection of data rather than a scientific publication but demonstrates the large amount of development which had taken place not least in the collection of corrosion data. The quality of the publication may be judged from the section dealing with alcohol in which the reader is assured that '. . . the wines and spirits used in the experiments were all of excellent quality . . . .'! Surviving data files from Firths actually contain considerably more corrosion information than given. Only 13% chromium steels with 0.2 and 0.3% carbon were dealt with in detail but there was mention of a new development, 'stainless irons'. The Monypenny book, which in its updated form was the basic reference work for many years, was a more scientific work but also included information on manipulation, corrosion resistance and applications.

Two developments of this period which gained considerable popularity and are still much used today appear to have been initiated at Brown-Bayleys. The 'stainless iron' is a 13% chromium steel but with lower carbon content (actually something less than 0.1%) to which feature it owed its name. While still hardenable to a certain degree there was a large amount of non-transformable ferrite so the steel could be softened more effectively and was more amenable to conversion into sheet and to manipulation in this latter form. The first commercial melt of this steel in Britain was made in 1920[26]. Firths followed this example (as did others) and produced a further data book dealing with it[28]. The other development in 1925 was given the name Twoscore[29]. The chromium content of the 0.2% carbon steel was increased to 17 to 20% in the interests of improved resistance to corrosion and the consequent adverse effect on hardening response (due to delta ferrite) corrected by addition of approximately 2% nickel, although some ferrite remained. The improved corrosion resistance made this the preferred grade for some applications and it was adopted in British Standards as S80 and En57. The steel was taken up by other steelmakers (for a time Firths used the trade name 'Saitie', an obvious derivative of S80.) Unlike many early developments both these steels have stood the test of time and are still widely used under 403S21 or 403 and S80, 431S29 or 431.

The early part of the decade saw much application development activity (aspect three) of an anonymous nature mainly being recorded in the brochures of steel manufacturers, the Firth's books being the forerunners of many. Perhaps a special note on the activities of W H Hatfield is justified. Hatfield was Brearley's successor as head of the Brown-Firth Research Laboratories and no doubt his efforts in stimulating the production and marketing of stainless steels were duplicated by others in other organisations but his activities were notable in the inter-war years and some of his popularisation efforts have been recorded in papers which he presented to the learned societies of a range of industries. A few examples are given in refs 30 to 33. The first of these is his first recorded effort (1919) to fight the myth that stainless steel blades are inferior in hardness and cutting ability. This had come about because of the refusal of some cutlers to accept that the new material required different treatment from the traditional ones and was typical of the difficulties which Hatfield and his contemporaries had in getting new materials used correctly by industries still dominated by the 'craftsman' approach.

Despite suitability for use in many environments, corrosion resistance of the 13% chromium types is limited as is the ability to undergo intricate cold forming. The data available from the mid-1920s indicate that applications were mainly of the light engineering type with the exception of steam turbine blading which was a very early use[25]. There was very little use as tanks for storage etc. While great attempts had been made to penetrate the domestic market, with the exception of cutlery, success was limited. It was with the advent of the austenitic steels that development in the domestic and other fields really 'took off'.

The austenitic steels (eg the '18/8' types) are not hardenable by heat treatment, the alloying element content being such as to depress the austenite to martensite change points to below normal ambient temperature. Nickel is the additional element used mostly for this purpose. The austenitic (fcc) structure is well suited for sheet manufacture and the mechanical properties (low limit of proportionality and high rate of work hardening) render it suitable for cold forming by a variety of methods. Moreover the lack of thermal hardening means that it is much more readily weldable with no need for post-welding heat treatment to soften welds.

As was the case with the chromium steels, the practical use of austenitic stainless steel had been anticipated metallurgically, without the corrosion resistance being identified, by Guillet[34] and by Geisen[19]. Maurer and Strauss working at Krupps' patented chromium-nickel steels in Germany[35] and Britain[36] in 1912 – 1913, although the composition ranges were very wide (not least in allowing carbon up to 1%) and certainly not all compositions possible could be described as stainless steels. Krupps went ahead with a grade they termed V2A which contained about 0.2% carbon, 20% chromium and 7% nickel. The British rights to the Krupp patent were purchased by the Firth-Brearley syndicate and both Firths and Brown-Bayleys developed their own versions of austenitic steel but not for a decade or more after the early patents and the 'discovery' of stainless steel. Firth's first commercial attempt was not a true stainless steel at all, although it was marketed because of its corrosion resistance. The patented range[39] was for up to 1.5% carbon with 2 to 5% chromium and 18 - 24% nickel the prime interest being in the low corrosion rate (as opposed to passivity) in acids. Perhaps it is significant that the patent application pre-dates that at which the Krupp rights were negotiated ('about the end of 1923'[29]). Hatfield commented on this steel during the discussion of one of his lectures in September 1923[40] giving the tradename of 'windwater' adopted because of good behaviour at the wind and waterline under marine conditions, the later being abbreviated to 'WW'. The steel has some interesting features but was short-lived commercially, quickly falling from the scene when attention was turned to steels with higher chromium contents. Again with these attention was primarily on corrosion with the production and fabrication aspects being identified later. Very soon the famous 18/8 (18% chromium and 8% nickel originally with about 0.2% carbon) was chosen and this must have been very soon after the Krupp agreement as already substantial data were being presented early in 1925[33] and there are numerous experimental results on file dated before this. Hatfield has given the development date as 1922[46]. Firths chose the trade name of 'Staybrite' for the austenitic steel and produced a further databook[41]. Concurrently, Brown-Bayleys chose a composition with 15 to 16% chromium and 10 to 11% nickel giving the trade name of 'Anka'. With time, production of the austenitic and martensitic steels was taken up by other suppliers under various trade names with numbers or secondary names to identify types. Examples are 'Immaculate' (Vickers – English Steel Company), 'Era' (Hadfields), 'Macilvry' (Edgar Allen), 'K E' (Kayser-Ellison), the 'R' series of Jessops and 'Silver Fox' (Samuel Fox). It is difficult now to date the involvement of these various Companies and apologies are tendered should important developments have been overlooked. Developments were paralleled elsewhere of course, Allegheny Steel Company and Republic Steel Company being early in the austenitic field in the USA[29]. Indeed Hatfield was moved to say in 1929[42] following a visit to the USA '. . . he found that 18/8 steel was being produced on a very extensive scale and was regarded as an indigenous product. It is only fair to state that the 18/8 composition originated in this Country in the author's own Laboratories, it is a British Development which spread to other Countries . . .'.

Two other austenitic steel developments are worthy of comment. Krupps introduced a 25% chromium, 20% nickel grade for heat resistance[43]. This has been widely used since, now as AISI type 310 and BS 970, 310S24. Firths, while obviously very pleased with their 18/8, patented another austenitic in 1927[44] this containing 11.5 - 13% chromium and 11.5 - 13% nickel with carbon less than 0.2%. The objective was to obtain a low hardness as annealed and a low work hardening rate with deep drawing fabrication in view, hence the trade name of Staybrite DDQ (deep drawing quality). While this has not been as widely taken up as the 18/8 and is not included in standards, it was widely used pre-war and continues to be produced both here and on the continent. An interesting early use was by the Swiss watch industry. When Firths started selling in Switzerland about 1930 this grade was chosen for watch cases being of low magnetic permeability with the low work hardening rate aiding fabrication. It remains the most used steel for watch cases.

A milestone in the stainless steel history was the erection of the first austenitic steel plant in the world at the ICI Works at Billingham in 1929, Figs 1 and 2. When the plant had already had some years of service, Hatfield acknowledged the enterprise of the chemical engineers in encouraging such a large undertaking. The nitric acid plant, largely of rivetted construction, was in Staybrite and was in service until after 1950. Chemical plant has continued to be a major application for stainless steels with the austenitic types predominating, besides giving rise to the desired 'fabricability' the nickel also reduces the corrosion rate in many acids when passivity is not operative. The weldability is also a major asset, Fig.3, especially after further developments outlined below. Availability of tubing was also a factor. While the original development was in plate and this continued to be the major form used for storage tanks, reaction vessels etc, the production of ever larger forgings and castings (for pump and valve bodies, pressure vessels etc) was pioneered for this industry, Fig 4.

Another milestone, this time not such a large one, was due to Hatfield. Always looking for ways to promote his favourite alloy he had his 1926 'bull nosed' Morris fitted with Staybrite radiator, bonnet, lamps, windscreen, hub caps, wheel nuts, discs and running board edging. It was inspected by the staff of the 'Auto-car' who wrote under a sub-heading of 'Stainless Steel as a labour saving agent for the Owner-Driver' of the pleasing results[45]. Hatfield developed on the theme of the motor car in the same journal in 1930[46] in an article which was brief but is nevertheless informative as regards stainless steel production and marketing at that time. The article arose because of the news[47] that Ford cars were to have 'rustless iron fittings' to be made from 'Allegheny Metal'. Hatfield showed patriotism (some might say chauvinism) by pointing out that the 18/8 composition which was involved was a British development and that he had made Allegheny personnel aware of its nature when they visited Firths in 1926 and when he had visited the Allegheny plant in 1928 at which time he had also visited Mr Ford in Detroit. To those who have been involved in trying to promote the use of stainless steel in cars the statement that 'Sir William Morris was much interested in the possibilities but . . . had not felt justified in increasing the price of his cars . . .' has a familiar ring. The writer commented that 'Mr Ford's enormous market gave him great opportunities since his requirements for tonnage in any material which he adopts are so great. In this Country, unfortunately, the opportunities for such large and centralised tonnages have been non-existent and the growth of the applications of this valuable steel to purposes other than chemical plant has only been gradual'. His words imply the 'chicken and egg' situation which applies with so many developments. A would use the new material if it was available in bulk at reasonable price while B would develop bulk supply with attendant economies if sales to justify this were assured. In his article, Hatfield noted indications of increased demand

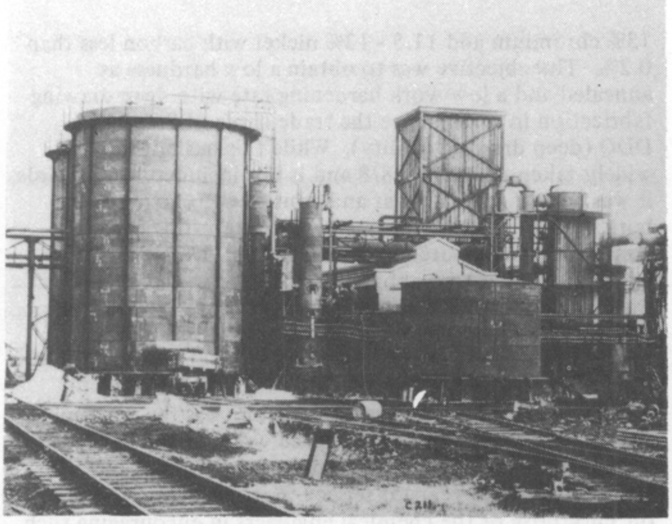


Fig 1 Nitric Acid Tanks at ICI Limited, Billingham '18/8' steel, 1929.

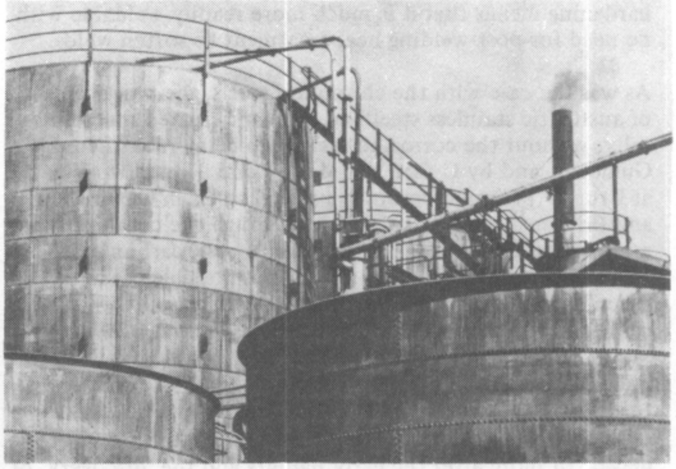


Fig 2 Detail from Fig 1 showing welded construction.

Fig 3 Early storage tank of welded construction (18/8 steel). c 1931.

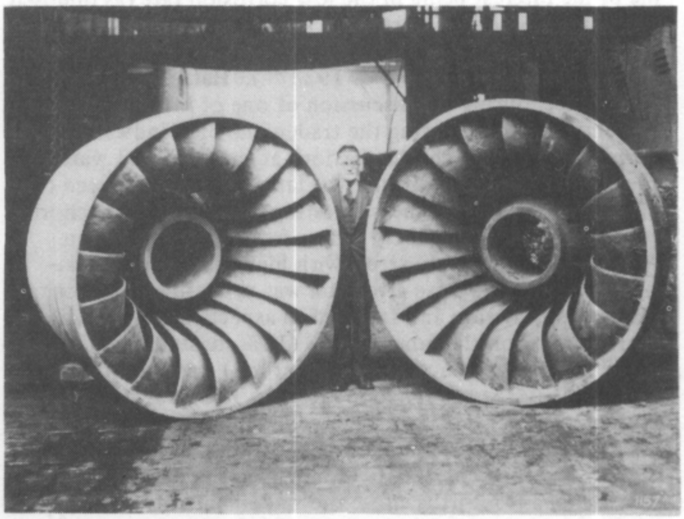


Fig 4 Hydro-electric turbine castings (13% Cr steel). 1933.

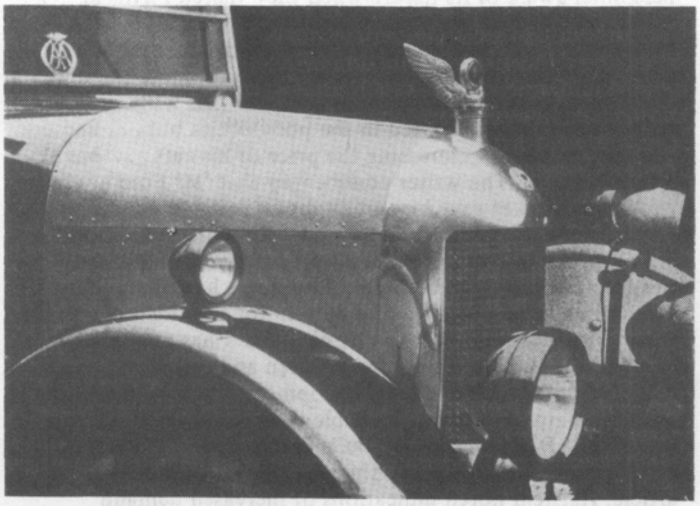


Fig 5 The first stainless steel motor car fittings (18/8 steel) (1926).

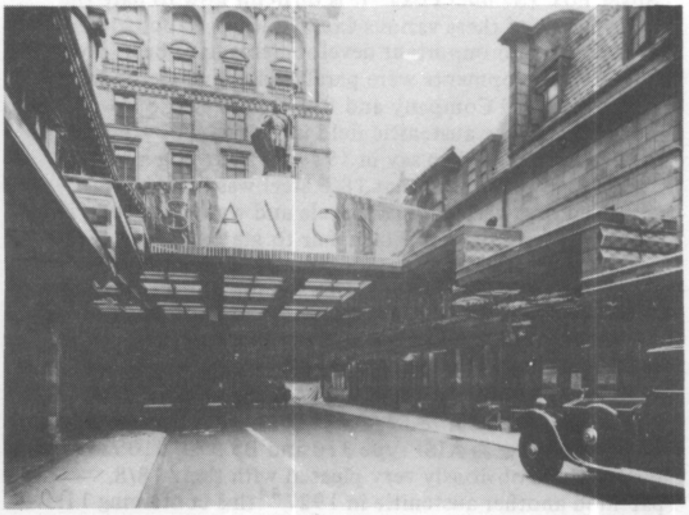


Fig 6 Entrance to the Savoy, '18/8' steel, 1930.

'. . . which justifies extended manufacturing equipment in connection with those large scale applications which have so important an effect on the cost of production'. Fig 7.

The first major set-back to the austenitic steels was the emergence of possible susceptibility to intercrystalline corrosion arising from certain details of thermal history and the high carbon content (by present day standards); where the thermal effect arose from welding heat, failure was known as weld decay. The manufacturers, users and academic organisations all rose quickly to this challenge. Most of the early studies of the phenomenon were not published but relatively early papers of note are in refs 48 - 50. One solution was to reduce the carbon content [48] which was no easy feat at that time but controlled carbon proprietary grades emerged and then standards (BS En 58E and AISI 304). Introduction of cold work to modify carbide distribution and special heat treatment to reduce dissolved carbon content were also proposed but were inconvenient. The solution most widely adopted for applications where there was a risk was to utilise steels with strong carbide formers added. Tungsten was first used by Firths[51]. Krupps favoured titanium and vanadium[52] while later Firths advocated titanium either alone or with tungsten[53]. In the USA niobium (then columbium) was preferred. In time additions of either titanium or niobium were adopted generally giving rise to another set of proprietary alloys. Firths used descriptive titles of FDP (Firths Disintegration Proof) for the titanium grade and FCB (Firths Columbium Bearing) for the niobium; the appropriate national specifications were En 58B or 321 and En 58G or 347 for BS and AISI standards respectively. The compounds introduced by these additions interfere with polishability so the unstabilised grades were used for domestic and food applications, the stabilised for heavy industry. The solution of this problem paved the way for bigger and more ambitious developments involving welding.

The only other major steel development pre-war was the introduction of molybdenum into the austenitic steel. The advantage in respect of corrosion resistance had been known at least to some since the early development period and there are data for chromium-nickel-molybdenum steels dated as early as 1923 in the Firths files. Grades of 18/8 with either 1½ or 2½% molybdenum (En 58H or En 58J) became increasingly popular for use in contact with aggressive environments; only the higher molybdenum level was favoured in the USA as type 316.

These then were the grades which satisfied the majority of applications up to the late 1930s, that is 13% chromium steel with 0.1% carbon or less, about 0.2% carbon or about

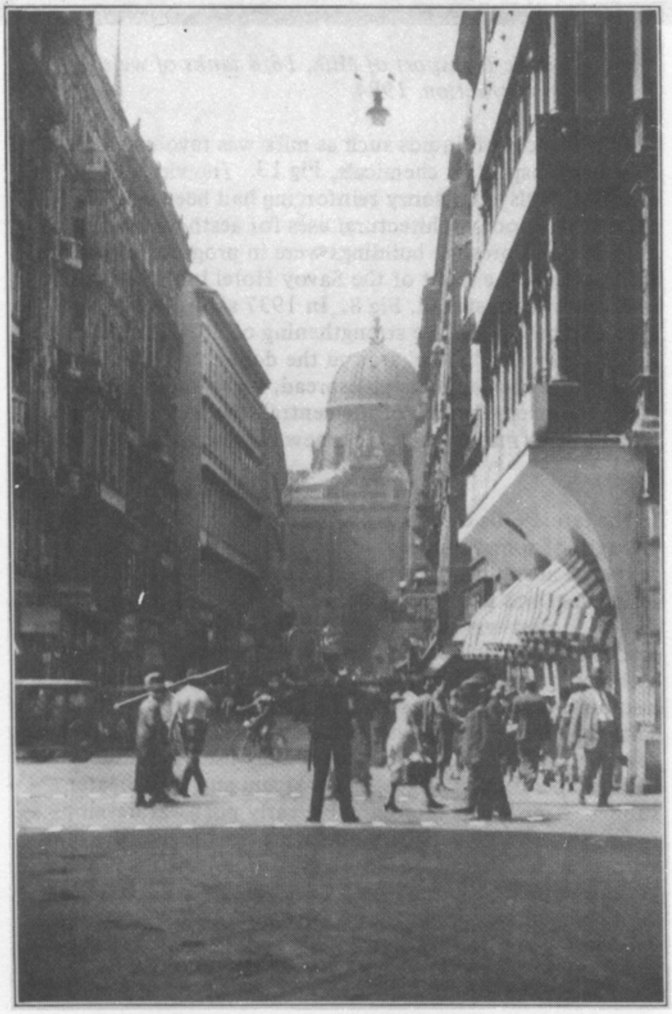


Fig 7 Forged 18/8 steel road studs in Vienna (1931).

