

# Tantalum Addition to Zirconium Diboride for Improved Oxidation Resistance

Stanley R. Levine  
Glenn Research Center, Cleveland, Ohio

Elizabeth J. Opila  
Cleveland State University, Cleveland, Ohio

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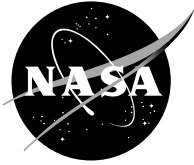
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# Tantalum Addition to Zirconium Diboride for Improved Oxidation Resistance

Stanley R. Levine and Elizabeth J. Opila<sup>a</sup>  
National Aeronautics and Space Administration  
Glenn Research Center  
Cleveland, Ohio 44135

## Abstract

Ultrahigh temperature ceramics have performed unreliably due to material flaws and attachment design. These deficiencies are brought to the fore by the low fracture toughness and thermal shock resistance of UHTCs. If these deficiencies are overcome, we are still faced with poor oxidation resistance as a limitation on UHTC applicability to reusable launch vehicles. We have been addressing the deficiencies of UHTCs with our focus on composite constructions and functional grading to address the mechanical issues, and on composition modification to address the oxidation issue. The approaches and progress toward the latter are reported.

## Introduction

The high melting points of refractory metal diborides coupled with their ability to form refractory oxide scales give these materials the capability to withstand temperatures in the 1900 to 2500 °C range.<sup>1</sup> These ultra-high temperature ceramics were developed in the 1960's<sup>2</sup>. Fenter<sup>3</sup> provides a comprehensive review of the work accomplished in the 1960's and early 1970's. Additions of silicon carbide are used to enhance oxidation resistance and limit diboride grain growth. Carbon is also sometimes used as an additive to enhance thermal stress resistance. These materials offer a good combination of properties that make them candidates for airframe leading edges on sharp-bodied reentry vehicles.<sup>1</sup> UHTC have some potential to perform well in the environment for such applications, i.e. air at low pressure. However, for hypersonic flight in the upper atmosphere one must recognize that stagnation pressures can be greater than one atmosphere. Thus their poor oxidation resistance can be an issue.<sup>4</sup> Low fracture toughness and large scatter in material properties leading to unreliable behavior under severe thermal shock and gradient loads or at attachments is also an issue.<sup>4</sup> The purpose

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<sup>a</sup>Cleveland State University;  
NASA Resident Research Associate at Glenn Research Center

of this study was to examine approaches to resolving these issues. Alloying approaches are being examined to improve oxidation resistance. Fiber reinforcement and functional grading are being examined to increase toughness and improve reliability. These approaches are being integrated to develop UHTC materials with improved robustness for leading edge applications. In this study, the preliminary results of alloying for oxidation resistance improvement are presented.

## Background

At very high temperatures in a flowing environment most of the  $B_2O_3$ <sup>5</sup> and  $SiO_2$ <sup>6</sup> will be lost by evaporation or active oxidation. Thus, the primary protective oxidation barrier for the refractory metal borides is the refractory metal oxide scale plus any residual  $B_2O_3$  and  $SiO_2$ . In the case of  $ZrB_2$  or  $HfB_2$  we are dependent on  $ZrO_2$  or  $HfO_2$ , respectively. Background information on these oxides can be found in the compilation edited by Alper<sup>7</sup>. These oxides, if perfect, would be good oxygen barriers. However,  $ZrO_2$  and  $HfO_2$  become nonstoichiometric by forming oxygen lattice vacancies under low oxygen partial pressure conditions. They are also readily modified by aliovalent cations of lower valence to form oxygen lattice vacancies. Oxygen lattice vacancies allow rapid oxygen ion transport through the scale. So, from a chemistry perspective,  $ZrO_2$  and  $HfO_2$  are not good choices for a protective oxide scale.

Another issue with  $ZrO_2$  and  $HfO_2$  scales is their phase instability. At high temperatures,  $ZrO_2$  and  $HfO_2$  are tetragonal. Upon cooling to room temperature they transform to the monoclinic structure with an attendant volume expansion. This phase transformation coupled with their high thermal expansion coefficient, and low thermal conductivity<sup>8</sup> can easily lead to cracking and spalling under thermal transient conditions.

One approach to resolve the oxygen transport issue and the cracking and spalling issue is to modify the scale with a cation that can stuff oxygen into the lattice and increase scale adhesion by phase stabilization. Thus we seek cations with higher valence. In addition, these cations must form a refractory oxide and they must also be derived from a refractory phase. The best candidates are niobium and tantalum. However, niobium pentoxide melts at only 1460 °C<sup>8</sup>. That leaves tantalum, with a pentoxide melting point of 1880 °C<sup>7</sup>, as the only viable candidate to add to the refractory metal diborides. Additions can be either as the element, carbide, silicide or boride. Evidence that Ta additions to zirconia decrease conductivity is given by Ewaida et al<sup>9</sup>.

