TEM Study of the High-Temperature Oxidation Behavior of Hot-Pressed ZrB$_2$–SiC Composites

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The oxidation behaviors of ZrB$_2$–30 vol% SiC composites were investigated at 1500°C in air and under reducing conditions with oxygen partial pressures of 10$^4$ and 10$^{-8}$ Pa, respectively. The oxidation of ZrB$_2$ and SiC were analyzed using transmission electron microscopy (TEM). Due to kinetic differences in oxidation behavior, the three layers (surface silica-rich layer, oxide layer, and unreacted layer) were observed over a wide area of specimen in air, while the two layers (oxide layer, and unreacted layer) were observed over a narrow area in specimen under reducing condition. In oxide layer, the ZrB$_2$ was oxidized to ZrO$_2$ accompanied by division into small grains and the shape was also changed from faceted to round. This layer also consisted of amorphous SiO$_2$ with residual SiC and found dispersed in TEM. Based on TEM analysis of ZrB$_2$–SiC composites tested under air and low oxygen partial pressure, the ZrB$_2$ begins to oxidize preferentially and the SiC remained without any changes at the interface between oxidized layer and unreacted layer.

I. Introduction

The transition-metal borides, carbides, and nitrides are classified as ultra-high-temperature ceramics (UHTCs). The UHTCs possess unique properties, including high melting points (>3200°C), good mechanical properties, strong oxidation resistance, and chemical inertness. Because of this, the interest in UHTCs has increased in the field of aerospace applications, for applications such as a thermal protection systems (TPS) on hypersonic aerospace vehicles and reusable atmospheric reentry vehicles. Among the UHTCs, ZrB$_2$ has the lowest theoretical density (6.09 g/cm$^3$), and has good thermal shock resistance because of its high thermal conductivity (65–135 W/mK). These attributes could be advantageous for TPS and other aerospace applications. Many attempts have been made to enhance the oxidation resistance of ZrB$_2$-based materials through the use of appropriate additives. The most common additive is SiC, which enhances the oxidation resistance via the formation of SiO$_2$ as well as mechanical properties and sinterability. The oxidation behaviors of ZrB$_2$–SiC composites have been well-defined previously. When ZrB$_2$–SiC composite is exposed to oxidizing environments (at a temperature of 1500°C), it forms a layer structure consisting of the following (1) a continuous, silica-rich layer, (2) an SiC depletion layer, and (3) an unreacted layer. This surface silica-rich layer prohibits the transport of oxygen through the oxide scales, and allows the ZrB$_2$–SiC composite to show parabolic mass gain kinetics.

II. Experimental Procedures

1. Preparation

Commercially available raw powders were used in this study. ZrB$_2$ powder (Hexagonal, $a = b = 3.17$ Å, $c = 3.53$ Å, $P6/mmm$, size 3–5 μm, >99%, Grade A; H.C. Starck, Munich, Germany) and α-SiC powder (Hexagonal, $6H$-polypeptide, $a = b = 3.07$ Å, $c = 15.08$ Å, $P63mc$, average size 0.45 μm, 98.5%, UF25; H.C. Starck) were used for hot-pressing. The batches consisted of 70 vol% of ZrB$_2$ powder and 30 vol% of SiC powder. Many previous studies have reported that ZrB$_2$–30 vol% SiC composites showed improved sinterability and mechanical properties, and notably high-temperature oxidation resistance. Therefore, composites with 70 vol% ZrB$_2$ and 30 vol% SiC were used for the oxidation tests in this study.

