HIGH-TEMPERATURE MATERIALS AND INDUSTRIAL APPLICATIONS

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1. Introduction

During the last decade there has been increasing economic pressure on productive industry throughout the world, and in Western Europe in particular, leading to major cut-backs in the old-established basic industries with consequent high levels of unemployment. While new industries have been established, and in some cases grown spectacularly, e.g. microelectronics, they have not been sufficient to counterbalance the falling employment in older labour-intensive industries, and in general have not been of a character to exploit the established skills of the work force. The cause of this changing pattern of industry and employment, and the possible courses of action to overcome the situation, are matters for careful consideration by political and social planners, as well as by industrialists themselves.

1.1. *Factors Leading to Reduced Industrial Activity in Europe*

1.1.1. One of the major factors leading to industrial recession in the Western World was the exceptional increase in energy costs, stemming originally from the oil-price increases imposed by the major producing countries in the early 1970s. Since oil formed the major primary source of energy for the generation of electricity in the industrialised nations of the world, the competing primary sources, principally coal and nuclear power, were not in a position to offer an immmediate economic replacement in sufficient quantity. All forms of transport, by air, sea or land, depend predominently on oil, so that the increased fuel costs bore heavily on all industry, but excessively so on the transport industries themselves. The consequent reductions in the rate of replacement of vehicles of all type led to growing unemployment in the aircraft, shipbuilding and automobile industries and in their materials supplies, particularly in steelmaking.

1.1.2. The introduction of labour-saving and equipment, ranging from simple mechanical aids to sophisticated electronic automation equipment, has reduced the man-power demands in all activities. In agriculture particularly, which historically has been a labour-intensive activity, level of employment has fallen considerably in spite of expending production, and much further reduction is to be expected as the European farming industry continues to rationalise its activities into larger units. Similarly in the engineering industry the introduction of mechanised "robots" is the reducing man-power requirements, while in commercial life the effects of computerisation of many aspects of information storage, selection and dissemination will continue to reduce demands for clerical and administratice staff at all levels of seniority.

1.1.3. A further major cause of rising unemployment in Europe is competition from emerging industrial countries with lower labour costs. This influence is particularly noticeable in the conventional old-establishment industries such as fabrics, clothing, etc. but is also serious in materials and engineering fields, e.g. steelmaking and shipbuilding, and even in the subcontractes production aspects of the newer industries, e.g. electronics.

1.2. *Action to Counteract Falling Employment*

1.2.1. To recover or expand employment in industries making established products at present suffering from competition by the emerging nations ideally requires increases in both productivity and in market demand. For while increase in European productivity without increase in total demand might recover a proportion of the market from the overseas competition, it would be at the expense of reduced man-power requirements. On the other hand increase in the demand without reduction of European costs would encourage the emerging nations to increase their own production using low-cost labour.

These industries must, therefore, seek to improve both productivity and marketing for established products, but more importantly must, by intensive research and development, seek new or improved products within their sphere of competence.

1.2.2. Expanded areas employment can be anticipated by the development of new industries based on entirely novel concepts arising from basic or speculative research. By definition, such developments cannot be planned to meet defined objectives, but can be stimulated by the provision of adequate facilities in appropriate establishments, and by the encouragement of creative research workers so that they are able to recognise potential openings for new products of processes.

2. The relevance of materials research

2.1. The major areas of interest demanding continuous research attention include energy, agriculture, manufacturing industry, health and the environment, transport, raw materials, etc. Between these broad areas, and perhaps embracing others not mentioned above, there is a good deal of overlap and interaction, so that an advance in one area may provide spin-off advantages to others, but on the other hand progress in another may be inhibited by lack of progress in yet another.

The provision of energy at economic rates and in a formal readily transportable is perhaps the most important factor supporting the widest range of activities, but of similar broad applicability is the subject of materials. Whether the materials are natural or synthetic, abundant or scarce, there are very few activities of mankind that do not involve the selection and use of approppriate materials or construction of goods, for the processing of other materials, or for the storage and dissemination of information.

2.2. The importance of research has been clearly recognised in both U.S.A. and Japan, the two nations of the Western world most closely competitive with Europe. In the U.S.A. the extent of materials research, both Federally sponsored and supported by private industry, is many times greater than current in Europe, while of the 12 new basic technologies itemised ofr immediate attention in Japan, 6 relate to materials.

It is clear that Europe must make a major commitment to materials research to maintain a competitive position with respect to these two nations, and to avoid being overtaken by emerging nations. With increasing technical competence, the emerging nations turn their attention first to the exploitation of their own natural resources. Whereas in earlier days they were content to export their natural or mineral resources with a minimum of processing, leaving the later stages of purification, processing and manufacture to more advanced nations, they now aim to retain for themselves as much as possible of the whole chain of production form initial raw material to the saleable product. With increasing familiarity with industrial techniques, supported by technical education gained from more advanced countries, the 3rd world nations will undertake more and more of the worlds' established industrial manufacturing.

Europe must therefore make every effort to preserve and extend its present competence in materials research, and above all to accelerate the exploitation in manufacturing industry of the results of its research.

3. Objectives of materials research

The position of materials research in respect of its application to industry has conventionally had two significantly different outlooks- first, to satisfy the needs of designers and manufacturers for materials with specified, or at least recognised, properties, and second, to explore the properties of existing or newly-found materials with the hope that exploitation of these properties would follow. In the present climate, in which the objectives of research activities are much more clearly expressed than in the past, the aims of materials research and development may be listed as follows:

3.1. *To meet demands for improved materials by existing industries.*

All designers and manufacturers of products recognise the shortcommings of their present materials, whether these be lack of strength, brittleness, poor corrosion or hot resistance, poor wear resistance of whatever. These characteristics limit the way in which the materials are used and, when clearly expressed, should enable research workers to seek improvements.

3.2. *To improve economics of existing usage.*

Material costs often form a high proportion of the coast of an article and there is much scope for economy by materials-oriented research. In the metallurgical field the comparative costs of casting, forging, powder compaction and electroforming need to be assessed, and the costs of machining and scrap recovery are relevant. Similar considerations apply to the use of non-metallic materials.

