

NEW METALS

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If people get the governments they deserve, perhaps it is equally true to say that engineers get the materials they deserve. What is certainly true is that they do not always get the materials they demand.

It is only quite recently that engineers have, in fact, demanded anything at all. For five or ten thousand years they were content to accept what the metallurgists provided and improvements in design came after improvements in materials. During this period the incentive behind the search for new materials, with the possible exception of the early steels, stemmed almost entirely from the metal-worker's own interest in his craft. Even the coming of the steam and internal combustion engines made little extra demand on metallic materials—steel and brass seemed amply sufficient for the new machines - and when the extraction metallurgists turned up with a genuine wonder-metal in the shape of aluminium all anybody could think of doing with it at first was to make it into a dinner service for Napoleon III.

A big change occurred, however, about 25 years ago, when the aircraft industry first became confident that it had a future, and designers turned their thoughts to structures having unprecedented combinations of strength and lightness. After centuries of independent development, the metallurgist suddenly found himself subject to exhortation from the user. The initial emphasis from the aircraft designers was on lightness, and to satisfy his needs magnesium alloys, based on a metal with a density of 1.7, were produced. For applications requiring higher strengths a remarkable series of aluminium alloys was developed, and these successes encouraged the belief that as far as new materials were concerned, to ask was to receive,

Then came the gas turbine, and with it a very considerable increase in the pace of demand. Materials capable of operating under far more severe combinations of temperature and stress than ever previously considered were now required, and density remained as important as ever. In an attempt to meet these requirements extensive programmes of metallurgical research were put into operation. An outstanding product of this research effort, without which little progress would have been made in the field of jet-propulsion, is the series of Nimonic alloys developed by a group of Birmingham metallurgists. Another important development was the rapid transformation of titanium from a laboratory curiosity into an industrial material. But difficult though it may be, it is easier to draw up an advanced design for an aircraft on paper than it is to produce the new structural materials with which to build it, and in spite of the successes scored by metallurgical research in recent years, the designers have moved on, and materials still lag behind in the gas turbine field.

In other fields too, new demands have arisen, mostly as a result of the coming of nuclear energy. Though already hard-pressed, metallurgical research has been asked to produce materials not only having high strength at elevated temperatures but conforming to the restrictions imposed by such considerations as neutron absorption and behaviour under neutron bombardment.

So far it has not been possible to control the 60-odd elements which rank as metals sufficiently well to provide something to suit all requirements, but metallurgists are doing their best to co-operate with nature in the production of materials which come nearer to the engineers' hearts desire than those at present available. For this purpose it will be necessary to depend very heavily on a group of metals which, because they have hitherto been relatively little used tend to be known collectively as the "new metals."

Properties of the New Metals

Nearly all the “new metals” which are likely to find more immediate use as structural materials fall within the group known as the Early Transition Elements. Essentially they are the Group IVa, VA and VIA metals of the first, second and third Long Periods. Titanium may be included within the group for the sake of completeness, though it may by now have lost its title to the name new metal. Beryllium (Group I, First Short Period) is the only new metal of any immediate importance lying outside this compact group of elements, though in Groups IIIA and VIIA are to be found the metals scandium, yttrium, lanthanum and rhenium which might prove to have useful properties if their fundamental scarcity could be overcome, and some of the rare earth elements may perhaps make a future claim to be included.

Present interest in the new metals is readily explained by a brief consideration of their properties in relation to current needs, which for the aircraft industry is above all high strength at high temperatures. It is obvious that a high-temperature material must have a high melting point, and this condition is fulfilled by all of the nine transition elements included among the new metals. Some of their melting points are very high indeed, as can be seen in Fig. 1.