Before hot-pressing, to reduce the particle size, the ZrB$_2$ raw powders were vibration milled for 30 min, using steel balls (~3 mm diameter spheres) and steel container; the median particle size and particle size distribution of vibration-milled
ZrB\textsubscript{2} powder were $D_{50} = 0.31$ μm and $D_{90}/D_{50} = 1.99$, while $D_{50} = 4.16$ μm and $D_{90}/D_{50} = 2.76$ in as-received ZrB\textsubscript{2} powder, respectively. During the vibration milling, 3.1 wt% of Fe impurity was introduced to ZrB\textsubscript{2} powder due to wear of steel balls. Fe impurity was reduced to 0.042 wt% level by acid treatment (3 M HCl, 1 h). The ZrB\textsubscript{2} powder were subsequently mixed with 30 vol% SiC powder and milled for 24 h in polyethylene bottles, with pure ethanol as the solvent and ZrO\textsubscript{2} balls (~4 mm diameter spheres) as the milling media. The powders were then carefully dried in a rotating evaporator, to prevent phase separation between the ZrB\textsubscript{2} (ρ = 6.09 g/cm\textsuperscript{3}) and the SiC (ρ = 3.21 g/cm\textsuperscript{3}). After drying, the powders were crushed with a mortar and sieved using 325 mesh sieves.

The powders were densified using hot pressing (HP2-1000-3560; Thermal Technology Inc., CA), with a temperature of 1950°C and a pressure of 32 MPa applied for 2 h in a graphite furnace, under an argon atmosphere. The powders were loaded into an 18-mm diameter boron nitride coated graphite die. The furnace was heated to 1800°C, a uniaxial load of 32 MPa was applied. After 120 min, the furnace was cooled to room temperature at a rate of 10°C/min, and then heated to 1950°C at a rate of 10°C/min with uniaxial load of 32 MPa. Above 800°C, both a thermocouple and a pyrometer (Infrared Thermometer, 620 A; Konica Minolta, Tokyo, Japan) were used to monitor the temperature of the furnace and the graphite die. When the die temperature reached 1800°C, a uniaxial load of 32 MPa was applied. After 120 min, the furnace was cooled to room temperature at a rate of 10°C/min, and the load was removed when the die temperature dropped below 1500°C. Specimens with a diameter of ~18 mm and a thickness of ~6.5 mm were fabricated, and samples with dimensions of 4 mm × 4 mm × 3 mm were diced from the specimens for the oxidation tests. The samples prepared for the oxidation tests are listed in Table I.

(2) Oxidation
The oxidation tests were performed using a horizontal tube furnace equipped with a MoSi\textsubscript{2} heating element. Before the tests, specimens were prepared using conventional polishing with a diamond abrasive, down to a 1 μm finish. They were then placed on an alumina boat filled with ZrO\textsubscript{2} balls as a buffer layer, and inserted into the center of the furnace, where the thermocouple was located. The oxidation tests were conducted at 1500°C for 10 h, under an air (Z3S-H) and low oxygen partial pressure (p\textsubscript{O\textsubscript{2}} = 10^{-8} Pa) atmosphere (Z3S-L). The heating and cooling rates were both 5°C/min. To create low p\textsubscript{O\textsubscript{2}} atmosphere conditions, CO gas containing 2000 ppm CO\textsubscript{2} was used, which produced an oxygen partial pressure of ~10^{-8} Pa at 1500°C. This oxygen partial pressure was selected based on the information obtained from a thermodynamic model, which predicted an oxygen partial pressure in the SiC-depleted region during the oxidation of the ZrB\textsubscript{2}–SiC composite. The alumina (Al\textsubscript{2}O\textsubscript{3}, 99.9% purity, 60 mm outer diameter × 5 mm wall thickness × 1 m length) tube was used for CO/CO\textsubscript{2} gas flowing and ends of the tube were sealed using gastight end caps. A gas flow was maintained with a flow rate of ~100 cm\textsuperscript{3}/min.

Table I. Summary of ZrB\textsubscript{2}–SiC Specimens: Compositions, Designations, Relative Density, and Conditions in the Oxidation Tests

<table>
<thead>
<tr>
<th>Composition (volume ratio) ZrB\textsubscript{2}–SiC</th>
<th>7:3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Designations Z3S-H Z3S-L</td>
<td>99.5 99.8</td>
</tr>
<tr>
<td>Relative density (%)</td>
<td>100%</td>
</tr>
<tr>
<td>Oxidation test conditions</td>
<td>2 × 10\textsuperscript{4} Air, 10\textsuperscript{-8} CO/CO\textsubscript{2}</td>
</tr>
<tr>
<td></td>
<td>high p\textsubscript{O\textsubscript{2}}, low p\textsubscript{O\textsubscript{2}}</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>1500</td>
</tr>
<tr>
<td>Time (h)</td>
<td>10</td>
</tr>
</tbody>
</table>

