OXIDATION OF ZIRCONIUM DIBORIDE-SILICON CARBIDE CERAMIC COMPOSITES IN DISSOCIATED OXYGEN

Hua Jin¹, Songhe Meng¹*, Weihua Xie¹, Chenghai Xu¹, Liyuan Qin¹
Center for Composite Materials and Structures Harbin Institute of Technology, Harbin 150001, China
* Corresponding author (mengsh@hit.edu.cn)

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Abstract

The oxidation behavior and oxidation products of hot-pressed ZrB₂-SiC ceramic composites are investigated under plasma conditions in the high temperature, low pressure partially dissociated oxygen stream of the home-made dissociated oxygen simulation set-up. Specimens are oxidized at different environments for exposure time of 30 min at surface temperatures ranging from 1000 °C to 1800 °C. The microstructures and composition of the oxide scale are characterized using environment scanning electron microscopy, x-ray diffraction, and energy-dispersive spectroscopy analysis, and the weight change is also measured. Consistent with the surface reaction and volatility diagram, the curve of the weight change could be divided into four stages. Comparison is made with specimens oxidized under similar temperature and pressure conditions in oxygen environment in which atomic oxygen concentrations are negligible. Both of active oxidation and passive oxidation uptake of the specimens are observed with silicon oxide and silicate formation. The results indicate that the active oxidation is found to have remarkable effect on phase composition of the surface oxide scale, and the oxidation behavior of hot-pressed ZrB₂-SiC ceramic composites changes under dissociated oxygen.

1 Introduction

During hypersonic flight through a planetary atmosphere and atmospheric re-entry, shock waves form as gases are rapidly compressed ahead of leading surfaces. High energy intermolecular collisions within the shock layer heat the gas and cause molecules species in the surrounding environment to dissociate, thus significantly add to the heat load [1]. Oxygen and nitrogen molecules are the relevant species in the Earth’s atmosphere, where oxygen is more easily dissociated than nitrogen, since it has a lower dissociation energy (~5.1 eV compared to ~9.8 eV). Ultra-high temperature ceramic composites (UHTCs) are considered as potential candidate material of thermal protective system (TPS) for re-entry aircrafts and supersonic vehicles because of their unique combination of high melting points, good thermal shock resistance, and excellent ablation/oxidation resistance [2-4]. The addition of appropriate amounts of SiC particles not only enhances the mechanical properties, but also improves the oxidation resistance of ZrB₂ as a result of the formation of a borosilicate scale on the virgin material when oxidized [5,6]. Numerous investigations [7,8] have been conducted on the oxidation behavior of ZrB₂-SiC ceramic composites, but these have mainly focused on static or flowing air studies under ambient pressures and low oxygen partial pressure, few studies on the oxidation in dissociated environment because the oxidation in a thermal furnace could not account for the effect of dissociated oxygen even at high temperatures.

Recent advances in space technology encourage serious studies on behavior of high-temperature materials under re-entry conditions, particularly dissociated environment. The investigation to the oxidation behavior of the ceramic composites under dissociated environment is needed in order to strengthen the understanding of the oxidation process of the materials in re-entry environments. The oxidation behavior of ZrB₂-SiC ceramic composites in such conditions one should take into account both the temperature and the plasma effects, where the plasma radicals can alter the degradation oxidation resistance of the material due to their high chemical reactivity. Recently some researches have evaluated the oxidation resistance properties of the ZrB₂ matrix ceramic composites in simulated dissociated environment set-up, which can be divided into two categories: high enthalpy facilities.
such as arc-jets, induction plasmatrons, and low enthalpy laboratory systems such as diffusion tubes or flow tubes. The former more closely reproduce aspects of the flow environments during hypersonic flight, but are also much more complicated to operate and generally generate temperature or heat flux data. In contrast, laboratory systems are more amenable to controlled and well-characterized experiments, such as MESOX (PROMES-CNRS) and diffusion-tube side-arm reactor facility (NASA) [9-11]. Because of the set-up shortage it is hard to be heated to 1800 °C for specimens. Few studied on the high temperature oxidation of ZrB$_2$-SiC ceramic composites in dissociated oxygen environment and the oxidation processing is still not clearly understood [12]. Hence, the objective of this paper is to investigate the oxidation behavior of hot-pressed ZrB$_2$ composites containing 20 vol% SiC under high-temperature, low-pressure dissociated oxygen environment. The oxidation products for the ZrB$_2$- SiC ceramic composites are to report formation and evolution using a home-made dissociated oxygen simulation set-up. Furthermore, the microstructures of ZrB$_2$-SiC ceramic composites after oxidized are analyzed and discussed.