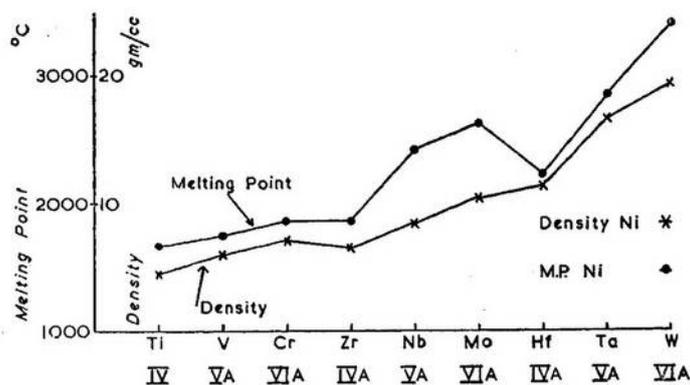


Fig 1. Densities and melting points

Low density is another desideratum for aircraft applications, in which strengths are usually compared in terms of the strength to weight ratio rather than absolute strength. Here beryllium with a density of only 1.8 would score, but for a high-temperature alloy a melting point above that of beryllium 1,200° C. would be needed, and obviously some compromise between melting point and density will have to be made. Comparison of the density plot with the melting point plot (Fig. 1) gives an immediate lead as to the elements likely to provide the best melting-point/density combination. For most of the elements considered, melting point and density go hand in hand, but at niobium and molybdenum there is a sudden large increase in melting point without a corresponding density rise. These, therefore, must be considered to be among the metals most likely to provide the basis for future high temperature materials.

Unfortunately strength is not the only factor on which the suitability of a high-temperature material depends. Reaction with atmospheric and fuel gases panicle, another very serious obstacle to the development of new materials for use in modern aero-engines. From, this point of view it has to be admitted that the performance of the otherwise favoured group of nine new metals ranges from poor to catastrophic as indicated in Table I. The difficulties are indeed formidable ; volatile oxides, liquid oxides, dissolution of oxygen in the metal all these are encountered, and with the exception of chromium, in no case is a protective oxide scale formed. Oxidation rates of several of the new metals are compared in Fig. 2 and those of niobium and nickel in Fig. 3. The heavy scale formed on a sample of a niobium—4 at % chromium alloy after 54 hours at 1,000° C, in air is illustrated in

Fig. 4. It is evident, therefore, that under the conditions in which they would be required to operate as high-temperature materials, nearly all the new metals in unalloyed form would be hopeless. From the oxidation point of view chromium stands out as the most promising, and this fact has justified its inclusion, with niobium and molybdenum, in the small group of metals most likely to become the high-temperature material of the future, even though its melting point and density do not promise so advantageous a strength to weight ratio at operating temperatures as for the other two elements. An additional disadvantage of chromium, is that it can be embrittled by very small quantities of nitrogen, which must be avoided during all processing and other operations.

Table I OXIDATION BEHAVIOUR OF THE EARLY TRANSITION METALS

Element	Oxidation Behaviour
Titanium	Dissolves oxygen rapidly at temperatures about 550° C.
Vanadium	Very poor oxidation behaviour owing to formation of low melting point oxide.
Chromium	Protective scale formed. Danger of nitrogen embrittlement.
Zirconium	Similar to titanium.
Niobium	Oxide scale non-protective. Oxygen dissolves in metal.
Molybdenum	Very poor oxidation behaviour owing to formation of volatile oxide.
Hafnium	Little information available. Metal severely embrittled by dissolved oxygen.
Tantalum	Similar to niobium.
Tungsten	Powdery, volatile oxide formed.

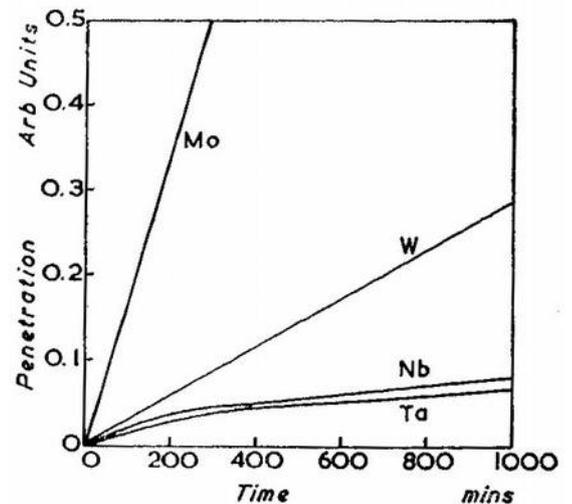


Fig 2. Relative oxidation rates for molybdenum, tungsten, niobium, tantalum. (From "Industrial and Engineering Chemistry")