(3) Characterization
The densities of the hot-pressed specimens were measured using the Archimedes method, and the theoretical densities of the composites were calculated using the rule of mixture. The microstructures of the cross-sections of both the as-made and oxidized specimens were characterized using scanning electron microscopy (FE-SEM; Philips, XL30 FEG, Eindhoven, Netherlands). To analyze the microstructures of the vertical sections before and after the tests, the specimens for both cases were cross-sectioned and mounted in epoxy, carefully polished with a diamond abrasive down to a 1 μm finish, and cleaned in an ultrasonic bath with acetone. The thicknesses of the resulting reaction layers were measured from the polished cross-sections. The tested specimens were prepared for TEM observations using ion thinning with a focused ion beam system (FIB; Quanta 3-D FEG, FEI, Eindhoven, Netherlands). Bright field (BF) images, SAED patterns, high-resolution TEM (HRTEM) images, and EDS data were acquired using a transmission electron microscope (Tecnai G2 F30 S-twin, FEI, Eindhoven, Netherlands) operating at 300 kV. The thermo-gravimetric (TG) properties of the ZrB\textsubscript{2} and SiC starting powders were analyzed using a TG/DTA instrument (TGA 97-18; SETARAM, Caluire, France). The temperature was raised to 1400°C at a rate of 10°C/min.

III. Results and Discussion

(1) Characterization of Sintered Composite
The bulk densities for the hot-pressed billets were measured, yielding densities of 5.22 and 5.25 g/cm\textsuperscript{3}. The theoretical density of the ZrB\textsubscript{2} 30 vol% SiC composite was 5.23 g/cm\textsuperscript{3}, determined using a rule of mixture calculation (6.09 g/cm\textsuperscript{3} for ZrB\textsubscript{2}, and 3.21 g/cm\textsuperscript{3} for SiC). Several assumptions for using a rule of mixture were used as follows: the 30 vol% SiC grains were well dispersed in 70 vol% ZrB\textsubscript{2} matrix and there are no reaction, substitution, and solid solution between ZrB\textsubscript{2} and SiC. The relative densities of specimens were over 99.5% to near theoretical density. This indicated that the porosity did not have a significant effect on the oxidation behavior.

Figure 1(a) shows a bright field TEM image of the hot-pressed ZrB\textsubscript{2}–SiC composite. The black grains in the figure are ZrB\textsubscript{2}, and the white grains are SiC. Intergranular faceted SiC grains with a grain size of 0.5–2.0 μm were observed at the ZrB\textsubscript{2} triple and quadruple junctions. The ZrB\textsubscript{2} grains also

![Fig. 1. Typical BF image of as-sintered ZrB\textsubscript{2} 30 vol% SiC composite. Intergranular faceted SiC grains were located at the triple and quadruple junctions of the ZrB\textsubscript{2} grains. The inset SAED patterns taken from circled areas are showing [0111] zone axis pattern from ZrB\textsubscript{2} and [0121] zone axis pattern from SiC.](image-url)
showed a faceted shape, with grain sizes of 3–6 μm. The inset SAED patterns taken from the circled areas are [0111] zone axis pattern of hexagonal ZrB₂ and [0221] zone axis pattern of SiC-4H polytype (hexagonal structure) in Fig. 1(a). The SiC-6H starting powder might partially transform to 4H-type during sintering and the most stable polytypes of silicon carbide at 1800°C–2000°C were 4H and 6H.²⁵

