OXIDATION OF ZrB₂ AND ZrB₂-SiC CERAMICS WITH TUNGSTEN ADDITIONS (PREPRINT)


University of Missouri-Rolla

FEBRUARY 2009

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MATERIALS AND MANUFACTURING DIRECTORATE
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AIR FORCE MATERIEL COMMAND
UNITED STATES AIR FORCE
4. TITLE AND SUBTITLE
OXIDATION OF ZrB₂ AND ZrB₂-SiC CERAMICS WITH TUNGSTEN ADDITIONS (PREPRINT)

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9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Air Force Research Laboratory
Materials and Manufacturing Directorate
Wright-Patterson Air Force Base, OH 45433-7750
Air Force Materiel Command
United States Air Force

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

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15. SUBJECT TERMS
tungsten additions, zirconium diboride-based ceramics, ultra-high temperature ceramics (UHTCs)

16. SECURITY CLASSIFICATION OF:
a. REPORT Unclassified
b. ABSTRACT Unclassified
c. THIS PAGE Unclassified

17. LIMITATION OF ABSTRACT: SAR

18. NUMBER OF PAGES 16

19a. NAME OF RESPONSIBLE PERSON (Monitor) Todd J. Turner
19b. TELEPHONE NUMBER (Include Area Code) N/A
Oxidation of ZrB₂ and ZrB₂-SiC Ceramics with Tungsten Additions


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The effect of tungsten additions on the oxidation behavior of zirconium diboride-based ceramics was studied. Four mole percent tungsten carbide was added to ZrB₂. The oxidation behavior was studied using thermal gravimetric analysis and isothermal testing in flowing air. Upon heating to 1500°C, the mass gain decreased from ~14 mg/cm² for nominally pure ZrB₂ to ~4.5 mg/cm² for tungsten containing ZrB₂. After heating to 1500°C for three hours, the scale thickness on nominally pure ZrB₂ was ~500 µm compared to ~100 µm for tungsten containing ZrB₂. Tungsten additions improved the oxidation resistance of ZrB₂ by modifying the morphology of the ZrO₂ scale by liquid phase sintering, making it a better barrier to oxygen diffusion.

Introduction

The borides, carbides, and nitrides of the early transition metals are considered ultra-high temperature ceramics (UHTCs) because they have melting temperatures above 3000°C. These materials have an unusual combination of strength at elevated temperature, high elastic modulus and hardness, high thermal and electrical conductivities, and stability in reactive environments (1,2). As such, UHTCs are candidates for applications involving extreme environments such as those associated with hypersonic flight, atmospheric re-entry, and rocket propulsion (3,4). In addition, these materials are under consideration for applications such as cutting tools, high temperature electrodes, microelectronic devices, nuclear fuel forms, and molten metal contact (5-9). More specifically for the present study, ZrB₂ has a combination of oxidation resistance and high thermal conductivity that makes it attractive for leading edges in hypersonic vehicles (3,10,11).

The oxidation resistance of nominally pure ZrB₂ varies with temperature. Below about 1000°C, a combination of porous, crystalline ZrO₂ and amorphous or liquid B₂O₃ forms on the surface (12,13). The B₂O₃ forms a continuous layer that acts as a barrier to oxygen diffusion resulting in parabolic mass gain kinetics. However, B₂O₃ has a low melting temperature (~450°C) and a relatively high vapor pressure (14,15). Between 1000°C and about 1200°C, the rates of B₂O₃ formation and evaporation are comparable, resulting in para-linear mass gain kinetics (16). At higher temperatures (1200°C and above), B₂O₃ evaporation is rapid. Loss of the protective layer allows for direct contact between the atmosphere and ZrB₂, which results in linear mass gain kinetics (17). Recently, Parthasarathy et al. have developed a mechanistic model that describes both the structural evolution and the rate-limiting steps at various stages of oxidation for ZrB₂, HfB₂, and TiB₂ (18,19).

Typically, oxidation resistance of the diborides is improved by adding compounds such as SiC, MoSi₂, or TaSi₂ that form a protective SiO₂-rich oxide scale at temperatures
For submission to proceedings of the 214th meeting of the Electrochemical Society above 1200°C (20-24). Compared to pure B$_2$O$_3$, borosilicate glasses are less volatile and provide a stable diffusion barrier during oxidation at intermediate temperatures (1200°C to 1600°C), which extends the temperature range for protective behavior (25). However, this approach only provides protection up to ~1600°C, not to the ultra-high temperatures that are predicted for hypersonic flight applications. At higher temperatures, loss of the SiO$_2$ scale again leaves a porous ZrO$_2$ scale on the surface of the diboride, resulting in rapid oxidation (26). In some cases, the ZrO$_2$ scale has been shown to densify, resulting in improved oxidation protection at temperatures of 1800°C or higher (26).