The choice of tantalum as an additive to the diborides is not new. Wuchina et al looked at TaB additions to HfC, HfN, and  $HfB_2$ .<sup>10</sup> They reported an increase in oxide scale density at 1500 °C for  $HfB_2$ . Talmy et al studied up to 20 % additions of  $TaB_2$  to  $ZrB_2$  – 20 % SiC.<sup>11</sup> Furnace oxidation temperatures up to only 1400 °C were used. They reported significant improvements in oxidation resistance and attributed these improvements to phase separation in the glass.

In addition to Ta acting as a  $ZrO_2$  or  $HfO_2$  scale dopant or  $Ta_2O_5$  acting as a glass modifier, one additional factor needs to be considered for Ta additions to the diborides. If  $Ta_2O_5$  were a major oxide scale constituent it could form an intermediate phase with  $ZrO_2$  (or possibly with  $HfO_2$ ) with a nominal composition of  $Ta_2O_5 \cdot 6ZrO_2$ . This intermediate phase has a lower melting point than either pure oxide.<sup>12</sup> Its presence could be either beneficial or detrimental. Evidence of solubility of Ta in  $ZrO_2$ , and of intermediate compound formation is shown in Figure 1. These observations support the phase diagram for  $Ta_2O_5 - ZrO_2$ .<sup>12</sup>

The approach chosen for oxidation resistance enhancement is the addition of tantalum via refractory compounds (melting points in parentheses):  $Ta_5Si_3$  (246 °C)<sup>13</sup>,  $TaSi_2$  (2200 °C)<sup>14</sup>,  $TaC$  (3880 °C)<sup>14</sup>,  $TaB$  (2040 °C)<sup>14</sup> or  $TaB_2$  (3140 °C)<sup>14</sup>. This paper deals only with  $TaSi_2$  and mixed Ta compound additions.

## **Experimental Procedures**

### **Processing**

The powder constituents used are shown in table 1. The powders were ground either individually or as blends using  $Si_3N_4$  media in hexane in a  $Si_3N_4$  mill for 24 hours. The powders were air dried, and soft agglomerates were broken down in a mortar and pestle.

Sufficient powder to yield a ~5 mm thick fully dense plate was placed in a  $2.54 \times 5.08$  cm graphite die cavity lined with grafoil. The powders were hot pressed in vacuum for either 1 or 2 hours hold time at peak temperature and 10 ksi applied pressure. The assembled die was heated at 20 °C per minute to 800 °C and held for 30 minutes. Heating rate temperature combinations were then 15 °C/min to 1200°C, 10 °C/min to 1500 °C, 7°C/min to 1750 °C, 5 °C/min to 1900 °C, and 3 °C/min to 2000 °C. After the hold at maximum temperature, the load was released and the die assembly was cooled at a rate of 10 °C per minute. After pressing, the plates were removed from the die, scraped to remove residual grafoil, and then machined into oxidation coupons and flexural test specimens per ASTM Standard.<sup>12</sup> Density was measured using machined coupons.

### **Mechanical properties**

Test bars (3 by 4 by 50 mm, with four long edges beveled) were machined from each plate of UHTC material. Specimens were tested in four-point flexure (20/40 mm inner/outer spans, steel fixture, 0.5 mm/min. loading rate) at room temperature. Three samples were tested per test composition.

## **Furnace Oxidation**

Sample coupons were 2.54 by 1.27 by 0.32 cm. Coupons were ultrasonically cleaned successively in detergent, de-ionized water, acetone and alcohol prior to exposure. Initial sample weights (to an accuracy of 0.00005g) and dimensions (to an accuracy of 0.001 cm) were recorded. Three samples were loaded into a slotted ZrO<sub>2</sub> refractory brick. Samples were exposed to ten-minute oxidation cycles in stagnant air at 1627 °C in a bottom loading box furnace with zirconia heating elements (Deltech, Inc.). One sample was removed after one cycle, five cycles and ten cycles. A maximum exposure time of 100 minutes was thus achieved. Weight change was measured, where possible. Some of the samples stuck to the sample holder during oxidation due to extensive glass formation. X-ray diffraction (XRD) was used to identify oxide phases present after exposure. After surface microstructural analysis by SEM and XEDS, samples were cross-sectioned and polished in non-aqueous 1µm diamond polishing media. Water was avoided to preserve any boron that might be present as an oxidation product.