2. Experimental Procedure

2.1 Materials processing

Commercially available ZrB$_2$ powders (Northeast Institute for Non-ferrous Metal Research, China) had a purity of >99.5% and mean particle size of 5 μm. The SiC powders (Xuzhou Hongwu Nanometer Materials, China) had a reported purity of 98.5% and mean particle size of 2 μm. The graphite flake (Qingdao Tiansheng Graphite Co., Ltd., China) had a purity of 99.5% and mean diameter and thickness were 15 μm and 1.5 μm, respectively. The powder mixtures of ZrB$_2$ plus 20 vol.% SiC were ball-mixed for 10 h in a polyethylene bottle using ZrO$_2$ balls and ethanol as the grinding media. After mixing, the slurry was dried in a rotary evaporator and screened. The resulting powder mixtures were hot-pressing at 1900 °C for 1 h under a uniaxial load of 30 MPa in Ar atmosphere. The furnace was cooled to the room temperature when hot-pressing time was elapsed. Then the sintered specimens were put out from the graphite dies. Specimen coupons in the size of Φ20×3 mm were cut across sections parallel to the hot-pressing direction by electrical discharge machining (EDM) method, and each specimen was polished with diamond slurries down to a 1 mm finish. The coupons were ultrasonically cleaned successively in deionized water and ethanol before oxidation test. The relative density of the sintered ceramic reached to 97 vol% according to experimental results by Archimedes method.

2.2 Experiment set-up

Figure 1 is a schematic illustration of the homemade oxidation set-up for ZrB$_2$-SiC ceramic composites with high temperature and low pressure dissociated oxygen environment. The homemade oxidation set-up associates a quartz tube reactor (length 60 cm and outer diameter 5 cm) placed at the focus of the copper coil with 35 kW induction heating equipment for specimen heating (up to 1800 °C) and a microwave generator (2450 MHz, 1500 W max). This quartz tube reactor crossing the refrigerated waveguide contains a Zirconia substrate holder which is placed in the axle centerline of the discharge, and the specimen (20 mm diameter and 3 mm height) is placed in the substrate holder which at the middle of the copper coil. Atmospheric entry conditions can be partially simulated, in which the pressure and temperature can be reproduced independently with a high accuracy. The temperature measurements on the surface of specimen realized using a multi-wavelength pyrometer with measurement range of 1000–2500 °C through the CaF$_2$ option window. The system is pumped with a one-stage oil rotary pump with the pumping speed of 7.2 m$^3$/h in the pressure range between 10 and 10$^5$ Pa. The flow of work gas (high purity oxygen and argon gases 99.998%) through the system is adjusted with a volume flow controller, and the pressure is measured with an absolute vacuum gauge and the pressure increases roughly linearly with increasing gas flow.

2.3 Oxidation of atomic oxygen

The specimens were pretreated in vacuum furnace (10$^{-4}$ Pa) at 500 °C for 2 h in order to eliminate gaseous impurities on the surface of the ceramic composites. Then the oxidation of ZrB$_2$-SiC ceramic composites were carried out in dissociated oxygen environment, which was a microwave discharge plasma-type ground-based dissociated oxygen simulation set-up. The atomic oxygen was the predominant component in the obtained oxygen plasma according to oxygen plasma emission spectrum and optical actinometry methods. The quantity of argon (5%) was introduced in the oxygen and the evolution of the intensities ratio $I_{o}/I_{A_{v}}$ of the 844.6 nm (O line) and 842.4 nm (Ar line) was
measured on the surface of specimen through the window. The experiment condition in the present research is listed in Table 1.

Fig.1 Schematic of dissociated oxygen simulation set-up.