Some researchers have reported formation of a SiC-depleted layer beneath the surface borosilicate glass layer during oxidation of ZrB$_2$-SiC ceramics (20,21,27). This layer is thought to form due to active oxidation of SiC beneath the scale, which is caused by low oxygen activity below the diffusion barrier (28). Formation of a SiC-depleted layer is likely to be detrimental to stability of the scale at elevated temperatures due to the increase in pressure of species such as SiO and CO in the porous SiC-depleted layer, which could cause rupture of the SiO$_2$ scale (25,26).

The purpose of this research was to examine tungsten additions as a possible route to improve the oxidation resistance of ZrB$_2$ ceramics. The initial motivation to explore transition metal additions was based on the possibility of modifying the microstructure of the ZrO$_2$ scale (29). Specifically, WO$_3$ forms a eutectic with ZrO$_2$ at ~1275°C. Formation of a liquid phase may promote liquid phase sintering of the ZrO$_2$, which could decrease porosity of the scale and reduce the rate of oxygen transport to the underlying ZrB$_2$, thereby reducing the rate of mass gain and/or the thickness of the resulting oxide scale. This paper describes the processing, mass gain characteristics, oxide scale morphology, and scale thickness for ZrB$_2$ ceramics containing 4 mole percent W.

**Experimental Procedure**

Specimens for this study were prepared from high purity (>99%) ZrB$_2$ powder (Grade B, H.C. Starck, Newton, MA) with an average particle size of ~2 µm. Two weight percent B$_4$C (Grade HS, H.C. Starck, Newton, MA) with an average particle size of 0.8 µm was added to all batches as a densification aid (30). For batches containing tungsten, four mole percent W was added in the form of WC powder (ACER, Czech Republic), which had an average particle size of ~1 µm. Hereafter, ZrB$_2$ ceramics that contained only B$_4$C as a sintering aid are referred to as “nominally pure ZrB$_2$” while ceramics containing four mole percent tungsten are referred to as (Zr,W)B$_2$.

Powders were mixed by dispersion, which was accomplished by ball milling the batched powders in methyl ethyl ketone (MEK) containing a dispersant (DISPERBYK-110, BYK-Chemie Co., Wesel, Germany) for 24 hours. Powders were milled in a high density polyethylene jar using WC milling media. After dispersion, one weight percent binder (Qpac-40, Empower Materials, Newark, DE) was added and the mixture was milled for an additional 24 hours. The slurry was dried by stirring at room temperature and allowing the MEK to evaporate. The dried powder cake was ground using an alumina mortar and pestle to form granules that were passed through a 50 mesh sieve. Cylindrical disks ~19 mm in diameter were formed by uniaxial pressing in a steel die at 18 MPa. The disks were further compacted by cold isostatic pressing at ~310 MPa.
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Test specimens were densified by pressureless sintering in a resistance heated, graphite element furnace (3060-FP20, Thermal Technology, Santa Rosa, CA). The heating schedule has been described in detail elsewhere (30). Briefly, pellets were heated at ~10°C/min in mild vacuum (~20 Pa) to 1650°C to facilitate removal of surface oxide impurities (31). After a one hour isothermal hold, the atmosphere was switched to flowing argon (~10^5 Pa) and the pellets were heated at 10°C/min to 2050°C and held for two hours for densification. For oxidation studies, specimens approximately 3 mm by 4 mm by 5 mm were cut from the pellets.

Additional studies on liquid phase sintering of ZrO_2 with additions of WO_3 were conducted by mixing four, six, or ten mole percent WO_3 (99.995%, Aldrich, Milwaukee, WI) with ZrO_2 (99%+, Alfa, Ward Hill, MA). Pellets were compacted in a steel die at ~18 MPa and then heated to 1300°C, 1372°C, or 1500°C for four hours in air

After densification, bulk density was measured using the Archimedes’ method with water as the immersion and saturating medium. Relative densities were calculated by dividing the measured bulk density by theoretical densities that were predicted from the nominal batch compositions assuming densities of 6.1 g/cm^3 for ZrB_2, 14.9 g/cm^3 for WC, and 2.5 g/cm^3 for B_4C. Phases present in the final specimens were characterized using x-ray diffraction (XRD; XDS 2000, Scintag Inc., Cupertino, CA) analysis. Lattice parameters were determined using Rietveld refinement (JADE 5.026, Material Data Inc., Livermore, CA) of XRD data. Microstructures and oxide layer thicknesses were observed using scanning electron microscopy (SEM; S-570, Hitachi, Japan) equipped with energy dispersive spectroscopy (EDS; E2V, Scientific Instruments, UK) for simultaneous chemical analysis.

