



Effect of surface oxidation on the flexural strength of ZrB₂–SiC composites

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ABSTRACT

The ZrB₂–20 vol.% SiC composites were oxidized at a constant temperature of 900 °C for 5, 30 and 60 min, respectively. Some of the oxidized specimens were immersed in water to remove the B₂O₃ glass from the surface in order to investigate the effect of surface microstructure and component on the flexural strength. The flexural strengths of immersed specimens are higher than original strength, but lower than those of the oxidized specimens. The increase in flexural strengths is strongly dependent on both ZrO₂ and outer glassy phase. For comparison, the ZrB₂–SiC composites were also oxidized at 1300 °C in air. The high oxidation temperature is detrimental to the flexural strength of composites, however, the reliability of specimen oxidized at 1300 °C is improved significantly. The effect of oxidation time was also investigated, and the flexural strength of specimens is not sensitive to oxidation time within a certain range.

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1. Introduction

Ultra-high temperature ceramics (UHTCs) are being considered as the potential candidates for aerospace application in the next generation of reusable aircraft, which are subjected to extreme aerodynamic heating during service [1–4]. As one important family of UHTCs, ZrB₂-based composites have attracted extensive research interests due to the excellent and unique combination of high melting point, retained strength at elevated temperature, good resistance to oxidation and relatively low theoretical density [5–7]. Monolithic ZrB₂ is not used widely in aggressive environments due to its poor oxidation resistance and unsatisfactory fracture toughness [8,9]. The addition of SiC as the second phase is considered as a new avenue to improve the oxidation resistance [10]. However, ZrB₂–SiC composites are brittle and extremely sensitive to the crack, pore and other flaws on surface. The inherent brittleness and poor reliability are still the obstacles for safety use in advanced thermal protection systems.

The flaws on the surface of ZrB₂-based composites, which can be introduced inevitably during fabrication and machining processes, can easily cause stress concentration and lead to catastrophic fracture [11]. In order to improve the mechanical properties, a fantastic method is proposed to tailor surface micro-

structure based on the surface oxidation. Houjou [12] and Zdenek [13] have demonstrated the flexural strength of SiC-reinforced Si₃N₄ and Al₂O₃ composites increased after oxidation owing to surface flaws healing. In addition, Zhang et al. [14,15] also investigated the crack-healing behavior of ZrB₂–SiC_w composites, and pointed out that the cracks could be healed completely in air at high temperature, but not healed in a vacuum; the crack-healing ability was strongly dependent on the surface oxide glass. The effect of oxidation at 1500 °C on the flexural strength of ZrB₂–SiC composites was also reported by Guo et al. [16], indicating that the increase in strength could be attributed to the healing of surface flaws by the outer glassy layer. However, the effect mechanism of surface oxidation on mechanical properties of ZrB₂-based composites has not been studied sufficiently. The increase in strength is simply attributed to the healing of surface flaws by oxide glass. Attempts should be made to further understand the influence of surface oxidation and microstructure on the strength of ZrB₂-based composites.

In the present work, the ZrB₂–20 vol.% SiC composites were oxidized at constant temperatures of 900 and 1300 °C for 5, 30 and 60 min, respectively. Some of specimens oxidized at 900 °C were immersed in water to remove the B₂O₃ glass from surface. The effects of surface microstructure, oxidation temperature and oxidation time on mechanical properties of ZrB₂–SiC composites were studied. The flexural strength of the oxidized specimen was evaluated and the effect mechanism of surface oxidation on strength increase was also investigated in detail.