## **Results and Discussion**

### **Processing and Mechanical Properties**

Surface area of some milled powder batches was measured by BET. The surface area was about 2 m<sup>2</sup>/g. Thus very little particle size reduction occurred.

The processing results are summarized in table 2. Greater than 95% of theoretical density was attained in all cases based on the rule of mixtures. The milling sequence made a difference with some powder batches, but not with others. In some cases large agglomerates were formed when individual powders were milled and then mixed. This resulted in undesirable consolidated microstructures. These could be broken down by further milling as in the case of the mixed tantalum additives. A more desirable route, as illustrated below, was to mill mixtures of the as received powders, a more common practice.

Sintering time had a significant effect on coarsening of the microstructure of the baseline ZrB<sub>2</sub>-20 vol % SiC composition as can be seen from figure 2. In going from one to two hours of hold time at 2000 °C density did not increase significantly and strength declined by about 25%. In both cases the scatter in strength was very large, but a high frequency of large agglomerates was absent. By using milling of mixed powders, a more consistent set of strength measurements was obtained. In a plate hot pressed for 2 hours, the average strength was almost as high as in the finer grained plate prepared by hot pressing a mixture of milled powders for 1 hour. Thus one can conclude that milling of mixtures is a more desirable route even for powders in which no large agglomerates formed.



## Oxidation

Figures 3 through 5 show the macroscopic appearance of specimens for the three compositions exposed at 1627 °C for 1, 5, or 10 ten-minute cycles. The ZrB<sub>2</sub> – 20 vol % SiC specimens were generally uniform in appearance except for the areas in contact with the zirconia setter along one edge and along a line to the left of center down the face. Here less oxidation occurred. The ZrB<sub>2</sub> - 20 vol % SiC plus mixed tantalum compounds was non-uniform and had clear evidence of liquid phase formation. The ZrB<sub>2</sub> - 20 vol % SiC – 20 vol % TaSi<sub>2</sub> performed very well forming a uniform compact oxide scale.

These macroscopic observations are supported by the oxidation results shown in figures 6 and 7. In all cases the oxidation kinetics are close to parabolic as indicated by the straight line plots in figure 7. Oxidation was slowest for ZrB<sub>2</sub> - 20 vol % SiC – 20 vol % TaSi<sub>2</sub> and fastest for ZrB<sub>2</sub> - 20 vol % SiC plus mixed tantalum compounds.

Figure 8 shows the cross-sectional microstructure of ZrB<sub>2</sub> - 20 vol % SiC – 20 vol % TaSi<sub>2</sub> after 1 and 10 ten-minute cycles of exposure at 1627 °C. A dense, compact and adherent scale is present in both instances. X-ray diffraction results show formation of monoclinic ZrO<sub>2</sub> as the major phase with minor amounts of cubic ZrO<sub>2</sub> present. X-ray energy dispersive spectroscopy shows SiO<sub>2</sub> present with ZrO<sub>2</sub> particles. No oxides of Ta were detected, but Ta may be dissolved in ZrO<sub>2</sub> or SiO<sub>2</sub> with other impurities. Also, Ta is difficult to detect due to peak overlaps with Zr and Si.

Figure 9 compares the microstructures of the oxide scales formed on ZrB<sub>2</sub> - 20 vol % SiC – 20 vol % TaSi<sub>2</sub> with that formed on a commercially prepared ZrB<sub>2</sub> - 20 vol % SiC after 10 ten-minute cycles of exposure at 1627°C. The difference is striking. On the latter the outer oxide layer, mostly SiO<sub>2</sub>, is about 10 times thicker than on the ZrB<sub>2</sub> - 20 vol % SiC – 20 vol % TaSi<sub>2</sub>. The total thickness of the scale and the two depleted zones is  $258 \pm 85 \mu\text{m}$  for the ZrB<sub>2</sub> - 20 vol % SiC on the side shown based on the average of 13 measurements. On the other side the scale plus depleted zone was  $515 \pm 253 \mu\text{m}$  based on the average of 12 measurements. The average for the 25 total measurements was  $381 \pm 224 \mu\text{m}$ . In the ZrB<sub>2</sub> - 20 vol % SiC – 20 vol % TaSi<sub>2</sub> the total thickness of the scale was  $6.3 \pm 1.6 \mu\text{m}$ . A depleted zone was not apparent.