Oxidation behavior was characterized using thermal gravimetric analysis (TGA) and furnace oxidation in flowing air. Mass gain was measured as a function of temperature using TGA (Netzsch STA 409C/CD, Germany), which was conducted by heating specimens at 10°C/min to 1500°C in flowing air. Isothermal oxidation studies were carried out in a MoSi_2-element tube furnace (Model 0000543 Rapid Temperature Furnace, CM Inc., Bloomfield, N.J.) equipped with gas-tight end caps. Specimens were placed on zirconia setters with raised ridges to minimize the contact area between the specimen and the substrate. Specimens were heated at ~5°C/min to 1500°C or 1600°C and held for one, two, or three hours in a flowing air atmosphere. After cooling to room temperature, mass was measured and specimens were sectioned to characterize the oxide layer thickness.

Results and Discussion

Liquid Phase Sintering

The potential for liquid phase sintering in the WO_3-ZrO_2 system was studied using powder mixtures. From the WO_3-ZrO_2 phase diagram, the solidus temperature for ZrO_2-rich compositions occurs at 1257°C (32). Above this temperature, ZrO_2-rich compositions should form a liquid phase containing about 70 mole percent WO_3, which will be in equilibrium with a solid phase containing about 96 mole percent ZrO_2. Based on the phase equilibria, WO_3-ZrO_2 mixtures containing four, six, and ten mole percent WO_3 were heated to 1500°C for 4 hours to look for signs of liquid phase formation and liquid phase sintering. From the fracture surfaces in Figure 1, all of the compositions
formed a two phase mixture after heating to 1500°C. The major phase consisted of rounded, darker gray particles. Analysis by EDS (not shown) revealed that the particles were primarily composed of Zr and O. In addition, the ZrO$_2$ particles had grown from their starting size of $\sim 0.5 \, \mu$m to nearly 20 $\mu$m in diameter. The minor phase, which was a lighter gray color, was present at the grain boundaries. Analysis by EDS showed that this phase was rich in W and O. More importantly, the minor phase appeared to wet the grains and form a thin, continuous layer that coated the grain surfaces. Based on these observations, it appeared that the addition of four mole percent WO$_3$ was sufficient to promote liquid phase sintering of ZrO$_2$.

Figure 1. Fracture surfaces of WO$_3$-ZrO$_2$ compacts heated to 1500°C for 4 hours. The compacts contained (a) 4, (b) 6, and (c) 10 mole percent WO$_3$ (balance ZrO$_2$).

To further assess the effectiveness of WO$_3$ as a liquid phase sintering additive for ZrO$_2$, mixtures of ZrO$_2$ containing 4 mole percent WO$_3$ were heated to temperatures from 1300°C to 1500°C (Figure 2). As shown below, the lower temperatures were not effective at producing a continuous liquid phase despite the fact that both were above the solidus temperature ($\sim 1257$°C). Heating to 1500°C was required to promote wetting of the ZrO$_2$ particles by the liquid phase. Hence, it appears that temperatures of 1500°C or higher are required to enable liquid phase sintering of ZrO$_2$ by a WO$_3$-rich liquid.

Figure 2. Fracture surfaces of WO$_3$-ZrO$_2$ compacts containing 4 mole% WO$_3$ (balance ZrO$_2$) heated to (a) 1300°C, (b) 1372°C, and (c) 1500°C for four hours.

Based on the liquid phase sintering studies, it was concluded that a minimum of four mole percent WO$_3$ would have to be incorporated into the ZrO$_2$ scale formed during oxidation of ZrB$_2$ to effectively modify scale morphology. Two ways to incorporate WO$_3$ into the scale were considered: 1) directly adding WO$_3$ to the ZrB$_2$ and (2) dissolving W into the ZrB$_2$ matrix so that WO$_3$ and ZrO$_2$ would form simultaneously during oxidation. The incorporation of WO$_3$ was not investigated based on the inhibiting effect that oxide impurities have on the densification of ZrB$_2$ ceramics. Hence, the dissolution of W into ZrB$_2$ was selected.
Densification, Microstructure, and Phase Analysis

