Oxidation Behavior of ZrB$_2$-SiC Modified Zr$_3$[Al(Si)]$_4$C$_6$ Composites Exposed to Air

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Abstract. The oxidation behavior of Zr$_3$[Al(Si)]$_4$C$_6$-matrix composites reinforced by adjusted content of ZrB$_2$-SiC with fixed molar ratio of 2:1 was investigated. The composites were exposed to air at medium temperatures, and the oxidation kinetics of the composites generally follow a parabolic law. With the ZrB$_2$-SiC content increasing from 0 to 40vol.%, the oxidation weight gain per unit surface area ($\Delta w/s$) and oxidation rate constant ($k_p$) of the specimens increase and then decrease at the same oxidation conditions. The high content of ZrB$_2$-SiC is benefit for improving the oxidation resistance of the composites. And, the lowest $k_p$ of the composite incorporated with 40vol.%ZrB$_2$-SiC is about $2.43 \times 10^{-6} \text{kg}^2 \cdot \text{m}^{-4} \cdot \text{s}^{-1}$ when oxidized at 1100°C, which is still higher than that of monolithic Zr$_3$[Al(Si)]$_4$C$_6$. In addition, the phase composition and microstructure of oxidation products and the oxidation mechanism of materials were analyzed and discussed.

1. Introduction

The design and fabrication of new materials with good comprehensive performance have been the main research hotspot of materials research. Zr$_3$[Al(Si)]$_4$C$_6$ (denoted as ZAC from this point on) is a newly found layered quaternary transition metal carbide, which has attract much attention due to its unique properties. This carbide is formed by adding Si and Al to ZrC. It combines the merits of both ceramics and metals, and it shows better strength, stiffness, toughness, and oxidation resistance than ZrC ceramic [1-3]. Especially, ZAC ceramic has good high-temperature mechanical properties [2, 3]. For example, it has a high Young’s modulus of 292 GPa even at 1600 °C, which is about 80% of the ambient value. And, the bending strength of ZAC ceramic can maintain up to 1400°C [2,3]. Therefore, ZAC is expected to be a novel promising ultra-high temperature ceramics (UHTCs). However, for high-temperature applications, its mechanical properties are still not satisfactory. To overcome the weakness, effective approaches need to be designed.

Usually, adding appropriate second phases to the ceramic matrix is an effective way to improve the properties of materials. Some works have been conducted to develop SiC reinforced Zr-Al(Si)-C
composites [4-7], and Zr-Al(Si)-C/SiC composites have improved mechanical properties and oxidation resistance compared with monolithic Zr-Al(Si)-ceramic. Incorporation of only one phase has limited effect, and a synergistic action among two or more strengthening and toughening phases have been reported, which can produce a more significant strengthening and toughening effect compared to individual reinforcing agents [8, 9]. So, incorporation of multicomponent is desirable to further improve the properties of ZAC. Binary ZrB₂-SiC is one of the main research subjects in the field of UHTCs, which shows promising properties such as high melting temperature, good thermal conductivity, excellent mechanical properties and oxidation resistance [10, 11]. Thus, ZrB₂-SiC can be ideal reinforcements for ZAC matrix. In our recent work [9], with an aim at developing a novel UHTC with good mechanical properties, ZrB₂-SiC (molar ratio 2:1, denoted as ZS from this point on) system were employed as binary reinforcements, and a novel Zr₃[Al(Si)]₄C₆-ZrB₂-SiC (denoted as ZAC-ZS from this point on) composite were designed and successfully prepared by in situ reaction hot-pressing. The composite shows much improved mechanical properties, especially at high temperature compared with monolithic ZAC ceramic.

For UHTCs, oxidation resistance is critical for their practical applications at high temperatures. As a potential ultra-high temperature structural material, the oxidation resistance of ZAC-ZS composites must be given consideration. Generally, materials will be subjected to different temperature, i.e., low, medium, and high temperatures, during oxidation. In many cases, the medium temperature oxidation of materials is of some importance. Thus, in the present work, the isothermal oxidation resistance of ZAC-ZS composites at 1000-1100 °C was investigated and the oxidation mechanism of the composites was analyzed and discussed.

