Bulletin of Electrochemistry 8 (8) August 1992, pp 407—410

0256-1654/92/$ 3-50

MATERIALS FOR HIGH TEMPERATURE APPLICATIONS

M HARIHARAN AND M P GUNASEKAR

Central Electrochemical Research Institute, Karaikudi-623 006, INDIA

The demand on materials with good strength for high temperature applications is ever increasing. Till recently hundreds of alloys such as austentic stainless steel, the cobalt base vitallium, nickel base hastelloy, inconel, etc have been developed. Addition of refractory elements like Mo, W, Ta, Nb, Zr, Ti and Hf improved the high temperature properties of these alloys. However with the advent of aerospace, gas turbine and most modern metallurgical industries, tremendous progress has been made in the area of ceramics and refractory hard metal technology. Some of the recently developed high temperature materials are received in this paper.

Key words: High temperature materials - carbides, borides, silicides, nitrides, aluminides and other special alloys, properties and applications.

INTRODUCTION

Advanced high temperature materials have become increasingly important in the past few decades because of the continuing need for engineering materials with better properties, longer life and lower costs. For instance, aerospace industries, gas turbine and jet engines, reactor technology and most modern metallurgical industries require materials with high mechanical strength, as well as oxidation and corrosion resistance at elevated temperatures even beyond 1250 K.

Many common metals and alloys, particularly the iron base alloys, developed for high temperature applications are useful only upto 1000K since it appears impossible to increase their recrystallisation temperatures which are related to the mechanical strength. Although nickel, cobalt and chromium base alloys recrystallise at higher temperatures they are also not useful beyond 1250 K.

High strength at elevated temperatures can be predicted for materials with very high melting points. Noble and refractory metals come as the next choice since they possess high melting points and high recrystallisation temperatures.

Noble metals such as platinum are excluded owing to the limited availability and excessive cost.

The applicability of refractory metals such as W, Ti and Ta as useful high temperature materials is also limited due to their unsatisfactory oxidation resistance at high operating temperatures.

As a consequence of the constant quest for such materials, a series of high temperature materials have come to use at present. They are mainly the metal oxides and refractory hard metals i.e. refractory metals hardened by inclusion in their lattice structure of tiny elements such as carbon, boron, silicon, nitrogen, etc. These interstitial compounds are respectively known as carbides, borides, silicides and nitrides.

The refractory hard metals possess extremely high melting points and as a consequence, high mechanical strength, outstanding oxidation resistance, high thermal and electrical conductivity, low density, poor tendency to thermal shock and so on. In this context, a broad outline of high temperature materials, their properties at high temperatures and the application possibilities of such ceramic materials needs attention.

PROPERTIES OF HIGH TEMPERATURE MATERIALS

First and foremost requirement of high temperature materials is the melting point or dissociation temperature. The higher the melting point, the higher is lattice strength and greater the possibility of its applications at high service temperature.

On an examination of a variety of materials, it can be stated that, primarily some of the carbides exhibit the highest melting points viz., ZrC, TaC, ZrC + TaC which lie in the range 4000 to 4250 K. Then comes the borides and refractory metals with melting points of 2300 to 3850 K and the oxides and nitrides whose melting points lie in the range 2100-3400 K and then the silicides and intermetallics with melting points from 1750 to 2550 K.

In view of the higher melting points with a consequent lower vapour pressure, these materials have a high negative free energy of formation and consequently thermodynamical stability at high service temperature.

An examination of the strength of metallic materials with increasing temperature show that even metals like Mo, Nb and Ta at about 1250 K have only 25% of their mechanical strength at room temperatures. Such a decreasing strength is also manifested in the alloys of W, Mo, etc. In contrast, the ceramic group consisting of the carbides, borides, silicides, metal oxides and nitrides show the highest moduli in the order mentioned. For instance, carbides and borides of the transition metals have a strength of 600 N. mm^{-2} at 1250 K.