3.3. *To ensure adequate supplies of strategic materials and to explore possible substitutes.*

Some critical materials are available only in limited quantities form know sources or only form politically sensitive areas. While stockpiling has been adopted to ensure strategic reserves for such materials, it is desirable also to continue to research for alternative sources or to discover adequate substitutes.

3.4. *To stimulate new applications leading to new industries.*

The careful study of the properties of known materials forms the basis for the design of goods made form those materials. Additionally, however, a full knowledge of properties, mechanical, physical and chemical, can lead to a realization of the suitability of the material for entirely novel applications. There is, therefore, a need for the systematic determination of the properties of all available materials.

3.5. *To discover new materials with properties capable of exploitation.*

Fundamental research on materials may from time to time reveal entirely new materials with novel properties for which no immediate application is apparent. The discovery of superconductivity is a case in point, which had to wait for over 50 years before significant applications could be developed. Other discoveries, however, e.g. the transistor, have led to rapid exploitation and the growth of new industries. Basic studies of materials with no targetted objective are therefore to be encouraged within reasonable limits.

4. MATERIAL TYPES

The broad field of materials covers a very wide range, extending from readily available natural products to specially made synthetics, some of which may be costly to produce, and includes an increasing variety of composite materials consisting of man-made assemblies of two or more constituents with specified geometric configurations. The main groups of materials which are of importance to man are categorised below:

4.1. *Natural Organic Products*

Timber has provided the major constructional materials throughout history and is likely to continue to form one of the main materials for moderately-stressed articles of many types. Animal and vegetable fibres have similary served as the basic materials for the making of fabrics of all types, although they are now being superseded in many fields by man-made synthetic fibres.

4.2. *Non-metallic Materials*

Stone quarried from natural deposits provides a plentiful material for buildings and civil engineering works, and is used in association with processed mineral materials such as cement and glass in many of these constructions. The thermal processing of selected minerals provides specialised materials such as refractories or high-temperature heat insulation and ceramics for domestic and industrial purposes.

4.3. *Metallic Materials*

The extraction of metals from their ores and the manufacture of alloys from them yield the essential materials for modern mechanical engineering. Irons and steels of hundred of different types and non-ferrous alloys running to thousands, provide characteristics of strength and ductility at sub-normal, normal and elevated temperatures, combined with particular physical attributes such as electrical conductivity or magnetic properties, or chemical properties such as resistance to attack by corrosive media, which enable an appropriate selection to be made for any particular application. The scientific study of metallurgy provides the basis for the continued development of improves metallic materials.

4.4. *Polymers*

The polymerisation of simple hydrocarbons derived from mineral deposits of oil or coal, and effected by treatment at high pressures and elevated temperatures, has led to a range of materials which are finding increasing applications in many fields, replacing natural fibres in fabrics, cords and ropes; timber in furniture and other domestic articles; and even metallic materials in light engineering. The properties of such materials and the extent of their application are likely to increase with continued research and development activity.

4.5. *Composites*

The combination of two (or more) different materials can often exploit beneficial characteristics of each. Some composite materials are already well-known and widely-used (e.g. steel-reinforced concrete, glass-fibre reinforced plastic) but much work in recent years has been aimed at developing improved composites by the study of the geometric effects of the lay-out and of the mutual stability of the different phases. The geometric pattern may be of particles or filaments distributed in a matrix, or of a laminar character, and the different phases may be from any of the groups mentioned above. The resulting properties depend both on the natural of the combined materials and on the details of the geometry.

From the above statements on the importance of materials and their clear relevance to the advancement and growth of industry, it may be concluded that both speculative and targetted research in the materials field should be strongly encouraged and supported. The extent of interests is so wide, however, that within the scope of this article it is not possible to deal in any detail with more than one selected topic. It is therefore proposed in what follows, to concentrate on materials for high-temperature service and the importance of this topic is explained in the following section. Least it be thought that other topics are of lesser importance, however, attention is drawn here to a fewer further selected materials areas which are also of major significance for industrial growth, and there are many others not noted here.

4.6. *Light Alloys*

These are mainly aluminium and magnesium alloys, but increasingly also included titanium alloys. Progress in this area has largely been for the immediate benefit of the aircraft and space technology industries. However, spin-off advantatges have accrued to many other industries, including the manufacture of consumer goods, so that the actual consumption of light alloys by the aero-space industries is now a relatively small proportion of the whole.

4.7. *Plastics*

The ubiquitous use of plastics, particularly in short-life products and consumer goods, is apparent to all. To maintain and extend this market needs continued research to ensure the economic competitiveness of the material as well as its functional suitability.

4.8. *Semi-conductors*

These materials form the basic of the electronics industry in its present form and research is active by the whole industry in a search for characteristics which will lead to the development of more reliable, cheaper or entirely novel devices.

5. High temperature materials

Materials operating in service at elevated temperatures are relevant to many processing and productive industries and hence provide an illuminating example of the desirability for materials research to be carried out with a broad view of the ultimate applications of the product, rather than in concentrating on the satisfaction of a single requirement. Nevertheless in the final stages of development of a material the detailed requirements of each potential application must be considered. Close cooperation is therefore demanded between, on the one hand a research organisation with a wide understanding of the basic sciences involved and the production and application problems arising in materials technology, and on the other hand the designers and development engineering engaged in individual industries.

The extent of interest in high-temperature materials can be appreciated by considering the main fields in which they are used.

5.1. *Energy Generation and Conversion*

5.1.1. High-temperature steam turbines

Oil- or coal-fired steam turbines provide the majority of power generation in the world, using maximum steam temperatures close to 600°C. In the steam-raising plant certain components reach higher temperatures and may be subject to severe erosive and corrosive attack; critical components are superheater tubes and tube supports. Piping and valves conveying steam from boilers to turbines are highly stressed and may also suffer steam erosion. In the turbines the casings and casing bolts are highly stressed due to the steam pressure, while the rotors, blades and nozzles have imposed stresses due to centrifugal forces, gas pressure and thermal changes.

