3000°C That’s not just hot—it’s EXTREMELY hot. It is above the melting or decomposition temperatures for most of the materials known to man. But in the world of extreme environment engineering, it is just a baseline. The list of materials with melting temperatures above 3000°C is limited to perhaps 15 elements or compounds (Table I). That is a pretty small palette of materials to draw from for an engineer or designer.

Table I. Materials with melting temperatures above 3000°C.

<table>
<thead>
<tr>
<th>Material</th>
<th>Melting Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>TaB₂, Re</td>
</tr>
<tr>
<td>W</td>
<td>HfC, BN</td>
</tr>
<tr>
<td>HfB₂</td>
<td>HfN, ZrC</td>
</tr>
<tr>
<td>TaC</td>
<td>ZrB₂, TiC</td>
</tr>
<tr>
<td>TaN</td>
<td>NbC, ThO₂</td>
</tr>
</tbody>
</table>

Since the late 1960s, the world of high-temperature materials has focused primarily on SiC and Si₃N₄ as the materials of choice. Entire industries have developed to produce ball bearings, armor, fibers, and even turbine blades. But recently, there has been a revival of sorts in materials originally studied in the 1960s for potential aerospace applications, driven by “the need for speed”—with new propulsion and hypersonics concepts as shown in Fig. 1. Current increasing interest in hypersonic vehicles and weapons points to the need for new ultra-high-temperature materials for wing leading edges and nosegits, as well as propulsion system components.

There are more than 300 materials with melting temperatures over 2000°C, including the aforementioned SiC, refractory metals (Hf, Nb, Ir, Re, Ta, W), oxides (HfO₂, ZrO₂, UO₂, ThO₂), a variety of transition metal carbides, nitrides, and borides as well as other compounds. For real engineering applications, though, melting temperature is only one of many of properties used in the materials selection process. Strength (room temperature and at application temperature), thermal conductivity, thermal expansion, density, fabricability, and cost are also important factors in determining the optimal material for a given application.

For the purposes of this paper, we will simply define UHTC materials by their usefulness in a real structural (load-bearing) application where the very high temperatures are generated rapidly by burning fuels or friction with the atmosphere (not steady state). This will quickly eliminate most of the materials mentioned above. While oxides are reasonable to consider for use in oxidizing environments, poor thermal shock resistance due to high thermal expansion and low thermal conductivity eliminates them from further discussion. The silicon based refractory compounds (SiC, Si₃N₄, MoSi₂, etc.) possess excellent oxidation resistance up to 1700°C due to the formation of a layer of SiO₂ glass that inhibits oxygen diffusion to the parent material. This is the primary reason for the popularity of these materials for a wide variety of applications. However, active oxidation (the direct formation of SiO₂ instead of a protective SiO₂ layer) can occur at very high temperatures (> 1350°C, depending on P_O₂) and reduced system pressures. In addition, decomposition of already-formed SiO₂, or the interface reaction between SiC and SiO₂ results in SiO(g) formation at high temperatures and reduced pressure environments. Other materials, such as TiB₂, TiC, NbB₂, NbC, while having high melting temperatures, form oxides with low melting points (TiO₂ – T_m = 1840°C and Nb₂O₅ – T_m = 1485°C). Graphite has the highest melting temperature of any material known, but starts to burn at 800°C. While it is a most widely used material in high-temperature applications, it must be protected by coatings for long-term use.

What we are left with are the borides, carbides, and nitrides of the Group IV & V elements, as well as mixtures based on these compounds. While these materials of interest have been known since the 1930s, it wasn’t until the seminal works sponsored by the U.S. Air Force as well as the work of Samsonov in the 1960s that the class of UHTC materials became more widely known. As the ZrB₂ and HfB₂-based UHTCs are the most widely studied of these materials due to their good oxidation resistance from room temperature to over 2000°C, we will start by discussing them.