Table 1. The dissociated oxygen experimental condition

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz Reactor (Pa)</td>
<td>40</td>
</tr>
<tr>
<td>Discharging Power (W)</td>
<td>1200</td>
</tr>
<tr>
<td>Flow of Oxygen (sccm)</td>
<td>95</td>
</tr>
<tr>
<td>Flow of Argon (sccm)</td>
<td>5</td>
</tr>
<tr>
<td>Test Time (min)</td>
<td>30</td>
</tr>
<tr>
<td>Surface Temperature (°C)</td>
<td>1000~1800</td>
</tr>
</tbody>
</table>

2.4 Characterization of oxidized specimens

The microstructure on the surface and oxidation layer of oxidized specimens was detected using environment scanning electron microscopy (ESEM, Quanta 200F, FEI, Holland) along with energy-dispersive spectroscopy (EDS, EDAX, USA) for chemical analysis. Specimens were prepared for microscopy by cutting cross-sections and coating with aurum after oxidized. In addition to SEM/EDS, crystalline phases of oxidation products were determined by X-ray diffraction (XRD, X’Pert PRO, PANalytical, Netherlands) with Cu Ka radiation. The weight of each specimen was measured before and after oxidation to determine the weight change by the electronic analytical balance (BW, Sartouis, Germany).

3. Results and discussion

The surface macrographs of specimens were shown in Fig.2. Compared with the un-oxidized specimen, the surface of the specimen turned dark when the surface temperature was at 1000 °C, and it changed from gray to white gradually with increasing temperature. However it went back to gray when temperature was above 1700 °C, which was due to the different oxidation products on the surface. The morphology was different from that of specimens oxidized when they were exposed to high temperature air or pure oxygen [13].

Fig.2 Macrograph of specimens after oxidation for different temperature.

Fig. 3. X-ray diffraction of ZrB$_2$-SiC ceramic composites after oxidized in dissociated oxygen environment for 30 min with various temperatures.

The oxidized surface of ZrB$_2$-SiC ceramic composites, exposed to dissociated oxygen environment with different temperature, was studied using XRD, SEM and EDS. Therefore, the characterization of oxidized surface could be identified. In order to investigate the component of surface oxide, the X-ray diffraction patterns of ZrB$_2$-SiC ceramic composites after oxidized in low pressures dissociated oxygen environment for 30 min with various temperatures were shown in Fig 3. As shown in the image, most of the ZrB$_2$ and SiC was unaffected after oxidation at 1000 °C, and little ZrO$_2$ could be identified from the XRD pattern while the formation B$_2$O$_3$ and SiO$_2$ glass could not be identified. When oxidation at 1200 °C, a little ZrB$_2$...
and SiC was observed and the relative intensity of the ZrO$_2$ increased. Besides, the specimens shared the same composition and the main product on the surface was zirconia, the size and amount of zirconia should represent the oxidation degree of the ceramic composites, which suggest the specimens were slightly oxidized in temperature region from 1000 to 1200 °C and extent of oxidation strengthened with the increasing temperature. When oxidation above 1300 °C, only ZrO$_2$ could be identified and the ZrB$_2$, SiC peaks decreased, even disappeared, and the relative intensity of the ZrO$_2$ increased with rise of the temperature from 1300 to 1800 °C. This indicated the oxidation resistance of ceramics was deteriorated with rising temperature. The oxidation products consisted of zirconia crystals and amorphous borate silicate glass, and the latter could not be identified from the XRD pattern at 1400 °C but could be detected from the SEM and EDS, as shown in Fig. 4a. The XRD analysis didn’t detect the zircon phase ZrSiO$_4$ peak which presented in the other paper with lower oxygen partial pressure [12]. It meant the oxidation resistance was further deteriorated in comparison to oxidized at 200 Pa.

![Fig. 4. Surface morphology of specimens oxidized at temperature are (a) 1000, (b) 1100, (c) 1200 °C, (d) EDS.](image)

The oxidation behavior of ZrB$_2$-SiC ceramic composites were very complex especially at high temperatures dissociated oxygen environment. From the previous literatures, the oxidation behaviors of ZrB$_2$ and SiC in oxygen or low oxygen partial pressure had been studied extensively [14]. SiC was oxidized to SiO$_2$ and CO$_2$ at above 900 °C [15] with passive oxidation, and was oxidized to SiO and CO with active oxidation [16]. ZrB$_2$ was found to oxidize at about 700 °C and the oxides were ZrO$_2$ and B$_2$O$_3$ with passive oxidation which was exhibited below about 1100 °C, while the active oxidation occurred at temperatures above about 1400 °C resulting from the rapid evaporation of
B₂O₃ due to high vapor pressure [17,18]. Whereas the behavior of ZrB₂-SiC ceramic composites in dissociated oxygen environment was unclear due to ZrB₂ or SiC and atomic oxygen to take part in an oxidation reaction. Thus, in this paper, the expected main reactions were described as follows:

\[ \text{ZrB}_2(s) + \frac{5}{2}\text{O}_2 \rightarrow \text{ZrO}_2(s) + \text{B}_2\text{O}_3(g) \quad (1) \]

