Oxidation of ZrB₂ Ceramics Containing SiC as Particles, Whiskers, or Short Fibers

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The thermal stability of ZrB_2 -based composites containing SiCchopped fibers was tested in a bottom-up furnace at 1200°C, 1500°C, and 1700°C for 30 min. The oxidation behavior was studied by X-ray diffraction, scanning electron microscopy, and weight gain. The degradation induced by oxidation was also evaluated considering the strength decrease of oxidized bars. Baseline ZrB_2 -composites containing the same amount of SiC particles or SiC whiskers were tested in the same conditions for comparison.

I. Introduction

Z IRCONIUM diboride (ZrB_2) belongs to the class of materials called ultra-high temperature ceramics, attributable to its high melting point above 3000°C. It possesses interesting engineering properties, such as high hardness, strength, thermal and electrical conductivity, and finds application in refractory and energy production industries.¹ Increasing interest raised by ZrB_2 is related to its potential use for high temperature aerospace applications, such as hypersonic vehicles or rocket propulsion systems. The main obstacle to the use of ZrB_2 -based ceramics in a wider span of applications is the discrete oxidation resistance, associated to low thermal shock resistance and low fracture toughness.

Concerning the first issue, the addition of SiC has been proved to improve the oxidation resistance of ZrB_2 and HfB₂, owing to the formation of a protective SiO₂-glassy layer which hinders the oxygen penetration in the bulk.² The oxidation mechanisms and the microstructural features of ZrB₂–SiC composites have been extensively studied.^{2–7} The morphology of the oxidized scale is constituted by an outermost borosilicate-glassy layer, an underlying coarse or columnar ZrO₂ layer with SiO₂ filling the voids, and a ZrB₂ SiC-depleted region above the bulk. On the other hand, the addition of SiC fibers or whiskers proved to be effective in increasing the fracture toughness from 3.8 to 5.7 MPa·m^{1/2}, which is an increase of more than 50%.⁸

A previous study on HfB_2 -SiC⁹ revealed that the oxidation mechanisms occurring at ambient pressure at 2000°C for 1 h developed microstructural features very similar to those formed upon an arc jet test at lower temperature for shorter time.⁹ Arc jet tests are commonly used to study the material response in simulated re-entry conditions and the study pointed out that the oxidation in static air for 30–60 min could give indications on the microstructure evolution of a material during atmospheric re-entry. In this prospect, the oxidation behavior of SiC short fiberreinforced ZrB_2 ceramics was tested in a bottom-up furnace up to 1700°C for 30 min and was compared to a typical ZrB_2 material containing either SiC particles or SiC whisker. To assess the materials degradation, the pristine strength was compared to the strength of the oxidized specimens.

Is there a difference among the oxidation behavior of a ZrB_2 matrix containing SiC particles, fibers or whiskers? Can we obtain a tougher material than the conventional ZrB_2 -SiC without losing the oxidation resistance properties at high temperature? These issues will be the target of this study.

II. Experimental Procedure

The materials investigated in the present work were prepared by hot-pressing ZrB_2 with 5 vol% of Si₃N₄ and 20 vol% of SiC-chopped fibers (20f), or 20 vol% of SiC particles (20p), or 10–20 vol% of whiskers (10w and 20w, respectively).

Commercial powders were used to prepare the ceramic composites: ZrB_2 Grade B (H.C. Starck, Goslar, Germany), specific surface area 1.0 m²/g, maximum impurity content: 0.25 wt% C, 2 wt% O, 0.25 wt% N, 0.1 wt% Fe, 0.2 wt% Hf, particle size range 0.1–8 mm; α -Si₃N₄ Baysinid (Bayer, Leverkusen, Germany), specific surface area 12.2 m²/g, maximum impurity content: 1.5 wt% O; β -SiC BF12 (H.C. Starck), 3% α -SiC, s.s.a. 11.6 m²/g, silica ~1.65 wt%; SiC HI Nicalon-chopped fibers, Si:C:O = 62:37:0.5, 15 µm diameter, 1 mm length; for SiC whiskers, no data sheet was available, by image analysis: average diameter 0.6 µm and average length 30 µm. Details on the materials preparation, densification, and mechanical properties have been reported in a previous work.⁸

