Assessment of the State of the Art of Ultra High Temperature Ceramics

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1.0 Introduction

Ultra High Temperature Ceramics (UHTCs) are a family of materials that includes the borides, carbides and nitrides of hafnium-, zirconium- and titanium-based systems. UHTCs are famous for possessing some of the highest melting points of known materials. In addition, they are very hard, have good wear resistance, mechanical strength, and relatively high thermal conductivities (compared to other ceramic materials). Because of these attributes, UHTCs are ideal for thermal protection systems, especially those that require chemical and structural stability at extremely high operating temperatures. UHTCs have the potential to revolutionize the aerospace industry by enabling the development of sharp hypersonic vehicles or atmospheric entry probes capable of the most extreme entry conditions.

2.0 Background

UHTCs originated in the early 1960s. Some of the earliest and most thorough work to date was performed then by the company ManLabs, under a research program funded by the Air Force Materials Laboratory (AFML)[1-2]. Work on UHTCs was initiated to meet the need for high temperature materials that would allow the development of maneuverable hypersonic flight vehicles. Since then, intermittent research has made some progress, but several significant challenges remain in the use of UHTCs, and these materials have yet to be widely implemented.

Strong covalent bonding is responsible for the high melting points, moduli, and hardness of the UHTC family of materials[3-4]. High negative free energies of formation also give UHTCs excellent chemical and thermal stability under many conditions. In comparison to carbides and nitrides, the diborides tend to have higher thermal conductivity, which gives them good thermal shock resistance and makes them ideal for many high temperature thermal applications[4-5].

Bulk UHTCs are fabricated through hot pressing in either resistance- or induction-heated furnaces, using graphite dies, at temperatures ranging from 1900–2100 °C and pressures of 60–100MPa, in processes that have not changed much since the '60s. High melting temperatures make it extremely difficult to consolidate pure samples using conventional hot pressing. Work by ManLabs found that additives could eliminate billet cracking and make dense, fine-grained microstructures achievable[1]. In particular, adding SiC from 5-30 volume percent improved UHTC densification and oxidation resistance.

An example of today's state-of-the-art UHTC/SiC composite is shown in Figure 1. The gray areas are HfB_2 grains and the black areas are SiC grains.

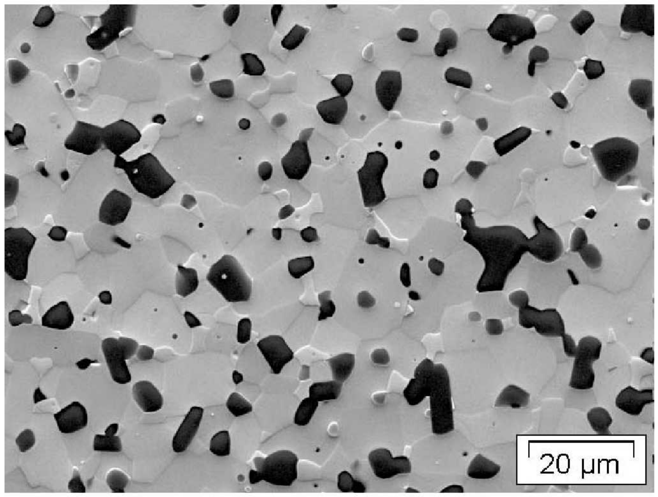

Figure 1. Baseline UHTC microstructure HfB_2-20 v% SiC

3.0 State-of-the-Art UHTC Development

Research on UHTCs slowed considerably after the work by ManLabs ended, until the early 1990s, when interest in the monolithic UHTC materials renewed. High costs of raw materials, in addition to the high temperatures and pressures required to hot press UHTC powders, have led to many new investigations into alternate ways of fabricating UHTCs. In addition to conventional methods, researchers are looking at reactive hot pressing and pressureless sintering by liquid infiltration and reaction[6-7]. These new reaction-based processes share the near-net shape and near-net dimension capabilities of gas-phase reaction bonding, as well as reduced processing temperatures and times required for solid state sintering.

Basic property evaluation of UHTCs and UHTC composites is being conducted at a number of government facilities within NASA and the military, as well as at some universities[8-12]. With this resurgence in basic research, UHTC carbides and nitrides are getting attention, as new processing techniques make the fabrication of these materials easier.