## Conclusion

Current UHTCs lack robustness (low fracture toughness, reliability and oxidation resistance). Ta additions using TaSi<sub>2</sub> appears to be a promising approach for improving the oxidation resistance of ZrB<sub>2</sub> – 20 v/o SiC. The rate of oxidation was reduced by > 10X at 1627 °C. However, the intended application for these materials is at higher temperatures in rapid flowing gas. The goal of Ta addition was to slow transport in the zirconia scale. One can not preclude at this point that the benefit of the TaSi<sub>2</sub> addition

results not from Ta, but from the additional Si that facilitates SiO<sub>2</sub> scale formation. Future work will address this issue by: (1) adding additional SiC to yield the same Si content as produced by the TaSi<sub>2</sub> addition; (2) using borides, carbides, and lower Ta silicides as Ta sources, and (3) most importantly testing at higher furnace temperatures (> 1900 °C), and under reduced pressures in a flowing environment.

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**Table 1.— Materials**

Material	Source	Particle Size	Purity, %
ZrB <sub>2</sub>	Cerac	< 10 um	99.5
SiC	H.C. Starck	< 5 um	>99.9
TaSi <sub>2</sub>	Cerac	80% - 325 mesh	>99.9
TaC	Cerac	– 325 mesh	99.5
TaB <sub>2</sub>	Cerac	– 325 mesh	99.5

**Table 2.—Processing and Flexural Strength**

Run	Composition	Powder Process	Processing	Density, g/cc	% ROM Density	UTS, Mpa	% strain	E, GPa
877-1	ZrB <sub>2</sub> - 20 v% SiC	mix milled, batch 1	2000C, 10ksi, 1h, vac			377.4	0.131	289.5
877-2						722.6	0.171	401.5
877-3						749.9	0.181	394.5
877-avg				5.22	94.6	616.6	0.161	361.8
882-1	ZrB <sub>2</sub> - 20 v% SiC	mix milled, batch 1	2000C, 10ksi, 2h, vac			381.4	0.086	416.8
882-2						588.8	0.106	531.2
882-3						486.9	0.098	472.3
882-avg				5.27	95.5	485.7	0.097	473.4
897-1	ZrB <sub>2</sub> - 20 v% SiC	milled mix, batch 2	2000C, 10ksi, 2h, vac			576.3	0.129	434.3
897-2						560.2	0.133	378.9
897-3						505.2	0.120	395.6
897-avg				5.32	96.3	547.2	0.127	402.9
878-1	ZrB <sub>2</sub> -19v/oSiC-5v/oTaB <sub>2</sub> -	milled mix	1900C, 10ksi, 2h, vac			838.7	0.178	448.0
878-2	4v/oTaC-7v/oTaSi <sub>2</sub> -14v/0HfB <sub>2</sub>					834.3	0.173	475.7
878-3						729.3	0.144	471.1
878-avg				7.11	99.9	800.8	0.165	464.9
889-1	ZrB <sub>2</sub> - 20 v% SiC - 20v% TaSi <sub>2</sub>	remill mix milled	1600C, 10ksi, 2h, vac			549.6	0.133	399.0
889-2						786.2	0.185	414.7
889-3						827.0	0.192	424.0
889-avg				5.92	97.7	720.9	0.170	412.6

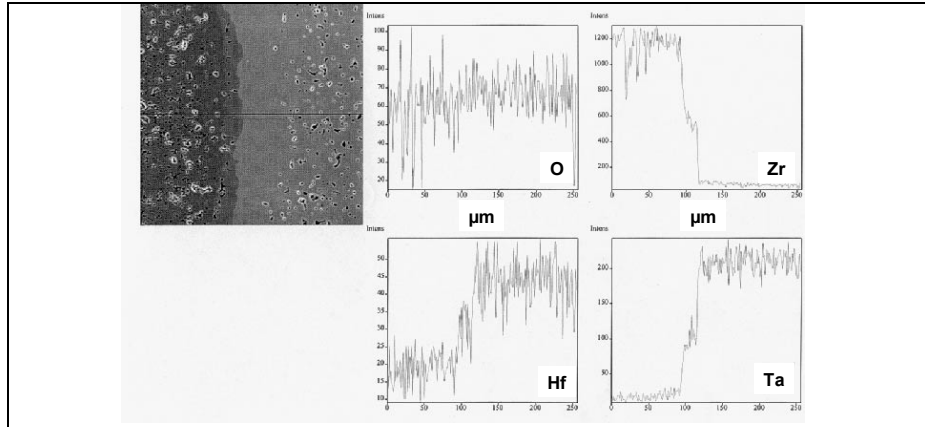


Figure 1. Microstructure and elemental concentration profiles in a zirconium oxide diffusion couple with tantalum oxide after 1 hour at 1450 °C.

