HIGH TEMPERATURE STRUCTURAL MATERIALS

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Summary

High temperature materials have played an important role in our lives by, for example, making possible modern jet aircraft that can take us to all corners of the world, and spacecraft that have taken mankind to the moon and back. The superalloys, ceramics, intermetallics, etc., developed for these and other applications in the past now provide a sound technological base from which current and future researchers can develop new or modified materials useful in improving the efficiency and general environmental friendliness of a variety of energy sources and transportation systems. To help accomplish this, the availability of high speed computers and massively parallel processing capabilities is now leading to the development of the field of "Computational Materials Science" in which the complex relationship between interatomic bonding and properties may be unraveled. It is suggested that such insights may well have a positive impact on developing new materials needed to improve the way we use our energy resources.

1. Introduction

The average person does not generally characterize materials in terms of their temperature capabilities. For example, very few people think of aluminum as a low temperature material; it is simply the material from which pots and pans or screen doors

are made. The situation is somewhat more obscure when it comes to high temperature applications because few individuals outside of specialists in the field can even name those materials responsible for making modern jet engines and space launch vehicles possible. The materials scientist or materials engineer on the other hand is very much involved in this business of characterizing materials according to how they perform under certain thermal conditions because it is a convenient way of quickly narrowing the field of possible candidates suitable for a particular application. To this end, there is no universally accepted temperature serving as a dividing line between low and high temperature materials, but most materials scientists tend to consider materials which maintain significant structural integrity above 600°C as high temperature materials, as will be assumed for the purposes of this discussion.

Included among applications that are viable only because there are materials that can survive the rigors of operating at high temperatures are gas turbine engines for aircraft and power plants, incinerators, blast furnaces, some fuel cells, rocket engines for launching vehicles into space including the Space Shuttle, nuclear power plants, and many more. Each one of these has somewhat different requirements and so development of the relevant materials often takes place within that technology area. For example, the specific requirements of aircraft jet engines and the need for ever greater efficiency and thrust has led over the past 60 years to the development of "superalloys" (usually nickel-base metal alloys) which are perhaps the most studied and most sophisticated high temperature structural materials to emerge from industrial innovation. Advances in the technology, therefore, tend to be driven by requirements or needs and as a consequence tend to be evolutionary rather than revolutionary. At least, that is the history of the subject up to the present time.

For an entity to be considered a useful high temperature material it often must be able to survive a variety of extreme conditions which in turn requires that it have most of the following properties. First of all, it must have a high melting point because generally its operating temperature, T, cannot exceed one-half the melting point, T_m, i.e., $T/T_m \leq 0.5$ (where the temperatures are in degrees Kelvin). An exception to this rule of thumb are the superalloys whose operating temperatures often approach $T/T_m = 0.8$. Second, it must resist catastrophic oxidation if it is to operate in an oxidizing environment or, in a more general sense, it must not react with its environment in a manner which degrades its performance. Third, it must be tolerant of the stresses that are imposed on it and generally this means that some ductility (or toughness) is required to avoid catastrophic mechanical failure. As will be noted below, many materials having high melting points, and therefore potential candidates for high temperature applications, tend to lack ductility under ambient conditions because the strong interatomic bonds that lead to their high melting points and strength at elevated temperatures are precisely the type of bonds that can lead to brittleness at lower temperatures. Fourth, many applications place a premium on weight reduction thereby eliminating many of the refractory metals such as tungsten which, although exhibiting a very high melting point (3370°C), has too high a density to be considered seriously for many uses except light bulb filaments and others for which weight is not a factor. Fifth, it must be possible to form the material into the desired shape, part, or piece of machinery at a reasonable cost consistent with the application. This can be a serious problem with some materials for which standard

forging, casting, rolling or other methods developed for relatively low temperature materials are simply not applicable.

To accommodate these critical and often conflicting requirements a number of different types of high temperature materials have been developed over the years with varying degrees of success. Some of the most noteworthy of these are reviewed in the following sections followed by a discussion of their applications and a look at what the future holds for the development of advanced high temperature structural materials.