In addition to the hot strength of a material, its suitability in various environments needs consideration. An analysis of the high melting metals and alloys and also of the ceramic materials indicates that even above 1750K the refractory metals (RMs) such as Re, Mo and W, the oxides and carbides of W, Nb, Ta Hf and Zr, and others such as Mo_2B, ZrN, TaN, Si_3N_4 and $MoSi_2$ are stable and can be used under reducing atmospheres. However, other than oxides, only SiC and some silicides and borides like ZrB_2, CrB and HfB_2 are stable in oxidising conditions above 1750 K.

Aerospace and in moving gas turbine parts (buckets) are subjected to thermal, vibratory and centrifugal stresses and materials with high specific strengths become of prime importance. High specific strengths are often and usually provided by light weight materials of density values below 4 g. ml^{-1} possessed by some berylides, oxides, carbides (SiC and B_4C) and nitrides (Si_3N_4 and BN) as well as the boride and silicide of titanium are advantageous from this angle.

Another important requirement of high temperature materials is the thermal shock resistance i.e. the ability of the material to withstand fluctuating temperatures without crack formation and propagation. Usually high values of tensile strength(S) and thermal conductivity (K) and low values of young's modulus(E) and coefficient of thermal expansion (∞) can favour resistance to fracture by thermal shock. The parameter $\frac{KS}{\infty E}$ can provide a quantitative basis for evaluation of thermal shock resistance [1].

In the choice of materials, time of residence at the service temperature too requires consideration. Distinction can be made between long and short term stresses of materials at service temperatures. For instance 1000 hours of life is sufficient in aircraft jet engines whereas power plant turbines are expected to last for more than 10 years. The materials used in aeroplane engines at higher operating temperatures do not satisfy power plant applications.

Rocket parts, such as nozzles face only short time exposure to high temperature stress and hence materials of good thermal conductivity with even poor oxidation resistance are of the immediate choice.

Various requirements of high temperature ceramic materials have been discussed above. However practical application of such materials demands the consideration, simultaneously, of a number of properties for a judicious selection.

Figure 1 summarises the advances in material developments in the last four decades [2]. It is evident that metallic materials capable of operation up to 1500 K are available at present. Further demand surely rests on ceramics. In case of heat exchangers also a similar picture can be presented. Figure 2 indicates that for service temperatures above 1250 K, ceramics alone can be considered [3].

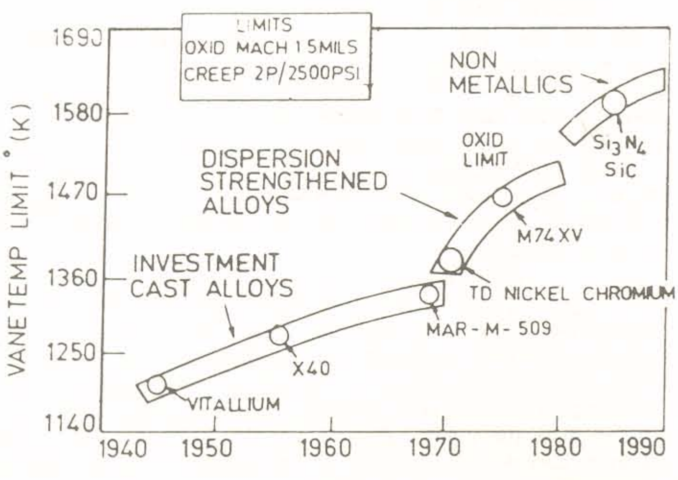

Fig. 1: Advances in materials developments.

FABRICATIONAL DEPENDENCIES OF HIGH TEMPERATURE MATERIALS

Ceramic parts for high temperature application are usually manufactured by powder metallurgy techniques and hence the retention of stoichiometry, the proportion of impurities and the particle size of the powders play an important role on the behaviour and material properties. In addition, manufacturing techniques have an important bearing on the microstructure of the formed product viz., size, shape, porosity and grain size.