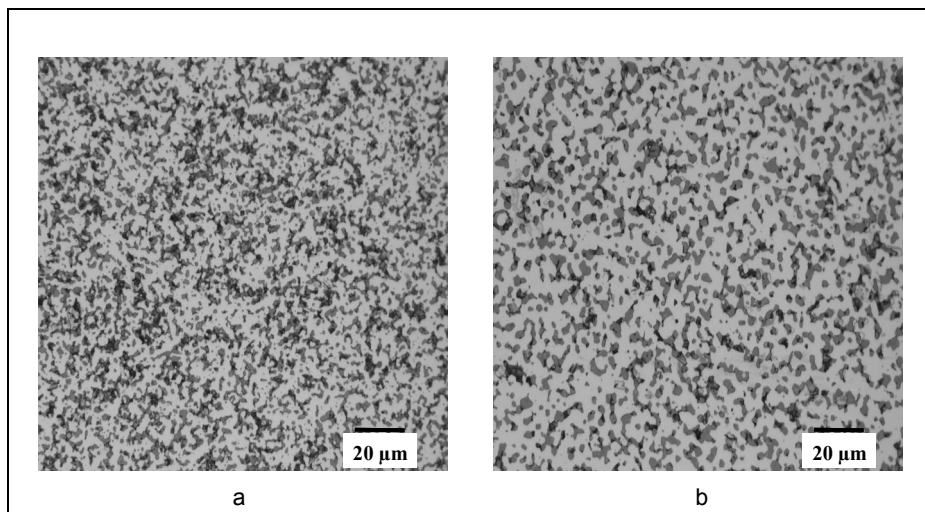


Figure 2. Effect of hot pressing time at 2000 °C and 10 ksi on the microstructure of  $ZrB_2 - 20$  volume % SiC. (a) 1h. (b) 2h.

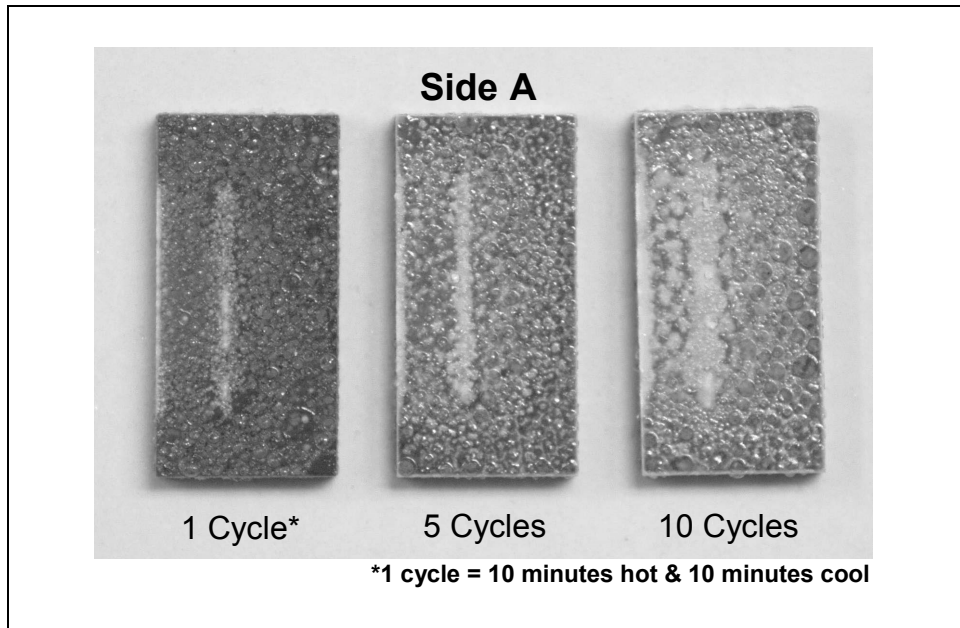


Figure 3. Appearance of  $ZrB_2 - 20 \text{ vol } \% \text{ SiC}$  after furnace oxidation at  $1627 \text{ }^\circ\text{C}$ .