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2. Experimental procedure

Commercially available ZrB₂ (2 μm, >99.5%, Northwest Institute for non-ferrous metal research, China), and SiC (1 μm, >99.5%, Weifang Kaihua Micro-powder Co., Ltd., China) powders were used as raw materials. The preparation procedure of ZrB₂–20 vol.% SiC composites was described in detail elsewhere [17]. Flexural strength of the specimens was tested in three-point bending on 3 mm × 4 mm × 36 mm bars, using a 30 mm span and a crosshead speed of 0.5 mm min⁻¹ (Instron-1186, USA). Each specimen was polished with diamond slurries down to a 1 μm finish and the edges of all specimens were chamfered to minimize the effect of stress concentration due to machining flaws. All specimens were fabricated with the tensile surface perpendicular to the hot-pressing direction, and at least 5 specimens were tested for each experimental condition. The oxidation was carried out in static air using furnace. The specimens on zirconia crucible were heated at the rate of 20 °C/min–900 and 1300 °C, respectively. The holding time for each target temperature is 5, 30 and 60 min, respectively. Some of the specimens oxidized at 900 °C were immersed in water (80 °C) for 5 h to remove the boron oxide glass from surface due to hydration of B₂O₃. One surface crack was introduced to the specimen with a Vickers indenter using a load of 98 N for 15 s to investigate the morphologies of surface crack before and after oxidations. The surface microstructure of specimens was observed by scanning electron microscopy (SEM, FEI Sirion, USA) equipped with energy dispersive spectroscopy (EDS, EDAX Inc., USA) for chemical analysis. Crystalline phases of the specimen after oxidation were analyzed by X-ray diffraction (XRD, Rigaku, Japan) at an incidence angle of 2°. The chemical composition of oxide scale was identified using X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, USA) with monochromatic Al Kα radiation.

3. Results

The surface microstructure of hot-pressed ZrB₂–SiC composites is presented in Fig. 1a. The small dark SiC are dispersed uniformly in the gray ZrB₂ matrix. The microstructure appears to be quite dense and homogeneous, and no pores, pits or other flaws can be observed in ZrB₂–SiC composites. The calculated relative density of ZrB₂–SiC composites is ~99.6% using the rule of mixtures based on the densities of 6.09 and 3.21 g/cm³ for ZrB₂ and SiC, respectively [18]. Fig. 1b shows the surface SEM image of the specimens oxidized at 900 °C for 5 min. It is obvious that the surface morphol-

ogy of oxidized specimen is significantly different from that of original specimen. The surface of the oxidized specimen is flat, but many microcracks distribute on the surface (the inset of Fig. 1b), that can be attributed to the volume mismatch between matrix and oxide products during oxidation [19,20]. Determination of the composition of the oxide layer by EDS is not possible due to its low sensitivity to light elements (i.e. boron). However, EDS analysis reported by other investigators [19] has shown that the outermost layer contains O, but is free of Si and Zr, which is consistent with the presence of B₂O₃. As the oxidation time increases to 30 min, the surface is completely covered with B₂O₃ glass, which could be responsible for the disappearance of microcracks, as shown in Fig. 1c. It can be seen from Fig. 1d that the surface of the specimen oxidized for 60 min is dark and covered with a tight and smooth B₂O₃ glass, it is reasonable to believe that the B₂O₃ glass layer becomes much thicker with oxidation time.

Fig. 2 displays the micrographs and EDS spectra of the surfaces of specimens oxidized at 900 °C after immersion. As shown in Fig. 2a, the surface of immersed specimen is quite rough, and no glassy phase can be detected owing to hydration of B₂O₃, which is significantly different from the surface oxidized at 900 °C for 5 min, as shown in Fig. 1b. From the micrograph inserted in Fig. 2a, a ZrB₂ grain is oxidized in situ to lots of nanoscale ZrO₂ grains, while obvious oxidation is not observed in the SiC grain. The microstructural skeleton of the surface after immersion is consistent with that of matrix. As the oxidation time increases to 60 min, there is no significant change in the surface of immersed specimen except for grain growth of ZrO₂ (Fig. 2b and c). Furthermore, EDS analysis in Fig. 2d also confirmed that the oxide scale is mainly composed of ZrO₂.