**Borides**

It is well known that Zr and Hf are very chemically similar elements, with their primary differences being density and nuclear capture cross section, so it is not surprising that the borides of these elements are also very similar. Both exist in hexagonal crystal structures of the AlB₂ prototype, with layers of B atoms in 2D graphite-like rings, alternating with Zr or Hf layers in a hexagonally close-packed array. Because of the very high strengths of the B-B rings and M-B bonds, these materials have very high hardness and temperature stability. While most extrinsic properties such as strength are dependent on processing and microstructure, the intrinsic thermal conductivities of the diborides are very high, approaching copper at room temperature, with little dropoff up to 2500°C. This makes ZrB₂ and HfB₂ very appealing for applications where thermal stress response is an important issue. A good example of this is rocket motor nozzles. In these applications, the temperature rise on the inside surface can approach 2000°C in less than 0.15
seconds, while the outer wall is still at room temperature. This $\Delta T$ generates a compressive stress on the inside (hot) surface, while the outside (cool) surface carries a tensile stress. Depending on the thickness of the nozzle, the thermal conductivity and strength will determine the success or failure of the part. A finite element model of thick and thin-walled cross-section (Fig. 2) shows the highest tensile loads in red. With higher thermal conductivity, the borides can more readily transmit the heat through the part and equilibrate the temperature within the cross-section, thereby reducing the thermal stress.

As mentioned previously, the strength of materials is dependent on processing and microstructure (as well as test methods used to measure the property). It is not surprising, then, that the strength values reported in the literature have a wide range. Because ZrB$_2$ and HfB$_2$ are hexagonal crystals, the properties exhibit anisotropic behavior within individual crystals. However, the bulk data reported are traditionally gathered from polycrystalline ceramics, and therefore do not show anisotropic behavior. As is common in ceramic systems, the strength of the diborides is generally shown to increase with decreasing grain size according to the Hall-Petch relationship. The influence of second-phase additions has also been reported. Silicon carbide was originally incorporated into HfB$_2$ and ZrB$_2$ by Cougherty, et al., in the 1960s as a grain refiner to improve its strength. More recent second phase additions include carbides and silicides. While these additions also influence the strength of the diboride ceramics, the primary interest of research on ZrB$_2$ and HfB$_2$ has primarily focused on improving their oxidation resistance.

The presence of a silica-forming species in the diborides greatly increased their oxidation resistance due to the in-situ formation of a borosilicate glass on the surface of the material, which impeded oxygen diffusion to the parent material. It was found that an optimal composition of ZrB$_2$ plus 20 to 30 vol% SiC, produced the highest oxidation resistance up to 2000°C. Pure diborides form liquid B$_2$O$_3$ during oxidation that can be protective up to around 1200°C, but the B$_2$O$_3$ evaporates at higher temperatures and no longer provides a diffusion barrier. The addition of the SiO$_2$-forming species helps increase the oxidation resistance by “tieing-up” the boria by the formation of a borosilicate glass that can be stable up to at least 1600°C.

A cross-section of a ZrB$_2$-SiC material oxidized at 1627°C in air is shown in Fig. 3. Efforts to model this oxidation behavior and the complex porous ZrO$_2$-glass scale are being undertaken by a variety of
researchers and will hopefully lead to further improvements in oxidation resistance. Hypersonic aerosurfaces will need to have lifetimes on the order of hundreds to thousands of hours to become cost-effective on reusable structures. One avenue to further increase the oxidation resistance has been reported by Talmy and Zaykoski. This involves the addition of transition-metal elements in the form of borides or silicides to produce complex immiscible glasses during oxidation to further reduce the oxygen diffusion rates through the glass. An example of the immiscible glass microstructure and a thermogravimetric oxidation curve showing the improvement of oxidation resistance is presented in Fig. 4.

**Processing**—While there has been a small amount of work describing the chemical vapor deposition of boride coatings, the vast majority of research on dense bulk boride materials has been in the form of powder-processed materials. Most boride powders have been synthesized by reduction, chemical or reactive processes. Carbothermal reduction of $\text{ZrO}_2 + \text{B}_2\text{O}_3$ is the most commercially viable process to produce $\text{ZrB}_2$, but often leaves $\text{B}_2\text{O}_3$ and carbide impurities. Other economically feasible processes for powder production include self-propagating high-temperature synthesis from the pure elements. The highly exothermic nature...
of these reactions makes them difficult to control, but can result in highly defective, very small crystals that have been linked to improved sinterability.

Densification of these materials has traditionally involved uniaxially hot-pressing in graphite molds at temperatures above 1800°C. However, recent work on the use of spark-plasma to minimize grain growth during hot pressing has drawn interest, and the reports of pressureless sintering by groups in Italy and the U.S. could lead to a wider use of borides in engineering applications by lowering processing temperatures and increasing the size and shape of articles that can be produced commercially.