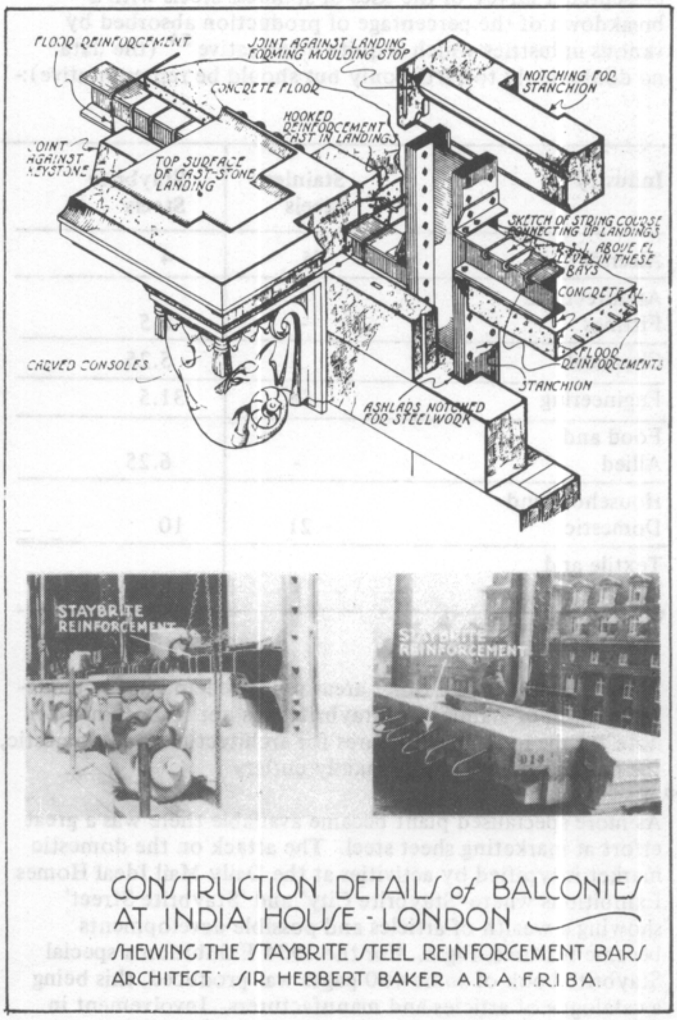


Fig 8 Extract from publicity showing the functional use of stainless steel in architecture. c 1930.

0.3% carbon, S80 (En57), the high carbon 18/8, the lower carbon 18/8, the stabilised 18/8s and the molybdenum bearing 18/8s. There were also numerous 'specials' some of which had their days and some of which have survived or developed but to detail these is beyond the scope of this paper. The ferritic grades (that is the stainless iron type but with higher chromium contents) were not popular at that time in Britain although there was a British Standard (En 60) but were more popular in the USA (430 or 446). They have certain limitations and are mainly used in small section form. Interest has increased each time there has been a nickel shortage largely to disappear afterwards but post-war a good market was developed for motor car trims. Improvements in melting techniques have increased the potential of ferritic steels but that is a later story.

In the early 1930s the production extensions predicted by Hatfield as essential for the promotion of stainless steels proceeded. In 1930 Thos Firth and Sons amalgamated with the steelmaking interests of John Brown and Company with consequent extension of production capability. Shortly afterwards induction melting was introduced. In 1934, stainless steel production of Firth Brown and the English Steel Corporation was concentrated in a new specialised Company, Firth-Vickers Stainless Steels with consequent expansion of plant availability and the introduction of new equipment. At this time (over the year 1934) Hatfield had presented a survey of the uses of stainless steels with a breakdown of the percentage of production absorbed by various industries which is quite informative [54] (the data no doubt apply to Firths only but should be representative):-

Industry	Stainless Steels	Staybrite Steels
Aircraft	15	4
Architectural Fittings	-	6.5
Chemical	1	5.25
Engineering	58	31.5
Food and Allied	-	6.25
Household and Domestic	21	10
Textile and Dyeing	-	3.5

There were obviously other areas not listed and unfortunately the ratio of stainless to Staybrite was not recorded. Of note are the quite small figures for architectural and domestic, the latter obviously being mainly cutlery.

As more specialised plant became available there was a great effort at marketing sheet steel. The attack on the domestic market is typified by activities at the Daily Mail Ideal Homes Exhibitions where 'Staybrite City' and 'Staybrite Street' showing a wealth of articles and possible developments became features, Fig 8. For the 1934 Exhibition a special Staybrite book of some 460 pages was produced, this being a catalogue of articles and manufacturers. Involvement in any prestige development was welcomed and publicised Figs 9 to 12 inclusive, (the Schneider Trophy seaplanes, the RMS Queen Mary, the Silver Jubilee Express etc) while there was popular advertising, for example as cartoons in 'Punch' Fig 14, and as posters in London and the Provinces.

If a personal view of the early domestic developments could be interjected, it is that there was too much emphasis on imitating traditional silverware with bright polishes; small scratches readily removed in the regular cleaning necessary for silver are difficult to remove from stainless steel. Although there were exceptions, not for many years were the virtues of simple lines and 'satin' finishes fully appreciated.

Fig 13 Bulk Transport of Milk, 18/8 tanks of welded construction. 1934.

Bulk transport of liquids such as milk was revolutionised as was the transport of chemicals, Fig 13. The virtues of stainless steels as masonry reinforcing had been quickly realised and soon architectural uses for aesthetic purposes on shops and prestige buildings were in progress; one of the earliest such, the front of the Savoy Hotel looks much today as it did when installed, Fig 8. In 1937 stainless steel was used extensively on the strengthening of St Pauls Cathedral and notably as a 'girdle' around the dome. Such activity has since no doubt been widespread, a post-war example being the strengthening of the central tower of York Minster with massive bolts in a new high strength stainless steel.

In the late 1930s came a growing awareness of the useful strength of some stainless steels at elevated temperatures. A special austenitic steel (actually developed for corrosion resistance) was used for vital parts in Whittle's jet engine in 1940. In post-war years there was development of special grades of martensitic steels used widely in gas and steam turbines [55] while special austenitic steels were prominent also for a time [56]. The standard austenitic steels with suitably controlled analyses were comprehensively tested for creep resistance [57] and were widely used for their high temperature strength, eg for steam and superheater tubing. Among the more notable early post-war developments were martensitic steels which combine high strength with good toughness, improved corrosion resistance and good weldability [58] (eg Armco 17/4 PH and FV 520 (B)) variants of these [59] being especially suitable for sheet production and fabrication finding applications in aerospace (eg Armco 17/7 PH and FV 520 (S)).

Although used as machined components, castings and forgings, it was in flat product form that the great increase in tonnage came notably with production continuously as wide strip instead of individual sheets which was pioneered in the USA and spread to Europe in post-war years.

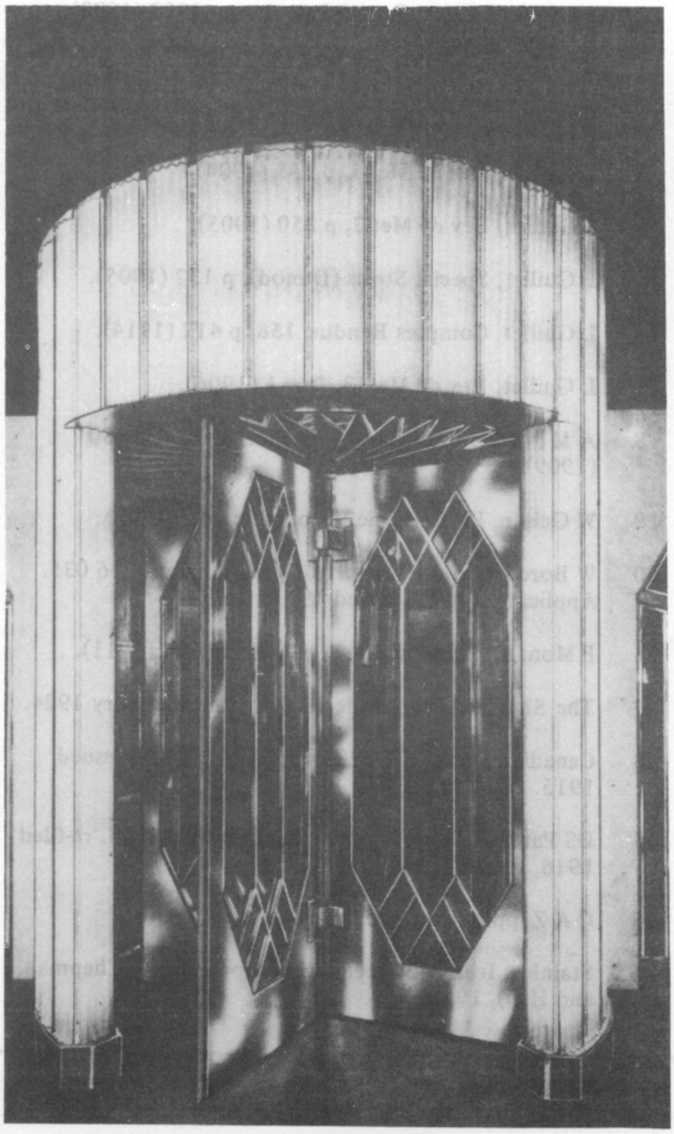
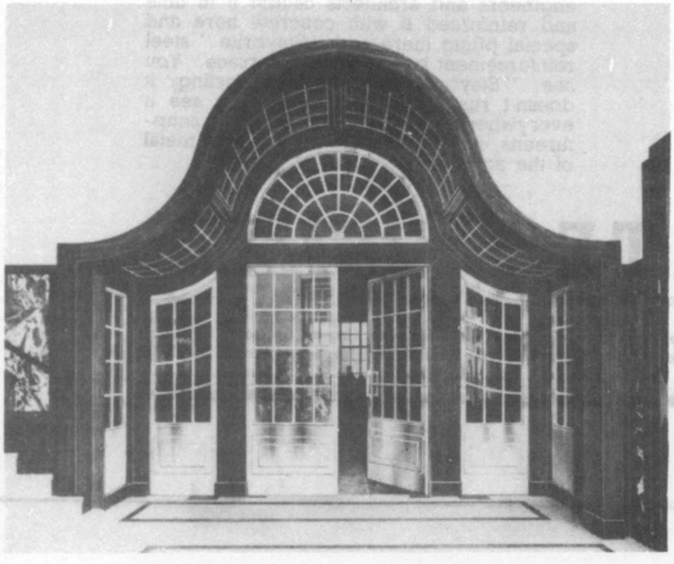


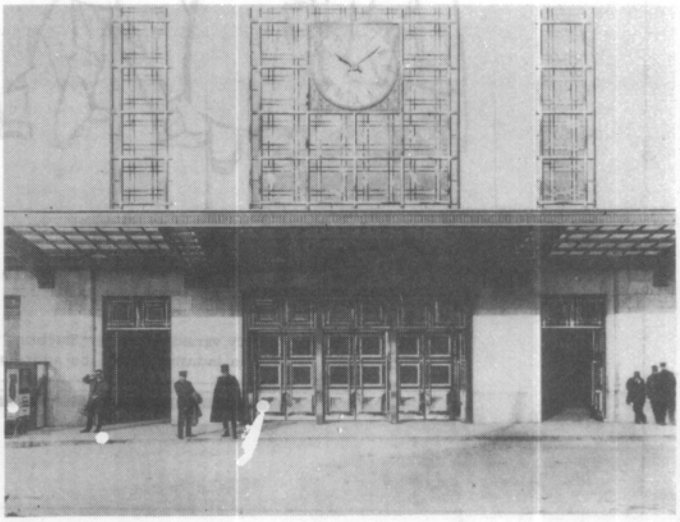
Fig 9 Entrance to Strand Palace Hotel (18/8 steel). c 1930.

Fig 10 Doors of Palace de Justice, Lausanne (18/8 steel). c 1930.

Fig 11 Entrance to Lyon's Corner House, Oxford Street (18/8 steel) c 1930.

Fig 12 Main Entrance to Railway Station, Geneva (18/8 steel). C1930.





Stainless steel had developed from a metallurgical curiosity to the metal for the man in the street and no matter how clever and interesting and technically brilliant the special steels and the larger items of heavy plant produced, it is the kitchen sink and its equivalents that consume the large tonnages.

Acknowledgements

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St. Paul's nearly collapsed ! And then clever engineers and architects caught it in time and reinforced it with concrete here and special piling there and "Staybrite" steel reinforcement bars all over the place. You see, "Staybrite" steel is everlasting, it doesn't rust away, that's why you see it everywhere to-day—shop-fronts, soup-tureens, cocktail-shakers—the wonder metal of the age . . .

"STAYBRITE" STAINLESS STEEL

REGD. TRADE MARK

★ All the best stores carry varied stocks of "Staybrite" Steel domestic equipment. Inquiries regarding the uses of "Staybrite" Super Stainless Steel in industry should be addressed to Firth-Vickers Stainless Steels, Ltd., Staybrite Works, Sheffield.

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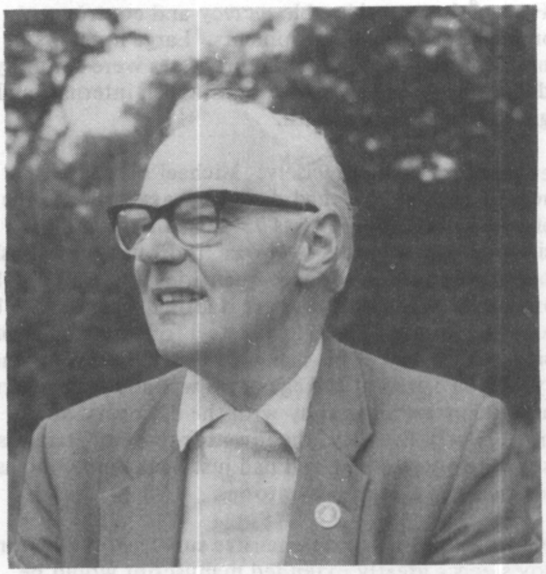
J Truman joined the staff of the Brown-Firth Research Laboratories in 1943 working as assistant in the corrosion laboratory and at the same time studying metallurgy at the University of Sheffield. While having spells with other subjects he spent most of the next thirty years working on various aspects of stainless steels including production in different forms and also research and development, during which he was leader of the corrosion and stainless steel research sections. On re-structuring the industry, direct involvement with most products except forgings has been lost, but a watching interest in all forms is retained.



A history of **alloy steels** with particular reference to Sheffield contributions

Samuel Keown

Synopsis

The discovery and development of alloy steels in the 19th and early 20th Century was strongly influenced by Sheffield industry and Sheffield metallurgists. Michael Faraday and James Stodart carried out the first experiments on alloy steels in 1818 concentrating on noble metal additions but their commercial trials at Sandersons in Sheffield were not successful. Robert Mushet discovered and developed the first alloy steel, an air-hardening high tungsten tool steel, in 1868 and this was exclusively manufactured by Samuel Osborn & Company from around 1871. A hundred years ago Sir Robert Hadfield discovered his famous austenitic manganese steel and silicon steels in addition to carrying out systematic investigations of many other alloy steel systems. Sheffield steelworks benefitted greatly from all these developments and from the requirements of new engineering industries and armaments. In 1912 Harry Brearley discovered stainless steel at Thomas Firth & Sons which further established Sheffield as the centre of the special steels industry.

Introduction

One hundred years ago, at the inauguration of the Metallurgy Department, Sheffield was at the centre of exciting and often quite secretive developments of new alloy steels. Gatty[1] claimed Sheffield to be 'the capital of steel with respect to the whole world' and according to Osborn[2] 'the Steel Age was in full swing'.

In 1884 the traditional constructional materials of cast and wrought iron were being replaced by the newly-developed Bessemer and Open Hearth Steels[3]. For specialised applications such as cutting tools and armaments, cementation or blister steel was being superseded by Huntsman's crucible steel. Low alloy steels were appearing in England, America and France[4] but considerable secrecy and controversy surrounded most new developments. Large numbers of patents were filed and industrial processes were carefully guarded as the inventors strove to establish international recognition and create wealth.

To set the scene more precisely: Michael Faraday, the 'pioneer of alloy steels'[5] had died 17 years earlier at the age of 75. Robert Mushet was 73 years of age and his 'special' high tungsten tool steel was 'thoroughly established'[6] and being produced in tonnage quantities by Samuel Osborn & Company in Sheffield. Robert Hadfield was only 26 but he had just 'invented'[7] his silicon steel following on from the important discovery of his manganese steel two years earlier. Henry Clifton Sorby at the age of 58 was about to resurrect his interests in metallography with the discovery of pearlite[8]. Harry Brearley, the inventor-to-be of stainless steels was 13 years of age and had just been employed as a bottle-washer in Firth's laboratories.

In order to provide a comprehensive survey of the history of alloy steels a greatly extended manuscript would be required to adequately survey the voluminous literature available. It seems appropriate, therefore, in this limited survey to celebrate the Centenary of Sheffield University's Metallurgy Department, to concentrate on the contribution of Sheffield's metallurgists and industry to the history of those special steels for which Sheffield has gained an international reputation. It is additionally and conveniently appropriate that the inauguration of the Department of Metallurgy in 1884 coincides with the beginning of the era of alloy steels.

The importance of Sheffield's contribution to the evolution of alloy steels has depended as much on foresight, industrial experience, commercial awareness, persistence and patience as it has to fleeting innovative ideas. Invariably, the metallurgists who were the innovators were also the industrialists who pushed through the ideas to commercial success.

Alloy Steels

Barraclough, in his history of Sheffield Steel to 1900[9], conveniently defines steel as lying somewhere between wrought iron and cast iron with respect to carbon content. In 1884 carbon contents of commercial steels ranged from 0.3 to 1.5%.

The following definition of 'alloy steel' or 'special steel' was given by Hadfield[10] in his definitive textbook on Metallurgy in 1925:-

'Steels which owe their properties to the presence of elements other than carbon, even though the carbon still plays a vitally important part in determining the characteristics of the alloy. This definition does not include as alloy steels those to which a small percentage of manganese, silicon, aluminium, titanium or other element is added in order to eliminate objectionable constituents or mechanical defects, such as blow-holes, from carbon steels.'

Alloys steels were developed during the 19th century to meet the growing demands of the engineering industries. At the beginning of the 19th century the available materials of cast iron, wrought iron and high carbon steel met all the requirements of the time[5] and there was no incentive to develop improved properties. It was mainly scientific curiosity that drove Michael Faraday and James Stodart to investigate the first alloy steels during the period 1818 to 1824 but these experiments on fairly exotic alloys did not lead to any immediate practical applications. Robert Mushet's discovery of the first commercially successful alloy steel in 1868 was motivated by industrial requirements for better tool steels and most subsequent developments were industrially orientated. Academic metallurgists of the period appeared to be more preoccupied with the 'β-iron controversy'[11] and the role of carbon rather than alloy developments.

The rapid growth of alloy steels is shown in Figure 1 [12]. Apart from a short-lived decrease due to the post-war depression, the startling growth rate was inspired by the new industries such as the automobile industry.

1818 — The Birth of Alloy Steels — Faraday and Stodart

At the end of the 18th century, Dr George Pearson, a Rotherham-born medical practitioner and scientist, was

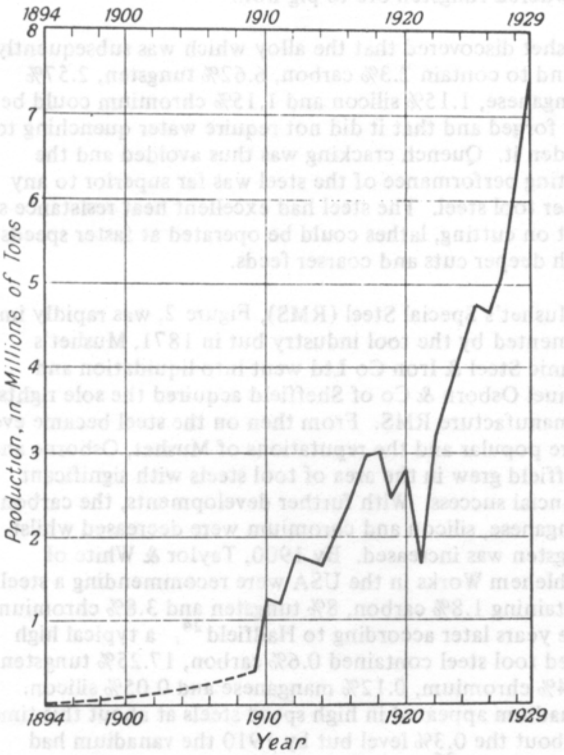


Figure 1 World Production of Alloy Steel To the year 1929[12]*. Note the post-war depression.*

asked by the Royal Society to investigate samples of the famous Indian Wootz steel. The results of this investigation published in 1795 [14] referred to James Stodart forging a penknife from Wootz steel and finding it to be superior to any other steel available at that time (Huntsman's crucible steel discovered in 1740 in Handsworth did not appear to be appreciated by Sheffield cutlers until much later). James Stodart was a practical metallurgist and businessman specialising in the manufacture of cutlery, razors and surgeon's instruments and, as a competent scientist, he had previously published papers on a variety of topics including Damascus steel.