5.1.2. Nuclear reactors

In all types of nuclear reactor high-temperature material problems arise with the fuel cans due to stressing by fuel expansion and to corrosion by the coolant. The majority of nuclear reactors at present operating, whether water cooled or gas cooled with carbon dioxide, generate steam at relatively modest temperatures in the range 300-400°C so that the material problems outside the reactor itself tend to be of the same character, though necessarily different in severity from those in fossil-fuel-fired power plant. Newer types of reactor, such as the advanced gas-cooled reactor, the high-temperature reactor (helium cooled) and the fast reactor (sodium cooled), have coolant temperatures exceeding 600°C and materials problems arise, particularly in heat exchangers, steams generators, transfer piping and valves by corrosive or erosive attack by the coolant.

5.1.3. Coal Conversion

Newer processes for the use of coal, in addition to conventional burning in lump or pulverised form, include fluidised-bed combustion, gasification and liquefaction, and may involve temperatures varying from about 400°C at high pressure in certain liquefaction processes, to as high as 1600°C in the flame zone of combustion processes, although the metal temperatures of plant components are normally restricted to less than 700-800°C. Nevertheless the combustion gases, containing carbon, sulphur, hydrogen, oxygen and their compounds as well as entrained ash, provide a severely corrosive and erosive environment. The components exposed to severe conditions include the internal parts of combustion beds or reaction zones, transfer pipes, valves, probes and heat exchanges.

5.2. *Transport*

5.2.1. Aircraft and Space Vehicles

The aircraft gas turbine provide the main stimulus for the development of modern superalloys, the term used to describe materials resistant to creep and fracture at temperatures in the range 700-1100°C. The alloys were originally required specifically for stator and robot blades to resist the high centrifugal or thermal stresses imposed on the blades, but with progressive increase in the severity of operating conditions similar alloys are now used for other gas-turbine components including discs, combustion chambers, casings and tail pipes. The aircraft gas turbine is likely to remain the primary application of the most advanced superalloys or competitive high-temperature materials.

The rocket motor for space travel has led to severe problems in high-temperature materials technology. The high temperature and velocity of the exhaust gas generates high thermal stresses and erosive action; refractory metals, particularly tungsten, and special forms of graphite have been used to resist these statisfactorily, even though the required life may be restricted to a few minutes. Similar problems arise with re-entry vehicles on account of aerodynamic heating, and these have led to the development of special refractory ablative tiles or coatings.

5.2.2. Marine

There is increasing use of gas turbines to power naval vessels and the materials problems arising are similar to those with aircraft turbines except that the corrosion problems caused by the marine environment and ingested salt are considerably aggravated. Merchant shipping mainly relies on the diesel engine in which a number of critical components are subjected to severe mechanical or thermal stresses and corrosive attack at high temperatures. The highest tenperature (about 800°C) is reached in pre-combustion chambers, but closely similar temperatures may be reached in exhaust valves, associated with high mechanical stress. The pistons, normally of cast iron, operate at moderate temperatures but may be protected by inserts or coatings of heat-resistant alloy to minimise thermal cracking or corrosion on the crown. Exhaust superchangers are similar in principle to gas turbines and pose similar problems of creep and thermal fatigue for the blades, but, with inlet temperatures around 550°C these are not severe.

5.2.3. Road and Rail

The diesel engines used for road and rail transport operate at higher engine speeds than marine diesels and this may lead to higher component stresses and temperatures. However the corrosion problems are less severe since refined fuels are used instead of the heavier residual oils used in marine engines. The critical components are those already mentioned.

Spark ignition engines for automobiles introduce two main components posing high-temperature problems. The exhaust valve, as with the diesel engine, may reach temperatures in the region of 700°C and is subject to corrosion by deposits from fuel additives, while spark-plug electrodes reach temperatures of about 800°C and are subject to spark erosion as well as fuel corrosion.

5.3. *Chemical Industry*

A wide range of chemical for the conversion of feedstock, from the oil industry or elsewhere, into required products, involve treatment at elevated temperatures and often at high pressures. The reactor vessel is usually in the form of a piping system constructed from heat-resistant alloys. Typical processes include the catalytic steam reforming of hydrocarbons to produce hydrogen and other gases used for the synthesis of ammonia, methanol, etc. and the thermal cracking of hydrocarbons for the production of ethylene. The systems consist of the reactor tubes, which typically are 12-15 m long and 100 mm bore with a wall thickness about 20 mm, which are connected by smaller bore "pigtail" pipes to a header and hence to transfer piping. Welding is an essential operation in the construction of such plant. The operating temperatures of the equipment may rise to 950-1050°C.

5.4. *Thermal Processing*

In many industries thermal processing is an essential step in the production procedure and for the construction of the plant it involves materials which are resistant to the temperatures and the environments involved.

The metal industry, particularly steelmaking, uses plant for the roasting of ores, reduction to metal and for melting, hot working and heat treatment of the products. The cement and refractory producers require kilns and furnaces for the treatment of their materials, while the ceramic and glass producers similarly operate melting and firing furnaces. While many of the plants involved in such processes are constructed of conventional refractory materials and burn crude fuels, more advanced techniques may all for specialised high-temperature materials for such articles as electric heating elements, conveyor belts, monitoring probes, permanent moulds, etc. For the production of glass fibre, for example, high-strength alloys are required for bushings and spinners operating at temperatures as as high as 1400°C.

6. Types of high-temperature alloys

The metallic materials used for high-temperature purposes range from the simplest plain carbon steels to the scarce and expensive metals of the platinum group, but they can be categorised into a few distinctive groups based on composition and structure. Typical compositions of representative alloys of the main groups are given in Table I and the principal characteristics of the structure and properties are indicated in the following sections.

6.1. *Irons and Steels*

6.1.1. Cast irons

Conventional cast iron has been used for many years for grates and burners of combustion stoves, but progressive internal oxidation following the path of the graphite flakes leads to growth and distortion. This can be overcome by the use of austenitic cast irons containing nickel at levels up to 20 or even 25 per cent together with chromium and silicon, and these materials find application in combustion and heat-treatment equipment where stresses are not high but corrosive and erosive conditions are severe. They are serviceable at temperatures up to about 750°C.