NASA Ames began working on UHTCs in the early 1990s, and in 1997 and 2000, in collaboration with the Air Force and Sandia National Labs, NASA conducted two flight experiments, SHARP-B1 and SHARP-B2 (Sharp Hypersonic Aero-thermodynamic Research Probes). These experiments briefly exposed the UHTC materials to actual reentry environments[13]. The SHARP-B1 vehicle tested a HfB2-SiC nose tip with a 3.5mm radius. The SHARP-B1 vehicle was not designed to be recovered, and thus post-test characterization of the UHTCs was not possible.

The second vehicle, SHARP-B2, was recovered. This test flew four segmented strakes on the exterior of the reentry vehicle. The strakes were designed to retract within the reentry vehicle at a predetermined altitude, after which a parachute was deployed, allowing the vehicle and UHTC materials to be recovered. Each UHTC strake comprised three segments, with each segment a different UHTC material (HfB_2 or ZrB_2). The flight experiment was a success, and the materials were recovered, but inadequate development had yielded materials with large agglomerates. These materials had poor mechanical properties, and a number of strake segments failed. NASA Ames is continuing to pursue experiments on these materials and has made progress in improving processing methodologies and resulting material properties, as demonstrated in Fig 1[14].

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Ames is pursuing a variety of approaches to modify and control the microstructure of UHTCs with the goal of improving fracture toughness, oxidation resistance and controlling thermal conductivity. The overall goal is to produce materials that can perform reliably as sharp leading edges or nose tips in hypersonic reentry vehicles.

Processing approaches include the use of preceramic polymers as the SiC source (as opposed to powder techniques), the addition of third phases to control grain growth and oxidation, and the use of processing techniques to produce high purity materials. Both hot pressing and field assisted sintering have been used to make UHTCs. Characterization of the mechanical and thermal properties of these materials is ongoing, as is arcjet testing to evaluate performance under reentry conditions.

The preceramic polymer approach has generated a microstructure in which elongated SiC grains grow in the form of an *in-situ* composite (Fig 2). This microstructure has the advantage of improving fracture toughness while potentially improving oxidation resistance by reducing the amount and interconnectivity of SiC in the material. Figure 3 shows a crack being deflected by these acicular SiC grains. Addition of third phases, such as Ir, results in a very fine-grained microstructure, even in hot-pressed samples (Fig 4). The results of processing and compositional changes on microstructure and properties will be reported, along with selected arcjet results.