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

\[ \text{SiC}(s) + \frac{3}{2}\text{O}_2 \rightarrow \text{SiO}_2(l) + \text{CO}(g) \quad (4) \]

\[ \text{SiC}(s) + 3\text{O} \rightarrow \text{SiO}_2(l) + \text{CO}(g) \quad (5) \]

\[ \text{SiC}(s) + \text{O}_2 \rightarrow \text{SiO}(g) + \text{CO}(g) \quad (6) \]

\[ \text{SiC}(s) + 2\text{O} \rightarrow \text{SiO}(g) + \text{CO}(g) \quad (7) \]

\[ \times\text{SiO}_2(l) + y\text{B}_2\text{O}_3(l) \rightarrow \times\text{SiO}_2 \cdot y\text{B}_2\text{O}_3(l) \quad (8) \]

Fig. 5. Surface morphology of specimens oxidized at temperature are (a) 1400, (b) 1500, (c) 1700, (d) 1800 °C.

The experimental results obtained after oxidation could only describe the last stage of oxidation. The SEM micrographs of the surface after being oxidized from 1000 to 1200 °C were shown in Fig. 4. EDS analysis showed a few ZrB₂ and SiC particles on the surface of the specimen, and some small ZrO₂ particles filled the pit between them, as shown in Fig. 4a. The determination of the composition of the glass layer by EDS was difficult due to its low sensitivity to light elements (i.e. boron), only the glass phase contained a lot of Si element and a small quantity of O element was detected in specimens oxidized in 1100 and 1200 °C (point B in Fig. 4b and c), which was consistent with the SiO₂·B₂O₃. This phenomenon is different from the previous research in the same temperature and oxidized time, but when oxidized time increasing to 5 hours at similar temperate, the glass phase could be found in some
litteratures [19-22]. The reason may be that the oxidized rate increased due to the atomic oxygen oxidation reaction. Besides, pores were found on the surface after oxidation at 1100 °C. When temperature above 1400 °C, the rate of vaporization of B₂O₃ was high compared to its rate of formation, so B₂O₃ may become “extinct” after it formed. The surface was covered with the dark glass layer that was confirmed by EDS (not shown here) analysis to be the SiO₂-rich layer deposited by the fresh SiO₂ liquids due to passive oxidation of SiC. A lot of small white ZrO₂ islands (spots) surrounded by SiO₂-rich lagoons, and pores were healed by SiO₂ liquids deposited, as shown in Fig. 5a. When oxidized under temperatures at 1500 °C, as shown in the Fig. 5b, the surface of the specimen was covered by honeycomb like zirconia particles, and the little silica glass filled the gaps between zirconia particles and the gaps between the particles. It indicated that besides the low oxygen partial pressure and high temperature would result in the active oxidation of SiC, the atomic oxygen could inhibit passive oxidation of SiC and promote active to passive oxidation transition, thus induced the formation of silica glass as shown in the chemical equation (6) and (7), which was consistent with the results in literature [23]. The gaseous products, such as CO and SiO tended to escape from the surface because vapor pressure exceeded the ambient pressure, which led to the presence of the pores. Further, these pores could act as the diffusion channels of gaseous products through outermost layer and oxygen toward to the unaffected substrate. In the further oxidation process, the surface covered by dense zirconia layer and grains grew with the increasing temperature owing to the extensive evaporation of silica glass and high temperature, which had been confirmed by Halloranetal [18]. The mean size of the zirconia particles reached to about 1.4 and 3 μm at 1700 and 1800 °C, respectively.

