Effect of Various Additives on the Oxidation Behavior of ZrB₂-Based Ultra-High-Temperature Ceramics at 1800°C

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The effect of various additives such as TiB₂, HfB₂, CrB₂, TaB, TaSi₂, LaB₆, La₂O₃, and AlN on the oxidation behavior of ZrB₂-based ultra-high-temperature ceramics (UHTCs) at 1800°C was investigated. The additions of CrB₂ and HfB₂ to the ZrB₂-SiC composites have minor effect on the structure evolution of the oxide scale and oxidation resistance. However, all the other additives, especially for Ti and Ta compounds, have changed the oxidation mechanism resulting in a marked detrimental effect on the oxidation resistance of ZrB₂-based UHTCs.

I. Introduction

MATERIALS with improved properties are needed for better thermal protection of hypersonic vehicles proposed for next generation space and atmospheric reentry vehicles. Sharp leading edges and nose tips will have to withstand exposure to high temperatures and severe thermal cycling in both neutral and oxidizing environments. These extreme conditions require materials that possess superior oxidation resistance, low creep, and excellent thermal shock properties.^{1–4} Currently available thermal protection materials cannot survive under such extreme temperatures. ZrB₂-based UHTCs are the most promising candidates for such applications due to the unique combination of properties, such as high melting point, high thermal conductivity, and resistance to erosion/corrosion.^{4–11}

Because of strong covalent bonding and low self-diffusion, high temperatures and external pressures are required to densify diborides. Generally, nitrides (i.e., AlN, Si_3N_4 , and ZrN) were as sintering aids for the improved densification of ZrB_2 .^{12–14} Other additives such as $MoSi_2$, $ZrSi_2$, and B_4C were also introduced to enhance densification.^{15–17} However, the influence of these sintering aids on the ultra-high-temperature performance of UHTCs is not well understood, especially for the oxidation behavior. ZrB_2 containing 15–30 vol% SiC additive are prominent UHTCs withstanding temperatures $1800^{\circ}C$.^{5–7,9–11,18–21} Intense research is ongoing to enhance the oxidation resistance of these composites. The introduction of the 10 mol% diborides improved the oxidation resistance of ZrB2-SiC at 1300°C and the weight gain decreased in the sequence of the modifying additives: CrB_2 , TiB_2 , NbB_2 , VB_2 , and TaB_2 , correlating well with the cation field strength for Cr^{3+} , Ti^{4+} , Nb^{5+} , V^{4+} , and $Ta^{5+.11}$ Beside diborides, other compounds such as TaSi₂, Ta₅Si₃, and MoSi₂ were also introduced to further improve the oxidation resistance of the UHTCs. The favorable effect of these additives on the oxidation resistance of UHTCs was observed below

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 1700° C.^{11,22-24} Unfortunately, the influence of these additives on the oxidation resistance of ZrB₂-based UHTCs at temperatures above 1700° C is very unclear.

The purpose of this work was to investigate the effect of the several representative additives (i.e., TiB_2 , HfB_2 , CrB_2 , TaB, $TaSi_2$, LaB_6 , La_2O_3 , and AlN) on the oxidation behavior and resistance of ZrB₂-based UHTCs at 1800°C. The oxidation mechanism and regularity were also discussed.

II. Experimental Procedure

The samples used here for oxidation testing were fabricated from commercial powders, including ZrB₂, SiC, TiB₂, HfB₂, CrB₂, TaB, TaSi₂, LaB₆, La₂O₃, and AlN, with a purity higher than 99%. The material compositions (vol%) are as follows: (a) ZrB₂; (b) ZrB₂-20SiC; (c) ZrB₂-20TaSi₂; (c) ZrB₂-20SiC-10TaB; (e) ZrB₂-20SiC-10CrB₂; (f) ZrB₂-20SiC-10TiB₂; (g) ZrB₂-20SiC-10LaB₆; (h) ZrB₂-20SiC-5La₂O₃ (i) ZrB₂-20SiC-10AIN.

The powder mixtures of these materials were ball milled in ethanol for 8 h and dried in a rotating evaporator. Milled powders were then uniaxially hot pressed in a boron nitride coated graphite die at 2000°C for 60 min and 30 MPa of applied pressure. Bulk density and theoretical density were evaluated using the Archimedes method and the rule-of-mixture, respectively. Sample coupons 2.0 cm \times 1.0 cm \times 0.35 cm were cut from the hot-pressed materials, and all surfaces were diamond polished to a 1 µm finish. Coupons were ultrasonically cleaned successively in detergent, deionized water, acetone and alcohol before exposure. Samples were loaded into a slotted ZrO₂ refractory brick and then exposed to 60 min oxidation in stagnant air at 1800°C, using a bottom-loading furnace with zirconia heating elements. Two samples of each composition were oxidized. X-ray diffraction (Rigaku, Dmax-rb, Tokyo, Japan) and scanning electron microscopy (SEM; FEI Sirion, Eindhoven, the Netherlands) along with energy dispersive spectroscopy (EDS; EDAX, Mahwah, NJ) were used to characterize the phase composition and microstructure of the surface and cross section of the samples after oxidation experiments.