(2) Oxidation Tests

Figure 2 shows the reacted depth as a function of exposure time for the ZrB₂–SiC specimens oxidized in air and low $\rho_{O_2}$ (10⁻⁸ Pa) atmosphere at 1500°C. In air, the shape of parabolic plots of oxidized depth versus time indicates that oxidation follows the parabolic rate law. The parabolic rate law of oxidation kinetics implies that the oxidation of ZrB₂–SiC composite in air is controlled by diffusion. It means the formed silica-rich oxide scale [reaction (1)] is protective because it is dense and smooth as seen in Fig. 3(a). Under low oxygen partial pressure (10⁻⁸ Pa), the oxidation kinetics at 1500°C is divided into two parts, parabolic kinetics at the starting 3 h and linear kinetics thereafter. In other words, oxidation kinetics deviates from the parabolic law and follow a linear law after 3 h of oxidation time. This indicates that the rate-limiting of oxide growth changes from the diffusion of oxygen through the reaction product layer [reactions (1) and (2)]; above 1300°C and 1100°C, respectively) to reaction between oxygen and SiC (reaction (3), SiO vaporizing below $\rho_{O_2}$ ~8.8 × 10⁻¹³ Pa at 1500°C), and SiO dissociation from SiO₂ (reaction (4); range of 10⁻⁵ > $\rho_{O_2}$ > 8.8 × 10⁻¹³ Pa at 1500°C).²⁵,²⁶ The parabolic-linear transition could be explained as the result of the gradual interconnection of the defects, such as pores crack and grain boundary.²⁹ The connectivity of oxidized ZrB₂–SiC grains becomes rough and loose and the number of grain-boundary interconnection is increased. Due to low oxygen partial pressure, the amount of SiO₂, which has relatively high partial pressure (~38.1 Pa) from SiO₂ increases greatly, possibly resulting in the formation of pores. When the defects interconnect with each other to form oxygen path (diffusion and transport) channels, the parabolic-linear transition of oxidation kinetics happens.

\[ \text{SiC(s)} + 3/2\text{O}_2(g) \rightarrow \text{SiO}_2(l) + \text{CO(g)} \]  

(1)

\[ \text{ZrB}_2(s) + 5/2\text{O}_2(g) \rightarrow \text{ZrO}_2(s) + \text{B}_2\text{O}_3 \]  

(2)

\[ \text{SiC(s)} + \text{O}_2(g) \rightarrow \text{SiO(g)} + \text{CO(g)} \]  

(3)

$\text{SiO}_2(l) \rightarrow \text{SiO(g)} + 1/2\text{O}_2$  

(4)

Figure 3 shows cross-sectional SEM images of the materials that were oxidized at 1500°C for 10 h in (a) air (2 × 10⁴ Pa) and (b) under low oxygen partial pressure (10⁻⁸ Pa). The oxidation of the Z3S-H [Fig. 3(a)] composites at 1500°C produced structures consisting of four layers: a surface silica-rich layer, an oxide layer, a ZrO₂/ZrB₂–SiC layer, and an unreacted layer. The thickness of the oxidized layers (silica-rich layer + oxide layer) was 45 ± 5 μm. Several previous studies reported that three layers (SiO₂ layer with SiO₂ + ZrO₂ layer: observed in some cases), SiC-depleted layer, unreacted layer) were consistently formed after oxidation tests at 1500°C.¹⁶,²¹,²³–²⁵ Because the ZrB₂ and SiC phases oxidize rapidly, it results in the formation of a ZrO₂ layer and silica-rich layer, via reactions (2) and (1), respectively.¹⁸