The oxidation tests were carried out in a bottom-up loading furnace at 1200°C, 1500°C, and 1700°C for 30 min on rectangular 13 mm× 2.5 mm× 2 mm bars in static air. Specimens were located in the furnace when the maximum temperature was achieved and then removed and airquenched after the exposure time. Mass and bars' dimensions were measured before and after the oxidation. The assintered material and oxidized specimens were examined on the surface using X-ray diffraction (Siemens D500, Karlsruhe, Germany) to identify the crystalline phases. Microstructural modifications induced by oxidation were analyzed by scanning electron microscopy (SEM; Cambridge S360, Cambridge, U.K.) and energy dispersive spectroscopy (EDS; INCA Energy 300, Oxford Instruments, High Wycombe, U.K.) on the surface and on the polished crosssection of the specimens. For comparison, composites containing 20 vol% of SiC particles, or 10-20 vol% SiC whiskers were also oxidized under the same conditions. For all the composites, four-point flexural strength tests were conducted on as-sintered materials at room temperature and at 1200°C on a universal screw-type machine, Instron 1195 (Instron 6025, High Wycombe, U.K.) with a crosshead speed

M. Cinibulk-contributing editor

Manuscript No. 29654. Received April 27, 2011; approved June 08, 2011. [†]Author to whom correspondence should be addressed. e-mail: laura.silvestroni@ istec.cnr.it

of 0.05 mm/min. For the high-temperature tests, the heating rate was 10° C/min, and a soaking time of 18 min was set to reach thermal equilibrium. The degradation after oxidation at 1700°C was evaluated by comparing the pristine strength of the as-sintered specimens and the retained strength of the oxidized specimens. These last set of specimens were tested at room temperature in three-point bending tests using the dimensions of the oxidized bars. Four bars were tested for each strength data presented.

III. Results and Discussion

By X-ray diffraction, the composites 20f and 10w showed diffraction peaks of only monoclinic ZrO_2 at all temperatures, whereas for 20w, the peaks of hexagonal ZrB_2 were visible up to 1500°C and they disappeared only after oxidation at 1700°C, when ZrO_2 was the only phase present.

The weight and volume gain increased with the temperature; 20w showed the lowest weight gain, whereas 10w showed the highest. Figure 1 shows the weight gain per unit surface area as a function of the oxidation temperature and it can be noticed that the materials containing 20 vol% of SiC in any form behaved very similarly.

On the surface of the composites after oxidation at 1200° C, the reinforcing phases were still recognizable, as the outside appeared as a discontinuous SiO₂ scale with ZrO₂ particles and the fibers or whiskers, which, however, looked cracked and damaged [Figs. 2(a) and (b)]. After oxidation at 1500°C, only the fibers were recognizable in the areas were bubbles formation and explosion occurred. For the whisker-containing ceramics, the surface was well covered by SiO₂ with rounded ZrO₂ particles dispersed in. Evidence of bubbling burst events was observed on 20f, 10w, and 20w specimens at 1500°C, due to the melting of SiO₂ and vigorous evaporation of gaseous species as SiO and B₂O₃. At 1700°C, islands of ZrO₂ in rounded particle or dendrite-like shape, were immersed in a



Fig. 1. Weight gain per unit surface area as a function of the oxidation temperature for the composites containing whiskers, fibers, or particles.

 SiO_2 continuous scale [Figs. 2(c) and (d)]. Two different immiscible glasses were observed in the composites containing whiskers: a darker one, surrounding the ZrO_2 particles, mainly constituted by SiO_2 , and a brighter one, containing Zr and other impurities coming from whiskers, such as Ca and Mg. It is probable that the darker glass resulted from Zr migration to form ZrO_2 precipitates, whereas in the brighter one, Zr concentration was still too low to generate particles.

The polished sections of the fiber- and whisker-reinforced composites are illustrated in Fig. 3 and they generally follow the typical aspect of oxidized ZrB_2 -SiC composites: an external SiO₂ layer, an intermediate coarse ZrO_2 partially filled with silica, and a SiC-depleted layer above the unreacted bulk. From Fig. 3, it can be noticed that the SiO₂ external thickness is comparable at 1200°C and 1500°C, while it dramatically increases at 1700°C. No SiC-depleted layer is present in the materials after exposure at 1200°C. Moreover, in the fiber-containing samples, after oxidation at 1500°C, graphite residuals are often observed surrounding the fibers themselves [see Fig. 3(b)]. For whisker-reinforced materials, this feature was not so evident, probably owing to the smaller size.