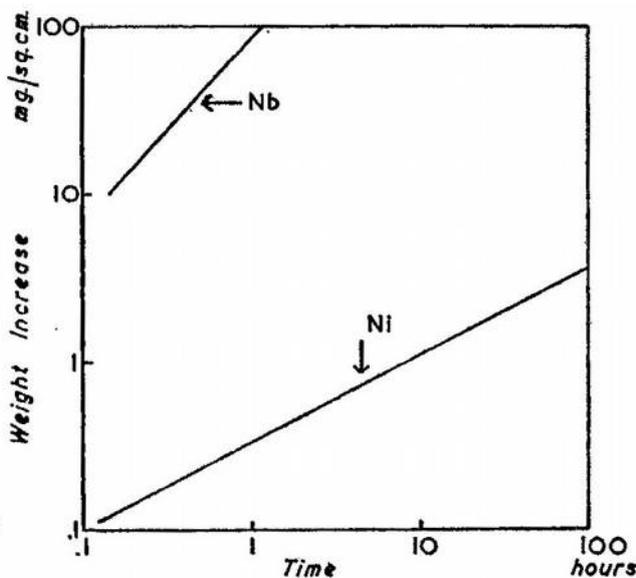


Fig 3. Oxidation rate of niobium compared with that of nickel. (From "Industrial and Engineering Chemistry")

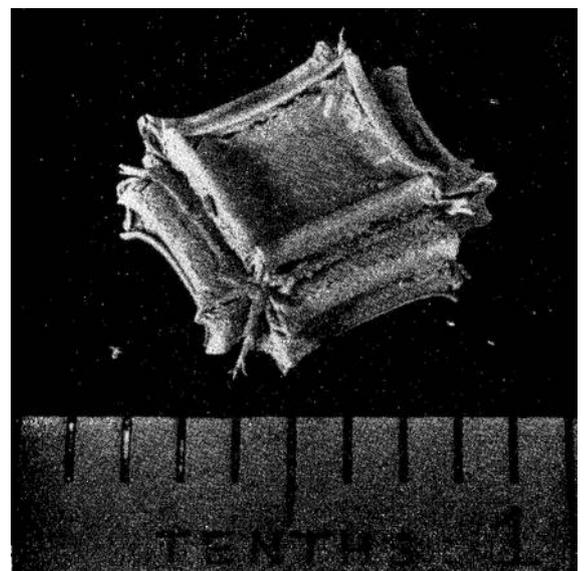


Fig 4. Oxide scale formed on a sample of niobium - 1/2at.% chromium alloy heated in air for 5 1/2 hours at 1,000°C.

Problems connected with high temperatures also occur in the nuclear energy field. Current plans to operate reactors at higher temperatures will require fuel assemblies and structural components which not only retain adequate strength under neutron bombardment at the new temperature level,

but which will also withstand attack by the moderator and the coolant, not merely for several hundred hours, as with aero-engine components, but possibly for years. Other reactor requirements demand that materials used must in general absorb as few neutrons as possible, must not give rise to excessively lethal or long-lived radioactive isotopes under neutron bombardment and must be capable of being fabricated to a variety of special shapes such as very thin-walled tubing.