XPS was also performed to verify the chemical binding state of the surface before and after immersion. Ar+ ion sputtered for 1 min to clean the surfaces, and the C 1s signal detected at 285 eV from adventitious carbon was used to calibrate the spectra. From

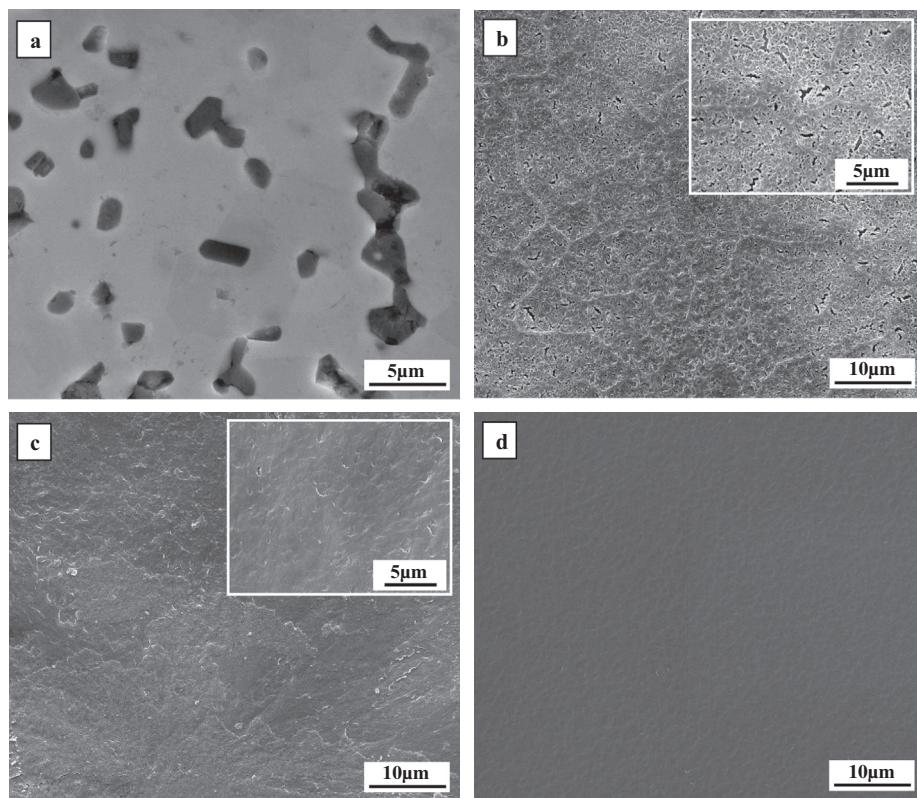


Fig. 1. Surface morphology of the original specimen (a) and the specimens oxidized at 900 °C for (b) 5 min, (c) 30 min and (d) 60 min.