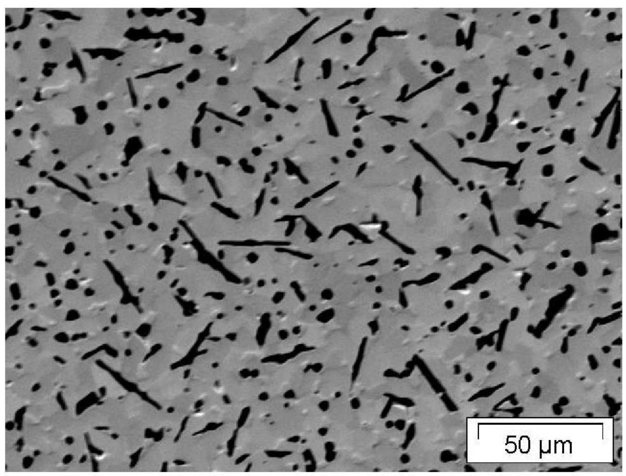

Figure 2: HfB_2/SiC UHTC microstructure with elongated SiC grains

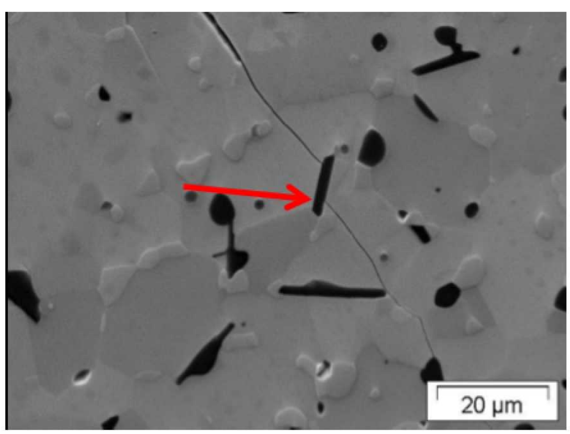

Figure 3 Crack deflection observed at the SiC-HfB_2 interface

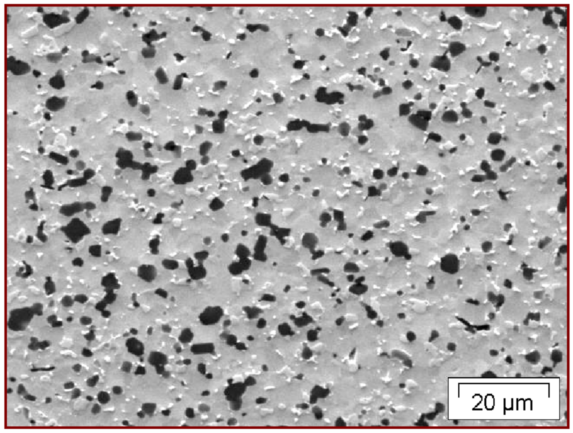

Figure 4: Very fine-grained microstructure observed in samples with Ir additions

Further work

Fiber reinforced UHTCs have the potential to be useful for sharp leading edges; however, suitable high temperature fibers have not been readily available. Some preliminary work on the use of the Ames materials as matrix materials will be discussed.

References

1. Kaufman, L. and Clougherty, E. V. "Investigation of Boride Compounds for Very High Temperature Applications," RTD-TRD-N63-4096, Part III, ManLabs Inc., Cambridge, MA, (March 1966).

2. Clougherty, E. V, Kalish, D. and Peters, E. T. "Research and Development of Refractory Oxidaton Resistant Diborides," AFML-TR-68-190, ManLabs Inc., Cambridge, MA, (1968).

3. Courtright, E. L., Graham, H. C., Katz, A. P. and Kerans, R. J. "Ultra High Temperature Assessment Study – Ceramic Matrix Composites," AFWAL-TR-91-4061, Wright Patterson Air Force Base, Ohio (1992).

4. Cutler, R. A. "Engineering Properties of Borides," in ASTM Engineered Materials Handbook, Vol. 4 – Ceramics and Glasses, Schneider, S. J., Technical Chairman, p. 787-803 (1991).

5. Guillermet, A. F. and Grimvall, G. "Phase Stability Properties of Transition Metal Diborides," Am. Inst. Phy. Conf. Proc., [231] 423-431 (1991).

6. Woo, S. K., Kim, C. H. and Kang, E. S. "Fabrication and Microstructural Evaluation of ZrB2/ZrC/Zr Composites by Liquid Infiltration," J. Mat. Sci. [2] 5309-5315 (1994).

7. Zhang, G., Deng, Z., Kondo, N., Yang, J. and Ohji, T. “Reactive Hot Pressing of ZrB2-Sic Composites,” J. Am. Ceram. Soc. [83] 2330-2332 (2002).

8. Levine, S., Opila, E., Halbig, M., Kiser, J., Singh, M. and Salem, J., “Evaluation of Ultra-High Temperature Ceramics for Aeropropulsion Use,” J. Europ. Ceram. Soc. [22] 2757-2767 (2002).

9. Bargeron, C. B., Benson, R. C., Newman, R. W., Jette, A. N. and Phillips, T. E. “Oxidation Mechanisms of Hafnium Carbide and Hafnium Diboride in the Temperature Range 1400-2100C,” Johns Hopkins APL Technical Digest, [14] 29-35 (1993).

10. Monteverde, F. and Bellosi, A. “Effect of the Addition of Silicon Nitride on Sintering Behavior and Microstructure of Zirconium Diboride,” Scripta Materialia, [46] 223-228 (2002).

11. Monteverde, F., Bellosi, A and Guicciardi, S. “Processing and Properties of Zirconium Diboride-Based Composites,” J. Europ. Ceram. Soc., [22] 279-288 (2002).

12. Shimada, S. “A Thermoanalytical Study on the Oxidation of ZrC and HfC Powders with Formation of Carbon,” Solid State Ionics, [149] 319-326 (2002).

13. Kolodziej, P., Salute, J. and Keese, D. L. “First Flight Demonstration of a Sharp Ultra-High Temperature Ceramic Nosetip,” NASA TM-112215, (December 1997).

14. Gasch, M., Ellerby, D., Irby, E., Beckman, S., Gusman, M., and Johnson, S., “Processing, Properties and Arc Jet Oxidation of Hafnium Diboride/Silicon Carbide Ultra High Temperature Ceramics,” J. Mat Sci, [39], 5925–5937 (October 2004).

15. Opeka, M. M., Talmy, I. G., Wuchina, E. J., Zaykoski, J. A. and Causey, S. J., “Mechanical, Thermal and Oxidation Properties of Refractory Hafnium and Zirconium Compounds,” J. Europ. Ceram. Soc., [19] 2405-2414 (1999).