Table II NEUTRON CAPTURE CROSS-SECTIONS FOR THE NEW METALS

Element	Cross-Section for Thermal Neutron Absorption (barns)
Titanium	5.0
Vanadium	4.5
Chromium	2.5
Zirconium	0.4
Niobium	1.2
Molybdenum	2.6
Hafnium	105.0
Tantalum	20.0
Tungsten	18.0
Beryllium	0.0085

No metal satisfactorily fulfils all these conditions, and it is customary to start from the least bad. The capture cross-sections for neutron absorption listed in Table II make it obvious that neutron absorption will be least for beryllium and zirconium, small for niobium, molybdenum, chromium, vanadium and titanium fairly large for tantalum and tungsten and very great indeed for hafnium. Beryllium and zirconium are likely, therefore, to be the best metals on which to base reactor materials if they can be made to fulfil the other necessary conditions sufficiently well.

In addition to low neutron absorption, beryllium can offer low density, an appreciably higher melting point than other light metals and hence a wider range of operating temperatures, very good corrosion resistance and an exceptionally high modulus of elasticity. The paramount problem associated with the use of the metal as a reactor material is the great difficulty experienced in fabricating the required shapes due to lack of ductility in directions parallel to the c-axis of the crystal.

Zirconium has generally good corrosion resistance to add to the advantage of its low capture cross-section, and, unlike beryllium being readily available, it is becoming more and more important as a structural material for nuclear projects. From the manufacturing point of view, zirconium, happily poses no major problems now that it is treated with due respect in the finely divided condition, and it has been found, furthermore, that industrial experience with its sister-element titanium can be of the greatest value in handling the newer metal. Some limitations to the usefulness of unalloyed zirconium have given rise to the development of zirconium alloys. These limitations stem from a rapid decline in strength with increasing temperature and from a tendency to catastrophic corrosion in the presence of water at high temperatures, the latter being especially severe when the metal contains dissolved nitrogen. Attack by carbon dioxide at elevated temperatures is another hazard to which zirconium is subject. Alloying, however, has alleviated both major difficulties, and most of the zirconium now required for nuclear purposes is supplied in the form of an alloy containing 1.5% Sn, 0.12% Fe, 0.05% Ni and 0.10% Cr, known as Zircaloy 2.

Though zirconium is at present the most generally useful nuclear engineering material for applications in which low neutron absorption is important, higher operating temperatures will call for an alternative. Guided by the capture cross-section list, the next choice falls on niobium. A small amount of this metal has already been used for nuclear purposes, but major advances in the high

temperature field will depend on our ability to overcome the basic difficulty of its high reactivity. In the unalloyed condition niobium will react with pile gases and with many of the materials with which it is likely to come in contact in the reactor at temperatures above 400°-500° C., and the problem may well be aggravated under neutron bombardment. The high temperature strength of niobium, however, will probably be adequate for most reactor requirements, and when pure, at any rate, the metal is sufficiently ductile to be fabricated into almost any form required. Use of niobium in future reactors, therefore, will be governed largely by the success or otherwise achieved in attempts to reduce the high-temperature reactivity of niobium without destroying its ductility - as indeed is the case for other potential uses of the metal.

Vanadium is another material which the possession of a low capture cross-section for neutron absorption and a high melting point has suggested for use in nuclear engineering, but so far it has found only limited application. Furthermore, for future high temperature requirements vanadium seems unlikely to compete with niobium, since it has the same limitations to an even worse degree, and smaller potential rewards in terms of high-temperature strength. In a similar way, titanium is unlikely to find appreciable uses in the atomic energy field because it can offer little more than zirconium and yet has a higher neutron absorption, though there may be a few special environments in which the corrosion resistance of titanium is sufficiently superior to that of zirconium to justify its use. No atomic energy applications have been suggested for chromium even though it is not a strong neutron absorber, its greatest disadvantage being the considerable risk of embrittlement which would exist under reactor conditions.

If reactors are made so efficient by the use of enriched fuel or by fundamental changes in design, that high rates of neutron absorption can be tolerated, capture cross-section will become a less important criterion of material selection, and under such conditions the really high melting point metals, molybdenum, tantalum and tungsten could theoretically be used. All have been mentioned in connection with nuclear engineering from time to time, but until further progress has been made in reducing their reactivity at elevated temperatures it seems unlikely that they could play a major part in extending the range of reactor operating temperatures.