Apart from the well-known oxidation reactions involving ZrB_2 , that foresee B_2O_3 development and subsequent volatilization at $T > 1100^{\circ}C$, and formation of columnar grains of zirconia, the most important differences between cycles at 1200°C, 1500°C, and 1700°C concern the oxidation modes for SiC. Irrespective of shape and dimensions of the SiC phase, possible reactions include (Table I): (1) formation of silica and gaseous CO, (2) formation of silica and graphite, and (3) active oxidation of SiC with formation of gaseous silicon oxide and CO.

For oxidation at 1200°C, reaction 1 leads to the formation of a stable silica layer and no subsurface oxidation occurs. When the temperature is raised to 1500°C, slow penetration of oxygen through the silica barrier induces a subsurface oxidation according to reaction 2, and leads to the formation of silica and solid graphite, that was hardly observed in ZrB₂–SiCp composites.^{5,6} When the temperature is further raised to 1700°C, reaction 1 takes place on the surface, but on the subsurface, active oxidation of SiC prevails with consequent formation of a SiC-depleted layer.^{5,6}

In terms of weight gain, it can be observed in Fig. 1 that all the samples display similar values, even if for a content of 20 vol% of whiskers, fibers, or particles, a lower weight gain was observed after exposure at 1700°C compared to 10w. Also, from the modified thickness it is evident that the higher the SiC content, the better is the oxidation resistance. It is interesting to understand the effect of SiC reinforcement dimensions versus the oxidation behavior. When talking about chopped fibers, we deal with SiC elements with typical dimensions of 100–300 μ m length and 15 μ m diameter. The whiskers are typically 30 μ m length and <1 μ m diameter. One interesting comparison is with previously characterized ZrB₂ ceramic containing ultra-fine SiC particles. Apart from all these analogies, one difference should be remarked. When a depletion region is formed, in the case of fine SiC particle,



Fig. 2. Surface morphology after oxidation of (a) 20f and (b) 20w at 1200°C; (c) 20f and (d) 20w at 1700°C.



Fig. 3. Polished surface of (a-c) 20f, (d-f) 10w, (g-i) 20w. From left to right: 1200°C, 1500°C, and 1700°C.

 Table I.
 Possible Reactions Involving SiC at Ambient Pressure (HSC Chemistry for Windows 5, Outokumpu Research Oy, Pori, Finland)

SiC possible reactions	Stoichiometry		ΔG (kJ)	
 Passive oxidation and CO formation Passive oxidation and graphite formation Active oxidation 	$\begin{array}{l} SiC+1.5O_2(g)=CO(g)+SiO_2\\ SiC+O_2(g)=C+SiO_2\\ SiC+O_2(g)=SiO(g)+CO(g) \end{array}$	1200°C: -831 1200°C: -589 1200°C: -405	1500°C: -809 1500°C: -541 1500°C: -457	1700°C: -793 1700°C: -509 1700°C: -491

a layer with small and fine porosity will form. In the case of fiber additions, the depletion region will contain large and long cavities, which should be taken into consideration for structural high-temperature applications. To this purpose, the strength degradation from room temperature to 1200°C and after oxidation is displayed in Fig. 4. The room temperature strength was comparable for composites containing whiskers and particles, whereas the addition of fibers induced a remarkable decrease due to the defect population change. At 1200°C, this trend changed: the materials containing whiskers or fibers maintained strength around 400 MPa, whereas the one containing particles collapsed to 250 MPa. The high-temperature strength is affected by several factors:

- 1. softening of amorphous phases that causes a strength decrease;
- change of the defect population induced by oxidation (indeed the materials spent about 30 min at temperature >1000°C) that causes a strength decrease;
- 3. sealing of small porosities by the borosilicate glass, that could induce a strength increase.

At 1200°C, all the composites underwent effects 1–3. The fact that whisker- and fiber-containing materials resulted in



Fig. 4. Strength values for composites containing 20 vol% of fibers, particles, or whiskers, at room temperature, at 1200°C and after oxidation at 1700°C for 30 min.

higher strength suggests that these reinforcing elements still have a strengthening effect at 1200°C. This, in turn, could be attributed to the fact that fibers and whiskers undergo a slower or incomplete oxidation and continue to exert a structural function, different from particles.

