ULTRA HIGH TEMPERATURE CERAMICS FOR HYPERSONIC VEHICLE APPLICATIONS

Dr. J NARSAIAH[1], Dr V SUDHEER[2], K KIRAN KUMAR[3]

[1]Associate Professor, Dept of Mechanical, AVN institute of engineering and technology, Hyderabad, TS, India.

[1]Associate Professor, Dept of Mechanical, AVN institute of engineering and technology, Hyderabad, TS, India.

[1]Mtech Student, Dept of Mechanical, AVN institute of engineering and technology, Hyderabad, TS, India

ABSTRACT:

HfB2 and ZrB2 are of interest for thermal protection materials because of favorable thermal stability, mechanical properties, and oxidation resistance. We have made dense diboride ceramics with 2 to 20 % Si C by hot pressing at 2000°C and 5000 psi. High-resolution transmission electron microscopy (TEM) shows very thin grain boundary phases that suggest liquid phase sintering. Fracture toughness measurements give RT values of 4 to 6 MPam1/2. Four-pt flexure strengths measured in air up to 1450°C were as high as 450 – 500 MPa. Thermal diffusivities were measured to 2000°C for ZrB2 and HfB2 ceramics with Si C contents from 2 to 20%. Thermal conductivities were calculated from thermal diffusivities and measured heat capacities. Thermal diffusivities were modeled using different two-phase composite models. These materials exhibit excellent high temperature properties and are attractive for further development for thermal protection systems.

INTRODUCTION

Reentry vehicles, regardless of their specific designs, require control surfaces with sharp leading edges if they are to be maneuverable at hypersonic velocities. Low-radius leading edges are subject to much greater aerothermal heating than blunt edges, such as those on the Space Shuttle, and they thus will reach temperatures that may exceed 2000°C during reentry. Available thermal protection materials will not survive such extreme temperatures and new materials are required for advanced thermal protection systems. The goal of this thre year project, which started in October, 2002, was to develop thermal protection materials based on zirconium and hafnium diborides that are more heat and oxidation resistant than materials presently available. Those diboride compounds and composites in which they are the primary constituent are referred to as ultrahigh temperature ceramics (UHTCs) because they have some of the highest melting points known, above 3200°C. Previous attempts to make these UHTCs had shown mixed results and the properties obtained were inconsistent. Achieving that goal required gaining an understanding of the performance-

limiting features of the UHTC specimens and using that understanding to make better thermal protection materials based on Zr and Hf diborides.

LITERATURE SURVEY

Introduction to ultra-high temperature ceramic compounds (UHTCC) There exists great interest in the development of materials that tolerate very high temperatures (>1600 °C), high pressures (> 50 KPa), strong localized stresses (mechanical contact and wear), and chemically aggressive environments (corrosive gases). Among the industries interested in these materials are the aeronautics and space sectors. Indeed, it is expected that the XXI century will see a revolution in supersonic and space flight, and in general the development of propulsion craft. Without a doubt, all these advances, as has been the case up to now, will be intimately related with the development of new materials.

With respect to supersonic flights, it is sufficient to consider that as the speed of the craft increases, the temperature of its surface grows exponentially due to the high friction. The speed forecasts are already for Mach 6, for which reason the estimated temperatures are greater than 1500 °C, as well as very severe wear of the surfaces. Therefore, one of the present challenges in supersonic technology is the manufacture of light materials that are resistant to oxidation, wear, thermal shock, and creep in conditions of cyclic and prolonged use at high temperatures.