Among the new metals under consideration hafnium has by far the greatest power of absorbing neutrons. It is indeed among the strongest neutron absorbers available, and could thus be of value when it is desired to slow down nuclear reactions, as for instance in reactor control rods. This point illustrates the errors into which normal chemical ways of thought can lead in the nuclear field. Chemically, hafnium and zirconium are so similar that they always occur together in nature and are very difficult to separate. Yet from the point of view of neutron absorption they are at the opposite ends of the scale, and the greatest care must be taken to reduce the hafnium content of zirconium destined for reactors to no more than a few parts per million.

Though the aircraft and nuclear energy industries are those which make the most severe demands on metals, new developments in other fields are bringing to light a variety of special requirements for new materials. The electronics industry, for instance, is making increasing use of tantalum in electrolytic condensers, for which the thin tenacious tantalum oxide film is especially suitable in having good dielectric characteristics and in being impervious to the electrolyte and self-healing. Other uses for new metals will also appear once the major applications have provided the incentive needed to initiate their development. The chemical industry, for instance, is taking increasing advantage of titanium, which in this particular connection remains a relatively new metal, and is now finding uses for the excellent resistance of niobium, tantalum and molybdenum to attack by various highly corrosive substances chiefly in the form of linings for large vessels. Small outlets for tantalum and titanium arise in bone surgery, for which purposes they have two valuable characteristics. they are impervious to corrosion by body fluids, and they provide surfaces on to which flesh can grow.

Present Knowledge of the New Metals

From the foregoing discussion, it appears that except for chemical applications the materials needs of modern engineering, taken as a whole, can be summed up as high strength with low density in the medium, temperature range, and high strength with oxidation resistance at high temperatures. In the high temperature case the lowest density that can be combined with the other two properties must be added. Whether for high or low temperature uses, the required properties must be combined with sufficient ductility to render the material fabricable, and for nuclear energy applications neutron absorption must be taken into consideration. Although these requirements can be stated fairly simply, their fulfilment will be far from simple, and if success is to be achieved without the kind of luck that wins £300,000 for 2d. all relevant scientific knowledge will have to be called upon in order to ensure that the effectiveness of the research effort devoted to new materials is as great as possible.

To provide a starting point it may be of value to review what is known about the new metals. As already mentioned, beryllium is a fairly straightforward divalent metal having unusually high elastic moduli but very limited ductility in some directions in the crystal lattice. Increased purity has, as is so often the case, brought improved deformability, but working remains difficult. For pure beryllium, the only lines of advance appear to be modification of manufacturing techniques and control of crystal arrangement in a way which permits the available slip planes to be used to maximum advantage. When alloying is permissible, attempts might be made to change the axial ratio of the hexagonal crystals, or to replace the hexagonal structure by a more ductile one. The latter alternative will be difficult, however, because for size factor and electrochemical reasons beryllium will tend to form inter-metallic compounds of complex structure with other metals, rather than the simpler type of phase which might be expected to be ductile.

The other new metals can be considered as a group. All can exist in a body-centred cubic form (although titanium, zirconium and hafnium are hexagonal at low temperatures and chromium may be face-centred cubic at temperatures near its melting point) and all are ductile when pure. Embrittlement is caused in each metal by the absorption of interstitial impurities, but sensitivity to small amounts of impurity increases on passing across the Periodic Table from Group IVA to Group VIA. It seems reasonable to associate this increase in sensitivity with a corresponding decrease in the solubility of oxygen, nitrogen, etc., which occurs on moving from Group IVA to Group VIA, arguing that in elements such as titanium and zirconium, in which interstitial impurities are extensively soluble, small amounts of interstitials will be dispersed throughout the structure and that though they would cause hardening due to their impeding effect on slip processes a considerable degree of ductility would be retained; whereas in the Group VIA metals, in which the solubility of oxygen and nitrogen is low, interstitial atoms would accumulate in the disturbed region of the crystal lattice at the grain boundaries, and though the individual crystals would remain ductile, the bulk material would be brittle because of the occurrence of intercrystalline fracture.