The influence of SiC distribution in the matrix should also be carefully considered. In case of particles, a faster oxida-

The values of the retained strength after oxidation are consistent with the analysis of the weight gain. Considering the absolute values, the composite containing particles had the highest value of retained strength, 220 MPa, followed by 20w and 20f, 180 and 160 MPa, respectively. The abrupt strength drop in the oxidized bars of 20w and 20f is mainly related to the flaws induced by oxidation (e.g., effect 2). From Figs. 3(c) and (i), it can be observed that the modified layer is ~200 μm for 20f and ~160 μm for 20w, whereas for ZrB₂ containing particles, this layer is <100 $\mu m.^{10}$ In particular, the SiC-depleted region in 20f, characterized by porosity of the same dimension as the former SiC reinforcement, is twofold thicker as compared to 20w and 20p.¹⁰

Finally, comparing the residual strength after oxidation at 1700°C to the pristine strength, it turned out that the retained strength of 20p and 20w after oxidation decreased of ~70-75% of the room temperature value, whereas for 20f, this value decreased only ~55%.

IV. Conclusions

The oxidation behavior of ZrB2-based ceramics containing SiC short fibers, whiskers, or particles was investigated and compared. Similar weight gains were measured and analogous scale morphology developed upon oxidation. The big size of the fibers allowed a more precise study of the oxidation of the reinforcing SiC, and the formation of graphite surrounding them was ascertained. Concerning the thermomechanical behavior, at room temperature, ZrB2-based composites containing small-sized SiC, that is, particles and

whiskers were stronger than the composites containing short fibers, but upon high-temperature degradation, all the three materials tended to converge to the same strength ~ 200 MPa. It can be concluded that the composites containing small-sized SiC had a steeper decrease of strength at high temperature, compared to fibers or whiskers containing composites, probably due to a faster oxidation of the network formed by the particles.

References

¹R. A. Cutler, "Engineering Properties of Borides"; pp. 787–803 in *Ceramics and Glasses: Engineered Materials Handbook*, Vol. 4, Edited by S. J. Schneider Jr. ASM International, Materials Park, OH, 1991. ²T. A. Parthasarathy, R. A. Rapp, M. Opeka, and R. J. Kerans, "A Model

for the Oxidation of ZrB₂, HfB₂ and TiB₂," Acta Mater., 55 [17] 5999-6010 (2007).

³S. N. Karlsdottir and J. W. Halloran, "Oxidation of ZrB₂-SiC: Influence of SiC Content on Solid and Liquid Oxide Phase Formation," J. Am. Ceram. Soc., 92 [2] 481-6 (2009).

⁴A. Bongiorno, C. J. Först, R. K. Kalia, J. Li, J. Marschall, A. Nakano, M. M. Opeka, I. G. Talmy, P. Vashishta, and S. Yip, "A Perspective on Modeling Materials in Extreme Environments: Oxidation of Ultrahigh-Temperature Ceramics," MRS Bull., 31 [5] 410-8 (2006).

⁵W. G. Fahrenholtz, "Thermodynamic Analysis of ZrB₂-SiC Oxidation: Formation of a SiC-Depleted Region," J. Am. Ceram. Soc., 90 [1] 143-8 (2007).

⁶F. Monteverde and A. Bellosi, "Oxidation of ZrB₂ Based Ceramics in Dry Air," J. Electrochem. Soc., 150 [11] B552–9 (2003).

⁷M. Mallik, K. K. Ray, and R. Mitra, "Oxidation Behavior of Hot Pressed ZrB2-SiC and HfB2-SiC Composites," J. Eur. Ceram. Soc., 31 [1-2] 199-215 (2011).

⁸L. Silvestroni, D. Sciti, C. Melandri, and S. Guicciardi, "Toughened ZrB₂-Based Ceramics Through SiC Whisker or SiC Chopped Fiber Additions, J. Eur. Ceram. Soc., 30 [11] 2155–64 (2010). ⁹C. M. Carney, "Oxidation Resistance of Hafnium Diboride–Silicon Carbide

from 1400 to 2000°C," *J. Mater. Sci.*, **44**, 5673–81 (2009). ¹⁰F. Monteverde and A. Bellosi, "Development and Characterization of Metal-Diboride-Based Composites Toughened with Ultra-fine SiC Particulates," Solid State Sci., 7 [5] 622-30 (2005).