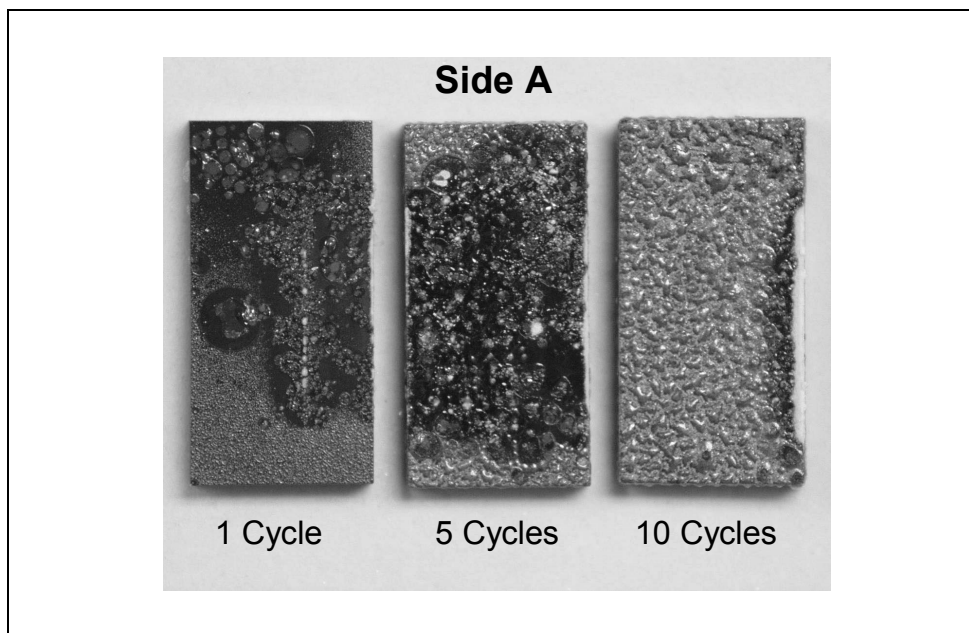


Figure 4. Appearance of  $ZrB_2 - 20 \text{ vol } \% \text{ SiC}$  plus mixed tantalum compounds after furnace oxidation at  $1627 \text{ }^\circ\text{C}$ .

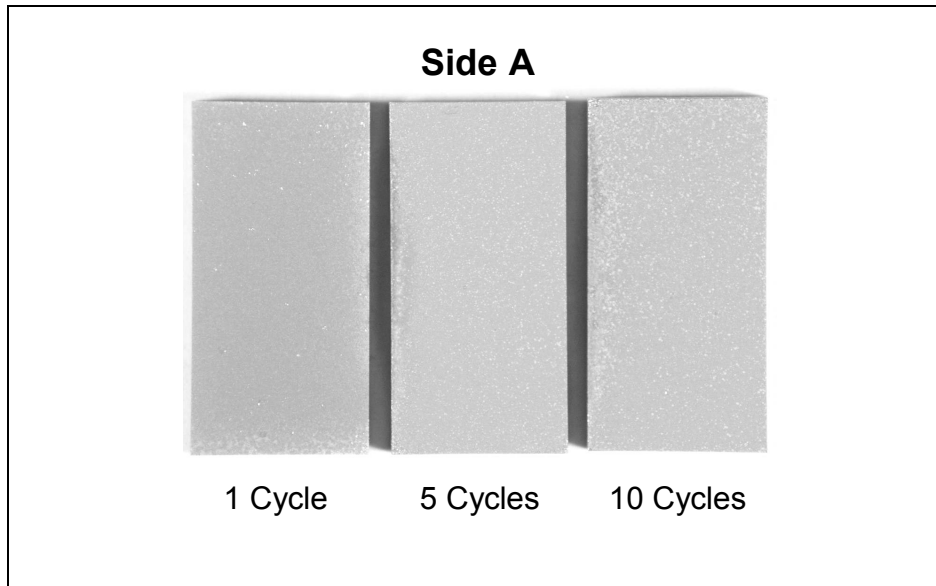


Figure 5. Appearance of  $ZrB_2 - 20 \text{ vol } \% \text{ SiC} - 20 \text{ vol } \% \text{ TaSi}_2$  after furnace oxidation at  $1627 \text{ }^\circ\text{C}$ .