6.1.2. Ferritic steels

Plain carbon and low-alloy steels are serviceable at moderate stresses at temperatures up to about 500°C but scaling due to oxidation limits their life at higher temperatures and the strength, in terms of creep resistance, falls steeply at temperatures above 400°C. The scaling resistence is improved by additions of chromium, usually in the order of 12 per cent, and strength by carefully balanced additions of molybdenum, niobium, vanadium, etc., so that there are many proprietary steels offering high strength and serviceability at temperatures up to about 600°C. Such steels are used for critical components, such as blades, in steam turbines.

6.1.3. Austenitic steels

These steels contain levels of nickel and chromium which are sufficient to stabilise the face-centred-cubic or austenitic structure at normal temperatures and to confer high corrosion resistance and, in general, good ductility. They range in basic composition from the simple 18 chromium, 8 nickel alloy normally used in the wrought form for a variety of corrosion-resistant applications, to 20 chromium, 35 nickel alloys used for moderately-stressed components in power plant. Many varieties of this broad class of alloy are commercially available with additions of molybdenum, manganese, titanium, niobium, etc. and with carbon up to about 0.5 per cent, to confer paarticular characteristics of strength or corrosion resistance. Most are used as wrought products but certain compositions are particularly chosen for use as castings.

6.2. *Nickel-chromium Alloys*

There is no structural difference between the basic austenitic steels referred to above and the high-nickel alloys containing up to 80 per cent nickel with smaller contents of iron. Such alloys, typified by 60Ni, 24Fe, 16Cr; 76Ni, 8Fe, 16Cr and 80Ni, 20Cr, are widely in use, for their oxidation resistance at high temperatures, as electric heating element and furnace parts and depending on the details of composition may be serviceable up to 1150°C.

6.3. *Superalloys*

This term has been adopted for alloys specifications developed to have high strength at temperatures in the range 700-1100°C. The alloys may be based on iron, nickel or cobalt, and normally require 15-20 per cent chromium to ensure satisfactory oxidation or corrosion resistance. The high strength is developed by the precipitation or dispersion of fine particles throughout the matrix, usually by additions of titanium, aluminium or carbide-forming elements.

6.3.1. Iron-based superalloys

These alloys are developments of austenitic steels with nickel contents in the range 20-40 per cent, chromium contents usually 15-20 per cent and sometimes with additions of cobalt. The strengthening precipitate is mainly the intermetallic compound γ' formed from additions of titanium and aluminium, but strength may also be conferred by carbides or nitrides of niobium or vanadium.

6.3.2. Nickel-based superalloys

The additional of small proportions of titanium and aluminium to the 80Ni-20Cr oxidation-resistant alloy produced the first of the now large family of nickel-base superalloys. The strengthening precipitate is the intermetallic compound $Ni_3(Ti,Al)$ termed γ', while the fracture resistance is promoted by grain-boundary precipitates of carbides. In the many alloys now in this group additions of cobalt, molybdenum or tungsten may be made to the matrix, while smaller additions of niobium, zirconium, boron and other elements control and modify the character of the precipitates. Such alloys provide the most advanced superalloys required for the rotor blades of gas turbines, while other alloys of the family are adopted for other gas-turbine components and for highly-stressed applications in many engineering fields. Most may be used as wrought components but the most highly developed are used in the vacuum-cast form.

6.3.3. Cobalt-based superalloys

Hardening by γ' precipitation has not been applied successfully to cobalt-base alloys, but carbide precipitations using stable carbide formers such as niobium, tantalum and vanadium can give attractive high-temperature strength, and this, combined with their ready castability, has caused the alloys to be used in many applications in gas-turbine technology.

Cobalt-base alloys are also prominent in the field of corrosion- and wear-resistant high-temperature materials. In these the corrosion resistance is conferred by chromium contents in the range 20-30 per cent and wear resistance is developed by large proportions of carbides formed from additions of molybdenum, tungsten or niobium with carbon contents up to about 2 per cent. These alloys are mostly used in the cast form, either as shaped castings or as weld-deposited coatings on other materials, and find applications as furnace parts in the metallurgical industry and as protective coatings on valve seats in internal combustion engines and various parts of steam turbines subject to steam erosion.

6.4. *Refractory Metals*

The metals with melting points above 1800°C have, as would be expected, high strength at elevated temperatures, but the commoner refractory metals, viz. molybdenum, tungsten, niobium, tantalum and vanadium all form volatile oxides, so that they cannot be used for long-time service in oxidising atmospheres without a protective coating. No alloying elements have been found to form a self-protective scale so that high-temperature applications of these metals have been restricted to short-time (e.g. rocket nozzles) or non-oxidising atmospheres (e.g. lamp filaments, vacuum furnace elements, etc.). Alloys based on these metals have mainly involved the addition of small proportions of reactive elements or dispersed oxides to act as grain-growth restrictions o maintain ductility.

6.5. *Other Metals*

The metals of the platinum group and alloys formed from them, in spite o their scarcity and high cost, are important high-temperature materials used for thermocouple wires, glass-melting and working equipment, crystal-growing crucibles, aircraft spark plugs etc. Other metals with high melting points, e.g. chromium, titanium, are important alloying constituents, but their high reactivity inhibits their use as a matrix for useful high-temperature alloys.

7. Metal and alloy production and usage

The problems arising in the use of metallic materials in high-temperature engineering range throughout the full range of the science and technology of metallurgy, from the mining and extraction of the virgin metals from their ores to the study and investigation of components in service and the analysis of failures. In all these areas there is scope for research and development action aimed at improving the serviceability or economics of the products. In the following sections of this paper the main areas are reviewed. It will be appreciated that many of the topics indicated as relevant to high-temperature materials are equally applicable to other metallurgical materials, but without progress in these directions the development of high-temperature engineering would be impeded.