Ductile/brittle transformations occur in the whole series of elements at temperatures depending on the amounts of impurities present. Even in commercially pure titanium and zirconium the transition temperature is below room temperature. Vanadium, niobium and tantalum on the other hand, have to be specially purified in order to reduce the transition temperature to an equivalent level, though this can be achieved without great difficulty. Chromium, molybdenum and tungsten normally have transition temperatures well above room temperature, and though success has been achieved in preparing samples which are ductile at room temperature a considerable amount of research is still being directed towards the improvement of the room temperature mechanical properties of these elements. The addition of small quantities of other metals having very high affinities for oxygen and

nitrogen, for example, has been tried as a means of removing harmful impurities from the grain boundaries, and some success has been achieved, especially with molybdenum.

Explanation of the decrease in the solubility of interstitial impurity elements on passing from Groups IVA to VIA may be sought in the relative sizes of the metal atoms and hence the dimensions of the interstitial space. As seen from Fig. 5 the atomic radii decrease markedly with increasing Group Number, and it could be suggested that in chromium, molybdenum and tungsten the interstices were too small to accommodate oxygen and nitrogen atoms, except at grain boundaries where the periodicity of the lattice is disturbed.

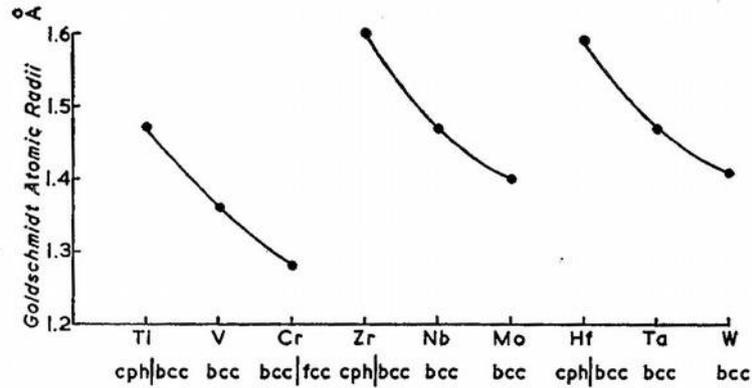


Fig. 5 The atomic radii and crystal structures of the new metals

Unfortunately this simple picture is spoiled by the fact that the solubility of hydrogen in the early transition metals follows much the same pattern as that of oxygen and nitrogen, even though the hydrogen atom is so much smaller than those of the other impurities that it is unlikely to suffer from the same spatial limitations. Factors governing the dissolution of oxygen, nitrogen and hydrogen in the new metals appear, therefore, to be a very worthwhile field of study which could help to overcome the fundamental difficulty of room-temperature brittleness.

Information is available on a number of the physical properties of the transition elements included among the new metals. It has been found, for instance, that Young's Modulus, which is low for Group IVA elements increases very markedly on moving from Group VA to Group VIA (Fig. 6). Electrical resistivity, on the other hand, does the opposite. As indicated by Fig. 7 specific resistivity falls markedly between Groups IVA and VA and less markedly between Groups VA and VIA, though even the Group VIA metals have high resistivities compared with those of non-transition metals. Magnetic susceptibility on the other hand is low for Group IVA elements, high for Group VA and low again for Group VIA.

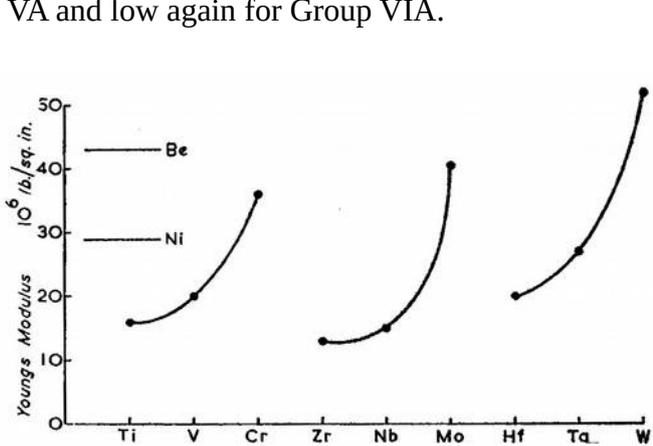


Fig 6. Young's modulus for the new metals.