In 1818 when Stodart was 58, he began a scientific collaboration with the much younger Michael Faraday (who went on to discover electromagnetic induction) on the chemical analysis of Wootz steel and on a much more ambitious investigation to study the effects of 16 different elements and 4 special compounds on 'steel alloys'. *

Metallic Elements:

13 in number, 7 being noble metals:-

1. Chromium
2. Copper
3. Gold
4. Iridium
5. Iron
6. Nickel
7. Osmium
8. Palladium
9. Platinum
10. Rhodium
11. Silver
12. Tin
13. Titanium

Non-Metallic Elements:

14. Carbon
15. Silicon
16. Sulphur

Other Ferrous Substances:

17. Wootz or Indian steel
18. Carburet of iron
19. Alumine alloy, so termed by Faraday in 1820, in imitation of wootz, also described as damascene steel. (Davy spoke of the added element as Aluminium).
20. Meteoric iron.

* (These lists are presented in the same way that Hadfield described the work[15].)

Thus Faraday and Stodart were attempting to improve the properties of iron and steel by alloying but since there was no engineering demand for better steels, their work was essentially aimed at simulating Wootz for the toolmakers and cutlers and for producing alloys suitable for mirrors. The alloy additions were mainly in the range - 2% and the base material was crucible cast steel.

Although two papers were published[16,17], much of the information on Faraday and Stodart's investigation is due to the subsequent work carried out by Hadfield[5] in 1930 – 1931 on samples from the Science Museum in London and from a previously undiscovered large wooden box containing 79 samples from the Royal Institution. It appears that the samples had lain undetected in the Royal Institution since Faraday's time until the reconstruction of the Institution building about one hundred years later [18].

Hadfield's analyses were able to show that the steels contained approximately 0.6 – 1.4% carbon, 0.2 – 0.3% silicon, $<$0.1% manganese, 0.02 – 0.5% sulphur and 0.03 – 0.13% phosphorus. As stated, most of the alloys analysed by Hadfield contained only small amounts of alloy addition but very large amounts of silver and platinum were used for some alloys. The noble metals were readily available from Faraday's associate Dr William Wollaston but the elements that we now associate with alloy steels, such as chromium and nickel, were then very difficult to obtain.

Faraday and Stodart considered that the steels containing silver, platinum, iridium with osmium, and palladium, represented the most 'valuable' series of alloys and they went on to make larger melts in collaboration with Sanderson's steelworks and Green Pickslay & Company in Sheffield. Faraday prepared the alloys as mixtures which were then taken by coach to Sheffield for melting, the journey taking 24 hours in 1822! In general, the commercial application and appreciation of Faraday and Stodart's work was disappointing. The rhodium steel was made into razors and the silver steel was used for cutlery, stove fronts and fenders. Unfortunately, little evidence remains of Sheffield developments of these steels and samples of the Sheffield experimental ingots have never been found. There is no evidence that Faraday ever visited Sheffield but Stodart was undoubtedly involved in close liaison with the Sheffield steelmakers and cutlers.

His experience of steels and their application brought a wealth of practical knowledge to the collaboration with Faraday [19] whereas Hadfield[5] tended to over-emphasise Faraday's contribution '. . . . Faraday, probably the greatest experimental investigator the world has ever known'.

However, Hadfield's conclusion on the importance of the work is probably quite accurate if Stodart is included in the tribute: 'The significance and value of Faraday's (and Stodart's) work on steel and alloys lay not in any immediate practical application of great importance but in the later developments in this field'.[20]

1868 – The First Commercial Alloy Steels – Mushet

Stodart and Faraday's work created much interest in other parts of the world and research of a similar kind was carried out in France and Russia but again without any significant commercial applications arising.

The next important work on alloy steels was that carried out by Robert Mushet in the Forest of Dean, following on the traditions of his father David Mushet (1772-1847) who made many contributions to the manufacture of iron and steel including the first manufacture of ferro-manganese. Robert Mushet was initially famous for his contribution to the Bessemer process, discovering that additions of the deoxidant spiegeleisen (ferro-manganese) were necessary for the process to be a commercial success. In subsequent patent and legal wrangles, Mushet failed to establish any monetary reward for his invention because his trustees failed to renew the patent fees and Mushet's process became public property!

Because of this experience, Mushet kept his alloy steel development tightly patented and great secrecy surrounded his processes in the Forest. Between 1856 and 1867 he took out 54 patents connected with steelmaking and alloy steels[21]. Mushet patented alloy additions of titanium (1859), tungsten (1859) and chromium (1861) and it might be inferred that he made a major contribution to alloying with manganese although the steels produced were not strictly manganese steels.

Hadfield, in his 1892 book on 'Alloys of Iron and Chromium'[4] accredits Mushet with the first suggested application of chromium to iron and steel manufacture although there is no evidence that Mushet produced chromium steels at this time. Julius Baur was the first person to manufacture chromium steels in association with the Chrome Steel Company of Brooklyn, New York, from about 1871[4]. The American work was followed by similar developments by M Brustlein of Holzier & Co of Unieux in France around 1878. All these steels were high carbon low chromium ($<2\%$) alloys, with applications mainly for projectiles or armour plating.

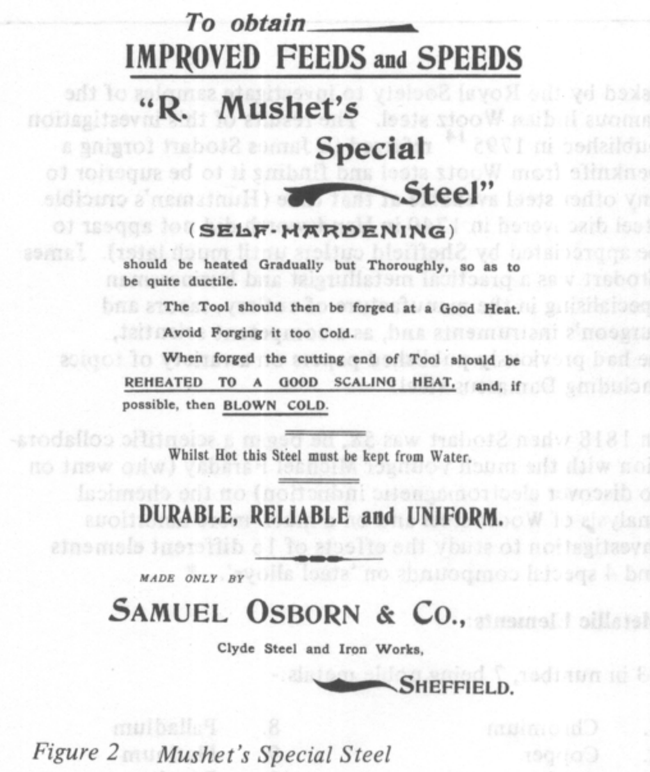
Although Mushet pioneered the manufacture of chromium steels he failed to achieve any degree of commercial success. The same was true of his titanium steels although it was adjudged by the British Association[22] that the steel exhibited an extraordinary amount of cohesive strength. Mushet was so convinced of the superiority of titanium steels that he called his business the Titanic Steel & Iron Company.

However, Mushet's disappointment with chromium and titanium alloy steels and his problems with his spiegeleisen discovery for pneumatic steel-making were soon dispelled when he discovered the first commercial alloy steel in 1868. This high tungsten steel was also the first air-hardening (self-hardening) alloy steel and the first high-speed tool steel.

As previously noted, Mushet had taken out a patent for tungsten additions to steel in 1859 but the discovery was not made until nine years later. Moreover, the process was important from 1868 until 1900 and the secrets of the process were only revealed on publication of Osborn's book in 1952[23]. The 'secret' was the addition of finely powdered tungsten ore to pig iron.

Mushet discovered that the alloy which was subsequently found to contain 2.3% carbon, 6.62% tungsten, 2.57% manganese, 1.15% silicon and 1.15% chromium could be hot forged and that it did not require water quenching to harden it. Quench cracking was thus avoided and the cutting performance of the steel was far superior to any other tool steel. The steel had excellent heat resistance so that on cutting, lathes could be operated at faster speeds with deeper cuts and coarser feeds.

R Mushet's Special Steel (RMS), Figure 2, was rapidly implemented by the tool industry but in 1871, Mushet's Titanic Steel & Iron Co Ltd went into liquidation and Samuel Osborn & Co of Sheffield acquired the sole rights to manufacture RMS. From then on the steel became even more popular and the reputations of Mushet, Osborne and Sheffield grew in the area of tool steels with significant financial success. With further developments, the carbon, manganese, silicon and chromium were decreased whilst tungsten was increased. By 1900, Taylor & White of Bethlehem Works in the USA were recommending a steel containing 1.8% carbon, 8% tungsten and 3.8% chromium. Five years later according to Hadfield[24], a typical high speed tool steel contained 0.6% carbon, 17.25% tungsten, 3.44% chromium, 0.12% manganese and 0.05% silicon. Vanadium appeared in high speed steels at about this time at about the 0.3% level but by 1910 the vanadium had reached 0.7%[25] so that the well-known and still used 18-4-1 tungsten-chromium-vanadium steel was close to being established almost 75 years ago.



To obtain

IMPROVED FEEDS and SPEEDS

"R. Mushet's Special Steel"

(SELF-HARDENING)

should be heated Gradually but Thoroughly, so as to be quite ductile.

The Tool should then be forged at a Good Heat.

Avoid Forging it too Cold.

When forged the cutting end of Tool should be REHEATED TO A GOOD SCALING HEAT, and, if possible, then BLOWN COLD.

Whilst Hot this Steel must be kept from Water.

DURABLE, RELIABLE and UNIFORM.

MADE ONLY BY

SAMUEL OSBORN & Co.,

Clyde Steel and Iron Works,

SHEFFIELD.

Figure 2 Mushet's Special Steel

Leaflet advertising R Mushet's Special Steels during the 1890s. Osborns had sole rights of manufacture of RMS after Mushet's Titanic Steel & Iron Company went into liquidation in 1871.

1882 — The Era of Special Steels — Hadfield

Both Robert Mushet and Robert Hadfield would probably like to have been immortalised as the 'Father of Alloy Steels'. Mushet, by extensive steel developments of an experimental nature based on vast experience of steel-making, might be called the 'Father of Commercial Alloy Steels'. Hadfield, however, by systematic and thorough scientific and metallurgical experimentation of thousands of alloys could claim to be the 'Father of Special Steels' for reasons to be expounded.

Robert Hadfield senior, started the Hadfield Company in 1869 for the manufacture of steel castings. In 1874 at the age of 16 the young Robert A Hadfield chose to enter his father's business rather than to go to Oxford or Cambridge. Five years later he received from his father a chemical laboratory of his very own and a cheque for £10,000. With the metallurgical world at his feet, Hadfield proceeded over the next forty years to systematically investigate alloy additions to steels including the following astonishing range of elements added in increasing percentages of single elements and in binary and ternary combinations: manganese, silicon, aluminium, chromium, cobalt, copper, molybdenum, nickel, titanium, tungsten and vanadium.

In 1882 Hadfield's investigations began when he found that a pair of defective (gritty) cast steel rolling mill pinions contained 1.5% of silicon due to faulty steelmaking practice in Hadfield's foundry. He contemplated that it might be possible to make grinding wheels out of silicon steel instead of the brittle emery wheels which were giving problems as indicated by the following extract from Hadfield's book[27] 'Emery wheels in those early days were comparatively weak, . . . an emery wheel used on a machine for grinding steel castings had burst into several pieces whilst revolving at very high speed. As a result a hole was knocked through a brick wall and the broken portions finally landed on the bed in the room of one of the workpeople living close by. Fortunately this was in the daytime so no-one was there to be hurt.' !

Hadfield set about manufacturing a silicon steel from steel scrap mixed with silicon spiegel. The spiegel actually contained high percentages of silicon and manganese and the resulting steel was found to contain 1.5% carbon, 3.96% silicon and 7.45% manganese. Although the steel was extremely hard it was almost as brittle as the emery wheels but the experiment led Hadfield to consider making steels containing single additions of manganese and silicon. Within four years Hadfield had developed his world-famous austenitic 12% manganese steel and his equally successful 4% silicon transformer steel (although it took considerably longer to achieve commercially significant tonnage applications).

The work on manganese steel commenced in 1882 and at his first attempt at single alloy additions, Hadfield produced a steel composition of 1.35% carbon, 12.76% manganese, very close to the present day austenitic manganese steel composition. It should be pointed out just how fortuitous it was that the ferro-manganese used for steelmaking had a manganese : carbon ratio of approximately 12 : 1 so that when aiming for 12% manganese, Hadfield obtained the 1% or so of carbon required to stabilise the austenite of which the steel is composed. (With Mushet's low carbon ferro-manganese a much different steel was produced!).

The steel was found to be soft but to strip the teeth off a file when trying to shape it. Unbelievably, the steel remained soft and extremely tough on water quenching from a high temperature and it was not magnetic!

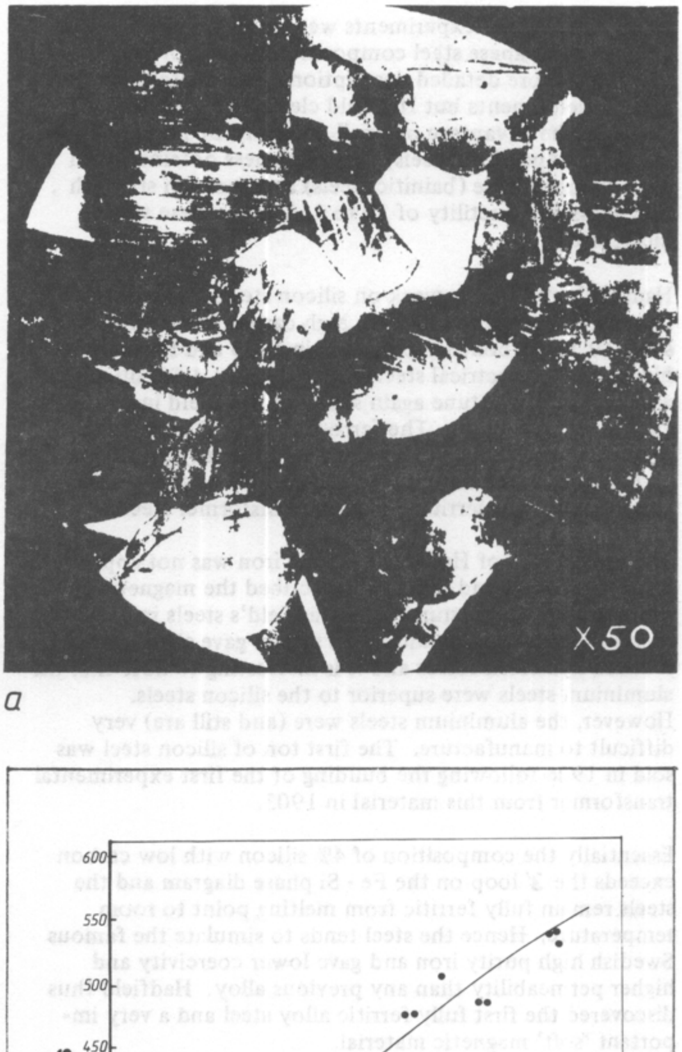


Figure 3 Hadfield's Manganese Steel

a) Hadfield's micrograph showing the austenitic microstructure in the quenched condition[7]

b) Strain hardening of the steel showing the high work hardening rate.

Hadfield had produced the first austenitic steel in history and at the same time the first work-hardening steel, Figure 3, the first non-magnetic steel and the toughest high strength steel available even to the present day.

Many hundreds of experiments were carried out on a wide range of manganese steel compositions. Lack of space prevents a more detailed description of the metallurgy of these developments but Hadfield clearly showed, for example, the advantage of small additions of 1 to 1.5% manganese (pearlitic steels) the brittleness obtained with 3 to 7% manganese (bainitic steels) and the high strength, toughness and ductility of 10 to 15% manganese steels (austenitic).

Hadfield's systematic work on silicon steels produced two important categories of steels, high carbon low silicon tool steels (0.7% carbon, 1.8% silicon) in 1883 and low carbon higher silicon electrical steels (0.2% carbon, 4.5% silicon) around 1888. Fortune again shone on Hadfield in his choice of ferro-alloys. The ferro-silicon used in his later experiments had a much lower carbon content (high silicon : carbon ratio) than anticipated and this led to the development of the fully ferritic electrical transformer steels.

The importance of Hadfield's silicon iron was not appreciated until W F Barrat and W Brown described the magnetic properties of a large number of Hadfield's steels in 1900[28]. Steels containing aluminium and silicon gave significantly reduced hysteresis losses and it is interesting to note that the aluminium steels were superior to the silicon steels. However, the aluminium steels were (and still are) very difficult to manufacture. The first ton of silicon steel was sold in 1906 following the building of the first experimental transformer from this material in 1903.

Essentially the composition of 4% silicon with low carbon exceeds the γ loop on the Fe - Si phase diagram and the steels remain fully ferritic from melting point to room temperature. Hence the steel tends to simulate the famous Swedish high purity iron and gave lower coercivity and higher permeability than any previous alloy. Hadfield thus discovered the first fully ferritic alloy steel and a very important 'soft' magnetic material.

Hadfield's silicon tool steel is still the basis of an important group of shock-resisting steels and further developments of carbon-silicon steels by other workers around the turn of the century produced spring steels (0.4% carbon, 1.8% silicon) ship plate (0.2% carbon, 1% silicon) and rails (0.6% carbon, 0.5% silicon).

It is difficult to accord Hadfield the tributes that he deserves in the space of this short article. His outstanding developments and methodical documentation appearing in almost 200 publications are a wealth of metallurgical knowledge requiring further study in the light of modern developments and understanding. Additionally, it should be noted that he made an enormous contribution to the wealth of Sheffield's steelmaking industry. Often his developments related to new armament materials for projectiles and armour plate. For example, one and a half million shells and six million 'tin hats' of manganese steel, were manufactured during the 1914-18 war. Government expenditure on munitions and materials during the Great War was £1.8 billion[29], much of this going to Sheffield industry. Hadfield's low hysteresis silicon steel was estimated to be saving the world about £80 million up to the year 1921 in terms of reduced energy losses[29].

1912 – Stainless Steel – Brearley

In the attribution of a particular alloy steel discovery, it is difficult to decide whether the idea, the manufacture or the successful commercial exploitation is the relevant stage of discovery. With tungsten steels and manganese steels, Mushet and Hadfield were clearly involved in all three stages and can undoubtedly lay claim to being the discoverers.

In the case of chromium and stainless steels, although there were a number of observations that chromium imparted corrosion resistance there was no successful manufacture or application of chromium steels for corrosion resistance until Brearley produced his first martensitic stainless steel containing 12.8% chromium and 0.24% carbon in 1912[30,31].

As previously stated, Robert Mushet first suggested the application of chromium to steel manufacture[4] and patented the idea in 1861[21]. Previously Faraday and Stodart had manufactured chromium steels in 1820-22[16,17] as did Berthier in 1821, Baur in 1871 and others[4]. Hadfield and Osmond came close to discovering stainless steel in 1892 when Osmond carried out metallography and etching experiments on high chromium high carbon steels including one which had the composition 1.27% carbon and 11.13% chromium. Osmond[32] noted that the steels resisted acid attack but neither investigator realised the commercial significance of the observations. Hadfield examined the samples 23 years later in 1915 and found them to be 'quite bright and practically free from rust'. However, Hadfield also noted that it was impossible to obtain low carbon ferro-chromium or chromium metal at economical prices for steel production at the time of their experiments in 1892.

Harry Brearley is the accredited discoverer of stainless steel (although B Strauss and E Maurer certainly independently discovered austenitic stainless steels in Germany at the same time)[33] because not only did he make the observation that the steels were etching resistant but he successfully manufactured and heat treated the steel and he found an application, in cutlery, for the steel. The story of his discovery is fairly unusual and deserves re-telling.

Brearley joined Thomas Firth & Sons in Sheffield in 1882 but was dismissed almost immediately because he was under age for employment. One year later at the age of 12 he rejoined Firths as a bottle-washer and chemical laboratory assistant. He became a skilled analyst and left Firths to set up a chemical laboratory at Kayser Ellison. Whilst there he collaborated with Fred Ibbotson, a lecturer at the University, to produce a book 'The Analysis of Steelworks Materials'[34]. Following three years as Works Manager of Firth's Riga works in Russia, Brearley returned to Firths in 1907 to take charge of the research department. In May 1912, engaged on armament development, Brearley visited a small arms factory with the object of studying the erosion of rifle barrels. He suggested that gun steels should have a high melting point and knowing that chromium raises the melting point of steel, he produced a series of steels adding between 6 and 15% chromium to a mild steel base (~ 0.25% carbon). The steels were submitted to a variety of heat treatments and examined metallographically. Brearley found that some of the samples and particularly an electrically melted 0.24% carbon, 12.8% chromium steel, resisted etching in the usual reagents after certain high temperature heat treatments. The steels were not utilised for ordnance purposes but Brearley recommended a number of applications including cutlery. Unbeknown to Brearley, Firths sent samples of the steel to two Sheffield cutlers for trials but the steel was rejected because of difficulties of forging, grinding and hardening.