Nominally pure ZrB$_2$ and (Zr,W)B$_2$ reached near full density after sintering at 2050°C for 4 hours. Both materials had minimal residual porosity and grain sizes of ~10 µm (Figure 3). Isolated B$_4$C particles, which had been added to react with and remove surface oxide impurities, were observed. Unlike B$_4$C, the WC that was added as a source of W in the (Zr,W)B$_2$ material was not observed after sintering. In contrast, XRD analysis revealed that diffraction peaks in specimens containing W were shifted to higher angles (30). Because W (1.4 Å) has a smaller radius than Zr (1.6 Å), W could substitute onto Zr sites in the ZrB$_2$, which decreased its lattice parameters and shifted the XRD peaks to higher angles. Dissolution of W into ZrB$_2$ is consistent with the reported W$_2$B$_5$-ZrB$_2$ phase diagram, which indicates a W solubility of ~13 mole percent in ZrB$_2$ (34). Hence, SEM observations and XRD analysis are both consistent with reported phase equilibria. All indicate that W should and did dissolve into the ZrB$_2$ matrix.

Figure 3. SEM image of a thermally etched cross section of nominally pure ZrB$_2$ sintered at 2050°C, which has the same grain size and shape as (Zr,W)B$_2$.

Thermal Gravimetric Analysis

Thermal gravimetric analysis showed that (Zr,W)B$_2$ had better oxidation resistance than nominally pure ZrB$_2$. As summarized in Table 1, (Zr,W)B$_2$ had normalized mass gain of ~4.5 mg/cm$^2$ after heating to 1500°C compared to ~14 mg/cm$^2$ for nominally pure ZrB$_2$. The initial mass gain for both materials started at ~700°C. However, the nominally pure ZrB$_2$ showed a transition to rapid mass gain at ~1200°C, which is the temperature at which B$_2$O$_3$ volatilization has been reported to become significant (18). As B$_2$O$_3$ was depleted from the oxide layer, mass gain became more significant since the porous ZrO$_2$ layer did not provide protection to the underlying ZrB$_2$. Oxidation of ZrB$_2$ to ZrO$_2$ results in a mass gain of ~10% after all of the B has been removed from the specimen by volatilization as B$_2$O$_3$. The addition of W appears to increase the temperature at which rapid mass gain begins to ~1400°C. Although the mechanism of improved protection is not evident from this experiment alone, the liquid phase sintering study described above supports the assertion that the presence of WO$_3$ as an oxidation product modifies the morphology of the oxide scale. Results indicate that oxidation was suppressed by better protecting the ZrB$_2$ from the external atmosphere. Two plausible protection mechanisms are that WO$_3$ acted as a liquid phase sintering aid that decreased the porosity of the scale
For submission to proceedings of the 214th meeting of the Electrochemical Society or that WO$_3$ itself acted as a barrier to oxygen transport to the underlying ZrB$_2$ due to the volume increase associated with oxidation of W to WO$_3$. In either case, the presence of W led to a significant decrease in weight gain during TGA experiments. Even though the results show that W additions were effective at improving oxidation resistance in ZrB$_2$, the TGA results do not reveal the full effect of W additions. Additional isothermal oxidation studies are needed to complement these results.

**TABLE I.** Summary of TGA results for nominally pure ZrB$_2$ and (Zr,W)B$_2$ for heating to 1500°C in flowing air.

<table>
<thead>
<tr>
<th>Material</th>
<th>Onset of Mass Gain (°C)</th>
<th>Onset of Rapid Mass Gain (°C)</th>
<th>Total Mass Gain (mg/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrB$_2$</td>
<td>700</td>
<td>1200</td>
<td>14.0</td>
</tr>
<tr>
<td>(Zr,W)B$_2$</td>
<td>700</td>
<td>1400</td>
<td>4.5</td>
</tr>
</tbody>
</table>

**Isothermal Oxidation Studies**

The addition of four mole percent W decreased the mass gain for (Zr,W)B$_2$ compared to nominally pure ZrB$_2$ at both 1500°C and 1600°C for oxidation times ranging from 60 to 180 minutes. For both temperatures, the decrease in mass gain was more significant at longer oxidation times (Figure 4). For example at 1500°C, the mass gain for nominally pure ZrB$_2$ increased from ~9 mg/cm$^2$ after 60 minutes to ~15 mg/cm$^2$ after 180 minutes. Over the same range of times at 1500°C, the mass gain for (Zr,W)B$_2$ increased from ~9 mg/cm$^2$ after 60 minutes to ~11 mg/cm$^2$ after 180 minutes, which is a decrease of ~25% for the W-containing material compared to nominally pure ZrB$_2$. Further, the trend in mass gain for (Zr,W)B$_2$ at 1500°C suggested that W additions may lead to the formation of a protective scale since the mass gain kinetics appear to be parabolic for (Zr,W)B$_2$. This is supported by observations for specimens oxidized at 1500°C for three hours (not shown), which revealed that the thickness of the ZrO$_2$ scale decreased from ~500 μm for nominally pure ZrB$_2$ to ~100 μm for (Zr,W)B$_2$. In contrast, nominally pure ZrB$_2$ exhibited linear mass gain kinetics at 1500°C and 1600°C. The reduced mass gain of (Zr,W)B$_2$ at longer times may also be due to time-dependent changes in the scale morphology, which will be discussed in more detail below.