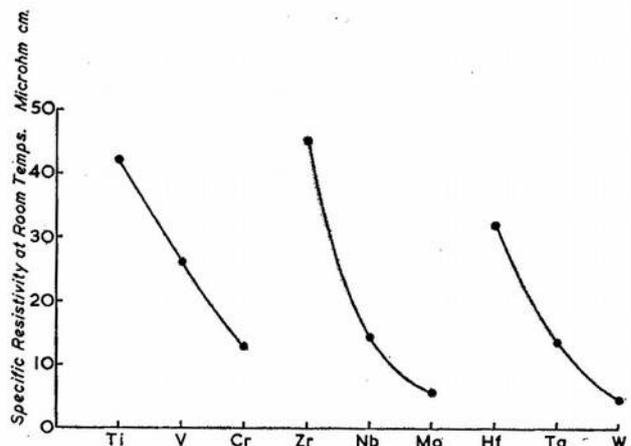


Fig 7. Specific resistivities.

It is obvious from the few examples given that the behaviour of the early transition metals conforms to an overall pattern. A number of attempts have, in fact, been made to put forward a coherent theory of the whole series of transition metals based on the properties already mentioned together with others such as soft X-ray spectra and electronic specific heats. The value of the paramagnetic susceptibility of the non-ferromagnetic transition elements, for instance, is proportional to the density of energy states at the Fermi-surface, and the temperature coefficient of susceptibility is related to the first and second derivatives of the density of states. Thus it can be argued that in titanium and chromium, for which the temperature coefficient of susceptibility is positive, the Fermi energy lies close to a minimum in the density of states curve for the d-band. Unfortunately, however, it is not possible to deduce from a series of such arguments for each separate metal the shape of the whole density of states curve, since a d-band of any given shape is unlikely to apply to the group of elements collectively. Similar difficulties tend to be encountered in any approach to the theory of the transition metals.

The position has been reviewed by Hume-Rothery and Coles¹, and more recently some further ideas on the electronic nature of the transition metals, based on data obtained from experiments on X-ray scattering together with the magnetic properties of transition metals and their alloys, have been put forward by Mott and Stevens.² No completely satisfactory picture has yet been formulated, however, and it appears that the next step forward must await the collection of sufficient experimental evidence, more particularly on the alloys of the transition metals with each other, to permit the formation of a strong empirical hypothesis which can then be tested more rigorously.

Lack of a basic theory of the transition metals does not necessarily mean that the development of useful materials from among the new metals must be done without the help of the more fundamental ideas of metallurgy. In producing materials of high strength, for instance, much of the recent work on the deformation of metals is of the highest value, and if strength were the only criterion for a new material, it would probably be possible to produce what is needed without very much difficulty.

First principles applied to the oxidation problem, however, produce smaller result. Fundamental investigations of oxidation reactions have indeed been carried out, and it has been fairly clearly established that the protectiveness of an oxide film depends on its physical fit with the metal on which the film is formed and the difference between the temperature coefficients of expansion of metal and oxide. If the film is protective its rate of growth is determined by the rate of transfer of anions, cations and electrons through the oxide layer, the chemical potentials of oxygen at the metal/oxide and oxide/gas interfaces, and the electrical conductivity of the oxide. Though, like all theories, that of oxidation does not necessarily fit all the experimental facts, it is sufficiently well substantiated to make it possible to write a rough recipe for an oxidation-resistant alloy. It is quite another matter, however, to prepare such a material from the ingredients at our disposal.