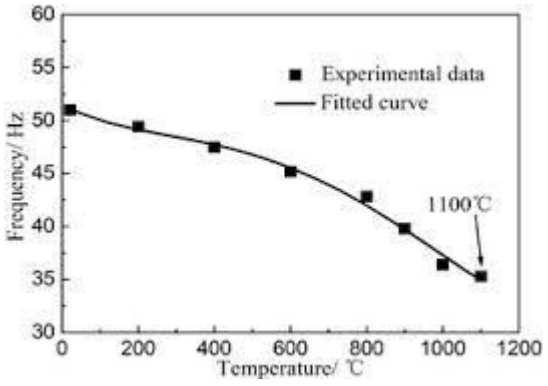
Ultra-high-temperature ceramics' ('UHTCs) are a class of refractory ceramics that offer excellent stability at temperatures exceeding 2000 °C being investigated as possible thermal protection system (TPS) materials, coatings for materials subjected to high temperatures, and bulk materials for heating elements. Broadly speaking, UHTCs are borides, carbides, nitrides, and oxides of early transition metals. Current efforts have focused on heavy, early transition metal borides such as hafnium diboride (HfB2) and zirconium diboride (ZrB2), additional UHTCs under investigation for TPS applications include hafnium nitride (HfN), zirconium nitride (ZrN), titanium carbide (TiC), titanium nitride (TiN), thorium dioxide (ThO2), tantalum carbide (TaC) and their associated composites. Thermodynamic properties In comparison with carbide and nitride-based ceramics, diboride-based UHTCs exhibit higher thermal conductivity (refer to Table 2.2), where we can see that hafnium diboride has thermal conductivity of 105, 75, 70 W/m*K at different temperature while hafnium carbide and nitride have values only around 20 W/m*K. Thermal shock resistance of HfB2 and ZrB2 was investigated by Man Labs and it was found that these materials did not fail at thermal gradients sufficient for the failure of SiC; indeed, it was found that hollow cylinders could not be cracked by an applied radial thermal gradient without first being notched on the inner surface. UHTCs generally exhibit thermal expansion coefficients in the range of 5.9– 8.3×10−6K−1.The

structural and thermal stability of ZrB2 and HfB2 UHTCs results from the occupancy of bonding and anti-bonding levels in hexagonal MB2 structures with alternating hexagonal sheets of metal and boride atoms. In such structures, the principal frontier electronic states are bonding and anti-bonding orbitals resulting from bonding between boron 2p orbitals and metal d orbitals; before group (IV), the number of available electrons in a unit cell is insufficient to fill all bonding orbitals, and beyond it they begin to fill the antibonding orbitals. Both effects reduce the overall bonding strength in the unit cell and therefore the enthalpy of formation and melting point. Experimental evidence shows that as one moves across the transition metal series in a given period, the enthalpy of formation of MB2 ceramics increases and peaks at Ti, Zr, and Hf before decaying as the metal gets heavier. As a result, the enthalpies of formation of several important UHTCs are as follows: HfB2> TiB2> ZrB2> TaB2> NbB2> VB2.

METHODOLOGY WITH RESULTS

Processing: One of the major accomplishments of this project was learning how to make superior UHTCs and then determining the properties needed to make intelligent design decisions. We made ZrB2 – Si C and HfB2 – Si C UHTCs with excellent properties in compositions as low as 2 vol% Si C. The results of the hotpressing experiments are shown in Figure 3, which is a plot of specimen density as a percentage of the theoretical value as a function of Si C content. Previous attempts by others to make thermal protection materials in these same systems required 20% Si C. The results of the present work demonstrated a wider range of compositions than was previously known, which gives designers more options in optimizing thermal protection systems (TPS).

The UHTCs studied here were made by hot-pressing powder mixtures in graphite dies. All specimens were sintered at 2000°C and 5000 psi, using a ramp rate of 20°C/min, held at 2000°C for one hour, and then cooled by turning off the power to the furnace. The hot press was a Cen torr model running under an atmosphere of gettered argon gas at 5 psi. The graphite dies were lined with Grafoil brand graphite tape (Union Carbide) to protect the dies from reacting with the powders. Samples with diameters from 2.54 cm to 6.35 cm were produced. The aspect ratios, or the height-to-diameter ratios, ranged from 0.12 to 1.10.



Material	Chemical Formula	Molecular Weight (g/mol)	Purity	Size	Density
Hafnium Diboride	HfB_2	200.11	0.995	325 mesh	10.5
Zirconium Diboride	$Zr B_2$	112.84	0.995	325 mesh	6.085
Silicon Carbide	Si C	40.09	0.990	325 mesh	3.22
Silicon Carbide average	Si C	40.09	0.999	<1 micron	3.22

The powders were prepared by mixing the diboride powder with the desired amount of silicon carbide and then milling the mixture. Both ball milling and attritor milling were used, as was dry milling in a Spe mill with a tungsten carbide Most samples were prepared by ball milling the powders using zirconia media in hexane for 8 to 10 hours. For attritor milling, the powders were milled using silicon carbide media and hexane for approximately 1 hour at 600 rpm. Batch size was 250 cm3. In the attritor milled samples, weight loss from the Si C media was added to the silicon carbide content of the powder to arrive approximately at 2, 5.

Microstructures: Measurements of the grain sizes gave information on grain growth, agglomeration, and the effect of silicon carbide on microstructures. After hot pressing, the HfB2 grains had an average diameter of 3.2 μ m, whereas the ZrB2 grains had an average diameter of 5.3 μ m. This can be seen in Table 6, where samples 3, and 27-33 are ZrB2 – Si C and 8-19 are HfB2 – Si C. Initial sample preparation used ball milling of the starting powders. Later samples used attritor-milled powders. Attritor milling is a generally more powerful milling method than ball milling and produces smaller particle sizes for a given milling time. Use of attritor milling should negate the effect of different initial particle sizes in the diboride powders.