Undeterred, Brearley had knives manufactured by Ernest Stuart the cutlery manager at Messrs R F Mosley. With Brearley's help, the knives were forged and hardened and were an immediate success, having the property of rustlessness which Stuart described as stainlessness after he had attempted to stain the knives with food acids.

Within two months Mosleys had ordered seven tons of another similar steel, Firth's Aeroplane Steel (FAS) which, quite remarkably, was an engine valve steel containing 13% chromium and 0.4% carbon. No-one, apart from Brearley, appeared to know that this was a stainless steel very similar in composition to his newly invented steel. However, stainless steel is not stainless unless it is polished.

The order was placed through the Amalgams Company and Brearley expected that Firths would be delighted. Brearley had extensive knowledge of steels and it was this knowledge that enabled him to suggest forging and hardening temperatures for the successful manufacture of cutlery knives by Mosleys. Brearley further suggested that the steel should be sold as heat treated blanks under his guidance so that the cutlers need carry out only simple finishing operations to produce knives. He further suggested that Firths might confer some privileges on him in respect of the manufacture and supply of the blanks in line with his contract of employment which stated that patents based on his discoveries should be the joint property of Firths and Brearley[30]. The steel was not patented, the 'heat treated blank' proposal was turned down and Brearley was asked to provide information and assistance as required. This he declined to do and shortly afterwards he resigned his position in the firm.

Subsequently Brearley obtained an American patent for his invention on September 5th 1916, the patent stating limits of composition and heat treatment: Brearley determined these limits with the assistance of an 'unknown' Sheffield company when the Firth facilities were no longer at his disposal. The patent withstood many challenges and eventually Firths bought a half share and formed the Firth-Brearley Stainless Steel Syndicate Limited in February 1917 issuing sub-licences for the manufacture of stainless steel throughout the world.

Thus the financial outcome for Brearley and Firths was most satisfactory with Sheffield becoming the centre of the stainless steel cutlery industry.

Harry Brearley, however, provided a final intriguing end to the story by placing a sealed packet with the Cutlers' Company in Sheffield on December 14th 1931. This declaration on the history of stainless steel, to give information on people, places, dates and companies involved in the discovery of stainless steel was to be opened on the day of the Forfeit Feast, June 29th 1960, 'by which time the persons concerned are unlikely to be living' 'to avoid causing inconvenience or giving offence'.

Amid great anticipation and interest in view of the wranglings between Brearley and Firths almost fifty years earlier, the declaration, Figure 4, was duly opened in 1960. Most observers and the Press denounced the declaration as insignificant but it is actually a useful document giving historical information which was known only to the principals and a few others. For example, the declaration names the two cutlery firms who dealt with Firths as George Ibberson & Company and James Dixon & Sons (blades manufactured by Innocents).

The steel company that assisted Brearley to define the limits of his patent application at the end of 1914 was the Vanadium Steel Company. Precise dates of the various happenings and the names of principals are also given. Probably most importantly the sealed packet was accompanied by a large display case showing the cutlery samples produced at the various stages of the discovery. These samples represent the first stainless steel ever produced and the world's first stainless steel cutlery. This display case, Figure 5, is now on public display in the entrance to the Cutler's Hall in Sheffield.

Metallurgically it is interesting to note that Brearley discovered martensitic stainless steels which require higher hot working and hardening temperatures than carbon steels, to allow them to be hot forged and to achieve maximum stainlessness. Using carbon steel hardening temperatures the steel would not be re-austenitised and a large proportion of the chromium would be in the form of chromium carbides which essentially reduces the chromium content of the matrix and lowers its corrosion resistance. With an Fe - Cr phase diagram and knowledge of the solubility of carbides it is easy to explain these observations but Brearley was successful because of his extensive practical knowledge of steels acquired over many years in the industry. 'I knew the temperature at which this particular steel could be most easily worked and most efficiently hardened'.[30]

Other Alloy Steels

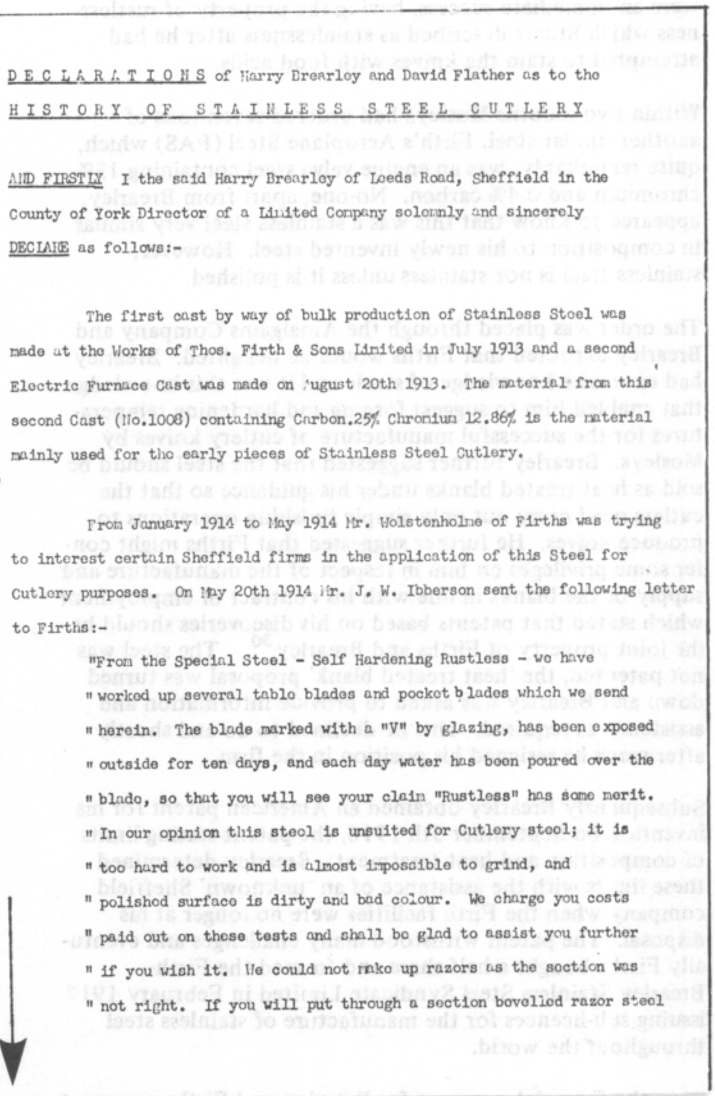
This survey has shown that Sheffield's metallurgists and industry made very significant contributions to the early history of alloy steels resulting in the development of steels depending on single large alloy element additions such as 9% tungsten tool steels, 12% manganese abrasion-resisting steels, 4% silicon electrical steels and 12% chromium stainless steels. Small additions of other elements to these base steels can, of course, improve the properties.

The only other element that is used as a large single alloy addition is nickel and the French and Americans were instrumental in discovering and developing nickel steels[35]. Britain was slow in applying nickel steels for armaments and industry although James Riley carried out excellent systematic pioneering work around 1889[36]. Austenitic stainless steels which contain large amounts of chromium and nickel were discovered in Germany[37] and very rapidly applied throughout the world.

Cobalt is added in large amounts to high speed, maraging and stainless steels but there is no cobalt-based steel. Molybdenum, vanadium, titanium, aluminium and niobium are usually added in small amounts and often in combination with other elements. Hadfield and many other Sheffield metallurgists were involved in these alloy steels but no claim to major alloy steel discoveries can be made. However, contributions such as that by Professor Arnold in optimising vanadium additions to tool steels[38] were typical of the local activities at the beginning of the 20th century.

Sheffield's metallurgists and industry made major contributions to the development of special stainless steels (Firth Vickers) and heat resisting steels (Jessop Saville) in the 1940s and 1950s[39]. Important work on the physical metallurgy of alloy steels was carried out in Sheffield at the United Steel/British Steel Corporation laboratories and in the University's Metallurgy Department during the 1950s and 1960s. In particular, the fundamental basis for micro-alloy steels was established in Sheffield during the 1960s[40].

Until 1970 European and American metallurgists led the world in the development and production of alloy steels. More recently the mantle for both alloy development and manufacture has tended to pass to the Japanese.



DECLARATIONS of Harry Brearley and David Flather as to the HISTORY OF STAINLESS STEEL CUTLERY

AND FIRSTLY I the said Harry Brearley of Leeds Road, Sheffield in the County of York Director of a Limited Company solemnly and sincerely DECLARE as follows:-

1. The first cast by way of bulk production of Stainless Steel was made at the Works of Thos. Firth & Sons Limited in July 1913 and a second Electric Furnace Cast was made on August 20th 1913. The material from this second Cast (No.1008) containing Carbon.25% Chromium 12.86% is the material mainly used for the early pieces of Stainless Steel Cutlery.

2. From January 1914 to May 1914 Mr. Wolstenholme of Firths was trying to interest certain Sheffield firms in the application of this Steel for Cutlery purposes. On May 20th 1914 Mr. J. W. Ibberson sent the following letter to Firths:-

"From the Special Steel - Self Hardening Rustless - we have
" worked up several table blades and pocket blades which we send
" herein. The blade marked with a "V" by glazing, has been exposed
" outside for ten days, and each day water has been poured over the
" blade, so that you will see your claim "Rustless" has some merit.
" In our opinion this steel is unsuited for Cutlery steel; it is
" too hard to work and is almost impossible to grind, and
" polished surface is dirty and bad colour. We charge you costs
" paid out on these tests and shall be glad to assist you further
" if you wish it. We could not make up razors as the section was
" not right. If you will put through a section bevelled razor steel

Figure 4 The Declaration of Brearley

Declarations of Messrs Harry Brearley and David Flather re the History of Stainless Steel Cutlery and the specimens exhibited to the Company of Cutlers in Hallamshire. 'To avoid causing inconvenience or giving offence I request that this declaration should not be made public before the 29th day of June 1960 by which time the persons concerned are unlikely to be living . . . Harry Brearley.'

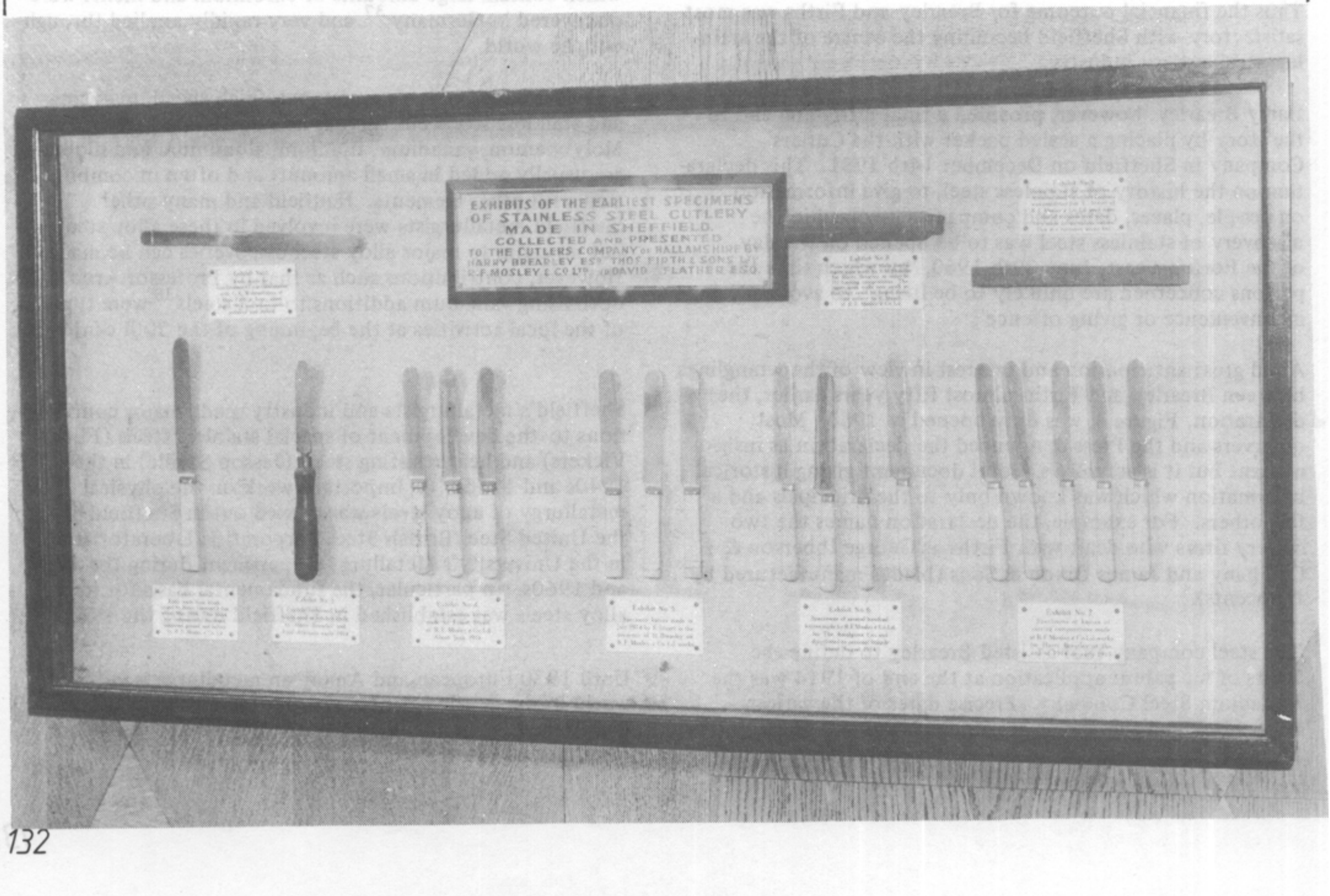


Figure 5 Exhibition of Stainless Steel Cutlery.

This exhibit, which is displayed in the Cutlers' Hall in Sheffield shows the first stainless steel cutlery ever produced. Details are given in Brearley's declaration.
Exhibits 1 & 2 are knives made by Ibbersons and Dixons.
Exhibit 3 is Brearley's hand-made knife with a blade fitted into a file handle.
Exhibits 4, 5 & 6 are knives made by Mosleys.
Exhibits 7 & 8 are knives and a small ingot from steel produced by the Vanadium Steel Co.
Exhibit 9 is a piece of scrap bar of aeroplane valve steel that was used for cutlery during the war.

Acknowledgements

The author gratefully acknowledges interesting discussions with Dr K C Barraclough, Mr J E Truman and Mr A L P Wood, CBE. The valuable assistance of Mr. T A Whitamore, Clerk to the Cutlers' Company, with respect to the Brearley declarations and exhibit is also acknowledged.

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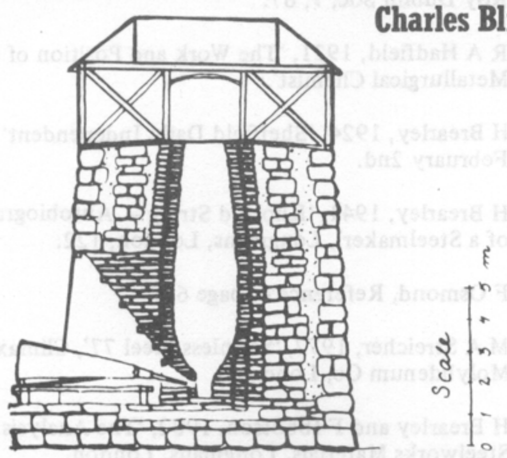
Early Blast Furnace News

Charles Blick



First an update on previous information:

Blaenavon Ironworks, Pontypool, Gwent.
MR SO 248093 (1790 to c 1900)

Progress on this site was reported in JHMS 18/2 p 135.

Stan Coates now reports (Nov '84) further steady progress, with a very useful work force employed almost full time, on the prodigious amount of work to be done. The feeling is that Welsh Office is determined to complete restoration, a satisfactory situation.

Coalbrookdale, The Old Furnace, Ironbridge, Shropshire
MR SJ 667048 (1638 to c 1818)

Dr Arthur Raistrick has written (Nov 1984) to say that he, and Mr Fred Williams, were driven to the conclusion that the 'aperture' in the lining, at the junction of the stack and the top of the bosh over the tymp, was the main tuyere in spite of its high position, because there was no other aperture.

They made a deep excavation in the crucible and on the drawing hearth and there was no hole of any kind which could have been a tuyere. They reached the bottom of the hearth and a great mass of 'bear', and that was all. They could only think of this hole as an unusually high tuyere, connected with the annular passage to it, as an experimental hot blast system.

Dr Raistrick thinks that, after the conversion of the furnace to cast the members for the Iron Bridge for which it was a melting furnace, it may never have been a smelting furnace again. At that time Coalbrookdale was preparing to take its cast iron from the several other furnaces the company was building.

We are very grateful to Dr Raistrick, at the age of 88 for harking back to the years 1948 to 1959 during which this work was done.

Dol y Clochydd blast furnace, Llanfachreth, Merioneth
MR 734222 (1597 - 1604).

Excavation of the north-west half of the furnace was carried out in 1984 by Peter Crew and Merfyn Williams, with students from the Snowdonia National Park Study Centre (see JHMS 18/1 p 48).

Note

Readers are reminded that most sites are on private property and access may not be possible. Where access is possible, permission to visit **MUST** be properly obtained before approaching a site.

The name of the Society may **NOT** be used as an excuse in the event of a dispute.

The lining and hearth base slab had been removed in antiquity, exposing a sand filled pit which seems to have been the only drainage arrangements. The outlet from this was choked with clay, which no doubt led to the demolition of the hearth, presumably with a view to reconstruction. Enough survives of the hearth and boshes to recover their dimensions. The front edge of the casting floor was uncovered, which appears to be undisturbed.


Dol y Clochydd, tapping arch excavated 1984.

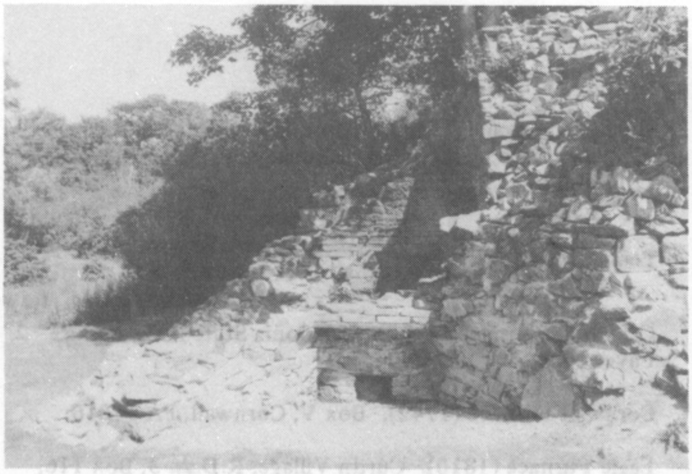
Following tree removal, the casting floor and blowing arch will be excavated during 1985, followed by consolidation of the remains.

Dolgun Blast Furnace, near Dolgellau, Merioneth.
MR SH 751187 (1719 to 1802)

Further work has been carried out by students from Plas Tan Y Bwlch, under the direction of Peter Crew and Merfyn Williams. Following the consolidation of the furnace (reported in JHMS 18/1, p 47-8), it has been possible to clear the tapping arch of rubble to expose the 2m high lining on the front wall which has been consolidated by rebuilding the front wall and the insertion of an iron lintel in the original slot.

Following a change of ownership, the National Park have negotiated a formal access agreement to this site.

Dolgun furnace, the tapping arch (scale: 1 metre)



Dolgun furnace, the tapping arch consolidated

Dovey Blast Furnace, Eglwysfach, Dyfi, Dyfed
MR SN 685952 (1755 to post 1796).

Dr Sian Rees reports that consolidation work is now virtually complete and that the car park, across the road, is nearly complete.

Moira Blast Furnace, Leicestershire
MR SK 314153 (c 1804 to c 1840)

David Cranstone has now finished excavation on the site. His final report is likely to appear in this Journal in 1985.

He reports that a number of interesting features appeared during the last weeks – possible remains of a cupola furnace, and details of the dam and casting floor, though this had been largely destroyed by later use of the site.

Chris Salter has taken samples of burden material recovered during clearance of the stack for microscopic and mineralogical study.