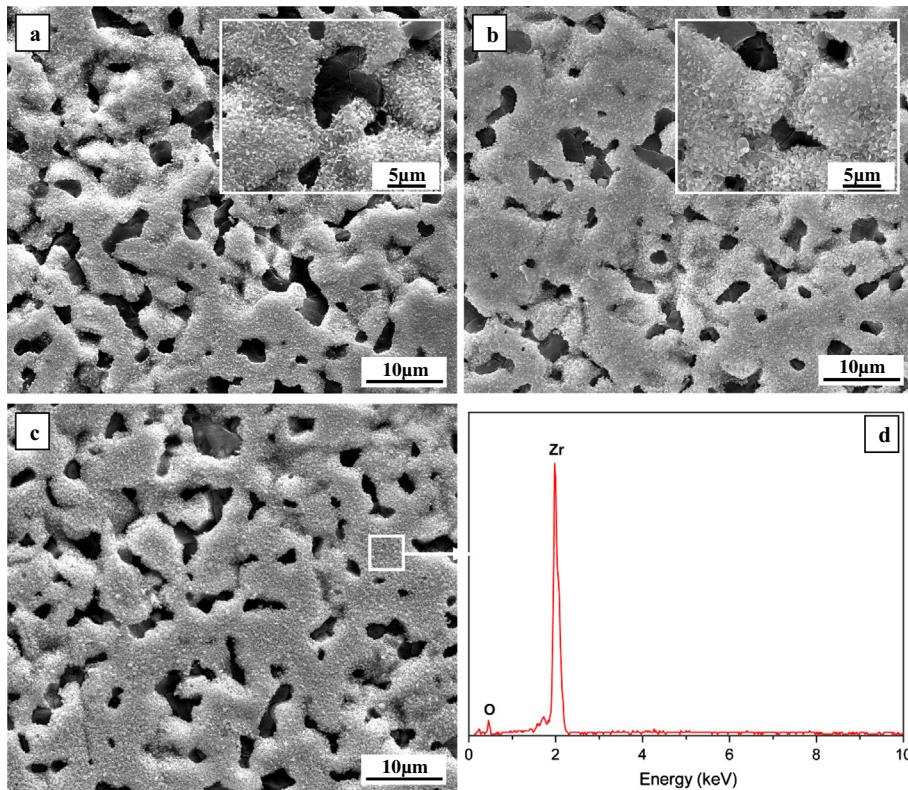


Fig. 2. Micrographs and EDS analysis of the surfaces for the specimens oxidized at 900 °C after immersion: (a) 5 min, (b) 30 min, (c) 60 min and (d) EDS spectra of (c).

Fig. 3a, a peak at 192.8 eV can be detected in B 1s spectra of specimen oxidized at 900 °C, which corresponds to B–O bond. However, the B–O bond disappears from B 1s spectra after immersion, while Zr–O bond can be observed at 182.7 eV ($Zr\ 3d_{5/2}$) and 185.0 eV ($Zr\ 3d_{3/2}$) as shown in **Fig. 3b**. It is suggested that B_2O_3 glass is removed from oxide scale due to hydration, inducing the exposure of ZrO_2 on surface. Similarly, the chemical shift between O–B (533.2 eV) bond and O–Zr (530.8 eV) bond can be identified after immersion (**Fig. 3c**). Furthermore, the peak located at 532.7 eV could be associated with intermediate compounds Si–C–O [21,22], and the large full width at half maximum (FWHM) of this peak indicates the high chemical inhomogeneity. The curve fitting C 1s spectra is presented in **Fig. 3d**, adventitious carbon on the surface of immersed specimen can be identified at 285.0 eV. Aside from C–C bond, C–Si bond and C–Si–O bond are observed at 283.2 and 287.1 eV, respectively. **Fig. 3e** shows that the intensity of Si 2p is very weak, suggesting a small quantity of Si element in the oxide scale. The formation of Si–O bond after oxidation at 900 °C confirms that there have been some slight oxidation reactions of SiC grains. The relative intensity of Si–O bond decreases significantly after immersion; meanwhile other component located at 100.6 eV is observed and identified as SiC.

The surface microstructural evolution of specimens oxidized at 1300 °C for different oxidation times is shown in **Fig. 4**. Compared with the specimen oxidized at 900 °C, the surface exposed to air at 1300 °C for 5 min is flat and dense, as shown in **Fig. 4a**, which is covered completely with the silica-rich glass. Many white phases mainly composed of ZrO_2 can be detected beneath the glass, indicating that the outer glass layer is quite thin. A continuous glassy layer was found to form above the ZrO_2 layer. The surface morphology of the specimen oxidized at 1300 °C for 30 min is not fundamentally different from that of the specimen oxidized for 5 min. The silica-rich glass becomes thick as the oxidation time increases, which results in reduction of the visible area of ZrO_2 (**Fig. 4b**). With

increasing the oxidation time to 60 min, many irregular ZrO_2 clusters are distributed in glass, which results from the transportation, agglomeration and growth of ZrO_2 with borosilicate glass (**Fig. 4c**) [23,24]. The XRD pattern of specimen oxidized for 60 min is shown in **Fig. 4d**. From that monoclinic zirconia as the main component in oxide scale as well as a small quantity zirconium diboride in matrix can be detected. In addition, there is a weak but very broad diffraction peak between 15° and 25°, which could be contributed to the presence of amorphous silica-rich glass on surface [17].

Fig. 5 shows the flexural strength of ZrB_2 –SiC composites treated under different oxidation conditions. As the oxidation time increases from 5 min to 60 min, the flexural strengths of the specimens oxidized at 900 °C as high as 974.7 ± 157.3 , 1166.2 ± 122.2 and 1045.1 ± 144.5 MPa, respectively, are significantly improved compared with the original strength of 815.6 ± 64.9 MPa. For the specimens after immersion, the flexural strengths are 938.6 ± 78.1 , 939.5 ± 80.3 and 896.6 ± 89.0 MPa, respectively. They are greater than that of original specimen, however lower than those of the oxidized specimens before immersion. After oxidation at 1300 °C, the flexural strengths of specimens are improved to 914.2 ± 58.9 , 905.9 ± 49.2 and 875.3 ± 55.9 MPa, respectively, which are lower than those of the specimens oxidized at 900 °C.