It is in tackling the latter problem that the lack of a complete picture of the electronic characteristics of the metals is the most serious handicap. At present hypotheses from which predictions regarding oxidation behaviour can be made must be built up by direct observation of oxidation processes in a wide range of metals and alloys, and only when sufficient experimental information has been collected will it be possible to estimate the chance of finding a sufficiently oxidation-resistant alloy among the new metals. On the other hand, of course, the next oxidation test carried out might reveal the ideal material, but it is not very likely.

An answer to the oxidation problem may require so fundamental a change in the character of the metals studied that there is a considerable danger of losing, partly or wholly, the properties which make them of potential value as high temperature materials. It must be hoped that with the successful outcome to the oxidation work will come sufficient understanding of the factors involved

to permit adjustments necessary to preserve the desired mechanical properties to be made without destroying oxidation resistance. The need to solve the two problems simultaneously is one of the strongest reasons for the emphasis placed on understanding at all stages in the process of alloy development. Without it, it would be very difficult to modify suitably an alloy found to have good oxidation characteristics but poor creep properties or vice versa.

Current State of the Work

Studies of the new metals aimed at high temperature materials have been going on, mainly in America, for the last five years or more, and work on beryllium and tantalum for a limited range of applications has been in progress for many more years.

Niobium research has revealed alloys which have oxidation resistance several hundred times better than that of the pure metal, which means that though the target has not yet been reached, there is good reason to believe that its attainment will be possible. The most oxidation-resistant materials prepared so far have had rather poor mechanical properties and have been difficult to work.

It is generally accepted that molybdenum-base alloys are unlikely to be of high-temperature use without a protective surface coating, and though coatings have been developed which are successful under some conditions, none has yet appeared which can withstand the rigours of the gas-turbine. Tungsten, which presents much the same problems as molybdenum is less far advanced.

Chromium has been held back by the handicap of room temperature brittleness. At one time it was thought that this might be an inherent characteristic of the metal itself, but intensive Australian work has shown that chromium can be ductile at room temperature if the nitrogen content is reduced to a very low level indeed. At present the very high purity material is prepared by a carefully controlled electrolytic process. If a larger-scale source of supply became available development of chromium alloys would be considerably encouraged, and though a year or two ago it was felt that the chances of ultimate success were slight there has been a recent resurgence of interest which may herald an important step forward.

The present position regarding vanadium is not hopeful. Thorough investigation of its oxidation behaviour led American workers to the conclusion that it was hopeless as a high temperature material, and no developments have occurred elsewhere which could challenge this view. Some people, however, see vanadium as a higher-strength rival to titanium in the low-temperature field.

Tantalum, though not a favourite for high-temperature use, has sufficient promise to have justified some alloy development work in America, but no great progress has been reported. A good deal is known, however, about the preparation and fabrication of the pure metal.

Of the Group IVA elements, titanium and zirconium are established industrial metals and for titanium, at any rate, the alloys have been widely studied. Hafnium is only just beginning to come into the picture and little is yet known about it.

The toxicity of beryllium has confined work on this metal to a few special laboratories whose interests are such as to discourage publication of the results. The aircraft industry, however, is believed to be interested in the possibility of high-strength beryllium alloys, and if the metal eventually becomes available for non-nuclear purposes it is probable that alloy development work will have to be undertaken.

Future Outlook

In the foregoing discussion the difficulties of obtaining the new materials made necessary by modern technological development have been emphasized. The example of history suggests, however, that if the result is needed badly enough success will ultimately be achieved. The materials we now call new metals will always be expensive compared with the common constructional materials because of the basic difficulties of obtaining them from their ores, purifying the product, and melting and processing without contamination, quite apart from paying for the very large amount of research which will be needed to develop them to a useful state, but increased demand and the savings resulting from experience will very probably have their usual effect of reducing the price to an acceptable level, as has already happened to a large extent with titanium and zirconium. If and when this happens, the metals discussed in the present article will no longer be new, but will become a vital part of our transport and power producing industries.

REFERENCES

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2. N. F. Mott and L. W. H. Stevens, *Phil. Mag. 8th Series II*, 1364, 1957.