7.1. *Mining, Extraction and Refining*

The provision of adequate supplies of the constituent elements of an alloy in a suitable form and of satisfactory purity is an essential first step. Since the natural occurrence of the element in the ore deposits is often at a low level (less than 1 per cent) and at regions of difficult access in politically unstable or antagonistic countries, problems of transport, energy availability, manpower and economic balance arise, and may play an essential role in the section of the most suitable procedure.

The major steps in the recovery process are:

(a) Mining: the deposits may be near the earth's surface and recoverable by open quarrying, or in deep mines; they may be soft, so that they can be dealt with by mechanical shovels or drags, or hard, needing explosives to break up the rock.

(b) Beneficiation: to separate the desired ore from the unwanted gangue or waste rock, methods vary from hand-picking to sophisticated magnetic or grind the ore to a fine particle size, and for flotation methods, to treat with surface active agents to select the ore form the gangue.

(c) Roasting and reduction: depending on the composition of the ore it may need roasting to convert to oxide, for example by expulsion of sulphur dioxide. The oxide is then reduced to crude metal by thermal treatment using carbon or hydrogen as the reducing agent.

Alternative processes now being more widely used are hydrometallurgical in character and involve the solution of the ore in chemical reagents and the reprecipitation of selected compounds of the required metal, which then provide the feed material for subsequent reduction.

(d) Refining: the crude metal will normally contain appreciable quantities of other elements and, particularly for the manufacture of high-temperature alloys, these may be deleterious to the properties of the final alloys. Refining is therefore necessary and may be carried out by processes such as chemical solution and reprecipitation, electrolytic deposition, vaporization, etc. While the processes may be genelalised in character the details must be specifically developed for the metal in question.

In addition to the supply of primary metal by the processes outlined above, significant contributions to the current industrial demands are made by recycling used materials —so-called secondary metal. For most materials secondary metal is used for lower-grade products in which some contamination can be tolerated, but with the possible future reduction or exhaustion of primary supplies and the consequent increasing costs, the need for improved recycling procedures is apparent. The system currently used for the precious metals provide a basis for extension to other metals as the economic or supply situations justify it.

The process of recovery of metals from their ores and the provision of them at the site of application is highly energy intensive and consequently very careful study of the energy consumption at all stages, including transport, is necessary to ensure the most economical process.

7.2. *Development of Alloy Composition*

Most current high-temperature alloys have been developed by essentially empirical methods over a period of years, but parallel studies of a basic scientific nature have provided guidance as to the effects of composition and structure on mechanical properties. Studies of the mechanisms of creep and fatigue in pure metals and single- and multi-phase alloys, have all contributed to an understanding of the way in which composition affects properties, and have enabled the alloy developers to improve their products by the adjustment of contents of the major constituents, by the elimination of injurious contaminants, and by the addition of trace elements having a beneficial effect on structure (e.g. boron and zirconium in the effects on grain-boundary structures and o yttrium on protective scale formation). Continuing research of this nature is therefore essential to support and stimulate metallurgical developments of all types.

7.3. *Alloying and Consolidation*

The primary metals may be supplied in a variety of forms ranging from cast pigs to powder and either as nominally pure metals or as intermediate alloys (e.g. ferro-alloys for the production of alloy steels or iron-based alloys). The conversion of these to the required alloy composition usually involves remelting under carefully controlled conditions to minimise contamination by unwanted elements. High-temperature alloys are conventionally, and still to a large extent, melted in electric arc or induction furnaces open to the atmosphere but under a cover of a protective slag. The slag is chosen to minimise atmospheric pick-up (both oxygen and nitrogen) and also aids in the removal from the melt of unwanted low-melting-point elements. For the more advanced superalloys, however, air melting is inadequate, and improved techniques have been adopted. First, electro-slag refining, in which an air-melted alloy is cast in the form of suitable ingot electrodes and then remelted by electric arc under a complete cover of reactive slag; further refining takes place in the molten pool and progressive solidification gives an improved structure to the ingot, aiding subsequent hot working. Second, vacuum refining or complete vacuum remelting, usually by induction methods, enables atmospheric contamination to be eleminated and reduces the content of unwanted volatile constituents. It has been established that even very low contents of some elements (e.g. lead, silver, bismuth) measured in a few parts per million are detrimental to high-temperature properties of advanced superalloys.

The molten alloy, adjusted to the required composition, may be cast into ingots for subsequent hot working or into bars for remelting for castings, but, particularly for larger components such as rotor discs for gas turbines, the ingot structure may be too segregated and coarse grained for satisfactory forging or to give uniform properties. The alloy may therefore be blown by inert gas to produce an alloy powder for subsequent consolidation. The powder may be pressed to form in shaped dies as in conventional powder metallurgical techniques; but for critical components in advanced high-temperature alloys is more likely to be hot isostatically pressed. This involves enclosing the powder in an evacuated metal container and hot pressing using an inert gas as the pressure medium. A very uniform fin-grained compact is thereby obtained, suitable for further hot working.

An additional advantage of the powder route to consolidated material is that dispersion-strengthened alloys are readily produced. In such materials finely dispersed stable non-metallic compounds, usually oxides, are incorporated to the extent of a few per cent by volume, and provide additional strength at temperature higher than those at which intermetallic compounds are effective.

7.4. *Working*

The consolidated material in the form of cast ingot or pressed powder compact is now required to be shaped to be an intermediate form from which the final component is to be machined. Hot-working processes are normally used and these serve to break down the coarse grain size and segregated structure of the ingot, thus improving the uniformity of properties of the material. Hot working may be by hammer or press forging, extrusion or hot-rolling, and the conditions of temperature, deformation rate, lubrication, etc., need to be separately developed for each particular material and for the form of product required. Some products such as sheet, tube and wire require further stages of cold working which again require careful development to ensure that a satisfactory and consistent material is obtained.

The more advanced high-temperature materials are not workable even at temperatures close to their melting points, and hence must be cast to form. Precision casting by developments of the lost-wax technique are used, and to avoid atmospheric contamination may be carried out entirely in vacuum. Improvements in pattern production, moulding, melting and pouring techniques all contribute to advancement of this art in high-temperature materials technologies and may be expected to be applicable to other metallic materials.