4. Discussions

When ZrB_2 –SiC composites are exposed to air at 900 °C, the oxidation rate of SiC is much slower than that of ZrB_2 , resulting in the preferential oxidation of ZrB_2 grains [25]. ZrB_2 is oxidized to ZrO_2 and liquid B_2O_3 with the increase of volume, and then the resulting B_2O_3 glass covers the surface of oxide scale. However, the B_2O_3 glass is very unstable since it would react spontaneously with water or moist air [26]. The oxidation of SiC can be observed at 1300 °C, and the product SiO_2 can further react with B_2O_3 to form borosilicate glass, which effectively inhibits the vaporization

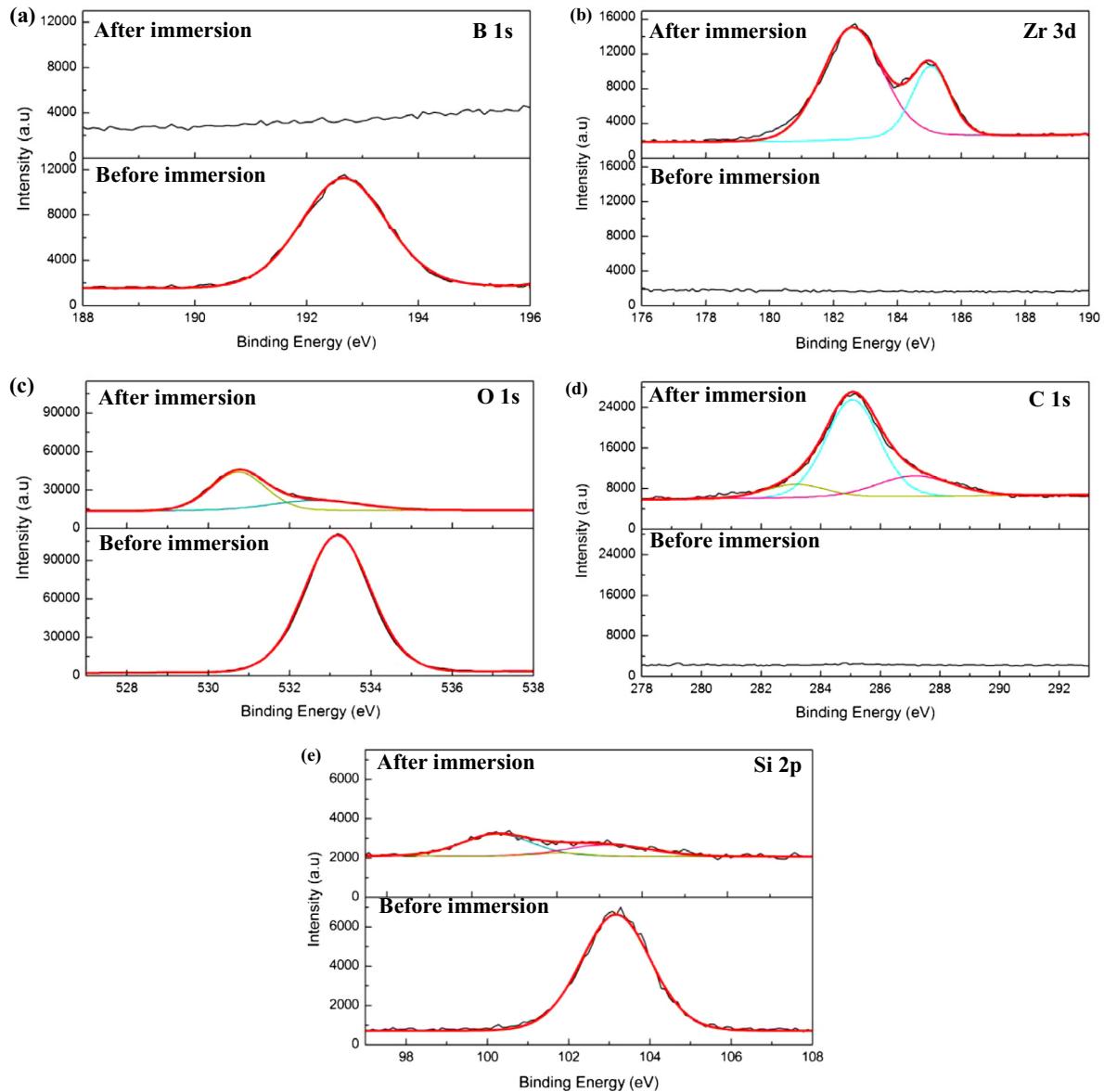
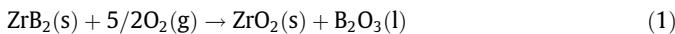