Among the sintering techniques, the pressure sintering technique has an edge over the normal sintering process. Complicated shapes requiring no further treatment can be formed by simultaneous application of pressure and heat to a forming die in a single operation. Pressure sintering ensures densities close to the theoretical values and no shrinkage occurs.

The influence of density on the strength [4] of the ceramic materials can be seen from the fact that in the case of chromium carbide bodies at 12% porosity, the modulus rupture is only half that at zero porosity. An increase in porosity, in general, causes a decrease in strength. In addition, circular (spherical) pores have less detrimental effect on strength than flattened pores. Likewise an increasing grain size can lead to a sharp decrease in shear strength.

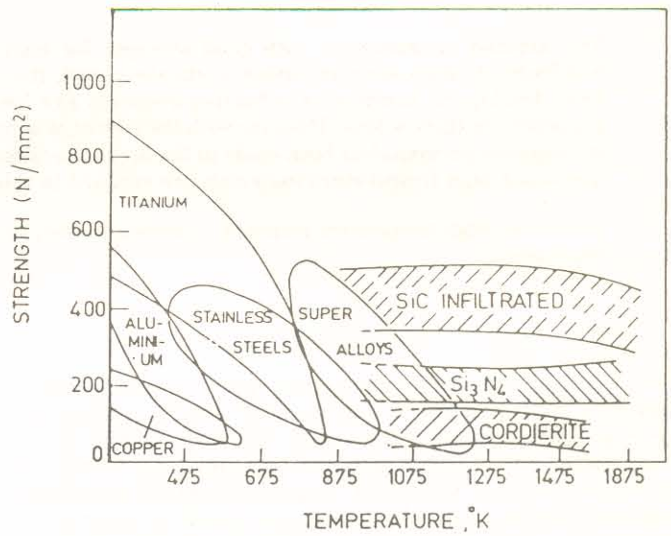

Fig. 2: Service temperatures of ceramic materials.

As regards the particle size of the starting powders of ceramics, the general rule is that smaller size particles aid sintering at lower temperatures and result in densities close to the theoretical values. As pointed out above, the strength of ceramic materials is related to the porosity.

A similar dependence exists for thermal shock resistance, though here the dependence proceeds in the opposition direction. While the strength decreases with porosity, the thermal shock resistance increases. For example, graphite which has only moderate strength has extremely good thermal shock resistance. Silicon nitride is valued more for its good thermal shock resistance coupled with good hot mechanical properties. On the contrary, MgO with poor thermal shock resistance has no place when the situation demands high fluctuation of temperature.

In the application of high temperature materials where thermal shock resistance is highly important, a compromise is therefore inevitable between an adequate hot strength and thermal shock resistance.

Usefulness of hard metals and oxide ceramics for high temperature applications depend on the various properties listed above. If the hot strength and oxidation resistance alone are taken into consideration, without stressing on the brittleness and sensitivity to thermal shock, several oxide ceramics and hard metals offer promising applications. Questions regarding the relative merits and promises of the two class of materials - ceramic and hard metals are difficult to answer. However, hard metals, particularly the borides of the transition elements, exhibit chemical stability including oxidation resistance equivalent to that of ceramics, even beyond 1300 K. They also have high short time strength at elevated temperatures. They possess metallic conductivity and exhibit high thermal conductivity as well as good thermal shock resistance. In this respect the borides are superior even to ceramic materials developed for gas turbine and similar applications.

Evaluation and comparison of properties of a wide variety of materials show that the transition metal borides, on account of a combination of the properties of ceramics and hard metals, offer immense scope for high temperature application.

APPLICATIONS OF HIGH TEMPERATURE MATERIALS

As already indicated only the ceramic materials are suitable for use at high service temperatures under stringent working conditions.