III. Results and Discussion

Macrographs of ZrB₂-based UHTCs after oxidation at 1800°C are shown in Fig. 1. Extensive oxidation and swelling of the sample were observed in the pure ZrB₂ after oxidation. Moreover, cracking and spalling were also found in the oxide scale as can be seen in Fig. 1. The formed ZrO₂ are very stable and adherent to the unreacted ZrB₂ at temperatures below 1200°C. However, the formed ZrO₂ would not adherent to the unreacted ZrB₂ at temperatures upon conversion of ZrB₂ to ZrO₂ during oxidation associated with phase transformation of ZrO₂ and the evaporation of B₂O₃ are responsible for the occurrence of the cracks and spallation. The color of the samples significantly changed after oxidation as shown in Fig. 1. This mostly depends on the additive cations. Ta

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containing samples oxidized at 1800°C formed a pink oxide, whereas Al and La containing coupons formed a white oxide. The additions of CrB₂ and HfB₂ to the ZrB₂-SiC composites have minor effect on the oxidation behavior. However, all the other additives have a detrimental effect on the oxidation behavior of the ZrB₂-based UHTCs. Particularly, the UHTCs containing TaSi2 and TiB2 as shown in Fig. 1 revealed a catastrophic increase in oxidation rate at 1800°C. Surprisingly, the samples with TiB₂ and TaSi₂ additions exposed at 1800°C for 1 h were completely consumed, which are also less resistant to oxidation than monolithic ZrB₂. It should be noted that the existence of the silica glass significantly increase the temperature range of the glass as the primary oxygen barrier leading to enhanced oxidation resistance of ZrB2. However, these materials containing silicides exhibited poor oxidation resistance, which indicated that the additions of Ta and Ti are both quite detrimental to the oxidation resistance of ZrB2-based UHTCs at ultrahigh temperature. The oxidation resistance of ZrB₂-20TaSi₂ and ZrB_2 -20SiC-10TiB₂ is far less resistant to oxidation than ZrB₂-20SiC at 1800°C. It was also found that the addition of TiB_2 significantly reduced the oxidation resistance of ZrB_2 -SiC composite in the previous study.²⁵ The thickness of oxide scale for ZrB_2 -20SiC-10TiB₂ is five times higher than that for ZrB_2 -20SiC under the same arc jet testing conditions. Additionally, the oxide scale with a porous structure was formed in TiB2 containing UHTCs after oxidation. Similarly, porous scale was also observed in this case. The formation of the porous structure was probably due to the outward diffusion of the cations.^{26,27} The additions of CrB₂ and HfB₂ to the ZrB₂-SiC composites have minor effect on both the structure evolution and oxidation resistance. The structure of oxide scale for ZrB2-SiC-CrB2 composites is analogous to that of ZrB2-SiC composites as shown in Figs. 2(a) and (b). Similar structure was also observed in the oxidized ZrB_2 -SiC-HfB₂ (not shown). The additions of CrB_2 and HfB₂ have minor effect on the structure evolution of the oxide scale. Interestingly, the addition of HfB₂ is beneficial to the oxidation resistance of ZrB2-SiC composites whereas the introduction of CrB₂ is detrimental to the oxidation performance of the materials. This is most likely attributed to the

difference of the oxidation resistance of these diborides in which ZrB_2 is more oxidation resistant than CrB_2 while is less than HfB_2 .