Fig. 3. XPS spectra of the oxidized specimens before and after immersion: (a) B 1s, (b) Zr 3d, (c) O 1s, (d) C 1s and (e) Si 2p.

of B_2O_3 and improves the stability of oxide scale [27,28]. The main oxidation reactions of $\text{ZrB}_2\text{-SiC}$ composites are described as follows,



After exposure to air at 900 °C for 5 min, the flexural strength of $\text{ZrB}_2\text{-SiC}$ composites increases by ~160 MPa. The surface morphology of specimen after short time oxidation is changed evidently, which is responsible for the variation of mechanical properties. The literatures [14–16] have reported that glassy phase can heal the flaws and cracks on the surface of specimen, which is the main reason for the increase in flexural strength. As the oxidation time increases, the flexural strengths are further improved to

1166.2 ± 122.2 and 1045.1 ± 144.5 MPa, respectively, which is because the surface of specimen is completely covered with B_2O_3 glass. For the specimens after immersion, the flexural strengths are higher than original strength, whereas lower than those of the oxidized specimens before immersion. It is suggested that not only the outer glass but also the resulting zirconia have an influence on the mechanical properties of $\text{ZrB}_2\text{-SiC}$ composites. Fig. 6 shows the variation of the indentation morphologies before and after oxidation. The profile of oxidized pre-crack does not change obviously. However the cracks after oxidation become vague and dispersed, and the length of these cracks induced by indentation is shorter than that of cracks without oxidation. It is evident that large numbers of fine zirconia grains grow and fill the cracks (the inset of Fig. 6b). A great increase of volume (>300%) results from oxidation of ZrB_2 to ZrO_2 and B_2O_3 , which has a great effect on the morphology of flaws [19,20]. According to Griffith fracture criterion [11], the decrease in flaw size is beneficial to reduce concentrated stress. Additionally, the morphology of the surface of immersed specimen is fundamentally different