![Fig. 6: The change curve of weight change/unit area with different temperature.](image)

To further substantiate the analysis based on the reaction production of ZrB₂-SiC ceramic composites at different temperatures, the weight change was also measured as a variation of temperature exposure to the dissociated oxygen environment, as shown in Fig. 6. The change curve of weight change/unit area with increasing temperature was nonlinear and wave, likely attributed to volatility driven mass loss and oxides formed gain. The change curve of weight change/unit area could be divided into four regions, an initial stage (1000–1300 °C), middle stage (1300–1400 °C), middle-late stage (1400–1600 °C) and late stage (1600–1800 °C), which was consistent with the surface oxidation reaction (1–8) and volatility diagram of ZrB₂ and SiC [24,25]. In the initial stage, ZrB₂ exhibited preferential oxidation and a few B₂O₃ volatilized, which result in the oxides were consist of solid ZrO₂ and glassy B₂O₃-rich phase and gas B₂O₃, thus the sum of weight increased marginally. When temperature above 1300 °C, though liquid B₂O₃ transition to gas entirely, the weight increased to 3.66 mg/cm² quickly in the middle stage which was attributed to both oxidation of SiC and diffusion of the SiO₂-rich
glass into the pores. The oxides were solid ZrO$_2$ and SiO$_2$-rich glass. When temperature was above 1400 °C, the lower oxygen partial pressure and atomic oxygen lead to the active oxidation of SiC under relatively lower temperature. In addition, the formation of protective silica film on the surface further lowered the oxygen partial pressure in the inner part, which aggravated the active oxidation of SiC. Therefore, a large amount of SiO gas escaped from the surface and weight decreased sharply to 3.18 mg/cm$^2$ in the middle-late stage because the weight of the solid oxides ZrO$_2$ and a few SiO$_2$ formed was less than the weight of ZrB$_2$ and SiC consumed. In the late stage, ZrO$_2$ covered the surface and oxidation reactions occurred at the ZrB$_2$-SiC substrate-scale by the inward diffusion of oxygen through the open pores in the oxide skeleton. Meanwhile, the vapor species and gas oxide escaped to the surface through the oxygen diffusion path was smaller than solid oxide formed. Thus, the weight increased in high temperature.

4. Conclusion

In the present work, isothermal oxidation of the ZrB$_2$-20 vol.% SiC ceramic composites were carried out in high temperature 1000~1800 °C, low pressure and dissociated oxygen environment by an homemade dissociated oxygen simulation set-up. The morphology of the specimens oxidized for 30 min were different from that exposed to high temperature air or pure oxygen. The XRD and SEM indicated that the ZrB$_2$ and SiC completely oxidized when temperature above 1300 °C and the ZrO$_2$ increased with rise of the temperature. The rate of vaporization of B$_2$O$_3$ was higher compared to its rate of formation when temperature above 1400 °C, additionally, the white ZrO$_2$ particles was covered with the SiO$_2$-rich layer. Then SiC occurred active oxidation from the gaseous products, for instance, CO and SiO tended to escape from the surface lead to the presence of the pores. At the interface between oxide scale and substrate, oxygen was first transported through grain boundaries, and reacted with SiC grains by active oxidation, leaving the ZrB$_2$ skeleton with large amounts of pores which acted as channels for oxygen diffusing into the substrate. The oxidation products and the microstructure of oxide scale in dissociated oxygen were similar to those in molecular oxygen. The change curve of weight change/unit area with increasing oxidation temperature was composed of four stages according to the increase in oxidation temperature: initial, middle, middle-late and late. It was consistent with the surface oxidation reaction and volatility diagram of ZrB$_2$ and SiC. In the initial stage, the chemisorption nuclei formed on the surface of the specimen and the weight increased marginally because the ZrB$_2$ oxidized to form more ZrO$_2$ and partial volatilized of B$_2$O$_3$ with temperature rising. The oxidation reaction of the ZrB$_2$-SiC ceramic composites in the middle stage was mainly controlled by the SiC oxidized and diffusion of the SiO$_2$-rich glass into the pores lead to weight increased. The presence of many pores resulted in the weight change/unit area in the middle-late stage being controlled by the active oxidation of SiC and a large amount of SiO gas escaped from the surface. Besides, the weight change/unit area with increasing temperature followed up trend in the late stage, which was contributed to further oxidized in the substrate-scale by the inward diffusion of oxygen and atomic oxygen. Furthermore, comparison of specimens after testing in dissociated oxygen environment with different temperature suggested that atomic oxygen had high reaction activity and significantly promoted the oxidation of ZrB$_2$-SiC composites, corresponding the temperature of passive-active transition was decrease. The active-passive transition in the oxidation of SiC depended strongly on the oxygen partial pressure in reaction region and oxidation component.

References