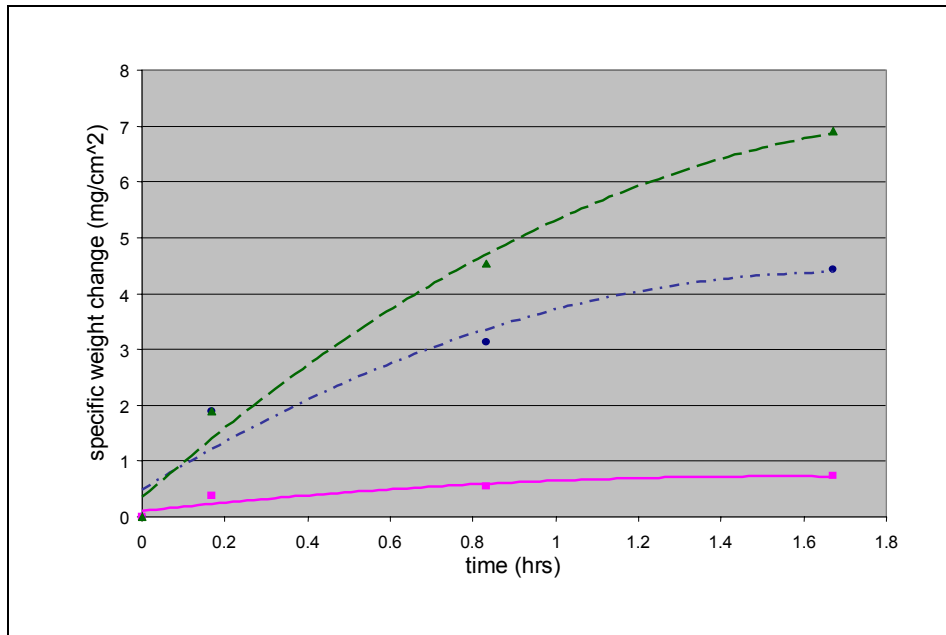


Figure 6. Oxidation behavior expressed as specific weight change versus. time for  $ZrB_2 - 20 \text{ vol } \% \text{ SiC}$  (◆),  $ZrB_2 - 20 \text{ vol } \% \text{ SiC} - 20 \text{ vol } \% \text{ TaSi}_2$  (■), and  $ZrB_2 - 20 \text{ vol } \% \text{ SiC} - \text{mixed tantalum compounds}$  (▲) at  $1627 \text{ }^\circ\text{C}$ .

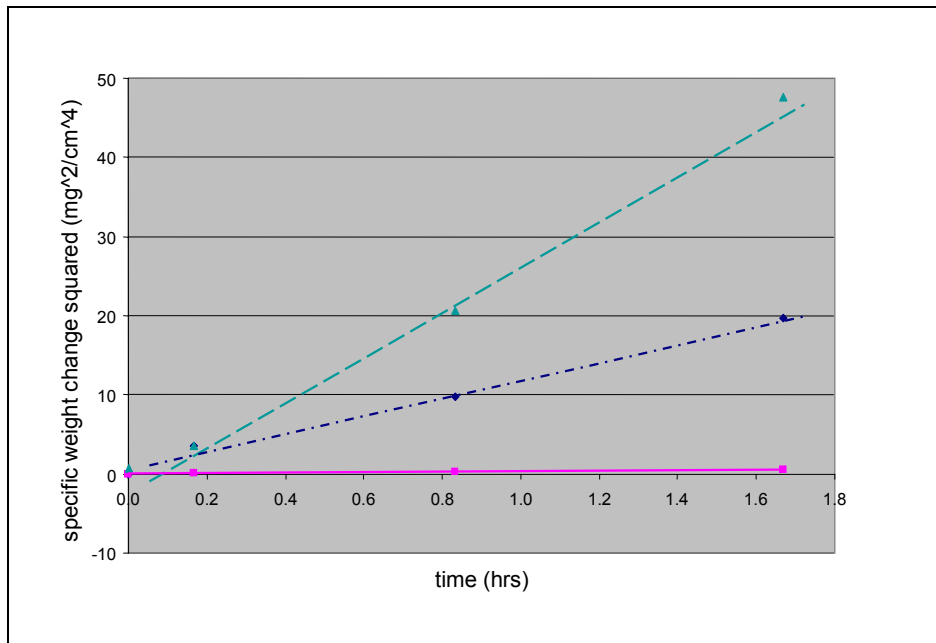


Figure 7. Oxidation behavior expressed as specific weight change squared versus time for ZrB<sub>2</sub> – 20 vol % SiC (◆), ZrB<sub>2</sub> – 20 vol % SiC – 20 vol% TaSi<sub>2</sub>(■), and ZrB<sub>2</sub> – 20 vol % SiC – mixed tantalum compounds (▲) at 1627 °C.