Oxygen diffusion through the ZrO₂ skeleton phase, liquid glass phase, cracks, and pores are the dominant routes of the oxygen transport in the oxide scale. Therefore, reducing the amount of the pores and oxygen diffusion rate in condense phases are effective ways to decrease the inward oxygen diffusion resulting in enhanced oxidation resistance. Apparently, oxygen transport through the skeleton phase can be reduced by changing the composition of this phase. It is well known that ZrO₂ become nonstoichiometric by forming oxygen lattice vacancy under low oxygen partial pressure conditions. Oxygen lattice vacancy allows rapid oxygen ion transport through the scale. One approach to resolve the oxygen transport issue is to modify the scale with higher valence cations (i.e., Nb^{5+} and Ta^{5+}) into the ZrO₂ that can reduce oxygen vacancy concentration and ion diffusion. Recent studies revealed that the addition of tantalum via refractory compounds to ZrB_2 matrix UHTCs led to higher oxidation resistance. Levine *et al.*²² added tantalum to zirconium diboride for improved oxidation resistance. The oxidation rate of ZrB₂-20 vol% SiC was significantly reduced with the addition of TaSi₂ at 1627°C. Talmy et al.²³ studied up to 20% additions of TaB_2 to ZrB_2 -20 vol% SiC. 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. Another explanation for this improved behavior is that Ta additions result in substitution of Ta on the Zr site in ZrO₂, reducing the concentration of oxygen vacancy in the ZrO₂. However, the Ta (i.e., $TaSi_2$ and TaB_2) addition performed poorly at ultrahigh temperatures since the existence of Ta2O5 would lower the melting point of oxide scale through forming an intermediate phase (i.e., $Ta_2O_5 \cdot 6ZrO_2$) leading to the melting and degradation of the ZrO₂ skeleton, which acts mechanical support for the oxide scale. Apparently, the decrease of melting point for oxide scale has a detrimental effect on the oxidation resistance at ultrahigh temperature. The integrity of ZrO₂ skeleton was not formed after oxidation at 1800°C. Furthermore, the



ZrB2-20%volSiC-10%volLaB6

ZrB₂-20%volSiC-5%volLa₂O₃

ZrB2-20%volSiC-10%volAlN

Fig. 1. Macrographs of the oxidized ZrB_2 matrix ultra-high-temperature ceramics with various additives at 1800°C for 1 h.

vporous structure, including spalling and cracking, was also found in Ta containing UHTCs after exposure to air at 1800°C as shown in Fig. 2(c), which resulted in the accelerated oxidation. It is generally accepted that gas phase diffusion through the cracks and pores, even in the Knudsen diffusion regime, is much easier than diffusion in condensed phases. Therefore, improvement of UHTC oxidation resistance by Ta additions is strongly dependent on the oxidation conditions, especially temperature.

Addition of other additives, such as LaB₆, La₂O₃, and AlN, into UHTCs has an analogous effect on the structure evolution and oxidation resistance. The introduction of these additives leads to a double detrimental effect. On the one hand, addition of other additive cations, such as Al^{3+} , Y^{3+} , or La^{3+} , into the scale would lower the eutectic temperatures of the oxide scale, leading to an instability of the skeleton and an accelerated transport of the zirconia to the surface. On the other hand, the concentration of oxygen vacancy increases due to introduction of the cation with a lower valence to ZrO_2 , which resulted in a reduced oxidation resistance. Figures 2(d) and (e) show SEM cross-section micrographs of La added ZrB_2 –SiC oxidized at

1800°C for 1 h. EDX analysis evidenced that the bright zones contained Zr and La oxide while the dark zones consisted of silica glass. The formed scale is strongly different from that without additives. These additives promoted the phase agglomeration leading to a reduction of the oxidation resistance. Although La was added to the material in the different compounds, they have a similar effect on the structure evolution and oxidation resistance of UHTCs. This means that the effect of additives to oxidation behavior of UHTCs is significantly dependent on the metallic element cations.

Remarkable transport of ZrO₂-rich oxides from inner scale to the surface layer in La-containing UHTCs was also detected after oxidation. This feature was not observed in ZrB₂–SiC composites in which a dense oxide layer was formed. SEM studies showed the evidence of the phase agglomeration in the oxide scale of La-modified samples after furnace oxidation tests as can be seen in Figs. 2(d) and (e). Agglomeration of silica-rich glass cannot act as an effective barrier to the inward diffusion of oxygen resulted in accelerated oxidation rate. The addition of cations with lower valance will increase the oxygen transport



Fig. 2. Scanning electron microscopy micrographs of the cross-section of ZrB_2 -based ultra-high-temperature ceramics after oxidation at 1800°C for 1 h. (a) ZrB_2 -20 vol% SiC, (b) ZrB_2 -20 vol% SiC-10 vol% CrB₂, (c) ZrB_2 -20 vol% SiC-10 vol% TaB, (d) ZrB_2 -20 vol% SiC-10 vol% LaB₆, (e) ZrB_2 -20 vol% SiC-10 vol% SiC-10 vol% LaB₆, (e) ZrB_2 -20 vol% SiC-5 vol% La₂O₃.

through the ZrO_2 phase resulting in increased oxidation rate of ZrB_2 , which can be validated by the thickness of the SiC-depletion layer. SiC depleted layer was not clearly detected in the La containing UHTCs suggesting that the oxygen transport through the ZrO_2 was the rate controlling step, which is significantly different from that without additives in which the dominant route of the oxygen transport is pores in the SiC depleted layer.^{18,19,28,29} The increase of the inward oxidation diffusion through ZrO_2 -rich oxides and outward cationic diffusion was probably responsible for the enhanced oxidation rate.