However, three different layers (silica-rich layer, oxide layer (SiO₂ + ZrO₂), and unreacted layer) were observed in this study; there was no SiC-depleted layer and the oxide layer consisted of ZrO₂ and amorphous SiO₂ contained unreacted SiC. (Therefore, we call this layer “oxide layer” in this study) The formation of the SiC-depleted layer in the ZrB₂–SiC system depends not only on the surrounding pressure and temperature conditions but also on the volume distribution of the SiC in the ZrB₂ matrix.³² In some cases, concretely, SiC-depleted layer is not formed because of the volume ratio of SiC/ZrB₂, SiC distribution, and internal oxygen partial pressure. The volume ratio of SiC and ZrB₂ is 3:7 in this study, and it is considered that the SiC fraction is relatively high. The high fraction of SiC increases the degree of SiC interconnectivity. The $\rho_{O_2}$ value in this region cannot be defined clearly, but it is above 8.8 × 10⁻¹³ Pa (boundary condition of reaction (3) is dependent on the oxygen partial pressure), considering the $\rho_{O_2}$ for the ZrB₂–ZrO₂ equilibrium at 1500°C.³⁶ Therefore, the SiC is oxidized to an amorphous SiO₂ phase rapidly and it disperses along the ZrO₂ grain boundaries at 1500°C. The reaction (1) was more dominant than reaction (3) in this region. Consequently, the SiO₂ phase was increased by the internal
The SiO$_2$ oxide scale on the surface is protective in an air atmosphere, because SiO$_2$ is significantly less volatile than B$_2$O$_3$, and acts as a barrier against inward oxygen transport.$^{21,22}$ The volume increase upon the oxidation of ZrB$_2$–SiC could also have been one of the driving forces for the amorphous SiO$_2$ viscous flow to the surface.$^{23}$ Thus, a silica-rich layer provides the passive oxidation behavior with a parabolic increase in oxidation depth. The oxide layer was located underneath the surface SiO$_2$ layer, and the microstructure of this region was similar to the original structure, because the SiC was removed by active or passive oxidation.$^{38}$ The SiO$_2$ might have remained at the ZrO$_2$ grain boundaries under certain conditions (conditions for passive oxidation of SiC, temperature range from 1200°C to 1600°C and above $p_{O_2} > 8.8 \times 10^{-13}$ Pa)$.^{23,32}$ At the interface between the unreacted layer and the oxide layer, even under high oxygen partial pressure conditions ($p_{O_2} > 10^{-3}$ Pa), SiO (g) phase was transported to the surface via reaction (3), after reaction (1) occurred near the interface between the unreacted layer and the oxide layer. This occurred because this region had a lower oxygen partial pressure compared with that outside of the specimen. However, it consequently showed passive oxidation behavior because of the surface SiC. Therefore, the amorphous SiO$_2$ viscous flow to the surface. $^{37}$ Thus, a silica-rich layer that acted as a SiO (g) barrier layer.

In contrast to Z3S–H, in Z3S–L, the silica-rich layer was not formed on the surface and, only two layers (oxide layer, unreacted layer) were observed. The depth of the oxidized layers [layer II of Fig. 3(b)] was 135 ± 3 μm, much thicker than that measured for Z3S–H. A few studies have reported on the oxidation behaviors of the ZrB$_2$–SiC system under reducing conditions. Rezaie et al. explained that the high vapor pressure of SiO (g) under reducing conditions leads to the active oxidation of SiC.$^{25}$ The SiC is removed directly by active oxidation ($10^{-15}$ Pa < $p_{O_2} < 8.8 \times 10^{-13}$ Pa) [reaction (3)], or it oxidizes to SiO$_2$ [reaction (1)], which is then removed by volatilization ($8.8 \times 10^{-13}$ Pa < $p_{O_2} < 10^{-5}$ Pa) [reaction (4)]. Likewise, the ZrB$_2$ is stable below $p_{O_2} \sim 1.9 \times 10^{-11}$ Pa, or will oxidize to form ZrO$_2$ and B$_2$O$_3$. In other words, the oxidation behaviors of the ZrB$_2$–SiC system depend on the precise $p_{O_2}$. The oxygen diffuses to the inside of the bulk more easily, due to the absence of a SiO$_2$ layer on the surface and the smaller amounts of SiO$_2$ at the grain boundaries under reducing conditions.