Morley Park Blast Furnaces, Heage, Derbyshire
MR SK 380492

It is most satisfactory to receive a report from Keith Reedman (Nov '84) that sufficient funds have been received to enable work to start on making good the 1818 furnace.

New information has come to hand concerning the following sites:

Backbarrow Blast Furnace, Newby Bridge, Cumbria
MR SD 355847 (1711 to Feb 12 1966)

Public Works contractors, having been allowed access to the site for certain buildings, should have cleared all by the end of September.

Thereafter, as the structures on site, the furnace and its surroundings, are now in a very parlous condition, HBMCE (formerly DoE) will be seeking to try to encourage their preservation.

Coed Ithel Blast Furnace, Llandogo, Gwent
MR SO 528027 (c 1648 to c 1796)

This scheduled site was excavated by R F Tylecote in 1964 and reported in JISI April 1966.

The site was recently put up for sale and, when visited, there was alarm at the growth of trees, some very large and many small. To avoid damage to the stack, experienced help will be required to remove two large trunks. This is being sought while the smaller growth, it is hoped, will be cleared by an organisation administered by local County Councils.

Darkhill Blast Furnace, Forest of Dean
MR SO 590087 (c 1818 to 1847)

Some excavation and consolidation work has been carried out by the owners, The Forestry Commission, since 1976, but recent information is that deterioration is now causing concern.

Leighton Beck Blast Furnace, Slackhead, Cumbria
MR SD 485778 (1713 to c 1806)

We are indebted to J Kenneth Major for two excellent colour prints of this site.

The original and almost unique feature at Leighton was the use of peat as the fuel which was available in large quantities within a very short distance. Prior to its 'blowing up' about 1806 it was an active and profitable concern.

One print shows the site which can be read quite easily – the dam, the leat, the site of the waterwheel, mounds some still containing charcoal, and the mound of masonry which was the furnace with its casting floor. But the second print shows the barn, 80 ft long by 26 ft wide which is in reasonable condition but not really used for farm purposes.

Newent Blast Furnace and Charcoal Store, Oxenhall, Forest of Dean (c 1647 to c 1751)

This site was visited by members, under the guidance of David Bick, on 8th May 1982.

Recently it was noted that the roof of the charcoal store had been removed as a preliminary, it was learned, to complete demolition.
Application was immediately made to the Inspectorate of Ancient Monuments for protection. It is most gratifying to report that this was, as a result, urgently recommended.

Venallt Blast Furnaces, Cwmgwrach, Neath Valley
MR SN 864050 (1842 - c 1860)

It is gratifying to report that the conservation scheme reported in JHMS 18/1, p 49, has now been completed. Consolidation of the structure has been carried out which revealed an extension to the furnace platform confirming that there were two furnaces.

Overseas

Delfos blast furnace (1918-1921), ISCOR, Pretoria, South Africa. Professor Nik J van der Merwe (member) was asked if this furnace still existed. Most helpfully a train of correspondence was started which yielded much information. P F de Villiers, general works manager, Iscor, Pretoria, confirmed opening of Cornelis Delfos Museum in old boiler and blowing house as a national monument (sic CRB), but added that one of their retired Acid Bessemer steel converters (1942 - 1982) had been installed outside the Pretoria Works – from the photograph sent, **exactly** like the one from Workington outside Kelham Island Museum, Sheffield.

Grateful thanks to those mentioned – and to Peter Smithurst for following up our initial contact.

Hopewell furnace (1771-1883), Hopewell Village National Historic Site, R D No 1, Box 345, Elverson, Pennsylvania 19520, USA. Most grateful to Elizabeth E Disrude, Superintendent, for copy of their new **Hopewell Furnace** handbook on their fully conserved furnace and village surrounding, which is **excellent.** This follows earlier receipt of photographs and book on the whole project.

Saugus ironworks. Most grateful, too, to Cynthia Pollack, supervisory Park Ranger of this so well known site, for copy of E N Hartley's 'Ironworks on the Saugus'.

Also sent was the following list of preservation sites in the USA:

The following sites preserve other vestiges of the early iron industry. At some sites only the furnace stack remains; others have been largely restored. The site administrator should be contacted for information on hours and facilities.

Alabama

Tannehill Furnace (1855). Tannehill Historical State Park
Route 1, Box 124, McCalla, AL 35111.

Main

Katahdin Ironworks (1843). Katahdin Ironworks Multiple Use Forests, c/o Katahdin Ironworks Gate, Katahdin Ironworks Road, Brownville, ME 04414.

Maryland

Catoctin Furnace (1774). Cunningham Falls State Park, Thurmont, MD 21788.

Lonaconing Iron Furnace (1836). Allegany County Historical Society, 218 Washington Street,Cumberland MD21502.

Nassawango Iron Furnace (1830). Furnace Town Foundation, Inc, PO Box 111, Snow Hill, MD 21863.

Massachusetts

Saugus Ironworks (1646). Saugus Ironworks National Historic Site, 244 Central Street, Saugus, MA 01906.

Missouri

Maramec Ironworks (1826). The James Foundation, 320 S Bourbeuse Street, St James, MO 65559.

New Jersey

Batsto Village (1766). Wharton State Forest, R.D.# 4 Hammonton, NJ 08037.

Howell Works (1790). The Board of Trustees of the Deserted Village at Allaire, Allaire, NJ 07727.

Ringwood Ironworks (1742). Ringwood State Park, Box 1304, Sloatsburg Road, Ringwood, NJ 07456.

Ohio

Buckeye Furnace (1851). Historic Site Manager, Buckeye Furnace, State Memorial, 123 Buckeye Park Road, Wellston, OH 45692.

Pennsylvania

Caledonia Furnace (1837). Caledonia State Park, R.D.# 2 Fayetteville, PA 17222.

Cornwall Furnace (1742). Box V, Cornwall, PA 17016.

Eagle Furnace (1810). Curtin Village, R.D.# 3, Box 116, Howard, PA 16841.

Greenwood Furnace (1837). Greenwood Furnace, State Park, R.D.# 2, Huntingdon, PA16652.

Hibernia Furnace (1793). Chester County Park, 235 West Market Street, West Chester, PA 19380.

Joanna Furnace (1792). Hay Creek Valley Historical Association, Box 36, Geigertown, PA 19523.

Lock Ridge Furnace (1868). Lehigh County Court House, Fifth & Hamilton Streets, Allentown, PA 18101.

Pine Grove Furnace (1764). Pine Grove Furnace, State Park, R.D.# 2, Gradners, PA 17324.

Pottsgrove Manor (1752). Pottstown, PA 19464.

Scranton Furnaces (1842). Scranton Anthracite Museum, Complex Headquarters, R.D.# 1, Bald Mountain Road, Scranton, PA 18504.

Book reviews

Eugenia W Herbert, Red Gold of Africa; Copper in Pre-colonial History and Culture, *University of Wisconsin Press, 1984,* **$***32.50 (Cloth, Octavo). pp 413.*

Most of the author's papers have been on the European-African copper trade which is a subject of great interest to the metallurgist when it is understood that a considerable proportion of the medieval and post medieval output of the European copper plants, such as those of the Fuggers, went into this trade. This forms the meaty middle of the book but it is introduced by four very fascinating chapters on early copper working in Africa and techniques of mining, smelting and fabrication. The third part deals with the role of copper in traditional African society.

Today 'copper' is almost a byword for Africa, as the copper belt of Zambia and the mines of Katanga are so well known to modern metallurgists, not to mention the more complex mineral deposits of South Africa. But there are many smaller deposits that have been worked for longer than the above, beginning with those of Sub-Saharan Africa at Akjoukt in Mauretania and in the area around Agadez in Niger. We now have C-14 dates for some of these which go back to the 2nd millennium BC, when they probably merely worked the native copper which seems to occur in most of the smaller surface deposits. The lack of fuel and water would have made large-scale washing and smelting difficult in these areas.

While there are indications that the early Portuguese colonisers were interested in the copper of the Congo region in the 16th century, there is little documentary evidence before the 18th century. But the extent of the ancient workings in Katanga suggest an enormous output long before this. C-14 dates for this deposit from the Zambian side of the frontier have given dates between the 9th and 14th centuries AD. Excavation shows that mining began by the 4th century AD.

By the 16th century, German miners were imported by the Portuguese to work the Bembe (?Congo) mines and the period of colonial exploitation had begun. But this period at this time was short-lived and African exploitation continued. It is during this that we begin to get light shed on the relationship between the miner, the smelter and the smith – an aspect of ethnology that interests anthropologists and metallurgists alike. The author puts the question 'Who were these African metalworkers? Who mined and smelted the copper? Who fashioned it into various forms found in the length and breadth of the continent?' This is a question that many Europeans ask themselves about their own areas. Here we may have the answer which is complex and varies from place to place. On the whole, the smith worked imported copper and brass and didn't mind whether it came from Europe or Africa. In some cases the smith occupied an inferior position amongst those who despised manual work as opposed to pasturalism. But in most African societies this position is rare. The smith functions as priest, artist, shaman and magician because he has the esoteric skills to manipulate the dangerous forces at play in the extraction of ores and can convert them into metal. This brings him into competition with the gods; he must be master – a specialist. Clearly we have similarities here with the Celtic – Aegean traditions. But there is confusion between the smith as fabricator and the smith as a smelter. Accounts of copper mining and smelting in Katanga emphasize the secret knowledge of the master smelter. It is regrettable that the mining historians have not dwelt on the sources that Eugenia Herbert has produced here, but we learn of rituals before a shaft is dug and other rituals during the actual mining.

Similarly when smelting is about to begin we have a series of rituals which are not unknown to one in connection with iron smelting. Indeed, iron smelters came to Katanga in the 19th century to be initiated into the mysteries of copper. The degree of specialisation varied from part-time to full-time. In some areas mining and smelting were dry season occupations. In other areas, however, the entire village moved to the mining site where crops were planted and mining carried on while the crops ripened – a form of trans-humance. In other cases the miners and smelters spent their whole time working rich veins and casting ingots which they exchanged for food with neighbouring groups. This compares with the 'extra-tribal' society mentioned by Childe.

The itinerant or 'gypsy smith', now not accepted by the prehistorians of today, does exist in Africa, in S-E Nigeria. Although the 'mining camp' idea in which people travelled long distances to dig for ores which they carried back to their villages to smelt, was certainly extant. This latter bears some resemblance to the Egyptian expeditions to the Palestinian Negev in the 12th century BC. But the Lemba of the Transvaal were travelling copper-smiths who obtained their copper from the mines in the Venda mountains in the form of bars which they carried to the villages of their clients.

The next chapter deals with the techniques of mining and smelting furnaces. Early mining engineers and anthropologists managed to mount 'command performances' of which the author disapproves since they can be misleading. It is true that former smelters have often forgotten their techniques and prove unsuccessful, but even so a lot of useful information can be gleaned by interrogation of former specialists by modern specialists.

Mining in Katanga was done with iron axes, and fire-setting was used where necessary and ore was passed to the surface in baskets. Shafts were up to 35m deep and seem to be more like bell-pits rather than modern mines, probably because of the lighting and timbering problems. Horizontal drifts were no more than 20m long. Malachite was the only mineral taken.

Up to 30 temporary furnaces might be built consisting of a basin 5-6 cm deep and 40 cm in diameter, with a shaft up to 70 - 75 cm high made of anthills, with 3 tuyeres bored through near the bottom. The furnace was filled with charcoal and wood, and ore was piled on top. Bag-bellows provided the blast. The metal was formed in the basin at the bottom and little slag was produced from such rich ore. At Phalaborwa in the 8th century AD iron flux was used and the metal was tapped, with quite large slag heaps around the furnaces.

African output of copper is difficult to assess but it is estimated that in Katanga, before 1850, 57 tonnes were produced annually. Mrs Herbert reminds us that the annual **world** output in the first decade of the 19th century was only 18200 tons.

The smithing and casting side is fairly well known to the European reader, but wire drawing may have come after the 15th century. Open stone moulds and lost wax seem to be the preferred processes, the latter using both beeswax and latex. The author here discusses possible Portuguese influences but, as we know so little about Portuguese or European techniques at this time, discussion is difficult. When we come to alloys, which show the predominance of brass, we seem to feel the impact of the foreign penetration, which is so fully discussed in the next section. There would be no difficulty in making bronze, as tin occurs both in Nigeria and the Transvaal, but zinc ore is rare and the making of brass unknown. On the other hand there is the famous caravan found in Mauretania which yielded 1 tonne of brass bars dated to about the 12th century AD and containing 20% of zinc. These were cast and very porous.

In this section we have a detailed discussion of the types of alloys available in Africa before and after European contact. There is little doubt that brass vessels were imported from Europe although the manillas (arm torcs), which were withdrawn as currency as late as 1948 in Nigeria, were found to be 60 - 65% Cu and 25 - 30% Pb. Yet it is quite clear that when trade developed with the Europeans the African purchasers were very particular as to what they exchanged both in form and composition.

The copper trade before the colonising period was mainly a question of the exchange of copper for gold. The former being valued more highly in Africa than the latter. It is this fact that triggered off the European trade in manillas and other ornamental items. We learn here of the intricacies of the trade in manillas (modelled on LBA dress fasteners with expanded terminals?) neptunes (brass vessels of all kinds), and their compositions.

The author makes attempts to calculate the extent of the trade and the intense competition between the colonial powers to keep this trade.

As far as British exports were concerned the record of the Royal African Co give export of copper bars and brass ware for the period 1673 - 1704. But some copper was exported probably from one part of Africa to another by sea, as land transport was too difficult.

The final section deals with the role of copper within African society, as a medium of exchange, as a medium of art, power, and its place in myth and legend. The types of currency have been discussed by many before and African art is now known to all, as a result of the discovery of the Benin 'bronzes'. But we can learn something from the profusion of 'currency bars' in Africa (croisettes), and the ingot shapes bear an extraordinary resemblance to the oxhide ingots of the Mediterranean in the LBA.

The book concludes with an 18th century quotation to the effect that gold is no longer considered by the Gold Coast: negroes in the careless light that it was when the Europeans started to trade with them. But is one really surprised that the wondrous colour of natural copper was considered superior to the yellowish metal of gold? It is only the world scarcety value that has up-graded the value of gold – Africans had their own gold – red gold.

So much for the contents. One must thank the author for giving us this full account of a very important subject which does not seem to have had due regard from most historians of metallurgy and comparatively little from anthropologists as compared with iron. The book is well arranged and the references collected at the end, but in this case clearly related to the pages to which they refer. This system is to be recommended to the authors of future works. The book contains a good bibliography and a useful index.

R F Tylecote

Edmund Teesdale, The Queen's Gunstonemaker, being an account of Ralph Hogge, Elizabethan Ironmaster and Gunfounder, *Linden Publishing Co, Seaford, 1984, £5.50, 125 pp, 2 maps, 2 plates, ISBN 0 9502354 66.*

In this brief book, the author, now the owner of Ralph Hogge's house at Buxted, discusses Hogge's origins, his early work for William Levett, first successful founder of one-piece iron guns in England, and the years of Hogge's output of iron guns and ammunition for the Crown, 1560-85. He refers also to the Henslowe family, into which Hogge married, important for the survival of certain accounts connected with ironworks in a book later used as a diary by Philip Henslowe, the Elizabethan theatre manager. On the technical side the book is disappointing; although there is no specific evidence for the gun-casting methods used at Hogge's Sussex furnaces, enough research has now been done for the appendix on blast-furnace and gunfounding practice to be drawn from a wider and more recent literature than Nef and Schubert. The author has found a small but welcome number of fresh original references relevant to the Hogge family, although in the main he has relied on secondary sources for this pleasantly-written essay.

David Crossley

D McDonald and L B Hunt, A History of Platinum and its Allied Metals, *Johnson Matthey, London, ISBN 0 905118 83 9 450 pages.*

This handsomely produced volume is a revised and rewritten text of the book originally written by Donald McDonald entitled: **A History of Platinum from the Earliest Times to the 1880s** and published by Johnson Matthey in 1960, a work which has long been out of print. The present volume sets out to rectify this situation, and there is no comparable work available which deals with the history of the platinum group metals (platinum, osmium, iridium, ruthenium, rhodium and palladium) from the earliest prehistory to the present.

The book is divided into 24 chapters covering 422 pages of text with both name and subject indexes. References are given at the end of each chapter. The work is very much a history rather than a scientific examination of the subject in the light of present-day knowledge, and there are few equations, chemical formulae or analyses of historical interest given in the text. The main intent of the book is to trace the development of knowledge of the subject, by historical research, through the individual scientists and other workers who have made important contributions to platinum group metals; their extraction, fusion, refinement and characterisation.

In antiquity, the only major utilisation of platinum was by the Indians of the pacific littoral in the region of the Ecuadorian-Colombian border in South America.

The earliest accounts suggest that the panned platinum group metals were first discarded by the Spanish settlers, before platinum began to arouse the curiosity of scientists in Europe. It is largely with this historical period that the book is concerned and it includes much fascinating information concerning the prominent investigators together with biographical details and many black-and-white and colour plates of portraits and illustrations of people, materials and processes. The illustrations do not carry figure numbers and there are no illustrations of any metallurgical sections or phase diagrams connected with the structure, extraction or alloying of the platinum metals. This is, obviously, not a book designed as a compendium of scientific information on the platinum metals: it is intended as the title suggests, to be a history. In this sense, the book is full of erudite scholarship, and much additional information has been brought to light by the researches of Dr Leslie Hunt. The book will continue to be an important source for the history of the platinum group metals for many years to come and can be recommended both as a well-written and well-produced volume.

D A Scott, Institute of Archaeology

J F Clarke and F Storr, The Introduction of the Use of Mild Steel into the Shipbuilding and Marine Engine Industries, *Occasional Papers in the History of Science & Technology, No 1, Faculty of Humanities, Newcastle upon Tyne Polytechnic, 1983, 98pp.*

Extensive quotations from contemporary literature show that steel at its best was much superior to iron, but despite care in tensile testing the new material, unpredictable brittle fracture was liable to occur during manufacture during test or during service. Some of the problems can now be attributed to working the steel in the blue-brittle temperature range. By 1880 mild steel was the established boiler making material.

In 1858 the first British boats were constructed from puddled steel, but one, at least, corroded rapidly when put into service on the Zambesi River. However, puddled steel was used extensively in the period 1862-1870. Bessemer steel was unreliable, and it was not until about 1885 that steel generally replaced wrought iron. The use of Bessemer steel was prohibited by Lloyds in 1907.

J K Almond

Laurence Ince, The Neath Abbey Iron Company, *De Archaeologische Pers, Nederland, A4, £6.00 soft cover, £7.50 hard cover, £2.00 postage in either case, 138pp plus plates.*

The Neath Abbey Iron Company, which had works near the Welsh town of Neath, achieved considerable fame in its day. The derelict remains of the two masonry blast furnaces and some other buildings, now converted to other uses, can be seen from the main road and the main railway line from Neath to Swansea and it is obvious that there was once considerable industrial activity on the site. Yet very little has been written about the company and no complete history of it has appeared before the present volume.

Neath Abbey Ironworks was of Cornish origin, a fact explained by the close association in the 18th century of the Cornish copper mines and the Swansea copper smelters. The Quaker family of Fox had financial interests on both sides of the Bristol Channel and in the shipping of copper ores to South Wales and coal from there to the Cornish mines. Seven members of the Fox family, together with others, set up an iron foundry near Falmouth in 1791, and in the following year the same partners took over the lease of the Neath Abbey Ironworks. This works was of little importance but the Foxes changed all that. They erected two new blast furnaces and in due course expanded into general ironfoundry work and, later, into the building of stationary steam engines, marine engines, ships, locomotives and gas works plant.

From the beginning the partners made use of the best technology available at the time. By 1793 they had a Boulton and Watt blowing engine for the furnaces and when the American industrialist Joshua Gilpin visited the works in 1796 he described it as being '. . . of the most modern and capital construction' The furnaces, he said '. . . produced 80 tons of iron per week', that is 40 tons each. If they did actually produce 40 tons a week each, they were large – though not exceptional – for their day.

Another visitor, the Swede E T Svendenstierna, recorded a weekly output of 15 to 16 tons of pig iron. But we have to remember that what a furnace could produce and what it did produce are not necessarily the same thing; both observers could have been right. What does matter is that contemporary evidence shows that the company had blast furnaces at work.

Then came problems. The partnership had become unwieldy by 1817 and the works was actually advertised for sale. It was, however, taken over by a new partnership of only four, two members of the Fox family and the brothers H H and J T Price and it was the Prices who led the company into its most prosperous years.