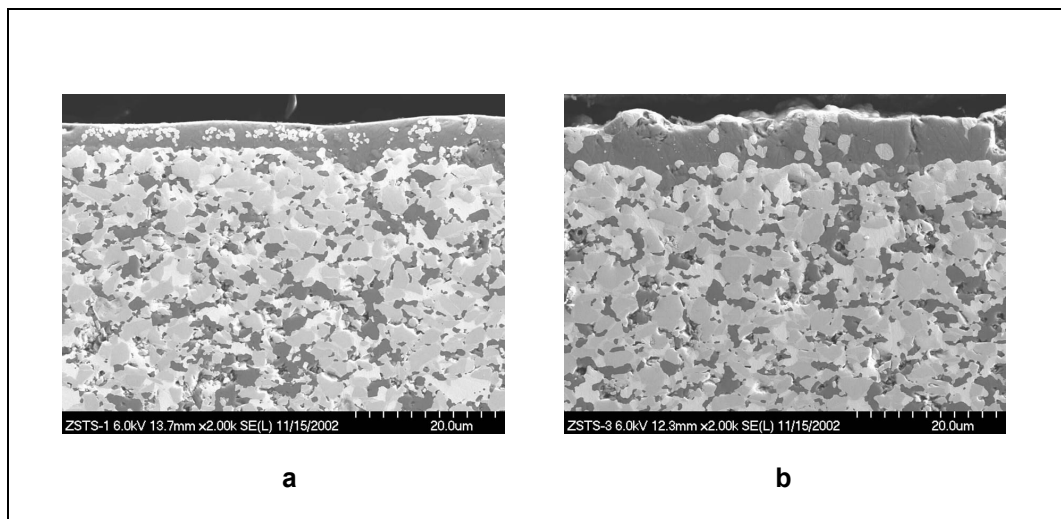


Figure 8. Microstructures of ZrB<sub>2</sub> – 20 vol % SiC – 20 vol % TaSi<sub>2</sub> after oxidation at 1627 °C for (a) one and (b) ten 10 minute cycles.



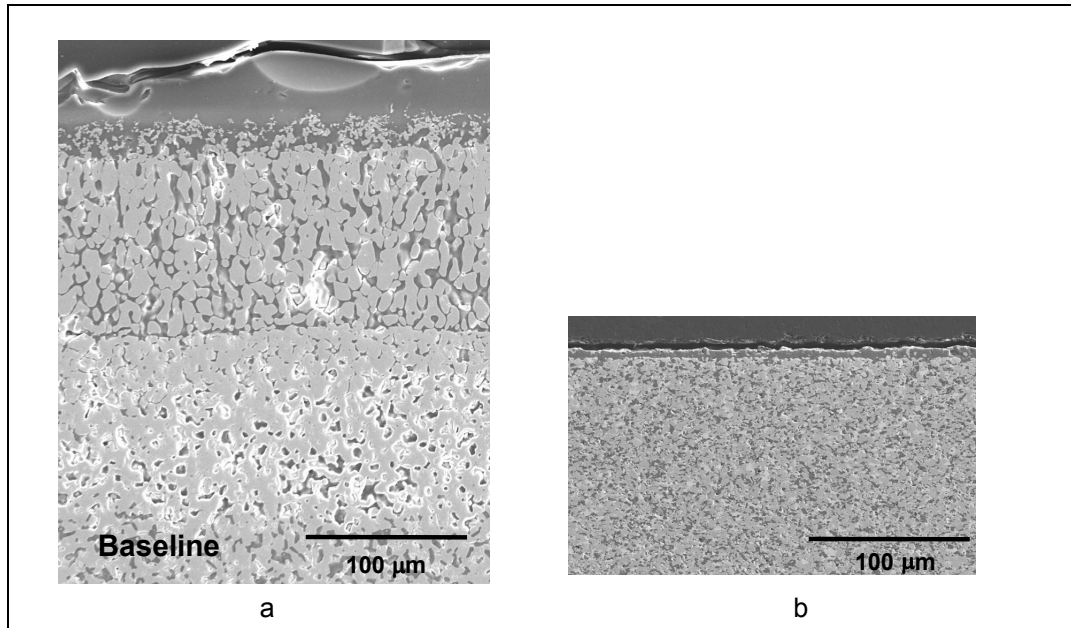


Figure 9. Comparison of oxidation attack of industry baseline  $ZrB_2 - 20 \text{ vol\% SiC}$  (a) with  $ZrB_2 - 20 \text{ vol \% SiC} - 20 \text{ vol \% TaSi}_2$  (b) after ten 10 minute cycles at  $1627 \text{ }^\circ\text{C}$  in air.

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<b>13. ABSTRACT (Maximum 200 words)</b>  Ultrahigh temperature ceramics have performed unreliably due to material flaws and attachment design. These deficiencies are brought to the fore by the low fracture toughness and thermal shock resistance of UHTCs. If these deficiencies are overcome, we are still faced with poor oxidation resistance as a limitation on UHTC applicability to reusable launch vehicles. We have been addressing the deficiencies of UHTCs with our focus on composite constructions and functional grading to address the mechanical issues, and on composition modification to address the oxidation issue. The approaches and progress toward the latter are reported.				
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