2. Review of Current High Temperature Structural Materials

2.1. Ceramics and Ceramic Matrix Composites (CMCs)

Within the group of high temperature materials identified as ceramics, the metal oxides and nitrides are far and away the most important from a technological and commercial point of view. The use of oxides, and particularly magnesium oxide (MgO), as a refractory material dates back many years having served the steel industry in the form of magnesia bricks that are used to line blast furnaces and other hot metal processing equipment. For that application the refractory bricks are ideal since the poor thermal conductivity of the MgO serves to thermally insulate the molten metal from the surrounding furnace structure and the material suffers no degradation from oxidation since it is already an oxide. On the other hand, cracking and spalling are problems since MgO shares the one drawback of many ceramics-it is a brittle material.

Efforts to overcome the seemingly inherent brittleness of oxide ceramics have taken several forms. In one, considerable success has been achieved in inhibiting crack propagation in zirconium oxide (Zr_2O) through the use of "transformation toughening". This mechanism involves the partial stabilization of a second phase, a tetragonal phase, within the monoclinic matrix that is the normal room temperature phase. The toughening phase takes the form of small particles which are in the metastable tetragonal state due to the use of small additions of stabilizing oxides, such as MgO, and because of the elastic constraint of the matrix. However, the stresses at a crack tip can induce the particles to transform from the metastable state to the equilibrium monoclinic state. This transformation is accompanied by a volume change which introduces compressive stresses that impede crack propagation since cracks tend to expand under tensile forces. Since the discovery of transformation toughened materials in the early 50's, and the availability of commercially produced material in the 60's, more recent work has shown that the toughening mechanism can be extended to other matrices, for example alumina (Al_2O_3) to give what is known as zirconia-toughened alumina (ZTA).

Another scheme for toughening ceramics involves the use of continuous ceramic fibers embedded in a ceramic matrix to form CMCs. One of the most successful of these makes use of high performance silicon carbide (SiC) fibers (exhibiting excellent strength and creep resistance up to 1300°C) which are imbedded in a SiC matrix. The key to obtaining acceptable properties for the CMC is in controlling the strength of the interfacial bonding between the fibers and matrix. If the bond strength is too great, the behavior is that of a non-composite, i.e., brittle. On the other hand, if the bond is too weak, the fibers are not able to take part in the load bearing process-again resulting in

brittle and weak behavior. What is desired then is a fiber/matrix interface of intermediate strength and to this end pyrolytic carbon coatings on the fibers have been developed which can provide just the right interfacial properties. Under these conditions if small microcracks develop in the matrix when it is under load, the cracks are blunted by being deflected along the fibers thus preventing catastrophic failure. The problem is that when at elevated temperatures the matrix may react with the fibers thereby altering the properties of the interface which, in turn, generally causes the properties of the CMC to degrade. The control and stabilization of this interfacial strength is the focus of much activity in the CMC arena but at present it is safe to say that no CMC can operate for 1000 hours above 1300°C as would be desirable for jet engine applications.

Another type of ceramic that has come to prominence in recent years are the nitrides, particularly silicon nitride (Si_3N_4) and the related SiALONS which are solid solutions based on Si_3N_4 formed by substitution of aluminum for silicon and oxygen for nitrogen. Since these ceramics sublime instead of melting the only way they can be formed into shapes or bulk material is through the consolidation of powders, there being three different ways of doing so. The first method, sintering, involves compacting the powders and then heat treating them at very high temperatures (up to 1800°C) in a nitrogen atmosphere to prevent sublimation. The resulting solid can be made fully dense in this manner especially if sintering aids such as yttria (Y_2O_3) are employed but there is an incredible amount of somewhat uncontrolled shrinkage that occurs during the sintering process so the method cannot be used to make net shapes. Instead, parts such as turbine blades must be machined from blocks of material which adds greatly to their cost. The second method, hot pressing, involves the use of special equipment that can apply pressure to the powders while at the same time the powders are heated to about 1700°C. Fully dense material can be made in this manner and parts can be made near net shape especially if the part is not too complicated in form. The third process, reaction bonding, starts with silicon metal powders (instead of Si_3N_4 powders), and involves consolidating the powders to the shape desired and heating in a nitrogen atmosphere for long periods of time (up to 24 hours) until the reaction which converts the silicon powder to Si_3N_4 is complete. Fortuitously, no shrinkage or expansion occurs during this process making net shape formation quite viable. However, it is very difficult to achieve full density in this manner and as a consequence the mechanical properties of reaction bonded Si_3N_4 are generally inferior to, for example, hot pressed material.