**Carbides**

The transition-metal carbides have also been considered as UHTC materials of interest due to their extremely high melting points—exceeding those of the aforementioned refractory borides. The monocarbides of Ta and Hf are of particular interest because they possess the highest melting temperatures of any compounds (3980 and 3928°C, respectively), as well as very high hardness and elastic modulus. Many of the monocarbides exist in the NaCl-type face-centered cubic crystal structure. The carbides are not as commonly studied as the borides due to the low-temperature “pesting” that occurs during oxidation, which will be described later. However, for applications where there is a rapid rise to temperatures above 2000°C, the carbides have become of considerable interest.

Many transition-metal carbides have potentially tailorable thermomechanical and thermophysical properties due to a wide phase stability field that allows a large number of vacancies to exist in the crystal lattice. The extremely high melting temperatures of TaC and HfC are due to their interatomic bonding, which while most researchers agree is a mixture of metallic, covalent, and ionic—the strongest component in the monocarbides has been determined to be covalent. These highly covalent bonds not only affect the melting temperature, but contribute to the high elastic modulus of these materials as well. However, the precise nature of bonding in these compounds is not well understood, as discussed in these recent reviews.

As shown in Fig. 5, the phase diagrams for Hf-C and Ta-C show a wide homogeneity region for the stability of the monocarbides. While the chemical formula is generally written as MeC, MeC₂ is more appropriate, where x is the C/Me ratio. The properties of the materials across this stability range will obviously be a function of the interaction between the dislocations and vacancies in the lattice. This interaction increases the Peierls stress (the force needed to move a dislocation through the lattice) and also changes the bonding character (reduced contribution of C atoms to cohesion by reducing the number of Me-C bonds that need to be broken during dislocation motion as well as reducing the strength of the Me-Me bond by increasing vacancy concentration) that will decrease the Peierls stress.

A number of studies on the oxidation behavior of HfC over a wide range of temperatures have shown excellent oxidation behavior at temperatures above 1800°C, when the oxide formed can densify. At temperatures below 1500°C, the oxide grains formed are not able to sinter, causing them to spontaneously spall off the parent carbide, a process known as pesting. At low temperatures, the HfO₂ forms a porous scale (due to the evolution of CO₂ during the oxidation), and the oxidation kinetics are linear. At higher temperatures, the kinetics can be parabolic due to the slower diffusion of oxygen through a dense scale. Bargeron studied the oxidation behavior of HfC films, and described the presence of an oxycarbide interlayer between the HfO₂ outer later and the parent carbide. He concluded that the diffusion of oxygen through that the oxycarbide was the main rate controlling mechanism for the oxide growth. While others have also found evidence of oxycarbide at this interface (Fig. 6) after arcjet testing at higher temperatures (> 2200°C) in reduced pressure environments (using NASA Ames AHF arc-jet facility), both Shimada and Wuchina noted the presence of carbon (both graphitic and amorphous) at the interface after furnace oxidation at lower temperatures (800-1500°C). The effect of pressure on oxidation of the carbides has not been well studied, but the oxidation of carbon and HfC is controlled by the P₀₂ at the interface, with the reaction:

\[
\text{HfC} + \text{O}_2 \rightarrow \text{HfO}_2 + \text{C} \quad (1)
\]

describing the oxidation reaction at low P₀₂, while at higher oxygen pressures, the C would oxidize as well, leaving HfO₂ and CO₂ as the reaction products.

The effect of carbide stoichiometry has also been studied. In furnace testing (below 1600°C), HfC₀.₆₇ had a thinner oxide scale than HfC₀.₉₈, as shown in Fig. 7. The oxide on the subcarbide was also denser, with less porosity and cracking, than on the higher carbide. The main difference between HfC and TaC is the melting temperature of the oxide formed. While HfO₂ is itself a high-temperature ceramic, with a melting temperature of 2758°C, TaO₂ has a much lower melting point of 1872°C. This difference is a major component in the materials selection process. For high-temperature applications in oxidizing environments, such as engine propulsion or hypersonic leading edges, where a shape-stable, non-eroding oxide is needed, TaC is not likely to be used because the oxide formed will readily slough off, especially in high-shear flight environments, as shown in Fig. 8. HfC is a much better choice due to the HfO₂ stability. However, when P₀₂ is considerably lower, it is possible that the oxide will not form on TaC, whereas HfO₂ will form on HfC at even very low oxygen pressures. Under these conditions, TaC would be a better material option.
structural material. Agte\textsuperscript{29} reported a maximum in the melting temperature in TaC-HfC solid solutions, but more recent studies in this system have indicated that the melting temperatures fall within the melting temperatures of the pure components.\textsuperscript{30}