7.5. *Machining*

The conversion of intermediate forms to the required final shape of component involves machining of the material. The hardness, and in general rapid work-hardening characteristics of high-temperature alloys, make this often a difficult process and although conventional high-speed steels and sintered carbide tools are widely used, alternative methods are being sought and brought into use. Spark machining and electrochemical methods are already established and other high-energy methods, such as the use of lasers, electron beams and ultrasonics are of interest. Continuing research on this topic can yield benefits to many fields of engineering production.

7.6. *Heat Treatment*

The properties of high-temperature alloys are critically dependent on the metallurgical structure developed by controlled heat treatments, which may be carried out before or after machining to final form. The treatments often need to be effected in controlled atmospheres or environments to avoid detrimental surface reactions, or to produce surface layers with improved mechanical or corrosion-resistant characteristics. Heat treatments may also be designed to minimise internal stresses or, in special component shapes to develop favorable stresses to combat the initiation of fatigue failures. The study of heat treatment and its association with controlled mechanical deformation is a fruitful field of investigation for all metallic materials.

7.7. *Joining*

Particularly for larger complex installations such as boilers and petrochemical plant, the individual components must be joined together either by dismountable mechanical joints or by permanent or semi-permanent methods. Welding is the most widely used permanent joining method and for the less ductile of the high-temperature materials difficulties arise due to cracking in the weld metal itself or in the heat-affected zone alongside the joint. The choice of welding method and of the consumable materials −electrodes or filler wires− depends critically on the parent alloy and the dimensions of the parts to be joined, as well as on their location and mobility. Much research is in progress on the welding problems associated with high-temperature materials and should continue, particularly on the high-energy-input processes such as electron-beam welding and laser welding.

The higher strength high-temperature alloys are not weldable even in quite thin sections, and semi-permanent joints made by brazing, or perhaps diffusion bonding, are possible alternatives. Brazing alloys with melting points in the range 900-1200°C have been developed specifically for use with high-temperature alloys, the most familiar of which are the gold-nickel alloys or those based on palladium alloys. Improvement in these alloys and in the techniques of their use, as applied to the superalloys and the refractory metals, could lead to benefits in other engineering fields.

For all types of joint data are required relating the mechanical strength of the joint to that of the parent material at the temperatures and stress levels of interest.

7.8. *Protection*

The search for high strength at elevated temperatures has eventually led to alloys which have inadequate inherent resistance to environmental corrosion at the service temperature and hence to the need to develop protective coatings.

7.9. *Data Determination*

To enable the design engineer to assess the merit of a particular material in relation to his own specific requirements it is necessary to provide an extensive body of data covering the mechanical, physical and chemical characteristics of the candidate materials, as well as the comercial aspects of economics and availability. The need for the simple standard mechanical properties such as modulus, tensile strength, ductility and impact strength, determined on specially prepared test pieces at normal temperature is readily apparent for all materials, while for high-temperature materials similar properties at the anticipated service temperatures are required, supplemented by data on the creep, stress-rupture and fatigue properties for times extending as far as possible to the expected life of the component. To satisfy such requirements demands an extensive programme of testing to cover the whole range of temperatures, stresses and times of interest. Still further extension of testing requirements arises, however, from the consideration that the properties of a specially prepared test sample are not necessarily reproduced in a component with a different production procedure in terms of working reduction and critical stress-bearing section. Facilities for the testing of components, and even of assemblies of components, at temperatures and in environments of interest, and under multiaxial stress conditions, may therefore be considered desirable. Rig-testing installations of this character are available for normal temperature engineering, principally in the aero-space industry, but have not yet been provided for elevated temperature testing.

The physical properties of materials are also of importance to the design engineer. For high-temperature applications the thermal characteristics –expansion, conductivity, heat capacity and emissivity– are of particular relevance. Electrical and magnetic properties may be of significance for some applications.

The corrosion behaviour of materials is determined primarily by the reactivity of the constituents to the environment, and this is defined by the thermodynamic diagrams relating the stability of potential compounds to temperature. The rate at wich corrosion progresses is controlled by the diffusion rates of the reacting species within the layers of scale already formed (or in the protective coating referred to above) and within the parent material itself, so that studies of solid-state diffusion are relevant to the control of high-temperature corrosion processes.

The collection and validation of property data is, therefore, essential for the optimum selection of materials for engineering purposes and to ensure the economical usage of existing materials and of their constituent elements.

7.10. *Specifications and Testing*

In order to ensure the reliability and consistency of materials used for engineering purposes it is necessary that specifications should be established for the benefit of producer and user. These may be individually arranged between the two parties or established by industrial, national or international bodies. The specifications normally define the composition of the material and the type and limits of specific property tests required. The formulation of specifications should be in the hands of both engineers and material scientists, so that all factors of importace are taken into account.

Similar considerations apply to the preparation of design codes which define the way in which material property data are used in engineering design. Such codes are of especial relevance in high-temperature engineering where interpolation or extrapolation of property data in terms of time or temperature is often necessary. The various attemps being made to correlate creep and fatigue data by mechanistic or phenomenological methods are aimed at giving greater confidence in these procedures. The acceptance of materials in their part-processed form and as finished components rests on testing to specification requirements and to such proof testing and non-destructive testing as is feasible. The latter field, embracing radiography by X-rays or γ-rays, ultrasonics inspection and various electrical and magnetic tests is a progressive field of research the results of which are generally applicable to all materials.

7.11. *Failure Investigations*

Inevitably from time to time failure occur in service and much can be learnt by careful scientific study of these. Material faults may be diagnosed or design faults identified, and steps then taken to remedy the shortcomings. In the same area of study are the attempts being made to assess the remaining life of high-temperature components after a period of service, for this would enable the safe life of plant to be extended without risk of early failure. Recovery treatments by thermomechanical processing are also possible, and indeed are already partly in use, particularly for aero-engine gas-turbine blades.