During the 70's and 80's the Defense Advanced Research Project Agency (DARPA) and the Department of Energy (DOE) in the USA sponsored huge programs which aimed at developing all-ceramic gas turbine engines for (1) automotive and (2) electric power generating applications. The motivation was to develop engines that would operate at high temperatures with improved fuel efficiency, be light in weight (for the automotive application), be low in emissions, and have multi-fuel capacity. Although a number of materials were studied and evaluated during the course of the program, the major emphasis was on developing Si_3N_4 and the SiALONs to the point where they could serve as materials for blades and rotors operating at 60,000 rpm and at temperatures up to 1400°C. The programs were comprehensive in that they not only focused on materials development but also on design-with-brittle-materials concepts, proof-testing methodologies, and non-destructive evaluation techniques, but in the end

the brittle behavior of the ceramics proved to be an obstacle that the researchers and engineers could not overcome. None-the-less, some engines were run at design speed for relatively short periods of time (up to 85 hours) and the extensive materials research led to the development of advanced cutting tool materials that perform much better than conventional tungsten carbide tools for some purposes.

Although the highly efficient, light weight ceramic gas turbine automobile engine envisioned by researchers in 70's and 80's did not materialize, the work paved the way for the "adiabatic" diesel engine which is now being developed for use as truck power plants. In this case, the use of high temperature ceramics to replace lower temperature steel components in the engine allows the engine to run uncooled thus eliminating the water pump, radiator and cooling fan leading to improved efficiency. Perhaps the 00's will be the time for ceramics to come of age and be utilized for applications not possible before.
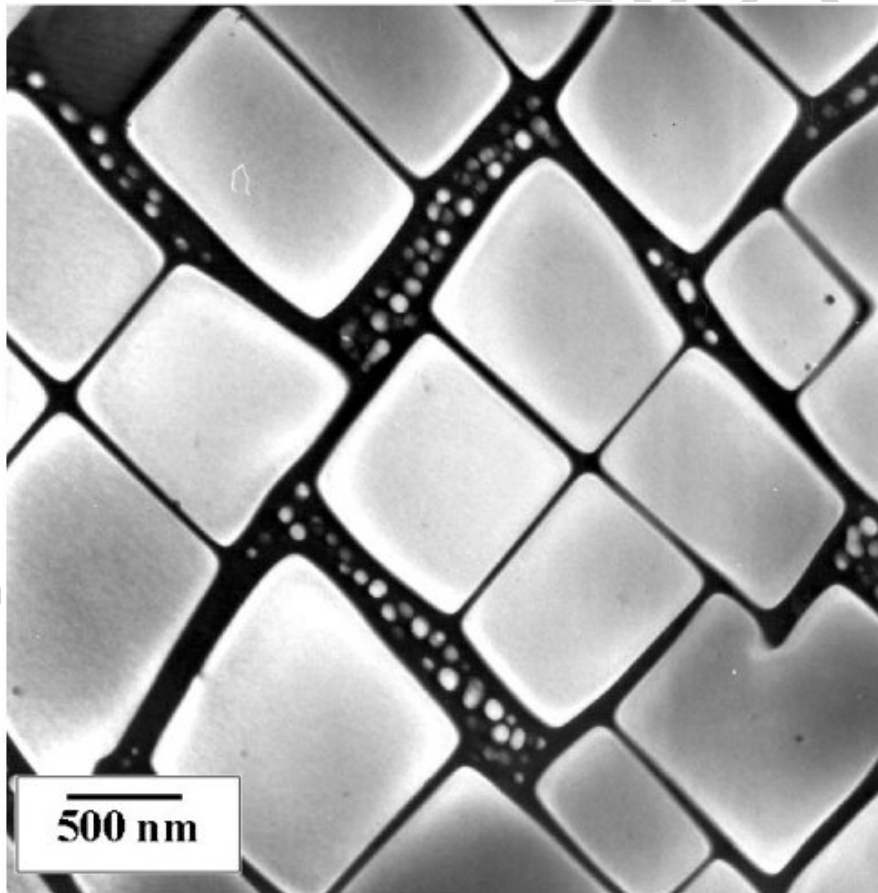
2.2. Nickel-base Superalloys