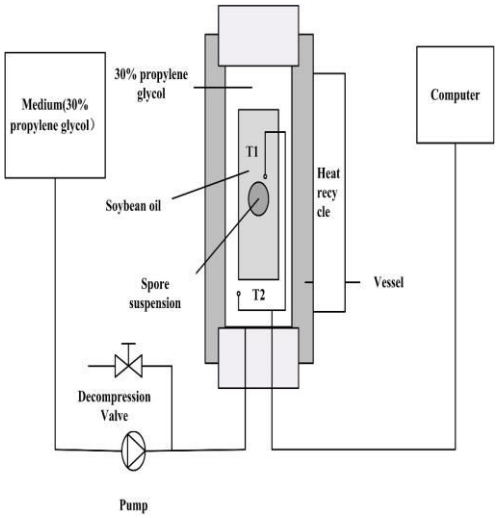
Evidence of agglomeration of Si C is present in sample 27. Agglomerates are typically detrimental to ceramic strength because of these stress concentrations. The Si C appeared to act as a grain growth inhibitor in the ZrB2 samples. The ZrB2 grains were significantly larger (greater than one standard deviation from the mean) in the 2% Si C than they were in either the 5%, 10% or 20% Si C samples. The HfB2 grain size appeared unaffected by the presence of Si C. The HfB2 grains were all tightly clustered around the mean grain size of 3.2 μ m.

The results of the spectral image analysis of the diboride UHTCs show small regions at the grain boundaries with compositions that are probably derived from impurities present in the starting powders. Some regions show presence of a Si-Mg-Ca-Zr-Al-O phase that is probably glassy. These regions are very thin and were not apparent in conventional scanning electron microscopic analysis. The lack of spectral image analytical capability may be the reason that other researchers have failed to observe these thin grain boundary impurity regions. None of those elements observed in this study

would have been present in pure starting powders and only the Zr, Ca and O might have been introduced from processing (from wear of the Ca-stabilized ZrO2 milling balls). The solubility of impurity elements in the diborides is probably very low, so they would be

rejected to the intergranular regions during the 2000°C hold in the hot press. The fall off in strength above 1000°C depicted in Figure 20 could be due to softening of intergranular impurity phases. If true, one approach to achieving better high temperature properties would be to devise synthetic routes to higher purity starting powders.

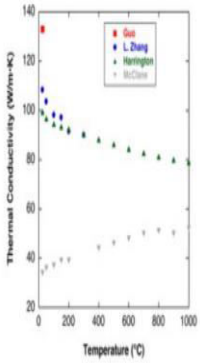
Processing: Because all subsequent tasks depend on availability of high quality UHTC materials, we devoted most of our initial effort to developing the process for making them. The plan was to try hot pressing initially and to attempt reactive hot pressing only if hot pressing did not produce good UHTCs. In fact, hot pressing was extremely successful and reactive processing was unnecessary.



As can be seen, this LDRD project succeeded in making fully dense HfB2 and ZrB2 UHTCs with Si C contents down to 2%. Before this work no one had ever reported nearly full density UHTCs with less than 20% Si C and conventional wisdom was that the larger amount of SiC was necessary to achieve full density in hot pressed HfB2 and ZrB2. These results provide a much broader range of possible compositions for application as thermal insulation and, as discussed above, properties such as strength, thermal conductivity, and oxidation resistance vary with Si C content.

Mechanical properties: Hot pressed specimens with 2% or more of Si C typically were at least 95% of theoretical density and were generally free of internal defects. With experience we were able to achieve room temperature strengths of 400 – 500 MPa and fracture toughness values of 5 – 6 MPam½. Weaker material either had large internal process flaws such as pore or agglomerates, or the test bars had machining flaws.

Properties improved with practice, for example changing from ball milling to attritor milling and substituting Si C milling balls for zirconia.