8. Refractories and ceramics for high-temperature service

8.1. *Conventional Refractories*

Non-metallic materials have a long history of usage in high-temperature technology, mainly as thermal insulating and containment materials for such purposes as metal-melting concibles, hearths and linings for pottery kilns and for industrial furnaces of all types. For such applications strength is an important factor but is not the primary requirement, since failure usually results from thermal cracking due to temperature changes, or from reaction with the contained material. The high-tonnage refractory materials of this type are mainly mixed oxides or silicates and the commercial materials have been developed to balance performance against cost. For more critical applications pure single oxides are increasingly used, alumina, zirconia, magnesia and beryllia being the commonest, since these generally have higher melting points than the mixed oxides.

8.2. *Advanced Ceramics*

Non-metallic materials other than oxides have become of increasing importance in high-temperature technology in recent years. Silicon carbide, long known as an abrasive and also for many years as a high-temperature electrical furnace element, is finding increasing use in a variety of advanced refractory applications, particularly in the self-bonded or reaction-bonded form. The high strength and low density of this material make it a strong candidate for certain aero-space components. Similarly silicon nitride provides competitive levels of strength and hot-corrosion resistance. Both these materials are formed from cheap and abundant elements so that there are no problems of availability, and the cost of components made from them will depend on energy costs and the level of commercial demand. Many other non-metallic materials, elemental or compound, are being examined in the light of their possible merits as high-temperature materials, and these include oxides, carbides, nitrides, borides and silicides, predominantly of the higher-melting-point refractory metals, but also of the more reactive metals such as aluminium, magnesium and calcium which can form compounds of high thermal stability.

In the same class of advanced non-metallic refractory materials must be included carbon. Although its oxidation resistance is generally poor, so that it can only be used at high temperatures in a protective atmosphere or vacuum, it can be obtained in a range of crystalline or vitreous forms, depending on the production process adopted, so that its extremely high melting point can be exploited.

8.3. *Production and Consolidation Processes*

The constituent compounds of ceramic materials are derived either from naturally occuring deposits of suitable precursors, which may be purified by conventional chemical means and then thermally decomposed to yield the oxide, or by high-temperature exothermic reactions between the elements to be combined or between selected compounds of them, often gaseous, e.g. ammonia to produce nitrides. The required compounds are usually obtained in the form powders or crystals, which may need milling to refine the grain size, and they must then be consolidated. This is the step that offers considerable scope for the development of special methods appropriate to individual materials. The common methods include slip casting, cold pressing or paste extrusion, all followed by sintering; hot pressing; hot isostatic pressing; activated or reaction sintering; fusion casting; and deposition by chemical vapours or by pyrolytic decomposition. In most all these processes the effect of particle size of the powders, and of the presence of small proportions of impurities or added compounds, may have critical effects on the properties of the resultant material.

The shaping of ceramic or refractory materials to the required form presents considerable difficulties since many of them, and certainly the more advanced fully-densified materials, can only be machined by the use of diamond tools. The tendency, therefore, is to employ the materials in relatively simple forms which can be produced directly by the consolidation process, or to machine in the "green" or partly-sintered condition, with allowance for shrinkage infinal sintering to be within acceptable limits. Research on consolidation and processes and their effects on shrinkage and resultant mechanical and physical properties are hence of major relevance in the application of these materials.

8.4. *Joining*

The commoner refractory materials pose few problems in joining, since suitable refractory cements are available, but the more advanced materials present difficulties, particularly if stress-carrying joints are involved. Mechanical joints, often with flexible interface materials to minimise stress concentrations, may be adapted, while reactive brazing metals offer promise. The established techniques for glass-to-metal seals used in the manufacture of vacuum devices provide a basis for the development of similar procedures for advanced ceramics.

8.5. *Mechanical, Physical and Chemical Properties*

Ceramic materials are essentially brittle in character and their mechanical properties cannot be directly compared with those of ductile metallic alloys, since different testing procedures are adopted. Bend tests normally take the place of tensile tests and the fracture stress is reported on a statistical basis since the results are more scattered due to the influence of minor flaws. Nevertheless measurements of bend strength against temperature and of time to fracture against bending stress provide a suitable basis for the comparison of different high-temperature ceramics and for the assessment of their temperatures of serviceability. These data need to be supplemented by determinations of impact strength and thermal shock resistance, which properties, in general, are much lower than those for metals. Application of recent developments in fracture mechanics should improve the confidence with these brittle materials can be used.

The physical and chemical properties of ceramic materials are required for design guidance, with particular attention being paid to the influence of environmental attack on fracture characteristics. Surface changes may promote or inhibit crack propagation.

8.6. *Testing*

Procedures for inspection and testing, and analysis of service failures must be developed and applied in exactly the same manner already referred to for metallic materials.

9. New techniques for high-temperature materials

The above review of the metallic and non-metallic materials used for high-temperature service and the problems arising in their technology has not referred to a number of new techniques which hold promise of providing improved materials but which still require further research and development before their potentialities can be fully exploited. The most notable of these are given below:

9.1. *Directional Solidification*

Since the long-time rupture of alloys under creep conditions is commonly nucleated at, and propagated along, grain boundaries improved life can be obtained by the growth of long columnar crystals with their axes along the direction of maximum stress in a component, thus avoiding boundaries transverse to the stress. Further advantage is obtained if the crystallographic axis of the columnar grains is favourable in regard to mechanical properties. Techniques have been developed to produce such structures in certain nickel-base superalloys by controlled directional solidification when casting gas-turbine blades.

9.2. *Single Crystal*

By further modification of the process of directional solidification it has been possible to produce single-crystal gas-turbine blades in which the complete absence of grain boundaries provides still greater resistance to creep or thermal fatigue failures. Further work is required on all aspects of directional solidification to explore the effects of crystal orientation on creep and fatigue properties and to extend the applicability of the process to other alloys and to other engineering components.