(A) Oxidation Test at High-$p_{O_2}$ Atmosphere (Air, 2 × $10^4$ Pa): Figure 4(a) shows a typical BF image taken from the region slightly below the interface between the unreacted layer (I) and the oxide layer (II) in Fig. 3(a). Several samples were prepared to find this interface at varying depths. In this region, some ZrB$_2$ grains were oxidized and their shapes were changed from faceted to uneven, while the SiC grains remained stable. Some parts of the ZrB$_2$ grain began to oxidize, and its phase was transformed. The ZrB$_2$ grain was, therefore, divided into two grains: unreacted ZrB$_2$ grain and oxidized ZrB$_2$ (ZrO$_2$ phase). It is well-known that below 1100°C, the oxidation of SiC (cr) is much slower than that of ZrB$_2$, and that above 1100°C, SiC is oxidized rapidly via reaction (1) to form SiO$_2$. At 1500°C, the oxidation of the ZrB$_2$ phase exhibited rapid linear kinetics. Even when the oxygen partial pressure of this region was much lower than that of the surface, the ZrB$_2$ phase was oxidized preferentially, while the SiC phase was rarely oxidized. Figure 4(b) shows an HRTEM image taken from the squarred area in Fig. 4(a), at the interface between partially oxidized ZrB$_2$ and unreacted ZrB$_2$. The atomic arrangement of the right region clearly revealed it to be a hexagonal structure with a planar spacing of 3.5487 Å for the {001} plane of the ZrB$_2$ phase. The atomic arrangement of the right region also clearly showed structure and planar spacing. A monoclinic ZrO$_2$ structure was revealed and the planar spacing of the right region did not match any of the SiC polytypes. This region had a planar spacing of 3.1639 Å for the {111} plane of the monoclinic ZrO$_2$ phase. There is a large difference in lattice volume at the interface between the ZrO$_2$ ($V_{\text{lat}} = 140.7$ Å$^3$ in monoclinic ZrO$_2$) and ZrB$_2$ ($V_{\text{lat}} = 30.7$ Å$^3$) grains. Therefore, stress might be concentrated at the interface between ZrO$_2$ phase and ZrB$_2$ phase. The deformation (transformation) also occurred to minimize the strain energy at this incoherent interface. The interface between ZrO$_2$ and ZrB$_2$ might have moved leftward (in the direction of the inward ZrB$_2$ grain) as the oxidation time increased. The partially oxidized ZrB$_2$ grain was also confirmed by element maps in Fig. 4(c). The Zr and O elements were detected at right region which had a planar spacing of the monoclinic ZrO$_2$ phase in ZrB$_2$ grain and grain boundary while Si and C elements were only detected in SiC grain. From the results of Fig. 4, it seems the oxygen might be diffused and oxidized along the ZrB$_2$ grain boundary preferentially and preceded to inward ZrB$_2$ grain.

The BF image of Fig. 5 shows the microstructure of the oxide interlayer [layer II of Fig. 3(a)] between the surface SiO$_2$ layer and the unreacted Z3S–H layer. It is closer to the outer silica-rich layer than to the un-oxidized ZrB$_2$–SiC layer. The microstructure was different from that of the unreacted layer, and the shape of the grains changed from faceted to rounded. Almost all of the ZrB$_2$ grains were oxidized to form an oxide phase (ZrO$_2$); the grains were then divided into smaller grains with a size of 0.5–1.5 μm, and they changed shape to minimize the surface energy. Many grain boundaries were created and the number of oxygen diffusion path was increased due to the oxidation of ZrB$_2$. In addition, the number of oxygen vacancies in the non-stoichiometric zirconium oxides (ZrO$_{2-x}$) might increase due to the low oxygen partial pressure.$^{40}$ They accelerated the oxidation of the specimen, until the surface was covered with the SiO$_2$ amorphous
phase. The surface of SiC grain also oxidized and transformed to amorphous phase of SiO$_2$ with volumetric increase and viscous flow. Unreacted SiC remained at the midmost of SiO$_2$ and showed island structure.

The SiC grains might also have been oxidized and transformed to give an amorphous SiO$_2$ phase with flowing viscously into the grain boundaries. Based on the volatility diagram, the $p_{O_2}$ in this region was not low enough to allow the active oxidizing reaction [reaction (3)]. The $p_{O_2}$ for this region was above 8.8 $\times 10^{-13}$ Pa, considering the $p_{O_2}$ for the ZrB$_2$–ZrO$_2$ equilibrium at 1500°C. If the $p_{O_2}$ value was lower than 8.8 $\times 10^{-13}$ Pa, the SiC in the ZrB$_2$–SiC would oxidize to form SiO (g), and a layer of SiO$_2$ (l) would not form in this region. A slight $p_{O_2}$ gradient was likely to exist across the layers.