Engineering at Neath Abbey, as distinct from ironmaking, had started quite early, with the production of Trevithick type steam engines in 1804-6 and under the Prices – particularly J T Price – this trade was developed greatly. In fact, it is as engineers rather than as ironmakers that Neath Abbey is best known. Between 1820 and 1829 the company built more than 40 stationary steam engines. In the latter year the building of railway locomotives started and in due course marine engines, ships and gas works plant were added to the list.

With the growth of the engineering side of the business ironmaking was transferred to a new site and a separate company, the Abernant Iron Company, was formed to operate the new furnaces. Ironmaking probably ceased at Neath Abbey from about 1845 but expansion of the engineering side continued.

J T Price died in 1854 and with the loss of his guiding hand the Neath Abbey Iron Company entered into a slow decline. As is often the case, the company's reputation carried it on for a time and in fact some parts of its business continued to prosper – railway locomotives are an example. But the company had clearly lost its earlier spirit of enterprise and in 1874 the partners closed the works. It was taken over by a new partnership of local men but its plant was old, its site restricted and the capital for modernisation was not forthcoming. So the works just slowly ground to a halt. It finally descended into such obscurity that the exact date of closure is unknown. Even the local newspapers failed to record it.

The author, Laurence Ince, tells us that his interest in the Neath Abbey Iron Company started when, as a schoolboy, he '. . . played among some strange ruins in the village of Neath Abbey'. Many others must have wondered, as he did, what these massive structures were. But unlike the others, he took the trouble to find out. It was not an easy task he set himself. Some of the Neath Abbey drawings have been preserved and the author has made good use of them as he has of every source, published and unpublished, he could find. His bibliography shows how widespread his search had to be.

The result is a very comprehensive and detailed account of a company which played quite an important part in 19th century industrial history. It is well written, very readable, and pays due attention to every aspect of the business – personal, economic and technical. It sets the scene for the establishment of the company, with a brief account of the geology of the Neath area and of the industrial developments prior to the setting up of the 1792 Neath Abbey partnership.

Neath Abbey Iron Company was, in its heyday, a good, sound, undertaking, with an excellent reputation for its products. It was, at least in the time of J T Price, a good employer and paid more attention to the welfare and training of its employees than did many other companies of similar type.

Neath Abbey was a company of medium size, employing at most, when busy, in the region of 300. In many ways, it could be said of Neath Abbey that it was good but average for its time. It never even approached the size of some of its Welsh ironmaking contemporaries, such as Dowlais or Ebbw Vale. Nobody of the status of Bessemer, Mushet or Hadfield was ever associated with it, though it trained some very good engineers; Benjamin Baker, of Forth Bridge fame was its most famous ex-apprentice.

But it is exactly because Neath Abbey was, in the context of the 19th century, ordinary, that it is important. The great strength of Britain's industrial position at that time lay in the large numbers of Neath Abbey type enterprises that existed, not in the few outstanding ones, the names of which are still well known.

Because the Neath Abbey Iron Company was so representative of its time its history needed recording. Laurence Ince has done it very well.

There is only one serious criticism. The book lacks an index. It is not intended simply to be read as a matter of interest – though it certainly can be so read. It is a work of reference and as such should provide the reader with a quick and reliable guide to its contents. Compiling an index is a tedious and wholly uninteresting task (this is a comment from one who has done it several times) but it does need to be done. Someone – author, publisher or professional indexer – should have done it in this case.

W K V Gale

Jack Ogden, Jewellery of the Ancient World, *Trefoil Books Ltd, April 1983. £30.00, 24 x 25 cm, 183 pp.*

This well produced book with excellent illustrations, many in colour, might well escape the attention of someone wanting to learn something about the techniques and materials employed in ancient jewellery. It covers a period from the beginnings of the Bronze Age to the end of the Roman period. Its author is a practitioner of the art of jewellery making and is secretary of the Society of Jewellery Historians. He has studied both the art and science of the subject and this study contains a full scientific treatment and should be read by all those concerned with the techniques used in manufacture and to wrestle with the problem of genuine versus forgery.

The main items are concerned with the precious metals and gemstones. There is an interesting discussion on the sources and impurities present in gold and silver and how they change with time.

The chapter on goldsmithing techniques is probably of greatest interest to the historian of metallurgy and deals with a lot of tricks of the trade, not generally known to the metallurgist. Attention is paid to metal-graining techniques and wire making. The author gives full treatment to the latter. He does not accept the squarish bronze plates from Late Bronze Age Isleham as drawplates because of the holes being too big. From block twisted and coiled wire we go to beaded wires made by suitably shaped tools. One series of techniques is fine chain making; techniques that were invented millennia ago and are still in use today.

Soldering and granulation is the next section, with plating thrown in for good measure. He mentions the pressure welded gold boxes from Ireland but states that this technique is not often applicable to gold jewellery, and that soldering with copper is preferred. It is claimed that gold droplets will adhere to sheet just below their melting points and that this can be confused with the soldering. This is true but one might term it low pressure welding or diffusion bonding.

In early times blow pipes were used to increase temperature locally, as seen in Egyptian tomb paintings and wall paintings from Pompeii. Medieval techniques of great ingenuity were used for the assembly of jewellery details, including various techniques of casting-on. Fasteners such as bayonet-type fittings were used from the 1st century BC, as in the Broighter gold torc. But the sliding safety catch on the Roman cross-bow fibulae and the use of screws (left-hand threads) are also reported (4th century AD).

The author then discusses plating and gilding. Even the gold plating of iron in 15th century BC, followed by metal inlay and the setting of gemstones. This section forms a large part of the book and is followed by a chapter on glass, enamel and faience. One aspect of faking is again dealt with under 'ancient imitation and altered gemstones'.

The final chapter reviews the life of the jeweller, the growth of the industry, the shop, the man and the guild. Altogether a very satisfactory treatment of a most interesting subject. There is an extensive bibliography. An index would have added to the usefulness of the book.

R F Tylecote

Jochem Wolters, Die Granulation – Geschichte und Technik einer alten Goldschmiedekunst, *Callway Verlag, München, 1983. Price DH 248. 28 x 30 cm, 331 pp, index, 39 plates (28 in colour), 45 figures.*

Granulation is one of most sophisticated techniques developed by goldsmiths and one which has an unbroken history from the third millennium BC until the 19th century. It also plays an important role in the art of present day goldsmiths and silversmiths. Jochem Wolters has collected in his book perhaps all the information available about its history and technology and supplemented this with excellent photographs (the colour plates are very beautiful indeed) and an extensive bibliography.

The beauty and the extent of the employment of granulation perhaps justifies the size – and no doubt the price – of this most comprehensive book on this subject.

The volume is divided into three general parts. The first part gives a definition of granulation, including the etymology of the term in the German, English and French languages. According to the author, granulation can be defined as a decorative technique which uses small metal spheres attached by metallic bonding in ornamental or figurative order to a metal surface.

Granulation can first be classified according to the material used (gold, silver, platinum and copper), the basic pattern of granules (singular, linear, flat, etc) and their shape and number. In this chapter the author also gives some very interesting examples of the technique which he calls protogranulation which employs spherical headed nails and also draws attention to an object from Troy II where granules are drawn out of a wire. There is also a long paragraph describing various methods of producing imitations of the granulation technique proper.

These general remarks are followed by the classification of objects on which granulated decorations have been used, ranging apparently from personal adornments, through cult objects to weapons.

The second part is devoted to the detailed description of the technique of granulation including the historical background. Apparently the methods of binding small spheres onto metal surfaces are numerous and varied through the centuries and across the globe. Even in antiquity, in the jewellery from Early Dynastic Mesopotamia for example, one can already find two different types of granulation which can often be recognised with the naked eye: one which shows traces of the use of a solder and another where no traces of solder can be found. Reading Wolter's description of various methods of creation of granulation one has the impression that, at least in historical time, there were as many bonding techniques as goldsmiths using granulation. Nevertheless, in early prehistoric times solderless bonding was the most common practice.

The chapter on the technique includes also results of some chemical and microscopic analyses of various types of granulation; the chemical reactions involved in the various processes are carefully explained. The most common utensils and binding agents (organic and inorganic) are described. Additionally there is also included an extensive table representing all known solders used for noble metals throughout history in chronological order (138 alloys in all), giving their composition, liquidus temperatures, the earliest source in which they are mentioned or the earliest object which has been analysed and proved to contain a given type of solder.

All historical jewellery with granulation can be divided on technological grounds into two groups: one in which some sort of solder (usually characteristic for the given time and place) has been used to bond the granules and another where there are no traces of solder. The second group includes most of the jewellery produced before the 1st century AD and also many XIX century objects. In this case the technique most commonly used for bonding included the use of copper salts which reacted with the metal during heating in the presence of charcoal to form an 'invisible' joint or weld between the granule and the base; due to the formation of a lower melting point alloy with copper. This technique has also been used for other fine goldsmiths work and references to the methods used by the artists are numerous. A large field of research into these techniques still remains, of course, by extensive analytical work on ancient granulated jewellery.

The third, and most extensive part of the book comprises an exhaustive history of granulation, embracing not only Europe and the Near East, but also pre-Columbian America, China, Korea, Indonesia and India.

The text on ancient jewellery includes numerous drawings and several sketch-maps supporting the spread of the technique of granulation in prehistoric and antique times. In prehistoric times the method seems to have originated in Sumer and from there it spread through Assyria to Anatolia, Greece and Egypt. Later on Greek and Phoenician colonisation spread the technique throughout the Mediterranean and Black Sea regions. A similar process of diffusion apparently took place in Northern Europe, where the Hallstatt culture acted as the centre influenced by the Scytho-Hellenistic and Etruscan cultures. The history of granulation is taken in the book up to modern times.

The main text of the volume is followed by an appendix which includes extensive quotations from historical sources and documents on granulation, ranging from an Assyrian script to the description of his method for granulation by a modern goldsmith, Reinhold Bothner, written in 1982. This appendix in itself forms an extremely interesting section of the book.

'Die Granulation' by Jochem Wolters is a book which certainly should be included in any library of the history of art or the archaeology and history of precious metal working techniques. The volume will appeal to a wide audience, ranging from students of archaeology and the history of art to silver and goldsmiths interested in applying the technique of granulation today. This book represents the result of exhaustive research supported by a long technological experience and it has been produced in a most careful and elegant form which will appeal also to every book lover.

Z A Stos-Gale

Erratum

In the review of C W Roberts' book on 'A Legacy from Victorian Enterprise' the author was wrongly referred to as 'Charles Roberts'. He wishes it to be known that his names are Colin William.

News and notes

The Manufacture of Copper-Arsenic Alloys in Prehistory

Heather Lechtman (Massachusetts Institute of Technology) has been engaged for several years in research on copper-arsenic alloys (arsenic bronze) and their production in pre-history. Her work includes an assessment of the comparative mechanical properties of the arsenic and tin bronzes as well as an investigation into the extractive metallurgies developed to manufacture copper-arsenic alloys. The studies include bronzes with compositions ranging from 0.5 - 13 weight percent arsenic.

During August 1984, Ronald Tylecote (Institute of Archaeology, University of London) joined Lechtman for a month of experiments in Sussex, England designed to produce copper-arsenic alloys by several methods, including the smelting of sulfarsenide ores of copper. The work, conducted out-of-doors, continued experiments they had begun in Vermont in 1982 when they attempted to smelt rich enargite ores Lechtman had collected from mines in the northern sierra of Peru.

Concentrating on the prehistoric production of arsenical bronzes in the Andean zone of South America, the 1984 experiments in Sussex used Lechtman's ores gathered in the Andes and furnace types considered to have been used in the Central Andes for smelting or refining similar ores [see Shimada, et al, **Science** Vol 216 (1982)].

The investigators designed three experimental approaches to achieve alloys in the composition ranges desired: (1) the addition of arsenic-containing minerals to molten copper; (2) the direct smelting of roasted copper sulfarsenide ores; and (3) the co-smelting of copper sulfarsenide ores with oxide ores of copper. Several small furnaces were built for the smelting experiments, fashioned after those reported by Shimada and his colleagues for the Lambayeque valley, N coastal Peru.

All three sets of procedures resulted in the manufacture of copper-arsenic metal. The smelting experiments were particularly successful in producing plano-convex ingots of solid alloy. The investigators are currently studying these alloys and the mattes and slags associated with them. They hope to publish their findings in about a year's time. Other members of the Sussex team were Roger Adams (Wealden Iron Study Group, Sussex, England), Rodney Clough (Institute of Archaeology, London) and John Merkel (Center for Archaeological Research & Development, Harvard University).

Bryn y Castell Hillfort, Ffestiniog: A Late Prehistoric Ironworking Centre in North Wales, SH 728429.

Excavations by Peter Crew over the last six years are now nearing completion. Over 500 kg of smelting and smithing residues have been recovered, together with anvils, hammer stones and a wide range of other artefacts.

The hillfort 380m asl has three furnaces, one with evidence for an eccentric conical cover and one re-used for smithing. A unique snail-shaped hut had two phases of use, with at least twenty furnaces and hearths. Phase I c 50 BC to 70 AD, Phase II c 150 to 250 AD, with no change in technology and no Romano-British finds, despite a nearby fort and road. Site chronology is based on some twenty radiometric dates mostly archaeomagnetic determinations from the furnaces/hearths, which are particularly suitable material for this technique.

News from Washington DC

Professor Heather Nan Lechtman of MIT has been awarded a MacArthur Prize by the John D and Catherine T MacArthur Foundation. She will receive **$**236,000 over a five-year period. She is Professor of Archaeology and Ancient Technology with a joint appointment in the Department of Humanities and in the Department of Materials Science and Engineering at MIT. She is studying prehistoric technology in the Andes, particularly the archaeometallurgy of this area. Professor Lechtman is also Director of MITs Center for Materials Research in Archaeology and Ethnology (CMRAE). Dorothy Hosler has a two-year postdoctoral fellowship there for the study of prehistoric metallurgies of the Americas, documenting cultural relations between the ancient peoples of western Mexico and the Andes. Professor Lechtman and Dr Hosler are collaborating on a paper for volume 10 of the series 'Advances in Archaeological Method and Theory', edited by Michael B Schiffer, to be published in 1985. Their paper will be on metals and metallurgy, and they welcome suggestions. CMRAE's address is Room 8-138, MIT, Cambridge MA 02139. The telephone number is 617-253-1375.

Bismuth and magnesium were the subjects of two interesting papers published recently on the analyses of bronze artifacts. Professor Robert B Gordon's 'Bismuth bronze from Machu Picchu, Peru' (**Science 223** (10 February 1984) 585-6, with John W Rutledge, also of Yale's Kline Geology Laboratory) reported 18% bismuth in the bronze head of a llama cast onto a low-tin bronze knife blade.

A recent letter to the editor of **Metallography (17** (1984) 215-221) by L E Samuels explained the presence of magnesium, which has been reported occasionally in bronzes from Egypt, as a consequence of corrosion and not an original component of the alloy. Magnesium was detected by electron microprobe in the corroded interdendritic areas of a section supplied by Professor Joshua Pelleg which had been cut from a bronze arrowhead.

A new publication of interest is the Swedish journal for the history of technology, **Polhem, Tidskrift for Teknikhistoria.** It is a quarterly. The ISSN number is 0281-2142, and the subscription is 75 Swedish kroner per year. It is issued by the Swedish National Committee for the History of Technology (Svenska Nationalkommitten for teknikhistoria, SNT) Ingenjorsvetenskapsakademien, Box 5073, 102 42 Stockholm. Stig Blomgren and Erik Tholander have a paper in English on 'A prehistoric engraving tool of nickel-alloyed steel found in Sweden' in volume 1 number 3 (1983) 1-11.

Professor Tohru Ishino (Castings Research Division, Department of Metallurgy, Faculty of Science and Technology, Kinki University, 3-4-1 Kowakae, Higashiosaka 577, Japan) has just published (1984) a third beautifully illustrated volume on Japanese casting: 'Temple Bells in Japan, their History and Casting Technique'. An 18-page booklet with the English translation accompanies the volume, but the diagrams of the casting methods are themselves unusually clear and informative.

The proceedings of the 19th Annual Conference of the Microbeam Analysis Society, Bethlehem, Pennsylvania, 16-20 June 1984: 'Microbeam Analysis 1984', edited by A D Romig, Jr and J I Goldstein, contains the papers from the session on archaeological applications organized by Professor Michael Notis of Lehigh University. All but two of the eleven papers were on metals. They covered a wide range of topics: early copper from the middle east (M R Notis et al 240-2) and from Batan Grande (S J Thorpe and U M Franklin, 227-230), iron in early copper (J F Roeder et al, 243-6), early steel from Jordan (K H Liu et al, 261-3), brazing gold (G Demortier, 249-252), the Inariyama sword (T Murata and M Sasaki, 257-260), Saugus pig iron (K S Vecchio and A R Marder, 247), wrought iron (R B Gordon, 231-4) and the relationship among ore, slag and metal compositions (J A Todd, 235-9). The volume is published by San Francisco Press, Inc, Box 6800, San Francisco CA 94101-6800. The ISSN number is 0278-1727 and the price is **$**30.

Wootz has been produced in the United States by Mr Wallace M Yater of Boonesboro, Maryland, an amateur blacksmith, who was successful in producing a cake this June. It is thought that this is the first wootz produced in the United States using traditional Indian methods. The production of this cake will be the subject of the last article in Yater's four-part series on 'The Legendary Steel of Damascus' in **The Anvil's Ring**, published quarterly by the Artist-Blacksmiths' Association of North America (ABANA). The first three parts of the series were published in Spring 1982 (**10** (1) 2-8), Summer 1983 (**11** (2) 2-13), and Winter 83/84 (**11** (4) 2-17). Back issues are obtainable from Dr Carl VanArnum, ABANA Secretary-Treasurer, PO Box 1191, Gainsville Florida 32602, for **$8** per issue.

The Society of Jewellery Historians has announced that the Third International Symposium on the History of Jewellery Materials and Techniques will be held 4-6 November 1985 in London at the Society of Antiquaries, Burlington House. The British Museum will hold a symposium on Precious Metals: Conservation and Technology immediately following, on 7-8 November 1985. Further information can be obtained from the Hon Secretary of the SJH, Judy Rudoe, Department of Medieval and Later Antiquities, British Museum, London WC1B 3DG England.

It saddens me to have to announce the passing earlier this year after a long illness of one of the pioneers of archaeometry, Professor Earle R Caley of The Ohio State University. His contributions covered many areas but he is perhaps best known to archaeometallurgists as the author of 'The Analysis of Ancient Metals', the standard work in the field for many years. His research materials, including samples, data, correspondence, reprints and books, were generously donated by Mrs Caley to SARCAR, the Smithsonian Archaeometric Research Collections and Records facility where they will become available to other scholars. According to the director, Dr Ronald L Bishop, this is the first major donation to SARCAR. This facility is an activity of the Conservation-Analytical Laboratory, located in new quarters at the Smithsonian's Museum Support Center in Suitland, Maryland.

Dr G Kuppuram (2 Airport Colony, Trichy-620007, Tamilnadu, India) was the editor of the proceedings of the seminar 'Ancient Metal Industries of South India' which was held 15-16 March 1983 at Tamil University. All but one of the papers are in English.

Mr R Srinivasan, a graduate of the metallurgy program at the Indian Institute of Technology in Madras now a student in the history of science at the University of Pennsylvania. He has studied various aspects of South Indian archaeometallurgy and has analysed iron from the Karnataka iron pillar.

If you know of meetings being planned, or have other news to contribute, please call me at 202-287-3733, or write me at the Smithsonian Institution, Washington DC 20560.

Martha Goodway

Abstracts

GENERAL

F Barlow: Ironmaking in the Blast Furnace a Hundred Years Ago. *Refractories Journal, Sept - Oct 1983,* **5,** *18-20.*

In contrast with earlier massive structures of masonry, the blast-furnace of 1883 basically comprised a cylindrical wrought-iron casing internally lined with relatively thin refractory brickwork. The overall height and bosh dia were up to 100 and 25 ft, respectively. With some national and regional variations, the profiles were broadly curvilinear, dimensions and capacities had significantly increased, and charcoal firing had largely given way to the use of coke. With the exceptions of Scotland and south Staffordshire, open tops have been superseded by cup-and-cone arrangements permitting collection of the top gas and its use in heating the Whitwell-or-Cowper-type hot-blast stoves, the refractory structures of which are particularly discussed. As compared with 1860, the output/furnace had almost doubled, and in America a weekly pig-iron production of 1642 short tons has been reported for a 11½ ft hearth furnace blown with a 649° F blast at a pressure of 9 lb/in^2. At that time ironmaking in Japan was being effected in quasi-hemispherical holes in the ground, supplied via one or two clay nozzles with air from an ordinary blacksmith's bellows.

AATA

J E Dutrizac and J B O'Reilly: The Origins of Zinc and Brass. *Canad Inst Metals Bulletin, Sept 1984,* **77 (869),** *69-73.*

Describes the history of brass and zinc making from the Roman period to the mid 19th century, with special emphasis on the European situation.