Figure 3 shows the weight gains of ZrB2-based UHTCs modified by CrB₂, HfB₂, TaB, AlN, and La₂O₃, which are consistent with the oxidation performance observed from macrographs and oxide scales. Only addition of HfB2 was found to beneficial to the oxidation resistance and all other additions are detrimental to the oxidation performance. TaB addition exhibited poorest oxidation resistance among CrB₂, HfB₂, and TaB. The addition of AlN significantly decreased the oxidation resistance although only 5 vol% was added to the material. These additives, such as TiB₂, TaB, TaSi₂, LaB₆, La₂O₃, and AlN, exert a great influence on oxidation resistance through changing the structure evolution of the oxide scale and oxygen transport route during oxidation process. The effect of these additives on the oxidation resistance of UHTCs is significantly different from these at lower temperatures. The oxygen diffusion through ZrO₂ skeleton, silica-rich liquid phase and voids are the rate controlling step for ZrB2-based UHTCs. Oxygen lattice vacancies allow rapid ion transport through the scale.^{22,30} Obviously, the addition of lower valance cations to ZrB2-based UHTCs will increase the oxygen vacancy concentration of ZrO₂, resulting in increased oxygen diffusion. Therefore, the oxygen diffusion rate through ZrO₂ skeleton significantly enhanced, leading to the change of oxygen transport routes and increased oxidation rate of ZrB₂. This can be explains why no SiC depleted layer was clearly detected in La containing (i.e., LaB₆ and La₂O₃) ZrB₂-SiC composites and the oxidation resistance decreased. It has been reported that AlN significantly improved the densification of ZrB₂-based UHTCs.¹² However, the addition of AlN should be avoided in the viewpoint of oxidation resistance. Apparently, other lower cations, such as Y³⁺, La³⁺, and Mg²⁺, also should be excluded for the improved oxidation resistance. The introduction of higher cations (i.e., Ta⁵⁺) may decrease the oxygen vacancy concentration of ZrO2 leading to the decreased oxygen diffusion through the ZrO_2 skeleton, which is beneficial to the oxidation resistance.^{22,24} Meanwhile, the introduction of these higher cations would change the eutectic point of the scale resulting in the reduction of the mechanical stability of the scale and scale adherence and thus accelerated oxidation. Decreasing oxygen vacancy without significant decrease of the melting point may be a good way to improve the oxidation resistance of UHTCs. From this point, the addition of W may be a good choice since its oxide (WO₃) has both a higher valence and



Fig. 3. Plots of specific weight gain of the materials at 1800°C for 1 h.

higher melting point (2723°C). With respect to Ta compounds (i.e., TaB₂, TaB, TaSi₂), they are beneficial to oxidation resistance below about 1600°C due to the reduction of oxygen vacancy concentration whereas detrimental at higher temperature because the oxidation performance of remarkably affected by the decrease of eutectic temperatures for the oxide scale above approximate 1700°C. Therefore, we should take both the beneficial and detrimental aspects into account when we choose modifiers to improve the oxidation performance. In addition, we also need know whether beneficial or detrimental aspect is dominant under the certain condition.

IV. Conclusion

The additions of CrB₂ and HfB₂ to the ZrB₂-SiC composites have minor effect on the structure evolution and oxidation resistance at 1800°C and do not change oxidation mechanism. However, all the other additives, such as TiB₂, TaB, TaSi₂, LaB₆, La₂O₃, and AlN, have detrimental effect on the oxidation behavior of the ZrB2-based UHTCs. These additives have changed the scale structure and dominant oxygen transport route during oxidation process resulting in the change of the oxidation mechanism. Particularly, the UHTCs containing TaSi₂ and TiB₂ revealed a catastrophic increase in oxidation rate at 1800°C and the samples with TiB₂ and TaSi₂ additions exposed at 1800°C for 1 h were completely consumed, which are also less resistant to oxidation than monolithic ZrB₂. The effect of additives to oxidation behavior of UHTCs is significantly dependent on the metallic element cations. The additives with lower cations (i.e., LaB₆, La₂O₃, and AlN) would lower the eutectic point of the oxide scale leading to an accelerated transport of the zirconia to the surface and increase the inward oxygen diffusion through ZrO₂-rich oxides as a result of the increase of the oxygen vacancy concentration and thus reduced oxidation resistance. The effect of addition of higher cations (i.e., TaB and TaSi₂) could be either beneficial or detrimental, which is strongly dependent on the temperature. Ta additions performed poorly under ultrahigh temperature due to liquid phase formation leading to the degradation of the mechanical stability of the scale and scale adherence.

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