(B) Oxidation Test at Low-$p_{O_2}$ Atmosphere (10$^{-8}$ Pa): Figure 6 shows an STEM image of the specimen tested at low oxygen partial pressure; the image was taken from the interface between the unreacted layer (II) and the oxidized layer [layer I of Fig. 3(b)], which was thinned using FIB before TEM analysis. Although the analyzed area was much narrower than that of Z3S-H, two small layers (ZrO$_2$/ZrB$_2$–SiC section and ZrO$_2$/ZrB$_2$+SiC/SiO$_2$ section) were clearly observed in one specimen (except the unreacted ZrB$_2$–SiC section), while similar two sections were seen over a wide area in case of Z3S-H (Figs. 4 and 5). Because the oxidation behavior of ZrB$_2$–SiC at 1500°C under low $p_{O_2}$ is kinetically much active. Section 1 of Fig. 6 shows the unreacted region with faceted ZrB$_2$, and SiC grains. In section 2, some ZrB$_2$ grains are oxidized and their shapes are changed, but the SiC grains are stable. Section 3 contains ZrB$_2$ and SiC grains with ZrO$_2$ grains and SiO$_2$ amorphous phase.

Figure 7(a) shows a high-magnification BF image taken from section 2 (the interlayer between the unreacted layer and the oxide layer) in Fig. 6. ZrB$_2$, ZrO$_2$, and SiC grains were observed. Some ZrB$_2$ grains were oxidized and their shapes were changed, and some ZrB$_2$ grains were divided into several small ZrO$_2$ grains after the oxidation; the SiC was stable in this region. Figure 7(b) shows an HRTEM image taken from the circled area in Fig. 7(a). The interface between the fully oxidized ZrO$_2$ grain and the unreacted ZrB$_2$ was observed. The atomic arrangement of the grain on the left side of circled area clearly revealed a monoclinic structure with a planar spacing of 3.71 Å for the {011} plane of the ZrO$_2$ phase. The atomic arrangement of the grain on the right side of circled area also clearly showed planar spacing and its structure. A hexagonal structure and a ZrB$_2$ phase were revealed. This grain had a planar spacing of 3.58 Å for the {001} plane of the ZrB$_2$ phase.

Figure 8 shows a high-magnification BF image taken from section 3 of Fig. 6. The amorphous SiO$_2$ phase was dispersed along the grain boundaries between the ZrO$_2$ grains and the unreacted SiC grains, or at the SiC/SiC grain boundaries. The SiO$_2$ phase flowed viscously, and wetted the SiC and...
ZrO$_2$ grains after the SiC grains were oxidized and transformed to amorphous phase. In both cases (air and reducing conditions), the oxidation started from the formation of ZrO$_2$ at the interface between oxidized layer and unreacted layer. When ZrB$_2$ is oxidized, grain boundaries of ZrB$_2$ started to transform to ZrO$_2$ phase first. Then the oxidation proceeded through grain boundaries with oxygen diffusion and finally the oxidation extended to inward ZrB$_2$ grains. This phenomenon can be seen from images in Figs. 5 and 7, the ZrB$_2$ grain is located inside and ZrO$_2$ is located outside of ZrB$_2$ grain boundary. After that, the grains were divided into several small SiO$_2$ grains and the shape changed from faceted to round. As mentioned above, the oxygen might transport through ZrB$_2$ grain boundaries, ZrO$_2$ grain boundaries (created by rounded ZrO$_2$ grains formation) and oxygen vacancies in the non-stoichiometric ZrO$_2$. Due to the multipath for diffusion of oxygen, the oxidation kinetics of ZrB$_2$ was controlled by diffusion of oxygen through ZrB$_2$ grain boundaries. The oxidation rate of SiC was relatively slower than that of ZrB$_2$. The oxidation behavior of SiC started from the surface of SiC grain with transformation to amorphous SiO$_2$ phase and the oxidation proceeded to inward SiC grain. When the SiO$_2$ formed and covered on the surface of SiC grain, the oxygen is difficult to react with SiC because surface SiO$_2$ phase act as a barrier for oxygen diffusion. The surface SiO$_2$ prohibited the oxygen diffusion inside and retarded the oxidation of SiC. Therefore, unreacted SiC remained on the surface, SiO$_2$ at the grain boundaries, and the oxidation kinetics of SiC was controlled by diffusion of oxygen at surface SiO$_2$, i.e., diffusion-controlled kinetics.