9.3. *Composite Materials*

Fibre-reinforced non-metallic composite materials are well-known for normal-temperature applications, but little progress has been made in the field of high-temperature materials. Now that high-strength ceramic fibres of a number of different types −carbon, boron, alumina, silicon carbide− are becoming more widely available, their incorporation in metallic matrices is being explored. Some success has been attained in aluminium and titanium alloys and extension to higher-melting-point alloys can be anticipated. The major problem in this field is the degradation of the reinforcing fibres by reaction with the matrix, both during the fabrication fibres by reaction with the matrix, both during the fabrication process and on a longer time scale at the service temperature. Considerations of thermodynamic stability and interphase surface energy are important in controlling the rates of interaction between fibres and matrix.

In the same category are the so-called in-situ composites which consist of directionally-grown eutectic alloys. The second phase is in the form of rods or fibres regulary dispersed in the matrix phase and the structure is inherently stable at the eutectic temperature. Exceptionally high creep resistance has been obtained in certain alloys of this type, e.g. Ni_3Al-Ni_3Nb, but in these the hot corrosion resistance has been inadequate. Further work in this field is required.

10. Summary and conclusions

This paper has endeavoured to point to the importance of materials in all industrial activities and, by taking the case of materials for high-temperature service as a specific example, to indicate the very range of research and development actions that are necessary to ensure progressive improvement in the materials available to users. These range from basic scientific studies of the structure of materials and the way in which these influence the mechanical, physical and chemical characteristics sought by designers, to the development of commercially available materials at an acceptable economic price, and finally to the study and analysis of service failures to provide guidance for improvement in both materials and engineering design.

In the high-temperature materials field some particularly important directions for future action can readily be identified. The following may be considered amongst them:

i) Exploration of the effects of minor and trace contents of elements not specified in the compositions of established alloys.

ii) Studies of the influence of grain size and structure on the creep and fatigue properties of large-size components.

iii) Improvements in cutting tools or machining techniques applicable to rapidly work-hardening high-temperature alloys.

iv) Development of joining techniques applicable to heavier-section advanced superalloys.

v) Development of improved protective coating compatible with advanced alloys for operation in sulphurous and carbonaceous atmospheres.

vi) Establishment of an improved understanding of the mechanisms of creep and fatigue failures so that the long-time life of components can be more accurately predicted, or alternatively, a reliable method to assess non-destructively the remaining life of a component, thereby permitting a longer safe life for expensive plant.

vii) Development of engineering designs to permit the use of brittle ceramics for critical components such as gas-turbine blades; to seek for advanced ceramics with higher temperature capability than existing materials.

The above topics, although by no means exhausting those considered important for future action, indicate that progress in materials development could contribute significantly to continued improvement in high-temperature engineering. For this, adequately equipped laboratories, staffed by qualified and experienced scientists and engineers are essential. It is important that such laboratories should be large enough to embrace a wide range of technique and disciplines relevant to materials, even though specialist laboratories dealing with well-defined aspects of the subject are also desirable, e.g. casting, welding, electrodeposition. In addition to facilities for experimental work it is essential that arrangements are provided for the collection and dissemination of data, for it is common experience that many of the delays and disappointments arising in engineering development are due to lack of awareness of existing knowledge, rather than to actual absence of that knowledge.

It must be emphasised again that all major development projects whether they be directed to the energy industry (nuclear power, coal conversion, steam raising, gas piping), transport (aircraft, marine, automobile), agriculture (earth-working equipment, cropping machinery, fertiliser production, food processing), heath (chemical and drug production), environment (sewage control, urban waste combustion) or civil engineering and building (roads, bridges, airports, buildings) all depend critically upon the availability of suitable materials. Interaction and overlap between these different areas of interest must occur and there is, therefore, much advantage to be sought in a unified view on materials research and development.

The present fragmented state of materials research in Europe stems from the fact that each of the major countries of the community has its own national programme, while within each country the different industries are each seeking to solve their own immediate problems. While some international cooperation occurs, particularly in the energy field and in aircraft development, there appears to be a need for a well-planned and directed European programme on materials with the object of stimulating existing individual laboratories to cooperate with others and to provide for rapid interchange of information. The CEC could initiate such action by establishing a materials centre to serve as a clearing house for information on materials research and development.

The CEC, Joint Research Centre programme on high-temperature materials, operated from the Petten Establishment, was started to carry

Table I. Typical Compositions of Selected High-Temperature Alloys

Alloy Type	Commercial Name	Cast or Wrought	Composition										
			Fe	Ni	Co	Cr	W	Mo	Nb	Ti	Al	C	Others
Austenitic Cast Iron	Ni-Resist	C	Bal.	20	–	5	–	–	–	–	–	3	2 Si
Ferritic Steel	FV 448	W	Bal.	1	–	11	–	0.7	0.4	–	–	0.1	0.05 N
Austenitic Steel	AISI 321	W	Bal.	10	–	18	–	–	–	0.4	–	0.05	–
	HK40	C	Bal.	21	–	25	–	–	–	–	–	0.4	0.05 N
Nickel-chromium Alloys	Alloy 800	W	46	32	–	20	–	–	–	0.3	0.3	0.04	0.3 Cu
	Nichrome V	W	–	78	–	20	–	–	–	–	–	0.04	2 Si
Iron-based Superalloy	N 155	W	Bal.	20	20	21	2.5	3	1	–	–	0.15	0.15 N
Nickel-based Superalloy	Nimonic 90	N	–	Bal.	18	20	–	–	–	2.5	1.5	0.1	B, Zr
	IN 100	C	–	Bal.	15	10	–	3	–	5	5	0.2	B, Zr
Cobalt-based Superalloy	HA 188	W	1.5	22	40	22	14	–	–	–	–	0.1	0.08 La
Cobalt-based Wear-resistent Alloy	UmCo 50	C	22	–	50	28	–	–	–	–	–	0.1	–
Refractory Metal	TZM	W	–	–	–	–	–	Bal.	–	0.5	–	–	0.08 Zr
Platinum-Rhodium	–	W	–	–	–	–	–	–	–	–	–	–	80Pt,20Rh

out this function in relation to its own specialised field, and its success, and its acceptance by the interested industries during the 7-8 years since it was formed, suggests that organisation with much wider terms of reference might, with advantage, be established.