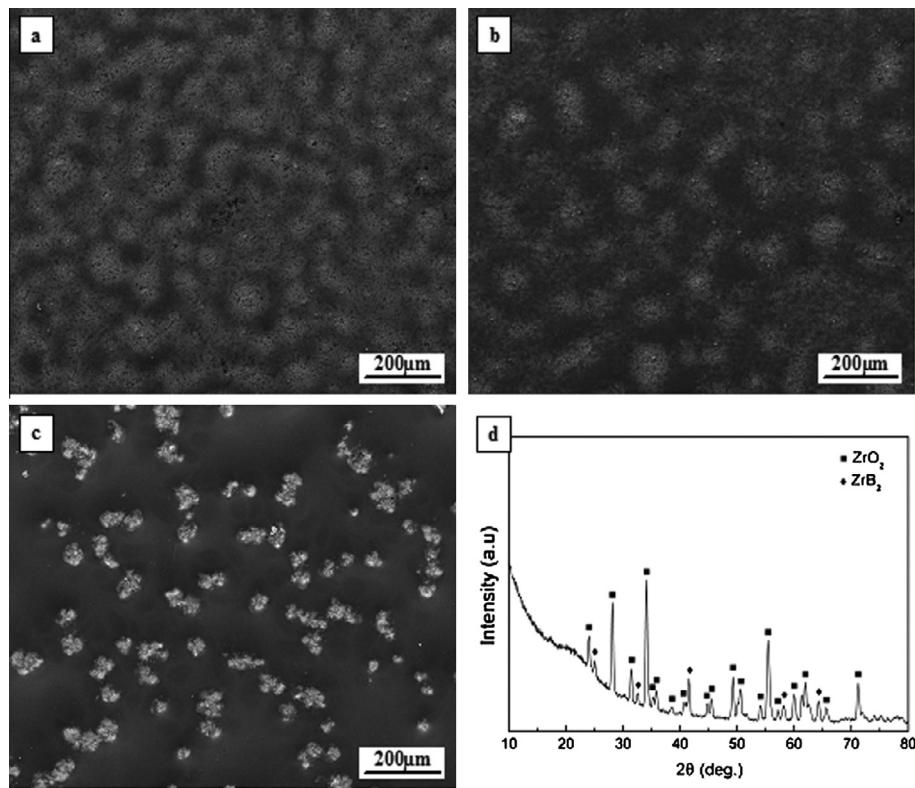


Fig. 4. Micrographs and XRD patterns of the specimens oxidized at 1300 °C: (a) 5 min, (b) 30 min, (c) 60 min and (d) XRD pattern of (c).

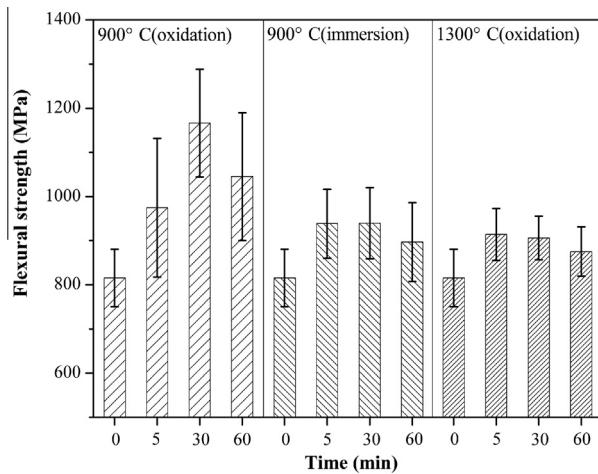


Fig. 5. Flexural strengths of the specimens oxidized at 900 and 1300 °C with different oxidation time.

from that of oxidized specimen before immersion. The surface of specimen oxidized at 900 °C is flat and covered with B_2O_3 glass, whereas the surface of the immersed specimen with the exposure of ZrO_2 is pretty rough. The pores and interstices in the irregular grain boundaries between ZrO_2 grains and/or SiC grain could be regarded as flaws, which could induce the crack nucleation under stress. The presence of glassy phase can seal the flaws on surface to further improve the flexural strength. The above results show that resulting ZrO_2 is responsible for the variation of morphology

of flaws, and outer glass further heals the flaws. Both ZrO_2 and outer glass have effects on the flexural strength of oxidized specimen.

Comparison of the flexural strength for specimens after oxidation at 900 °C and 1300 °C suggests that the oxidation temperature also affects, as expected, the mechanical properties of oxidized specimens. The flexural strength of specimens oxidized at 1300 °C is lower than that at 900 °C, which could be attributed to the difference in thickness of oxide scale. Fig. 7 shows that the oxide scale of the specimen after oxidation at 1300 °C for 5 min is much thicker than that at 900 °C for 60 min. The oxide scale is much loose and contains many flaws compared with ZrB_2 -SiC composites. A large number of flaws are introduced in the oxide scale after oxidation at 1300 °C, which can weaken the strength improved by the variation of surface morphology. The literatures have confirmed that thick oxide scale is detrimental to the flexural strength of composites [15,29]. In addition, it is should be noted that the error bars of flexural strength for the specimens oxidized at 1300 °C are much smaller than those at 900 °C. The borosilicate glass is very stable compared with the B_2O_3 glass produced at 900 °C, which is consistent with small distribution of flexural strength after oxidation at 1300 °C. Consequently, the flexural strength and reliability of oxidized specimens are strongly dependent on oxidation temperature.

For a limited oxidation time, there is little change in the flexural strength during different oxidation times. However, the variation of flexural strength caused by the slight oxidation in short time is significant compared with original strength, which indicates that the flexural strength of specimen is sensitive to surface morphology.