2. Experimental procedure

2.1. Materials preparation

Powders of ZrH₂ (99.9%, ≤53 μm), Al (99.9%, ≤74 μm), Si (99.9%, ≤53 μm), graphite (99.9%, ≤74 μm) and B₄C (99.9%, 3.5 μm) were used as starting materials. Zr₃[Al(Si)]₄C₆-ZrB₂-SiC (ZAC-ZS) composites with different ZrB₂-SiC (ZS, molar ratio 2:1) content of 10, 20, 30, and 40 vol.% were fabricated by in situ reaction hot-pressing process at 1850 °C. The detailed preparation process can be found in our previous works [9]. For the convenience in description, the composites were donated as ZAS1, ZAS2, ZAS3, and ZAS4, corresponding to the composites incorporated with 10, 20, 30, and 40 vol.% ZrB₂-SiC, respectively.

2.2. Characterization and tests

Isothermal oxidation test in air was carried out in a tube furnace (JinguangSGQ-10-14, Mianyang, China) at 1000°C and 1100 °C, respectively. When the given testing temperature was reached, the samples (3mm × 4mm × 8mm) were put into the furnace, held at the given testing temperature for target time, and then taken out. The weight gain of the specimens before and after oxidation were measured by an electronic microbalance (Sartorius BT224s, Beijing, China) with an accuracy of ±10⁻⁴ g. Phase analysis of the oxidized scale was carried out using XRD(Rigaku SmartLab, Tokyo, Japan). The microstructure of the surfaces of the oxidized specimens was analyzed by SEM(JEOL JSM-5900, Tokyo, Japan).

3. Results and discussion

3.1. Oxidation kinetics

Figure 1 presents the weight gain per unit surface area (Δw/s) of the composites oxidized at temperatures of 1000°C and 1100°C in air as a function of exposure time (t). And for comparison, the data of monolithic ZAC ceramic is also given. As can be seen, during the initial oxidation stage at each temperature, the Δw/s of all the specimens increases rapidly, and the oxide film forms quickly on the surface of materials, which plays a certain role in preventing further oxidation. After that, with the
further increase of exposure time at each oxidation temperature, the $\Delta w/s$ of the specimens increases slowly, indicating an oxide passivation stage. With the incorporation and increasing content of ZS from 0 to 40vol.%, the $\Delta w/s$ of the specimens increase first and then decrease at the same oxidation condition. For the composites, ZAS2 shows the highest $\Delta w/s$, and ZAS4 shows the lowest $\Delta w/s$. In addition, with the increase of oxidation time at each temperature, the $\Delta w/s$ of the composites have a tendency to be higher than that of monolithic ZAC ceramic, and the longer the oxidation time, the more obvious the phenomenon is. When oxidized at 1100 °C for 15 h, the $\Delta w/s$ of ZSC4 is about 0.365 kg·m$^{-2}$, which is about 21% higher than that of ZAC (about 0.302 kg·m$^{-2}$).

Figure 1. Weight gain per unit area versus oxidation time of specimens oxidized at different temperature: (a) 1000 °C, (b) 1100 °C.

Figure 2. Square of weight gain per unit surface area versus oxidation time of specimens oxidized at different temperature: (a) 1000 °C, (b) 1100 °C.

Figure 2 shows the square of weight gain per unit surface area $(\Delta w/s)^2$ of the specimens oxidized at temperatures of 1000°C and 1100 °C in air as a function of exposure time($t$), respectively. It can be seen that for all cases, a quite good linear relationship ($R^2 \geq 0.98$) between $(\Delta w/s)^2$ and $t$ is displayed, indicating that the oxidation kinetics for all the specimens follows the parabolic rate law [6]:

$$(\Delta w/s)^2=k_p t + c \quad (1)$$

where $k_p$ is the parabolic rate constant and $c$ is a constant. It implies that diffusion through the oxide scale is the rate controlling step of the oxidation process for all the specimens. The slopes of the fitting lines in Figure2, i.e., $k_p$, are plotted in Figure3. In accordance with the $\Delta w/s$ results shown in Figure1, with the incorporation and increasing content of ZS, the $k_p$ increases first and then decreases at the same oxidation temperature. Usually, the increased temperature results in an increased $k_p$, which becomes less obvious for the composites with high ZS content. It indicates that the higher content of ZS, i.e., 30 vol.% and 40vol.%, shows a certain improvement effect on the oxidation resistance of the composites. However, it is noted that the $k_p$ of the composites are higher than that of monolithic ZAC
ceramic at the oxidation temperature of 1000-1100 °C. Typically, the $k_p$ of ZAS3 and ZAS4 at 1100 °C is about $9.47 \times 10^{-6}$ and $2.43 \times 10^{-6}$ kg$^{-2} \cdot$ m$^{-4} \cdot$ s$^{-1}$, which is much higher than that of ZAC (about $1.74 \times 10^{-6}$ kg$^{-2} \cdot$ m$^{-4} \cdot$ s$^{-1}$). The above results suggest that the simultaneous incorporation of ZS reduces the oxidation resistance of materials below 1100 °C.

3.2. Phase composition and microstructure

As a typical representative, the XRD patterns of the oxide scales of ZAS3 composite are compared with monolithic ZAC ceramic [12] after oxidation at different temperatures for different time, which are shown in Figure 4. As can be seen from Figure 4(a), when oxidized at 1000 °C for 1 h, the surface of ZAS3 mainly consists of tetragonal ZrO$_2$ (t-ZrO$_2$), monoclinic ZrO$_2$ (m-ZrO$_2$), a little Al$_2$O$_3$ and unoxidized ZAC, which shows a very thin oxidation scale. With the increase of oxidation temperature and time, the surfaces of the composite have been oxidized completely. The peaks of Al$_2$O$_3$ and mullite almost disappear, and the oxidation products mainly consist of ZrO$_2$. In addition, t-ZrO$_2$ will transform to m-ZrO$_2$ with further oxidation. For the monolithic ZAC ceramic (Figure 4(b)), the surface of oxidized ZAC mainly consists of t-ZrO$_2$, a little Al$_2$O$_3$ and unoxidized ZAC. With the increase of oxidation temperature and time, the peaks of ZAC also disappear, showing a completely oxidized surface. The intensities of the peaks for t-ZrO$_2$ increase, and the peaks of m-ZrO$_2$ and mullite can be detected. These results show that both of the composite and monolithic ZAC ceramic have an
oxidation layer consisting of ZrO₂, Al₂O₃ and mullite after being oxidized. The difference is that lower content of t-ZrO₂, Al₂O₃ and mullite can be observed for the composite.

Figure 5. Surface micrographs of ZAS3 oxidized at (a) 1000 °C and (b) 1100 °C for 10h and ZAC oxidized at (c) 1000 °C and (d) 1100 °C for 10h, respectively.

Figure 5 shows the surface morphologies of ZAS3 composite and monolithic ZAC ceramic after complete oxidation. The oxidation surface of the composite is mainly covered by granular ZrO₂ and needle-like mixtures of ZrO₂ and Al₂O₃. The composite shows a very rough oxidation surface with some large cracks and deep holes. Such a loose oxidation surface has a poor protection effect to the internal materials. In contrast, the oxidized surface of monolithic ZAC ceramic is relatively smooth and dense. Also, granular ZrO₂ can be seen clearly on the oxidation surface, especially oxidized at 1100 °C. The above characterization results demonstrate that the oxidation resistance of ZAC-ZS composites is reduced with respect to monolithic ZAC ceramic when oxidized at medium temperatures, which is in good agreement with the results of oxidation kinetics.

3.3. Oxidation mechanisms analysis
Based on above results, in the case of monolithic ZAC ceramic, the following reactions will take place during the oxidation at 1000 - 1100°C:

\[
\text{Zr}_3\text{[Al(Si)]}_4\text{C}_6 + \text{O}_2 \rightarrow \text{ZrO}_2 + \text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{CO}_2 \quad (2)
\]

The oxidation products Al₂O₃ and SiO₂ will continue to react as follows:

\[
\text{Al}_2\text{O}_3 + \text{SiO}_2 \rightarrow 3\text{Al}_2\text{O}_3\cdot2\text{SiO}_2 \quad \text{(mullite)} \quad (3)
\]

For the case of ZAC-ZS composites, the incorporation of ZrB₂ will lead to the oxidation reactions as follows:

\[
\text{ZrB}_2 + \text{O}_2 \rightarrow \text{ZrO}_2 + \text{B}_2\text{O}_3 \quad (4)
\]

B₂O₃ has a high volatility at temperatures higher than 1000°C:
B₂O₃ (l) \rightarrow B₂O₃ (g) \quad (5)

Besides, the incorporation of SiC will also be oxidized, but due to the excellent oxidation resistance of SiC below 1100 °C, very few SiO₂ can be derived from the oxidation of SiC. Thus, the oxidation of incorporated SiC is very limited, which can be ignored. Therefore, it can be approximated that only two phases, i.e., ZrB₂ and ZAC, in the composites contribute to the oxidation.