Figure 1. Micrograph taken with an electron microscope of a nickel-based superalloy showing its two-phase structure. The blocky areas are the intermetallic Ni_3Al phase denoted as γ' (gamma prime). In between, is the nickel-rich γ matrix phase containing some secondary γ' particles. Other constituents such as boron and hafnium are added for grain boundary control in polycrystalline or directionally solidified materials. (Courtesy of Dr.Mahmoud Ardakani, Imperial College, UK)

It is safe to say that over the years superalloys have been the most studied, engineered and successfully used of all the high temperature structural materials. Research and development in this area has been going on for over 50 years mostly driven by the need to improve the performance and efficiency of aircraft gas turbine engines. The basic metallurgical structure of nickel-base superalloys consists of a nickel aluminum titanium $Ni_3(Al,Ti)$ ordered intermetallic second phase embedded in a predominantly nickel solid solution matrix, Figure 1. Historically the intermetallic phase is denoted by gamma prime (γ') and the matrix phase by gamma (γ). Many additions have been made to this basic system to accomplish a variety of objectives. For example, additions such as boron, carbon and hafnium are added to modify the grain boundaries with the intent of inhibiting grain boundary sliding and therefore inhibiting creep which is the tendency of turbine blades (in particular) to elongate under stress at elevated temperatures. The reason for the concern over creep rate is that tight tolerances must be maintained in modern jet engines for reasons of efficiency and any significant elongation of the blades during operation could prove catastrophic.

Along with these changes in chemistry, significant changes have also taken place in processing techniques which in turn have demanded further and more radical changes in chemistry. Starting in the early years, most blades were fabricated by forging techniques but this soon gave way to investment casting which in turn gave way to directional solidification wherein the blades were formed so that the grain boundaries ran parallel to the axis of the blade and grain boundary sliding became almost a thing of the past. However, one more major processing technique entered the scene in the 70's and 80's which was to cause metallurgists to rethink and remove many of the additives that had been introduced over the prior 50 years. Specifically, a variant of the directional solidification technique was introduced that made it possible to grow single crystal turbine blades, i.e., blades that were virtually completely free of grain boundaries, Figure 2. Actually it took some time for workers in the field to reluctantly admit that much of the work that had gone into alloy development for the sole purpose of grain boundary control now had to go out the window. But out the window it went and today with single crystal blades incorporated into virtually every commercial aircraft engine the alloy compositions tend to be much simpler.

It would be remiss not to mention why superalloys have the remarkable properties they do. Much of the success of these materials is due to their unique two-phase structure, which, as stated previously consists of γ and γ' as shown in Figure 1. The blocky γ' second phase has one characteristic which is almost unique among materials, that is its strength increases up to a point with increasing temperature instead of decreasing as occurs with most materials. In addition, the presence of the somewhat non deformable second phase requires the operation of a deformation mechanism in the matrix that is quite unlike that which would obtain if a single phase alloy of the matrix composition were deformed. More simply put, the matrix is more resistant to deformation than it would be minus the second phase and the second phase itself is intrinsically quite resistant to deformation. The result is a combination that makes possible modern jet engines and our ability to expand our horizons with world-wide travel.

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Biographical Sketch

Dr. John Venables received his PhD in Physics from the University of Warwick, England and served as Associate Director and Chief Scientist of Martin Marietta Laboratories, Baltimore, Maryland until his retirement in 1990. At Martin Marietta he used his background in physics and materials science to investigate the properties of transition metal carbides; domain structures in pyroelectric materials; electromigration effects in thin film conductors; grain boundary structures in hafnium-modified superalloys; sintering mechanisms in silicon nitride; and basic bonding mechanisms in adhesively bonded aerospace structures. He has over 80 scientific publications including co-authorship of the "Materials Science" entry in the Encyclopaedia Britannica and has served on many committees of the National Academy of Sciences. He is currently a consultant on advanced materials to the aerospace industry.