Processing—As with the diborides, monocarbides powders are commercially produced by either carbothermal reduction (sometimes with CaCO\textsubscript{3}) or direct reaction (SHS synthesis).\textsuperscript{31,32} Densification is typically done by hot pressing, but plasma spraying and hot isostatic processing (HIP) have also been employed. Plasma spraying has the advantage of producing near net-shape articles, but stoichiometry tends to be difficult to control due to loss of C at extremely high-temperatures in the plasma, while the HIP process is used when control of carbon content is of high importance. The metallic encapsulation necessary to densify the carbides from the powders is an effective diffusion barrier to the carbonizing atmosphere in the HIP vessel from the heating elements.

Nitrides

Transition metal nitrides are of critical importance in the microelectronics industry as a diffusion barrier between Cu interconnects and the SiO\textsubscript{2} insulation layer, as well as an interlayer/diffusion barrier in magnetic recording devices. In the world of structural ceramics, these materials offer a wide range of thermal and mechanical properties that are of use to a systems designer. As structural ceramics, the UHTC nitrides (ZrN, HfN, and TaN) are less well known than the diborides or monocarbides, but they do offer some advantageous properties.

Like the monocarbides, HfN (and ZrN) can exist over a range of stoichiometries, as shown in Fig. 9. With a melting temperature of 3387°C, it certainly qualifies as a UHTC material. That temperature was measured in an atmospheric pressure environment: at an overpressure of nitrogen at 60 atmospheres, the melting point increases to 3800°C.\textsuperscript{33} For long temperature applications at high temperatures, the loss of N from the lattice is thought to be a considerable problem to overcome. It is interesting to note that small N additions to the α-Hf with N additions lattice dramatically raise the melting temperature—from 1743°C for the pure metal to 2910°C for 30%N. The thermomechanical properties of α-Hf have been described in the literature.\textsuperscript{34} For the HfN phase, the thermal expansion and strength and modulus are all very close to that measured for HfC, while the thermal
conductivity is slightly higher.\textsuperscript{35} TaN is considerably less stable than HfN, with decomposition temperatures below 2700°C at atmospheric pressure.

Oxidation testing of HfN was carried out in a similar method as described for the HfC materials. While HfN\textsubscript{s2} did not have as significant of a pesting problem as HfC\textsubscript{s2} did, the scale formed was not protective and showed evidence of porosity and cracking. In higher-temperature arcjet testing, however, the HfN\textsubscript{s2} did show a very different response in forming an oxide scale. While the oxygen diffusion inward / N\textsubscript{2} evolution and NO\textsubscript{x} species formation / outward diffusion are not well-understood, the gas pressures at the interface must be significantly lower as the oxide that formed during testing formed a dense, adherent scale—so much so that subsequent oxidation caused the formation of a gas bubble behind the oxide scale, resulting in a “blowout” of the oxide towards the end of the 3 minute test, as shown in Fig. 10.

**Summary**

Ultra-High Temperature Ceramics are a family of compounds that display a unique set of properties, including extremely high melting temperatures (> 3000°C), high hardness, and good chemical stability and strength at high temperatures. Structural materials for use in high-temperature oxidizing environments are presently limited mostly to SiC, Si\textsubscript{3}N\textsubscript{4}, oxide ceramics, and composites of these materials. The maximum-use temperatures of silicon-based ceramics are limited to approximately 1700°C due to the onset of active oxidation (lower temperatures in water vapor environments). The development of structural materials for use in oxidizing and rapid heating environments at temperatures above 1700°C is therefore of great engineering importance. UHTC materials are typically considered to be the carbides, nitrides, and borides of the transition metals, but the Group IV-V compounds (Ti, Zr, Hf, Ta) are generally considered to be the main focus of research due to the superior melting temperatures and formation of stable high-melting temperature oxides. The combination of properties make these materials potential candidates for a variety of high-temperature structural applications, including engines, hypersonic vehicles, plasma arc electrodes, cutting tools, furnace elements, and high temperature shielding.

**References**

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Wuchina, et al.
(continued from previous page)

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Wuchina, et al.
(continued from previous page)