The diffusion coefficient of O²⁻ anion in mullite (about 10⁻¹⁶ ~ 10⁻¹¹m²·s⁻¹) and Al₂O₃ (about 10⁻¹⁶ ~ 10⁻¹⁹m²·s⁻¹) is several orders of magnitude lower than that in ZrO₂ (about 10⁻¹⁰-10⁻¹⁴m²·s⁻¹) in the investigated temperature range [13]. Thus, the formation of more mullite and Al₂O₃ will constitute a more protective oxide scale. For the composites, the incorporation of binary ZrB₂-SiC reduce the Al content, resulting in the limited formation of mullite and reducing the content of remained Al₂O₃. Moreover, the volatilization of B₂O₃ at 1000 - 1100 °C makes the oxide scales of materials loose, resulting in a poor oxidation protection. It indicates that ZrB₂ have negative effects to the oxidation resistance of materials at medium temperatures. But, SiC shows beneficial effects to the oxidation resistance of materials[14] in most cases. SiO₂ derived from the oxidation of SiC can react with Al₂O₃ and form mullite. Meanwhile, SiO₂ will also react with B₂O₃ and produce borosilicate glass, which will prevent the volatilization of B₂O₃ effectively. And, borosilicate glass will flow and fill up pores and cracks during oxidation, resulting in a dense oxide scale. But due to the excellent oxidation resistance of SiC, very few SiO₂ is produced below 1100 °C, SiC makes little contribution to the oxidation resistance of the composites. In totally, the incorporated ZrB₂-SiC reduce the oxidation resistance of materials at medium temperatures.

In addition, it is noted that stable t-ZrO₂ exists in the oxidation products. Generally, due to a lack of a stabilizing agent for ZrO₂, t-ZrO₂ will transform to m-ZrO₂ upon cooling to room temperature. It has been reported [15] that undersized trivalent Al³⁺ cations can be incorporated into ZrO₂, which can stabilize partially t-ZrO₂. This results in a coexistence of both t- and m-ZrO₂ phases in the oxide scales of the samples. And, the effects of constant strain on ZrO₂ from the grains around will also stabilize partially t-ZrO₂ [15]. Due to the loose oxide scales of the composites, the effects of grains around ZrO₂ are reduced. Thus, the lower content of Al in the composite and the loose oxide scale reduces the stabilization effect, and more m-ZrO₂ exists in the oxide scales of the composite.

4. Conclusions
The isothermal oxidation behavior of Zr₃₈[Al(Si)]₄₈C₆-ZrB₂-SiC composites at 1000 °C and 1100 °C in air has been investigated. With the increase of oxidation temperature, the Δw/s and k_p of the composites increase, and the oxidation kinetics of the composites generally follow a parabolic law. With the ZrB₂-SiC content increasing from 0 to 40vol.%, the Δw/s, and k_p of the specimens increase first and then decrease. The incorporation of high ZrB₂-SiC content is of some advantage to the oxidation resistance of the composites. But the Δw/s and k_p of the composites are higher than those of monolithic Zr₃₈[Al(Si)]₄₈C₆ ceramic below 1100 °C. When oxidized at medium temperatures, SiC in the composites has almost no effects on the oxidation, and mainly ZrB₂ and Zr₃₈[Al(Si)]₄₈C₆ in the composites are oxidized. The reduced oxidation resistance of the composites compared with monolithic Zr₃₈[Al(Si)]₄₈C₆ ceramic under this experimental conditions can be ascribed to the formation of a loose oxide scale, consisting of mainly ZrO₂, which cannot prevent the inward diffusion of oxygen element effectively.

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