Among the oxide ceramics, high alumina (more than 90% Al_2O_3) materials are used in metallurgical industries where severe conditions are present., e.g. casting and close systems. Magnesia and zirconia based materials are also used for such applications. Fully stabilised ZrO_2 is used for casting nozzles in the tundishes in continuous casting while partially stabilised ZrO_2 is used in sliding gate closure plates.

Efficient refractory lining of furnaces assumes importance in view of energy savings and the recent survey indicates the development of fibre materials which are predominantly based on Al_2O_3/SiO_2 compositions[5]. Such insulating materials are manufactured in the form of mats and modules. Application of fibrous refractories leads to reduction in heat losses and improved heat storage coupled with the reduction in the weight of the refractory materials.

A recent application of oxide ceramics has been in the development of oxygen sensors for monitoring the oxygen content of furnace atmospheres. The sensors coupled with a fuel control system help to regulate the flow of air into the furnace leading to the highest working efficiency. Such sensors consist of ZrO_2 electrolyte, usually stabilised with Y_2O_3, coated with platinum, and mounted in a refractory block. The device is inserted through the furnace wall into the combustion area for measuring the partial pressure of oxygen.

Similar oxygen sensors are finding increased use in automobile engines for regulation of air-fuel ratio to meet the fuel efficiency and emission standards[6].

An emerging class of ceramics based on a combination of oxides and nitrides are being developed for high strength and creep resistance and good sintering and hot pressing ability, 'Slalons', as they are designated, are mixed phases of Si_3N_4 and oxides primarily of Al_2O_3 [7].

Ceramic engines with practically no wear and tear based on stabilised zirconia are being developed and by the dawn of the 21st century revolutionary progress and achievements are anticipated in automobiles.

Among the hard metal carbides used as the tool materials, TiC appears most suitable as it possesses superior oxidation and thermal shock resistance properties. However, at higher temperatures TiC fails to form adherent protective coatings. TiC cemented with a Ni-Cr alloy is better and remains practically unchanged due to the formation of a dense, adherent protective layer.

A material consisting of about 65% TiC, 15% solid solution (NbC-TaC-TiC) and about 20% Co, commercially known as 'Kentanium' [8] is highly suitable for applications requiring strength, resistance to oxidation and thermal shock up to 1450 K and particularly useful for gas turbine blades, both rotor and stator up to an operation temperature of 1350 K. Various grades of kentanium are available that contain different compositions of TiC-NbC-TaC in combination with varying degrees of cementing elements viz., Co and Ni.

Still superior performance of TiC materials has been made possible by modification of binder composition i.e., by the incorporation of Cr or Cr-Co, Ni-Cr or Co-Ni-Cr alloys, and this class of alloys are known under the trade name "*WZ Hard Metals*" and find use in the fabrication of gas turbine parts.

Other than TiC, ZrC is well understood but finds limited study in view of its inferior oxidation resistance. However WC-Co cemented carbide with the addition of TiC has superior machining properties. Recently cemented chromium carbide materials have been developed with outstanding oxidation and corrosion resistance at elevated temperatures.

Other than the refractory metal carbides and cemented compositions, silicon carbide finds extensive high temperature applications. SiC bricks are used in blast furnaces as corrosion and abrasion resistant materials with their high strength and shock resistance properties. SiC fibres with a density of 3.4 g. ml^{-1} have become available recently.

Silicate bonded SiC heating elements are usable up to 1850 K. In recent years $MoSi_2$ and $LaCrO_3$ heating elements which can go up to 1950 K and 2050 K respectively have come of use in industrial furnaces.

The borides of the transition metals with their high melting point are the suitable choice for high temperature applications. They are considered even superior to carbides, because of better corrosion and oxidation resistance at extremely high temperatures.

Among the borides, the diborides of Zr and Ti are the most important. ZrB_2 is one of the hardest materials developed so far and in special tests a ZrB_2 product survived high temperature blasts better than any other material [9].