PTC

G Demortier: Analysis of Gold Jewellery Artifacts; Characterisation of Ancient Gold Solders by PIXE. *Gold Bull, 1984,* **17,** *27-38.*

BAA

D Glascock, T G Spalding, J C Spiers and M F Cornman: Analysis of Copper-Based Metallic Artifacts by Prompt Gamma-ray Neutron Activation Analysis. *Archaeom, 1984,* **26,** *96-103.*

BAA

P N Jones: A Short History of the Attack of Armour. *Metallurgist and Materials Technologist, May 1984,* **16** *(5), 247-250. Illustrated.*

To reproduce conditions at Agincourt (1415) a set of carburized wrought iron bodkin arrowheads (thin dagger type) were shot over velocity measurement devices at wrought iron plates of 3mm, 2mm and 1mm thickness. No penetrations were affected against the 3mm target, indicating that a head protected by a typical helmet would be safe. The 11mm penetration of the 2mm thick plate indicates that a typical breast-plate would protect the thorax from fatal damage. The 40-50mm penetrations of

1mm plate used for leg and arm defences would cause loss of mobility and fighting capacity to arms and legs. Mail armour would afford little protection.

At sea, the passage of cannon balls through ships timbers generated sharp splinters of wood which severely wounded sailors. This was countered by the introduction of the iron-clads. Subsequently development of armour defeating shell led to further development of armour. At Jutland (1916) deficiencies in British magazine safety features and inability of British shells to perforate armour before detonation, due to unstable explosive, inadequate fusing and poor metallurgical heat-treatment practice of the shell bodies gave rise to much more serious damage in British ships as compared to the German ships despite the use of similar thickness of armour.

A similar situation arose at Operation Goodwood (1944) when the guns on German tanks were much more effective against armour than those in British tanks.

APG

W W Krysko and J Krysko: Contribution to the History of Foundry Technology. *Giesserei Dec 1983,* **70** *(26), 692-698 in German.*

The beginnings of metallurgy, starting from the melting of Pb 9000 to 7000 BC are reviewed. Egyptian sculptures in Pb of 3800 BC are illustrated as examples of early specimens found in the British Museum. The beginnings of castings in open forms and of mass production in 2000 BC of artistic castings are examined. Techniques of wax melting and of hollow parts casting are traced. The paper gives its attention to artistic castings and discusses the later developments in Greece, Lebanon and other countries. Castings of early bronze and Fe figures are included. 26 ref.

AATA

T Lopez Navarro: The History of Cold Forming. *Deformacion Met June 1983,* **85,** *28-38 in Spanish.*

The history of cold forming is studied with reference to the techniques used by ancient man to manufacture jewellery, necklets, safety pins, funeral masks etc. The processes of stamping, wire drawing and deep drawing as used by ancient man are described and the metal working defects found on archaeological finds are analyzed to throw light on the precise manufacturing routes.

AATA

P J MacKinnon: The Early History of the Electrolytic Zinc Process. *Can Inst Metals Bulletin, Oct 1984,* **77 (870),** *86.91.*

Brief history from the L'Etrange process of the 1880s, through the developments in Germany, France, the USA and Britain and the Commonwealth during this century to the present dominant position of the electrolytic process in zinc production in the world today.

PTC

F R Morral: Manganese: a Chronology and a Bibliography. *Canadian Mining and Metallurgical Bulletin, Feb 1984,* **77 (862),** *72-75.*

A chronology of important dates in the discovery, use and production of Mn is presented. Important historical and current references on Mn are noted. World-wide production of Mn ore is tabulated for 1960, 1970 and 1980. Numerous ref.

AATA

D W Paddock: Assaying and Sampling: The State of the Art. *Metal Bulletin Monthly, Jan 1984,* **157,** *78-82.*

After briefly reviewing the occurrence and extraction of metals and the range of uses to which they can be applied the four main techniques currently in use for the analysis of metals and their alloys are described. They are: emission spectrography, used for the rapid analysis of steels, Al and Cu-base alloys; inductively coupled plasma emission spectrophotometry for the rapid and simultaneous analysis of major, minor and trace elements in all types of metal materials, including ores, minerals, steels, Al alloys, Cu alloys, Ni alloys and Ti alloys; atomic absorption spectroscopy for the analysis of minor and trace elements in alloys, metals, ores and minerals; and X-ray fluorescence spectrometry which is particularly useful in determining elements that are difficult to separate by chemical means, such as Nb and Ta, Hf and Zr or the rare earth elements. The role of independent analysts is also briefly discussed.

AATA

U Ruoff: Von der Scharfe bronzezeitlicher 'Rasiermesser' [The sharpness of Bronze Age Razors (a practical demonstration)], *Archaol Korrespondenzbl, 1983,* **13,** *459, pls.*

BAA

A Smith: Early Product Finishing: I, *Product Finishing, June 1983,* **36 (6),** *40-41.*

The origins and the original 1876 specification of the Barff process for forming a protective Fe_3O_4 film on iron and steel by decomposing steam on the heated surfaces are presented, the procedure described, the early apparatus illustrated. The lives of the Bowers and their extension of the Barff technique by introducing air and CO_2 as the reaction media are also discussed. 10 ref.

AATA

C Walton: Enamelling I : Introduction and Cutting Cells for Champleve Enamelling. *Aurum 1983,* **16,** *33-41.*

Work at C F Barnes and Co, London, on enamelling Au jewellery is cited. Enamelling is defined; transparent, translucent and opaque enamels and flux, are considered. The four main types of enamelling are discussed and illustrated; these are champlevé, basse taille, cloisonné and plique à jour. Techniques of champleve, cutting cells for champleve and metal preparation are included.

AATA

BRITAIN

(Ed anon): Tour into Cornwall to the Land's End . . . describing the Scilly Isles, the tin mines, Portsmouth, Stonehenge, etc etc. In letters by James Forbes to his wife's sister Ann . . . in 1794. *J Roy Inst Cornwall, 1983,* **9,** *146-206, refs.*

BAA

K Branigan and J Collis: Roman pigs – and unurned income! (Two very large lead ingots; Bronze Age urn at Carsington Reservoir, Derbys). *Rescue News, 1984,* **33,** *5, pl.*

BAA

C S Briggs: Copper mining at Mount Gabriel, Co Cork: Bronze Age bonanza or post-famine fiasco? *Proc Prehist Soc 1983,* **49,** *317-33, pl, figs, refs.*

BAA

G Briscoe: Bristol's Old Lead Shot Tower. *Industrial Archaeology. Spring (no year!),* **17** *(1), 35-38, 41-43, illustrated.*

An outline history of the first lead shot tower, built to exploit the 1782 patent of William Watts and demolished in 1968.

APG

R Brownsword and E E H Pitt: X-ray Fluorescence Analysis of English 13th - 16th Century Pewter Flatware. *Archaeometry, 1984,* **26** *(2) pp 237-244.*

Most of the thirty-six pewter items were found to have been made from high quality tin-rich alloys with low lead content, hardened with a small amount (0.5 - 3.0%) of copper; these were thought to be from the later part of the period. Three items, one with the highest copper content of all the alloys, were thought to be from the earlier part of the period. Five items with up to 2% of copper hardener but with lead levels up to 26.5% were though to be of provincial origin. A possible correlation of alloy composition and date and place of manufacture with rim-form is discussed. A wavelength-dispersive technique was used for the analyses.

Author

R Brownsword and E E H Pitt: A 16th Century Stone Spoon-Mould from Coventry. *Metallurgist and Materials Technologist. May 1984,* **16** *(5), 246. Illustrated.*

Made by turning and carving a piece of Liassic mudstone, the fragment was evidently discarded after repeated use had caused heat cracking. The technique for casting pewter spoon bowls is discussed.

APG

R Brownsword and E E H Pitt: A technical note on some 13th century steelyard weights (correlation between alloy composition and armorial bearings). *Medieval Archaeol, 1983,* **27***, 158-9, refs.* *BAA*

R Chadwick: Copper: the British Contribution. *Canadian Mining and Metallurgical Bulletin, Oct 1983,* **76 (858)***, 84-88.*

A chronological review from birth (1568) to demise (1980) of Cu smelting at Swansea on the South Wales Coast in UK is presented. Topics discussed are: ore purchasing methods; terms for leasing, including a sample lease writ, smelting companies from big land owners; a copy of the flow sheet for Welsh Cu smelting process developed in 1811. Strategies used to combat the 'Cu smoke' nuisance, gaseous releases containing mainly $S0_2$ and As_20_3 from the smelters at Tawe since 1717 are addressed. Evolution of the methods for producing sulphuric acid from $S0_2$ emissions and the subsequent use of H_2S0_4 in the production of other chemicals, such as HC1, $CuS0_4$ etc, and the manufacture and uses of other alloys at the various Cu smelters are also discussed. 23 ref.

AATA

C A Morris: A Late Saxon hoard of iron and copper-alloy artefacts from Nazeling, Essex. (Metalworker's hoard, 11th century deposition?). *Medieval Archaeol, 1983,* **27***, 27-39, pl, figs, refs.* *BAA*

S M Pearce: The Bronze Age metalwork of south-western Britain. *Oxford, Brit Archaeol Rep Brit Ser, 1983,* **120** *(i-ii), 740 pp, pls, figs, tables, ref. Price £30 for two vols (paper: 0 86054 242 4).*

BAA

M L Pearl: John Wilkinson, 1728-1808. Ironmaster and Inventor. *Metals Society World, May 1984,* **3***, (5), 14, 15.*

A brief biography.

APG

J Peatman: Sheffield Industrial Museum (Kelham Island); an exciting new approach to industrial museums. *Ind Archaeol (1983?),* **17 (1)***, 27-34, pls.*

BAA

D R Perkins: An analysis of lead musket shot from the wreck of an early 18th century man-of-war. *Int J Naut Archaeol. Underwater Explor, 1983,* **12***, 339-42, figs, tables.*

BAA

A Phillips: Early Colchester foundries (early 19th century, history and products). *Essex Archaeol Hist, 3 ser, 1982,* **14***, 102-110, pls, ref.*

BAA

J F Potter: Iron working in the vicinity of Weybridge, Surrey, (Iron Age and post-medieval). *Ind Archaeol Rev 1982,* **6***, 211-23, pls, fig, refs.*

BAA

H S Green: A Late Bronze Age gold hoard from Llanarmon-yn-Ial, Clwyd. *Antiq J 1983,* **63***, 384-7, fig, tables (refs p 392).* Gives analyses

BAA

H S Green, G Guilbert and M Cowell: Two gold bracelets from Maesmelan Farm, Powys ('Capel Isaf' type, MBA). *Bull Board Celtic Stud, 1983,* **30***, 394-8, pls. Analyses.*

BAA

J Hume: The presentation of an industrial monument. Bonawe iron works (Strathclyde). *Popular Archaeol, May 1984,* **5 (11)***, 44-7, pls.* (See also 84/1855).

BAA

B G Scott: An Early Irish Law Tract on the Blacksmith's Forge. *J Irish Archaeology, 1983,* **1***, 59-62.*

The text of an 8th century tract is summarised and considered in relation to the work of a blacksmith of that era, often carried out at best under flimsy structures open to domestic livestock etc. It is tempting to envisage the compiler as one who at some time had worked with hot metal himself.

APG

E C Scrivenor, E V Cooper, M C George and T J Shepherd: Gold-bearing Carbonate Veins in the Middle-Devonian Limestone of Hope's Nose, Torquay. *Trans Proc Torquay, Nat Hist Soc 1982-83,* **19***, 19-21 (Publ 1984).* An abstract. Gives mineralogy and petrology.

BAA

A Sheridan: A reconsideration of the origins of Irish metallurgy. *J Ir Archaeol, 1983,* **1***, 11-19, figs, refs.*

BAA

M L Simpson: A Cast Bronze Cauldron from Downpatrick, County Down. *Ulster J Arch 1983,* **46***, 162-164 (publ 1984).*

A typical 2-handled, 3-legged bronze cauldron of the period 14 - 17th century. The composition was 13.45 Pb, 7.08% Sn with 0.86 P, 0.50 Sb and 0.54 As. This compares well with Brownsword's figures for the early period (13 - 14th centuries).

RFT

Kim Colebrook: A History of the British Ironworks, Abersychan in Gwent. Local History. *The Journal of the Gwent local History Council No 54, Spring 1983, 6-22.*

The historical importance of industry in the Eastern Valley and the well documented centres of Blaenavon and Pontypool are noted, and attention is drawn to the need for research into other valley sites. Production commenced at the Abersychan ironworks in 1827, after serious geological problems at the site had been overcome. Six furnaces, each 48 ft high, with generous ancillary equipment were provided. The rolling of iron nails was begun in 1840 and by 1850 this produce was the entire commercial output. The company name was changed from British Iron Co to New British Iron Co in 1843 and in 1843 the lease was transferred to the Ebbw Vale Co. Production later centred upon Spiegeleisen, essential to the production of steel by the Bessemer process, which was in use at Ebbw Vale. Production ceased in 1881. Many particulars are given as to history, production, processes, wage rates, costs and other matters, illustrated by 4 photographs, 6 diagrams, a map, references and a bibliography.

HWP

C McCombe: The Early Development of Ironfounding in North-West England. *Foundry Trade Journal, 1984, June 21, 562-567.*

The burgeoning industries of Merseyside, Lancashire and the coastal strip of Cumbria were supported throughout the nineteenth century by the ironfounders of the north west. The writer shows that this dependance of the products of the foundry was especially true of the builders of textile machinery, marine and stationary steam engines, machine tools, ordnance, sugar refining equipment and steam locomotives. Reference is also made to some architectural uses of iron castings in the region and to the formation of the Friendly Ironmoulder's Society in 1809.

Author

G P Stell and G D Hay: Bonawe iron furnace (official guide). *Edinburgh, HMSO, 1984, 32 pp, pls, figs, refs, Price £0.75. (Paper: 0 11 492350 7).*

BAA

J Ypey: Rekonstruktionsversuch der Schwertklinge von Sutton Hoo [Reconstruction of the Sutton Hoo sword blade (damascening pattern)]. *Archaeol Korrespondenzbl, 1983,* **13**, *495-8, figs, refs.* *BAA*

E G West: Eros — an historical note on its Metallurgy. *Metallurgist & Materials Technologist, Nov 1984,* **16** *(11), 00-00.*

Various analyses have shown the presence of 0.5 - 1.0% Si, 0.27 - 1.5% Fe, 0.004 - 0.013% Mn, 0.001 - 0.009% Mg, 0.017 - 0.06% Zn and 0.01 to 0.75% Cu in the aluminium. Details are given of the inspection and cleaning carried out in 1947. A brief account is given of the origin of the statue and of the circumstances leading to the choice of aluminium. A replica of the statue was erected in Liverpool in the 1920s, but this was cast in an unsuitable aluminium alloy which had severely corroded thirty years later.

APG

EUROPE

OFFA - 40, 1983.

This is a festschrift to Hans Hingst and as such it is appropriate that most of it should be devoted to Early Iron. It contains the Proceedings of the Comité pour Sidérurgie Ancienne's Conference at Senkelmarkt in Schlesvig-Holstein held in November 1980. The volume as a whole forms an excellent statement on current research in early iron production generally and specifically on North/Central Europe. The following papers on iron metallurgy are included:

B G Scott: Some Problems in the Reconstruction and Interpretation of Indo-European Metallurgical Vocabularies, *pp 19-28.*

John Alexander: Some Neglected Factors in the Spread of Iron-Using in Europe. *pp 29-33.*

Z Bukowski: Neue Ergebnisse zur Problematik de Ältesten Eisenbearbeitung und Gewinnung im Bereich der Lausitzer Kultur, *pp 35-46.*

K Bielenin: Der Rennfeurrofen mit eingetieftem Herd und Seine Formen in Polen, *pp 47-61.*

R Pleiner: Neue Entdeckungen von römerzeitlichen Eisenhütten in den böhmisch mährischen Siedlungsräumen, *pp 63-68.*

A Hauptmann und Gerd Weisgerber: Eisen im Siegerland ein archaometallürgisches Projekt, *pp 69-75.*

P Galliou: Iron in Iron Age and Roman Armorica, *pp 77-83.*

M Mangin: Le Travail du fer et son role dans la naissance et la development d'Alesia, *pp 85-99.*

J S Brongers: Eisenproduktion aus heimschem Erz in den Niederlanden — end historischer Überblick, *pp 101-102.*

H Cleere: The Organisation of the Iron Industry in the Western Roman Provinces in the Early Empire, with Special Reference to Britain, *pp 103-114.*

R F Tylecote and R E Clough: Recent Bog Iron Ore Analyses and the Smelting of Pyrite Nodules, *pp 115-118.*

I Martens: The Norwegian Bloomery Furnaces and their Relation to the European Finds, *pp 119-224.*

A B Johansen: Problems of Origin and Cultural Background in Early Iron-Production along the Timber-line in South Norway, *pp 125-127.*

A M Rosenqvist: Report on Chemical and Mineralogical Analyses of Norwegian Ores, Slags and Iron, *pp 129-137.*

Gert Magnusson: Some Iron Production Sites and their Location, *pp 139-151.*

H Barbre and R Thomsen: Rekonstruktionsversuche zur fruhgeschichtlichen Eisengewinnung, *pp 153-156.*

J Piaskowski: Hypothetische Eigenschaften des in Schlesvig-Holstein geschmolzenen Rennfeuereisens, *pp 157-162.*

H Hingst: Das Eisenverhuttungsrevier auf dem Kammberg-Gelande in Joldelund, Kreis Nordfriesland, *pp 163-176.*

T Utecht and H Stumpel: Magnetische Sondierung im Eisenverhuttungsrevier von Joldelund, Kr Nordfriesland, *pp 177-182.*

I Keesmann, J Preuss and J Endres: Eisengewinnung aus lateritischen Erzen, Ruki Region, Provinz, Equateur-Zaire, *pp 183-190.*

G Bauhoff: Zur Geschichte Gusseiserner Ofenplatten, *pp 191-197.*

K W Struve: Zwei getriebene Bronzetassen der alteren Bronzezeit aus Schleswig-Holstein, *pp 241-256.*

M Müller-Wille and K-H Willroth: Zur eisenzeitlichen und fruhmittelalterlichen Neusiedlung von Angeln und Schwansen, *pp 275-320.*

G Ardwidsson and G Berg: The Mastermyr find. A Viking Age tool chest from Gotland. *Stockholm, Almqvist and Wiksell International, 1983, 57, pls, figs, refs, index (91 7402 129 X).*

BAA

S D Cappelen: Ulelos Jernvaerk: a lot that is old and a lot that is new. *Jernindustri, April 1983,* **64(4),** *101-104 (in Norwegian).*

325 years have seen many changes at the works, including the recent installation of a foundry plant incorporating two 2400 kw ASEA induction furnaces each capable of melting 4 t in 75 min. With a total production capacity of > 8000 t/year, wood fired furnaces now account for only 10% of production, compared with 80% thirty years ago.

AATA

J Day: The Continental Origins of Bristol Brass. *Industrial Archaeology Review, Autumn 1984,* **7 (1),** *32-56.*

Gives a brief history of brass and zinc making at Altenberg (Vieille Montagne), and Stolberg, in the vicinity of Aachen, together with a good description of the traces of the industry which survive to this day.

It is known that from Elizabethan times on, brassworkers from this area were encouraged to come and establish brass making industries in Britain. More specifically many Dutch and Flemish workers came to the Bristol area in the early 18th century connected with the naissant brass industry there. It is suggested that at least some of these workers came from Stolberg, although tried evidence is still lacking.

PTC

R Maddin, JD Muhly and T S Wheeler: Metal Working. Excavations at Athienou, Cyprus. *Kedem 16, Jerusalem 1983, pp 132-140.*

The evidence suggests strongly that on this site chalcopyrite ore was roasted to form the raw material from which copper was extracted in the 3rd millenium BCE. Alloying, casting and working may also have been carried out there. The use of rich ores and the nature of the process accounts for the absence of the usual slag residues. 120 kg of nodules, 2 - 6 cm diameter and 200 kg of slightly larger chunks about 10 cm diameter in fact represent the waste product. The structure of these chunks is investigated and probable origins discussed. It is suggested that Cyprus was an administrative centre for the distribution of metals in the Late Bronze Age, both importing some metals, probably tin and perhaps copper and contributing local copper to the trading effort. The authors speculate that (olive) oil-firing may have been used for roasting.