CONCLUSION

1. As stated in the introduction, the objectives of this LDRD project were to:
2. develop improved processing for HfB2 - and ZrB2 - based UHTCs
3. create a database of reliable UHTC physical and mechanical properties
4. determine the relation between UHTC microstructures and properties using advanced electron microscopic analysis
5. determine the origin and type of failure for UHTCs subjected to realistic stresses and feedback that information to improve processing
6. The results presented above show that we accomplished these goals. We developed hot pressing technique that reproducibly produced 3 in. diameter, 400 g billets of the Zr and Hf diboride UHTCs. We made the first reported, high quality diboride UHTCs with Si C contents as low as 2%. We used those specimens to measure fracture toughness, 4point fracture strengths to 1450°C, and thermal diffusivity, thermal expansion, and specific heat up to 2000°C. These measurements have produced high quality data on mechanical and thermal properties as a function of temperature for a wide range of diboride UHTCs.
7. Use of automated x-ray spectral image analysis (AXSIA) allowed us to determine compositions of small, thin impurity phases on the grain boundaries at a scale never before possible. Those results suggest that the high temperature properties of the UHTCs can be further improved through use of higher purity starting powders and by taking care not to add impurities during processing.
8. An unresolved scientific question is the densification mechanism for ZrB2 and HfB2 and what role the Si C plays in facilitating densification. As discussed above, adding as little as 2 vol% Si C to either HfB2 or ZrB2 greatly improves sintering behavior. The theoretical densities increase from 68-75% to nearly 100% under the same processing conditions.

REFERENCES

1. Campbell I. E. and Sherwood E. M. (Eds.), “High-Temperature Materials and Technology”, Wiley, New York, 1967.

2. Clougherty, E.V., Kaufman, L. “Investigation of Boride Compounds for Very High Temperature Applications,” Man Labs, Inc., Cambridge, MA, Air Force Technical Documentary Report No. RTD-TDR-63-4096, 1963.

3. Levine, S.R., et al. “Evaluation of Ultra-High Temperature Ceramics for

Aero propulsion Use," Journal of the European Ceramic Society, vol. 22, no. 14-15, 2002, p. 2757-67.

4. Fahrenholtz, William G. and Gregory E. Hilmas, organizers. "Draft: NSF-AFOSR Joint Workshop on Future Ultra-High Temperature Materials," National Science Foundation Workshop, Arlington, VA, 13-14 January 2004.

5. Upadhya, K, Jenn-Ming, Y and Wesley P. H, "Materials for Ultrahigh Temperature Structural Applications", the American Ceramic Society Bulletin, December 1997.

6. Monteverde, F., Bellos A. "Oxidation of ZrB2-Based Ceramics in Dry Air," Journal of the Electrochemical Society, vol. 150, no. 11, 2003, p. B552-B559.

7. Thermal Properties Research Center (TPRC), Thermophysical Properties of Matter, New York: IFI/Plenum, 1979.

8. Berkowitz-Mattu, Joan, "High-Temperature Oxidation, Part III. Zirconium and Hafnium Diborides", Journal of the Electrochemical Society, 908-914, 113, No. 9, September 1966.

9. Zheng, Zhen-Yan D, Naoki K, Jian-Feng Y, and Tatsuki O, "Reactive Hot Pressing of ZrB2-SiC composites", Journal of American Ceramic Society, 83 [27] 2330- 32 (2000).

10. Zheng "Oxidation behavior of ZrB2 powders below 1073 K in air", 381-387, 24 (#3) March, 2002.

11. Metcalfe A. G., Elsner N. B., Allen D. T., Hi-Z Technology, Inc., San Diego, California, U.S.A., and E. M. Opeka, Naval Surface Warfare Center, Division, West Bethesda, Maryland, U.S.A., and E. Opila, NASA Glenn Research Center, Cleveland, Ohio, U.S.A, "Oxidation of Hafnium Diboride", 196th Meeting of the Electrochemical Society, 17 - 22 Oct. 1999, Honolulu.

12. Thermal Diffusivity: The thermal diffusivities of the UHTC composites were measured from 250°C to 2000°C in increments of 250°C. The thermal diffusivities were affected by the porosity, the temperature, and the Si C content. The estimated error was also found to vary with temperature. At the higher temperatures some surface oxidation occurred that might have affected the measurements.

13. Porosity had the greatest effect on the thermal diffusivities. A visual comparison of the HfB2-SiC data and the ZrB2-SiC data (Figures 21 and 22) shows the dramatically reduced diffusivities of the porous samples, whereas all the nearly fully dense samples lie close together.

14. The thermal diffusivities of the UHTCs all decreased with increasing temperature, as expected. In all samples the thermal diffusivity exhibited a monotonically decreasing trend, which was the behavior expected in this temperature range. The limited number of data points were fit well by an equation of the form A + BT + CT -1. Though the thermal diffusivity of silicon carbide is known to have a power law dependence with temperature29, this is

not known for the diborides.