Figure 9(a) shows a TEM BF image of the oxide region in the oxidized layer [layer II of Fig. 3(b)] of Z3S-L. The amorphous SiO$_2$ phase was observed to disperse along the ZrO$_2$ grain boundaries, including many pores. Figure 9(b) shows a magnified BF image of a grain boundary composed of amorphous phase SiO$_2$ and a pore in Fig. 9(a). The microstructure of this region was similar to that of the oxidized layer at the interface between the unreacted layer and the oxidized layer, as shown in Fig. 8 (section 3 of Fig. 6). However, many pores were observed in dispersed SiO$_2$ at the grain boundaries with absence of SiC phase after the test—despite the fact that the region was sufficiently oxidized—indicated that the oxygen partial pressure of this region was not low enough to rapidly evaporate the SiO$_2$ phase from the SiO$_2$ phase. The oxidation of SiC started from the surface of SiC grain, the oxygen diffusion inside and retarded the oxidation of SiC. This result was caused by further reaction between ZrO$_2$ and amorphous SiO$_2$. The interstitial silicon diffuses and dissolves into crystalline ZrO$_2$ until the solution limit is reached when ZrO$_2$ and amorphous silica coexisted, thereafter by precipitation of ZrSiO$_4$.

IV. Conclusions

The ZrB$_2$-30 vol% SiC composites were oxidized in air ($pO_2 = 10^4$ Pa), and under reducing conditions ($pO_2 = 10^{-6}$ Pa) at 1500°C for 10 h. The microstructures and oxidation depths of the specimens were observed using SEM and phase transformation and microstructure of the grains/grain boundaries on each layer were analyzed using TEM.
Based on TEM results, the three layers (surface SiO$_2$ layer, oxide layer, and unreacted layer) were observed in Z3S-H and the two layers (oxide layer, and unreacted layer) were observed in Z3S-L with varying depths after oxidation test. The SiO$_2$ and residual SiC were dispersed in whole oxide layer in Z3S-H, because of the structural distribution of SiC in the ZrB$_2$ matrix and internal oxygen partial pressure. In contrast, active oxidation behavior and no surface SiO$_2$ layer were observed in Z3S-L, and the amorphous SiO$_2$ phase also remained at the ZrO$_2$ grain boundaries in Z3S-L.

The results from the TEM analysis, in both cases (air and reducing conditions), ZrB$_2$ was oxidized and transformed to ZrO$_2$ phase firstly and then, SiC was oxidized at the interface between unreacted layer and oxidized layer. The oxidation and transformation of ZrB$_2$ was started from grain boundaries and the oxidation proceeded to the inside of grain which showed outside ZrO$_2$ and inside ZrB$_2$ structure. Then, the grains were divided into several ZrO$_2$ grains after fully oxidizing with the shape changing from facet to round. The SiC started to oxidize and transform into SiO$_2$ from the surface of SiC grain. After that, the SiO$_2$ was dispersed in grain boundaries in whole oxide layer of composite due to high viscosity and volumetric increase. The unreacted SiC existed in amorphous SiO$_2$ which has an island structure.

The oxidation of ZrB$_2$ might be controlled by O$_2$ diffusion and transport through the ZrB$_2$ grain boundaries and ZrO$_2$ grain boundaries, respectively, and the oxidation kinetics of SiC might be controlled by O$_2$ diffusion through SiO$_2$ because surface SiO$_2$ acted as an oxygen diffusion barrier. The oxidation behavior in structural changes was similar, but the oxidation kinetics was different. TEM analysis is one of the good approaches for understanding oxidation behaviors of ZrB$_2$–SiC-based UHTCs.

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