APG

W Menghin: Das Schwert im fruhen Mittelalter. [The early Medieval Sword (c AD 430-720)]. *Stuttgart, Konrad Theiss, 1983, 368 pp, pls, figs, tables, refs, sheets in rear pocket. Price not known (3 8062 0362 8).*

BAA

J Piaskowski: Metallographische Untersuchungen zur Eisen und Stahltechnologie in Haithabu. *Berichte uber die Ausgrabungen in Haithabu 1983,* **18,** *45-62, in German.*

Detailed metallographic description of the iron work from Haithabu especially relating the composition and inclusions in the iron to the ores and the iron smelting process.

PTC

Christiane Eluère. Two unique golden helmets. *Gold Bulletin, 1984,* **17** *(3), 110-111.*

Two iron helmets, covered with bronze sheet, decorated with repousse patterns, coated with a thin sheet of gold foil are described. Their style and design would appear to date them between the third and fourth centuries BC.

ECJT

Gernot Piccottini and Ricard Mauterer. Kupferlegierungen auf dem Magdalensberg. *Zeitschrift f Archäometry, 1983,* **1,** *20-26 (to be continued).*

This paper is the first in a series of publications about non-ferrous objects and describes the development of a new and simplified method of determination for tin in archaeological objects. Analyses of furniture mountings are presented and discussed. These are mostly brasses and date from the Roman period.

Authors

Marek Gedl. Anfänge der Kenntnis des Eisens im Gebiet Polens. *Zeitschrift f Archaeometrie, 1983,* **1,** *8-19.*

An attempt has been made to describe the beginning of iron production in Poland. A series of results of excavations is evaluated as well as different publications in this field. The probability of different advanced hypotheses is discussed.

Author

Hans Jorg Köstler. Der Neubau des Holzkohlenhochofens Radwerk III in Vordernberg (Steiermark). *Der Anschnitt, 1984,* **36** *(2-3), 72-78.*

19th century furnaces with hot blast; some very interesting stove positions.

RFT

M Pietsch: Die römischen Eisenwerkzeuge von Saalburg, Feldberg und Zugmantel (Catalogue of Roman iron tools from Saalburg, Feldberg and Zugmantel). *Saalburg Jahrb, 1983,* **39,** *5 - 132, pls, figs, refs, index.*

BAA

E Riedel: Bibliography of the Raw Materials and Technology of Archaeological Iron Objects. (In German). *Berliner Beiträge Archäom, 1983,* **8,** *337-65,*

BAA

V Rychner: La Matière Première des Bronziers Lacustres. (The Earliest Material from the Lake-dwelling Bronze Workers). *Archaeologie Suisse, 1984,* **7 (2)**, *73-78.*

Deals mainly with the composition of small plano-convex ingots and waste material from Auvernier and Corcellettes. The ingots are impure coppers mainly containing As and Sb. A bracelet and a winged axe are of similar composition while the other objects and waste metal are tin bronzes and leaded-tin bronzes.

RFT

J-P Taavitsainen (with contributions from R Rosenberg and K A Kinnunen). A Copper Ring from Suovaara in Polvijarvi, Northern Karelia. *Fannoscandia antiqua I, 1982, pp 41-49. (In English).*

A Copper Age (mid 2nd millennium), copper ring about 5 cm dia of high purity thought to be made from native copper. The main impurities are As 380 and W 110 ppm. Unfortunately no structural examination has been made. It is considered that the copper is neither from Finland nor the USSR area of Karelia, but that it may originate outside the region of the last glaciation.

RFT

R Pleiner: Zur Technik der Iron Messerklingen Aus Haithabu, *Berichte uber die Ausgrabungen in Haithabu, 1983,* **18**, *63-92 (In German).*

A detailed and well illustrated metallographic and technical description of iron blades from the 9 - 10th century Viking settlement of Haithabu in Schleswig-Holstein.

PTC

R Pleiner and D Bialekova: The Beginnings of Metallurgy on the Territory of Czechoslovakia. *Bulletin of the Metals Museum, Japan Institute of Metals, December 1982,* **7**, *16-28. (In English, illustrated).*

Remains of copper wire ornaments occur earlier than 3000 BC. Several clay crucibles used for melting date from 3000 BC, The introduction of alloying and the increasing use of metal during the Bronze Age is outlined. Systematic production of iron began in Asia Minor in the second millenium BC but large-scale production of iron did not begin in Czechoslovakia until the latter half of the first millenium BC. The development of ferrous metallurgy is traced to the end of the 13th century AD.

APG

B Rothenburg: Ancient Copper Mines in Spain. *Bulletin of the Metals Museum 1983,* **8**, *22.*

Survey article of the author's excavations in SW Spain at Chinflon, and Rio Tinto from Chalcolithic to Roman times.

PTC

T A Wertime: The Furnace Versus the Goat. The Pyrotechnologic Industries and Mediterranean Deforestation in Antiquity. *J Field Archaeology, 1983,* **10**, *445 - 452. (Based on contribution to 1978 symposium on Deforestation, Erosion and Ecology in the Ancient Mediterranean and Middle East).*

This paper presents arguments and data to support the hypothesis that pyrotechnologic industries (lime-burning, ceramics, mining and metal extraction) were the prime factor in the deforestation of Mediterranean lands during antiquity, and that destruction by goats were a secondary, later factor. Energy costs of metallurgy and pyrotechnology for the whole of ancient history at Cyprus and Rio Tinto and for the 5th-1st centuries BC at Laurion and Populonia are estimated eg for Cyprus, 5 million tons of charcoal equivalent to 5 million acres of coppice, with another 5 million acres required for other purposes. Evidence of the need to economise in fuel in these areas is presented eg avoidance of roasting sulphide ores, recourse to fluxing techniques, tolerating loss of lead in slag, shift from copper to iron production in Cyprus. Evidence of transport of fuel to the ore, or ore to fuel is presented.

APG

K D White: Greek and Roman technology (general technological development; individual topics). *London, Thames and Hudson, 1984, 272 pp, pls, figs, tables, refs, index. Some on metallurgy, mainly on agriculture. Price £18.50 (0 500 40044 X).*

BAA

A J Wilson: New Light on Mining's Ancient History. *Mining Magazine. May 1983, 372-375. Illustrated.*

Based on the report 'Studies in Ancient Mining and Metallurgy in South-West Spain' by B Rothenburg and A Blanco-Freijeiro, published in 1982 by the Institute for Archaeo-Metallurgical Studies and distributed by Thames and Hudson Ltd, the article outlines the metallurgical history of the Huelva province as it is presently understood. The mines and stone mining tools dating from the Early Copper Age (4th and 3rd millennium BC) are the earliest known in Western Europe. A great deal was then known about fluxing, ore dressing, the preparation of a well balanced smelting charge. Developments in the area are outlined until in the second century AD the extensive Roman operations were brought to an end.

APG

S K Zacharias: Brass Making in Medieval Western Europe. *Canadian Mining and Metallurgical Bulletin, March 1984,* **77**, *(863), 110-114.*

The changes in Western brass making are traced by these historical metallurgy notes. The calamine process ($ZnCO_3$ plus charcoal in a closed crucible) was the only process used in Western Europe prior to the 18th century but the alloying process later took over. The Chinese had begun to produce metallic Zn by at least the 9th to 10th century AD while European Zn was not produced on an industrial scale until after 1743 AD. The ancient calamine and alloying practices are described and archaeological considerations with comments on the likely Zn content of brasses are presented.

AATA

G Zimmer: Giessereieinrichtungen im Kerameikos, Athens. (Casting Installations in Kerameikos). *Arch Anzeiger, 1984, 63 - 83 (offprint).*

Statue casting pits and moulds, crucible and tuyeres fragments. The remains cover the period 5th cent BC to 1st cent AD.

RFT

AFRICA

T Shaw and P T Craddock: Ghanaian and Coptic Brass Lamps. *Antiquity 1984,* **58,** *126-128.*

Several antiquities previously thought to be coptic on stylistic grounds have been shown to be 19th century on the basis of composition. They have over 33% of zinc, a figure never exceeded by the old cementation process which was not finally superseded in Europe until the 1850s.

PTC

Andrew Oddy: Gold in the Southern African Iron Age. *Gold Bulletin, 1984,* **17** *(2), 70-78.*

The finds of worked gold artifacts at Mapungubwe and other areas in the Southern African interior dating back to about the end of the first millennium AD are of great interest in revealing the level and techniques of manufacturing carried on in the region at this time.

Author

AMERICA

T Dalyell: Going for Gold. *New Scientist, 3rd November 1983,* **100 (1382),** *393-394.*

Au winning and working by the pre-1532 Incas are discussed in the light of exhibits in the Lima Museum of Gold. The Au largely washed from river gravels, was blowpipe-melted in baked clay/lime pot crucibles to give a relatively low melting point Au alloy which could be beaten to provide thin plates for covering base metals, etc. Various shades of Au were produced by careful alloying and some Inca cultures formed Au artefacts by lost-wax casting.

AATA

J E Dutrizac: The End of Horizontal Zinc Retorting in the United States. *Can Inst Met Bulletin, Feb 1983,* **76 (850),** *99-101.*

The history of the National Zinc Co smelters at Bartlesville, Oklahoma, USA is given, with detailed, illustrated description of the horizontal retort process which ran up to 1976. Zinc is now produced electrolytically on the site but some of the old furnaces still charged with retorts have been preserved.

PTC

D J Frurip, R Malewicki and D P Heldman. Colonial Nails from Michilimackinac. Differentiation by Chemical and Statistical Analysis. *Archaeological Completion Report Series,* **7,** *Mackinac Island State Park Commission, Michigan, 1983, pp 83.*

17 inclusions in 5 British nails and 10 inclusions in 3 French nails were semi-quantitatively analysed for silicon, phosphorus, sulphur, potassium, calcium and manganese in the scanning electron microscope. Using a computer, discriminant analysis of the result was carried out. It was shown that by using an appropriate technique, the origin of the nail containing each inclusion could be predicted with a high degree of accuracy. Silicon, phosphorus and manganese were the elements chiefly responsible for the separation. Sulphur, potassium, and calcium levels contributed much less. The former three elements would be present as a result of the composition of the ore, the latter three elements as a result of smelting, and refining techniques. Also discussed are eighteenth-century nail making practices, smelting and forging techniques and the manufacture of machine-cut nails.

APG

M Fiset, T Vo Van and A Galibois: Objects from the 'Forges of St Maurice': Metallographic and Chemical Study. *Canadian Mining and Metallurgical Bulletin, March 1984,* **77 (863),** *115-121. (In French).*

A group of 22 specimens originating from 'Les Forges du St Maurice' has been systematically studied by chemical analysis and metallographic examination to determine their characteristics and to evaluate their metallurgical quality. Most forged iron and steel samples are heterogeneous from both their microstructure and their chemical composition. Observation of a few finished products has shown that surface heat treating was applied although its metallurgical control was rather empirical.

AATA

R B Gordon and J W Rutledge: Bismuth Bronze from Machu Picchu, Peru. *Science, 10th Feb 1984,* **223 (4636),** *585 - 586.*

The decorative bronze handle of a tumi excavated at the Inca city of Machu Picchu, Peru, contains 18% Bi and appears to be the first known example of the use of Bi with Sn to make bronze. The alloy is not embrittled by the Bi because the Bi-rich constituent does not penetrate the grain boundaries of the matrix phase. The use of Bi facilitates the duplex casting process by which the tumi was made and forms an alloy of unusual colour. 27 ref.

AATA

H Lechtman: Andean Value Systems and the Development of Prehistoric Metallurgy. *Technology and Culture, Jan 1984,* **25,** *(1), 1-36.*

The author outlines techniques of gilding and silvering by depletion and by electrochemical replacement and shows how Andean metal workers would have used these techniques with the materials and salts which were available to them to make the characteristic artefacts which are discussed. Cultural, social and geographical conditions are considered to be responsible both for the evolution of these metallurgical techniques and for the complete absence of ferrous metallurgy in the area until the Spanish conquest.

APG

D C Stapp: Trace Element Analysis of Copper Trade Goods from the Pacific Northwest. *Paper presented at the 184th American Chemical Society National Meeting Kansas City, Missouri. Sept 1982*

X-ray fluorescence spectroscopical analysis was conducted on sheet copper and brass artefacts recovered from Indian burials dated to approximately 1800. Eleven types of copper-base metal sheeting were identified. It is shown that the copper originated from the sea-based fur trade rather than land-based trade.

APG

OA Tovar: Ferrominera: History, Present Prospects and Long Term Plans. *(Proc conf). 2nd International Iron Ore Symposium, Frankfurt, West Germany, 23-24th March 1981 G1 - G11.*

Includes a brief history of iron ore mining in Venezuela from 1743 to the present.

AATA

ASIA

Anon: Cast Iron Treasures from Korea. *Foundry Trade Journal, 1984,* **156,** *(3282), 261-262.*

Some exhibits in an exhibition of Korean art held at the British museum are briefly described. Technical features of a 9th or 10th century cast iron Buddha are illustrated and discussed.

APG

P T Craddock, I Freestone, L K Gurjar, K T M Hegde and I Sonowane. Early Zinc Production in India. *The Mining Magazine Jan 1985, 45-52.*

First detailed description of the excavation of banks of intact zinc smelting furnaces from Zawar, India. Each furnace contained 36 clay retorts. The process is seen as an interesting stage in the development of chemical industry and is probably ancestral to the process developed at Bristol by Champion, and all subsequent high temperature distillation processes.

PTC

N Gale: Mystery of Timna Iron Solved by Lead Isotope 'fingerprinting'. *IAMS newsletter, June 1984,* **6,** *6-8.*

Many rings and other small items of iron have been found at Timna amongst the more familiar copper artifacts and remains of copper mining and smelting. The origin of this iron has now been shown to be the local iron minerals normally used as fluxes in the copper smelting process. The presence of 0.1 - 2.0% of copper within the iron artefacts suggests the iron was made at Timna as a by-product of the copper refining. The raw copper was rich in iron which could be successfully separated, removed and worked.

PTC

P T Craddock: Tin and Tin Solder in Sumer: Preliminary Comments. *MASCA June 1984* **3 (1),** *7-9.*

Presents the analyses of 25 Sumerian bronzes from Wooley's excavations. Both arsenical copper and tin bronze are represented. One ED III copper bowl circa 2500 BC had silver lugs attached by tin solder.

PTC

K Horikawa: The Ancient Nails of Horyusi Temple Restoration of the Tatara Ironmaking Process. *Bulletin of the Metals Museum, Japan Institute of Metals, Dec 1982,* **7,** *29-38. (In English, illustrated).*

28 nails manufactured at various dates between 607 and 1833 AD were examined. Chemical analysis indicated that the carbon contents ranged from 0.09 to 0.45%, sulphur from 0.001 and 0.063%, phosphorus 0.009 to 0.074%, but very low levels of other metallic elements. Metallography showed very uneven carbon distribution and many nonmetallic inclusions. Later, a Tatara furnace was constructed and used to produce metal. 20 tons of iron sand and 22 tons charcoal produced nearly 4 tons crude steel and 0.7 tons pig iron. The results of chemical analyses are reported.

Experiments showed that the steel produced forge welded very well after it had been melted, cast, and forged to bar, as did steel of similar composition made by melting electrolytic iron and charcoal. However, a decarburised surface layer 0.6 to 2mm deep appeared to be necessary for good forge welding of the unmelted steel. As a result of these experiments, the author now considers that the nails were not made by forge welding steels of different compositions, but by simply reheating and forging crude iron made by the ancient method.

APG

U M Franklin: On Bronze and Other Metals in Early China. Chapter in The Origins of Chinese Civilization. *Edited D N Keightly. Univ of California Press, Berkeley, 1983, pp 279-296.*

A social order in which a large pool of forced labour could be mobilized and maintained to mine the ore and extract the metal was necessary for large-scale bronze production. In an appendix, the almost complete absence in early China of personal ornaments made of metal (eg metal bracelets) is discussed.

APG

H J Ming: Stack Moulding Techniques in Ancient China. *Foundry Trade International, December 1983, 242-246. Illustrated.*

The technique of stack-moulding appears to have been introduced in about 620 BC. Detailed examination of moulds and a firing kiln from the period AD 9 - 23, and the results of modern experimental work have enabled the processes and materials used to be described in detail. Attainment of a very high standard of design, patternmaking, moulding material preparation, moulding, coremaking, firing, metal melting and pouring enabled very large quantities (over 10^9) of identical castings of high quality components to be produced.

APG

Z Shoukang: Early Bronze in China. *Bulletin of the Metals Museum, Japan Institute of Metals, December 1982,* **7,** *3-15 (In English, illustrated).*

Examination of artefacts from recent excavations shows that Chinese bronze culture appeared before 2000 BC. Nearly all the artefacts contained no arsenic and only a few pieces show traces of it. Most of the artefacts were tools and in addition to tin bronze finds include lead-tin bronze, lead-copper and occasionally brass. Details are given of open pits, underground mines and adits and the remains of furnaces, slags and metal associated with smelting in the period 1000 BC to AD 20 at Tonglushan, Hubei Province. The production of tin began no later than the Shang dynasty (16th - 11th century BC). No remains from this era have yet been discovered, but a description of the process published in 1673 is quoted. The preparation and use of bronze is discussed and 'six rules for alloying' written down in the period 770 - 476 BC are reproduced and discussed.

APG

J F Merkel: Summary of Experimental Results for Late Bronze Age Copper Smelting and Refining. *MASCA J 1983,* **2,** *173-178.*

BAA

S Wachsmann and Kurt Raveh: Concerning a Lead Ingot Fragment from La-Hotrim, Isreal. *Naut Arch 1984,* **13,** *(2), 169-176.*

This fragment which has been cut-off through a hole could possibly be a piece of the type of ingot shown in Egyptian tomb painting along with copper oxide ingots. It measures 12 x 7.5 x 2cm thick. Two are to be seen being carried by porters in the tomb of Amenemopet (Thutmose IV).

RFT

B Rothenberg: Explorations and Archaeometallurgy in the Arabah Valley (Israel). *Bulletin of the Metals Museum (Japan), 1983,* **8,** *1-16.*

Article summarizing survey and excavations over the past 25 years on copper smelting sites dating from Chalcolithic to Roman times.

PTC

L Willies: Ancient Lead and Zinc Mining in Rajasthan, India. *World Archaeology, 1984,* **16 (2),** *222-233.*

Lead and zinc mines in Rajasthan, India, were examined in relation to the early use of zinc as a metal. Carbon dates of circa 2000 years before present established Zawar as the world's oldest zinc mines. Large scale mining for lead at Rajpura-Dariba goes back to circa 3000 years before present. Major features are described, emphasizing the considerable scale of operations, and the methods used.

Author

B Prakash: Metallurgy in India through the Ages. *Bulletin of the Metals Museum (Japan), 1983,* **8,** *23-36.*

Survey article on history of metallurgy in India dealing with many well known topics, viz Harappan copper, zinc distillation, Wootz steel etc.

PTC

W Rostoker, B Bronson, J Dvorak. The Cast iron bells of China. *Tech & Cult, 1984,* **25** *(4), 75-767.*

Bell metal (bronze) has traditionally been chosen because of its low damping capacity. But as regards price – cast iron was 1/10 the cost of bronze in 14th century China. As is well-known, grey cast iron has the highest damping capacity, (SDC) of any common metal bar lead. The Chinese no doubt stumbled on cast iron as a bell metal because much of the early cast iron was white as it was intended for malleablising. But its high hardness suggests that it should have a low SDC Experience with Chinese bells show that bronze and iron bells are comparable. Not all Chinese bronze bells were of good quality and it is suggested that this is due to faults in the casting. Likewise cast iron bells can vary.

This paper makes some other points. The holes near the top are for chaplets and being at the top do not affect the sound. Most cast iron bells do not have the piece mould parting lines removed because being white iron they were too hard. Later after the 11th century, bells had high S content and therefore were often coal smelted. The S content would favour white iron in spite of the silicon content and slow cooling.

Bells in Field Museum, Chicago:

Si	**C**	**S**	**HV**	**Iron**	**Date**
1.0	3.2	0.40	352	White	Ming
1.0	3.9	0.57	415	White	--
1.0	4.7	0.29	483	White	1591

RFT

Hans-Gert Bachmann, Andreas Hauptmann: Zur alten Kupfergewinnung in Fenan and Hirbet en-Nahas im Wadi Arabah in Suedjordanien. *(Ein Vorbericht). Der Anschnitt, 1984,* **36,** *(4), 110-123.*

A survey with slag analyses.

RFT

L B H(unt): Gold Treasures from Korea. *Gold Bulletin, 1984,* **17** *(3), 109.*

Excavations of royal tombs have yielded rich hoards of gold crowns, winged head ornaments, pendants etc. One of the gold crowns was made from gold sheet with pendants hanging from thick gold rings and with many jade ornaments. (Illustr).

Author

ABSTRACTS

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