Titanium diboride, with its extremely high melting point (3250K) and high tensile strength coupled with extremely good thermal conductivity finds application in rocket parts such as nozzles. TiB_2 is also stable in fluoride melts. This property combined with its excellent electrical conductivity offers scope for its investigation as alternate cathode material in aluminum cells. It is also useful in the manufacture of high temperature crucibles and evaporating basins for distillation of metals such as aluminum.

Another boride of commercial importance is chromium boride which offers scope as excellent coating material for oxidation and corrosion protection over steel substrates at high temperatures, particularly in heavy boilers.

The silicides also have similar properties. They possess outstanding oxidation and corrosion resistance at high temperatures. In addition, sintered silicide products deserve mention as high temperature materials requiring strength and chemical stability. Among this group of materials molybdenum disilicide, ($MoSi_2$) alone finds commercial application as heating element because of its outstanding oxidation resistance. $MoSi_2$ can be used up to 1970 K.

Another silicide worth mentioning is chromium silicide. Addition of chromium metal to chromium silicide gives a material with high temperature properties equivalent to standard cermets.

Among the nitrides silicon nitride Si_3N_4 has been investigated extensively for its application in gas turbine, truck and vehicle motors in view of its high hot strength. The present day concept of an automobile engine envisages a combustion chamber in SiC and inlet cone, stator ring, rotor disc and turbine blades in Si_3N_4[10].

Though the nitrides of the transition metals are stable and have high melting points, hardly any mention is made of their high temperature applications.

Aluminide such as nickel aluminide having considerably higher melting point (1900 K) offer itself for high temperature service conditions. Ni-Al has fairly good oxidation resistance properties up to 1400 K and good strength up to 1100 K, but loses its strength rapidly at high temperature[11].

Ti-Al has interesting strength-to-weight ratio. SiC reinforced Ti-A matrix has been prepared by plasma spraying method for gas turbine applications[12]. Aluminides are also being investigated for fuel cell applications.

Development of protective ceramic coatings against corrosion and oxidation of metals and alloys at high temperature, also needs mention in this context. Recent trends indicate the development of such coatings even over ceramic parts, particularly in special metallurgical applications where rapid wear, erosion and corrosion are predominant due to the molten slag and molten metal.

$MoSi_2$, TiN, TiB_2, ZrB_2, Al_2O_3, Cr_2O_3 spinels, etc are some of the coating materials useful for such applications and the coating is usually made by plasma spraying technique.

Further demand of this class of materials is ever increasing and scientists and engineers are constantly contributing to this important and interesting area of engineering materials.

REFERENCES

1. P Schwarzkoph and R Kieffer, *Refractory Hard Metals*, Mac Millan Co, (1953), p. 359.
2. L P Jahnke, *J Metals* **4** (1973)15.
3. H J Pahlmann, H R Maier and A Kravth., *Proc Brit Ceram Soc*, 26, (1978) p. 17.
4. A Majidic, La, *Ceramica* **34**–5(1981)26.
5. A Majidic, La, *Ceramica* **34**–5(1981)27.
6. R V Wilhelm and D S Edda, *Amer Ceram Soc Bull* **56** (1977)509.
7. R R Wills, R W Stewart and J M Wimmer, *J Amer Ceram Soc* **60** (1977)64.
8. P Schwarzkoph and R Kieffer, *Refractory Hard Metals* Mac Millan. Co, (1983) p. 387
9. P Schwarzkoph and R Kieffer, *Refractory Hard Metals* Mac Millan Co, (1953) p. 408.
10. D Mchaughlin, Proc. *Brit Ceram Soc* **26** (1978)183.
11. Robert Steinitz, *Proc Conf High Temperature Materials* (Eds) R F Hehemann and G Mervin Ault. John Wiley and Sons Inc, New York (1957) p. 182.
12. *High temperature technology*, Vol 8, No. 1, (1990) p. 59.