Figure 4. Normalized mass gain as a function of time for nominally pure ZrB$_2$ (squares) and (Zr,W)B$_2$ (circles) oxidized in flowing air (a) 1500°C and (b) 1600°C. Note the difference in Y-axis scales for the two plots.
Remarkably, the oxidation protection imparted by W additions is better at 1600°C than it was at 1500°C (Table II). Whereas mass gain after 180 minutes for nominally pure ZrB$_2$ increased from ~15 mg/cm$^2$ at 1500°C to ~22 mg/cm$^2$ at 1600°C, mass gain for (Zr,W)B$_2$ decreased from ~11 mg/cm$^2$ at 1500°C to ~8 mg/cm$^2$ at 1600°C. So, mass gain for (Zr,W)B$_2$ decreased by ~25% when temperature increased from 1500°C to 1600°C. Although a definitive analysis of the mechanism requires more investigation, two reasonable possibilities are that W is more effective at modifying scale morphology at the higher temperature or that the WO$_3$-rich phase somehow becomes a more effective diffusion barrier at 1600°C.

**TABLE II.** Comparison of mass gain after three hours at 1500°C or 1600°C for ZrB$_2$ and (Zr,W)B$_2$.

<table>
<thead>
<tr>
<th>Material</th>
<th>Mass Gain (mg/cm$^2$) 180 minutes at 1500°C</th>
<th>Mass Gain (mg/cm$^2$) 180 minutes at 1600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrB$_2$</td>
<td>15</td>
<td>22</td>
</tr>
<tr>
<td>(Zr,W)B$_2$</td>
<td>11</td>
<td>8</td>
</tr>
</tbody>
</table>

**Combined SiC and W Additions**

The mass gain of (Zr,W)B$_2$ ceramics containing 20 volume percent SiC was studied using TGA. As shown in Figure 5, the combination of SiC and W additions resulted in a lower mass gain compared to W additions alone. The onset of mass gain for all three ceramics was around 700°C. Nominally pure ZrB$_2$ underwent rapid mass gain above about 1200°C, resulting in a total mass gain of ~14 mg/cm$^2$ after heating to 1500°C. The addition of W suppressed rapid weight gain until about 1400°C, reducing mass gain to ~4.5 mg/cm$^2$ after heating (Zr,W)B$_2$ to 1500°C. With a combination of SiC and W additions, rapid mass gain was suppressed at temperatures below 1500°C, resulting in a normalized mass gain of less than 2 mg/cm$^2$. Adding a combination of W and SiC produced a silica-rich surface oxide that provided improved oxidation protection compared to the W addition alone. More detailed analysis of isothermal oxidation studies is in progress to understand the role of W in the oxidation of ZrB$_2$-SiC ceramics.

![Figure 5](image.png)

Figure 5. TGA results for nominally pure ZrB$_2$, (Zr,W)B$_2$ containing 4 mole percent W, and (Zr,W)B$_2$-SiC containing 4 mole percent W and 20 volume percent SiC.
Oxidation behavior was studied for ZrB$_2$ ceramics with W and SiC additions. Mass gain studies employing TGA showed that the addition of four mole percent W decreased mass gain from ~14 mg/cm$^2$ for nominally pure ZrB$_2$ to ~4.5 mg/cm$^2$ for (Zr,W)B$_2$ for heating to 1500°C in air. The beneficial role of W was further evaluated with isothermal oxidation experiments. The addition of W decreased both mass gain and oxide scale thickness compared to nominally pure ZrB$_2$. Remarkably, W additions appeared to provide more effective oxidation protection at higher temperatures, reducing the mass gain from ~11 mg/cm$^2$ for (Zr,W)B$_2$ oxidized at 1500°C for three hours to ~8 mg/cm$^2$ for (Zr,W)B$_2$ oxidized at 1600°C for three hours. Finally, W additions are also promising for improving the oxidation resistance of ZrB$_2$-SiC ceramics.

Acknowledgments

This work was funded by the Air Force Research Laboratory on contract number FA8650-04-C-5704 through the Center for Aerospace Manufacturing Technologies at the Missouri University of Science and Technology.

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