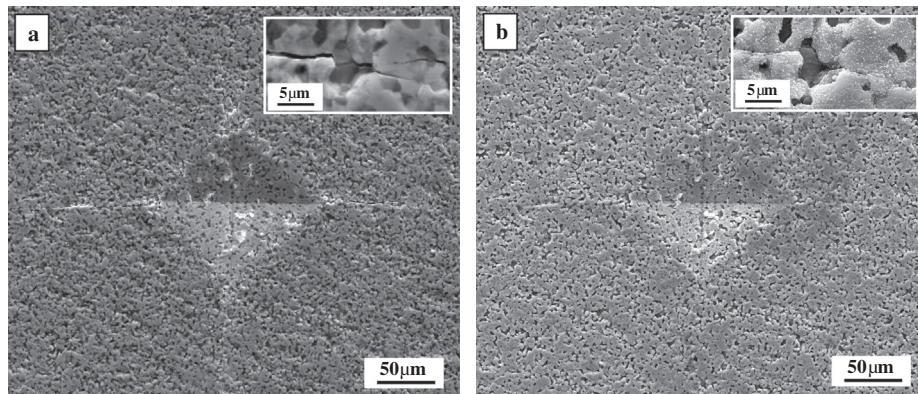


Fig. 6. Micrographs of the indentation on the surface of original specimen (a) and the oxidized specimen after immersion (b).

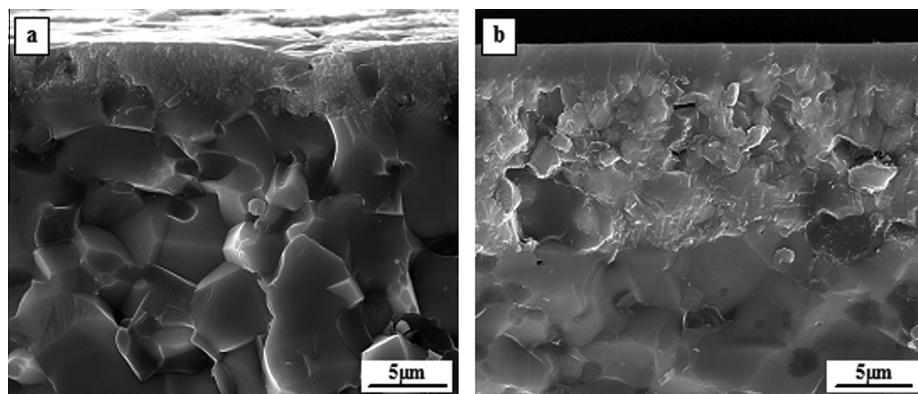


Fig. 7. Micrographs of fractured surfaces for the specimens oxidized at 900 °C for 60 min (a) and at 1300 °C for 5 min (b).

5. Conclusions

The ZrB₂–20 vol.% SiC composites were oxidized at constant temperatures of 900 and 1300 °C for 5, 30 and 60 min, respectively, and some of the specimens oxidized at 900 °C were immersed in water to remove the B₂O₃ glass from surface. The flexural strengths of specimen treated under different conditions are significantly improved as compared to the original strength of 815.6 ± 64.9 MPa. The flexural strengths of specimens after immersion are higher than original strength, whereas lower than those of the specimens oxidized at 900 °C for 30 min with a maximum increase of 50%. The variation of strengths for ZrB₂–SiC composites before and after immersion should be associated with the evolution of surface microstructure. The morphology and size of surface flaws are changed significantly by the resulting ZrO₂ during oxidation, and outer glass could seal the surface flaws to further improve the flexural strength. The flexural strength decreases as the oxidation temperature increases from 900 to 1300 °C, indicating that thick oxide scale is detrimental to the mechanical properties of composites due to the presence of flaws. On the other hand, the reliability of specimens oxidized at 1300 °C is improved. The flexural strength of specimen is not sensitive to oxidation time, whereas the flexural strength of specimen with slight oxidation in short time is much greater than original strength. In addition, the effect mechanism of surface oxidation on the mechanical properties can apply to not only ZrB₂-based composites but also other Si or B containing ceramic matrix composites, which proposes a promising method for improving strength of composites.

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