Influence of composition on microstructure, mechanical properties and oxidation behavior of ZrB2/ZrAlC composite ceramics

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ZrB2/ZrAlC composite ceramics were successfully synthesized from Zr, Al, graphite and ZrB2 powders by using a spark plasma sintering method. The volume content of ZrAlC has a major impact on the fracture toughness. ZrAlC-rich (>70 vol.%) composite ceramics exhibit much higher fracture toughness than do ZrB2-rich (>60 vol.%) composite ceramics. The evidently larger ZrAlC grains in the ZrAlC-rich composite ceramics lead to a longer crack propagation path for toughening. Both the Vickers hardness and Young’s modulus of composite ceramics increase slightly with an increase in the ZrB2 volume content. The evident oxidation of composite ceramics at 1000°C results in the formation of Al18B4O33 and Al4B2O9. At 1200°C, the composite ceramics exhibit a fluffy and porous top oxidized layer composed of whiskers of Al18B4O33 and Al14B2O9 grains, and the thickness of the oxidized layer and oxidation mass gain increase with an increase in the ZrAlC volume content. The ZrB2-rich composite ceramics with less than 40 vol.% ZrAlC content do not exhibit apparently larger oxidation mass gain than does the pure ZrB2 ceramic after oxidation at 1200°C and higher temperatures. The composition-dependent microstructure and properties provide a comprehensive insight for the development of high-temperature composite ceramics based on ZrAlC and ZrB2.

1. Introduction

Zirconium diboride (ZrB2) is a promising structural ceramic for potential high-temperature applications owing to its high melting temperature, strength and thermal conductivity.1–5) However, its poor sinter-ability, low fracture toughness and weak oxidation resistance are the main barriers to practical application. On the other hand, ZrAlC compounds (Zr3Al4C5, Zr2Al6C16, Zr3AlC5, Zr2Al2C4, etc.) show superior oxidation resistance and high fracture toughness and are promising high-temperature structural ceramics.6–10) In addition, ZrAlC compounds exhibit high-temperature mechanical properties comparable to those of the most promising ultrahigh-temperature composite ceramic ZrB2–SiC, whose strength degrades rapidly above 1400°C.5,6) Combining ZrAlC and ZrB2 to integrate their advantages would help create a new type of high-temperature composite ceramic.

The densification of pure ZrB2 ceramic through spark plasma sintering (SPS) requires a high temperature of at least 1900°C and a high pressure of 50 MPa in vacuum.11) In our previous studies, dense ZrB2/ZrAlC composite ceramics were obtained by SPS of a mixture of graphite powder and ball-milled ZrB2, Zr, Al powders at 1800°C and under 20 MPa in vacuum, or through in-situ reaction SPS of Zr, Al, B4C and graphite powders.12,13) In addition, the ZrB2/ZrAlC composite ceramics exhibited remarkably enhanced fracture toughness compared with the pure ZrB2 ceramic as well as better oxidation resistance than ZrB2 and ZrAlC ceramics.12–14) However, the composition (ZrAlC and ZrB2 volume contents)-dependent mechanical properties and oxidation behavior of the composite ceramics fabricated through a consistent approach are still unknown. It is necessary to establish the composition-structure-properties relationship in order to develop high-

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performance high-temperature composite ceramics based on ZrB2 and ZrAlC ceramics. This study systematically investigates for the first time the microstructure, mechanical properties and oxidation behavior of ZrB2/ZrAlC composite ceramics with various ZrB2 and ZrAlC volume contents. The experimental results are comparatively analyzed, and the mechanisms contributing to composition-dependent fracture toughness and oxidation resistance are discussed.

2. Experimental details

ZrB2, Zr, Al, graphite and Si powders were sufficiently mixed in an agate mortar for sintering ZrB2/ZrAlC composite ceramics by using SPS. Details of this operation are reported in previous papers.15),16) The molar ratio of Zr:Al:C was selected to be 2:6:2:4.8 in the starting powders, the Si powder (4 wt %) was added as a sintering additive for stabilizing the structure of ZrAlC compounds and improving their oxidation resistance,8),9) and excess Al was added to compensate for the loss of Al during the heating process of SPS.15),16)

The densification temperature of pure ZrAlC ceramic through SPS is only 1700°C, while the densification of pure ZrB2 through SPS requires at least 1950°C under 20 MPa in vacuum. To obtain almost dense and relatively uniform ZrB2/ZrAlC composite ceramics for comparison, we fabricated ZrAlC-rich samples with higher ZrAlC volume content and ZrB2-rich samples with higher ZrB2 volume content at 1700 and 1800°C for 5 min, respectively. Obtaining relatively uniform composite ceramic samples with the compositions of 60 vol.% ZrAlC and 40 vol.% ZrB2, and 50 vol.% ZrAlC and 50 vol.% ZrB2 under the preparation conditions was difficult. Thus, these were excluded as it is believed that the present results from the selected samples are sufficient to make systematic comparisons and reasonable conclusions.

Zr2Al3C5, Zr3Al4C6 and Zr2Al4C5 are designated as ZrAlC compounds owing to their similar layered crystaline structures, mechanical properties and oxidation behavior.6)-9) The samples with compositions of pure ZrAlC, pure ZrB2, and (10xN) vol.% ZrAlC and (100-10xN) vol.% ZrB2 are marked as ZAC, ZB, and NZAC/(10-N)ZB, respectively. For example, the sample with 90 vol.% ZrAlC and 10 vol.% ZrB2 is marked as 9ZAC/1ZB.

The open porosity of the samples was measured using Archimedes’ immersion method with water as a medium. The microstructure was studied using X-ray diffraction (XRD, Rigaku Ultima III, Cu Kα, 40 kV and 40 mA). The surface and cross-sectional morphologies were observed using scanning electron microscopy (SEM, Hitachi S-3400). The microstructure of composite ceramic was also studied using high resolution transmission electron microscopy (HRTEM) (JEOL JEM-2100F, Japan). The grain sizes were measured using the SEM images. A detailed description of the measurement of mechanical properties, including Young’s modulus (E), Vickers’ hardness (HV) and fracture toughness (KIC), was reported in previous work.15,16)

The ceramic samples were calcinated at high temperature to characterize the oxidation behavior. The samples for testing were prepared in sizes of 4 mm × 4 mm × 3 mm. They were cleaned by ultrasonic cleaning and then dried for weighing using a balance (BS210S, Germany). The mass of the as-prepared sample is \( M_0 \), and its total surface area is \( S \). The mass of the naturally cooled sample after high-temperature calcination in the air in a furnace (Nabertherm LHT04, Germany) is \( M_f \). The oxidation mass gain of the sample is calculated according to the following Eq. (1):

\[
\Delta M = \frac{M_1 - M_0}{S}
\]

The larger the oxidation mass gain, the worse the oxidation resistance, and vice versa.

3. Results and discussion

3.1 Microstructure and mechanical properties

As shown in Fig. 1, except for the 9ZAC/1ZB sample, one major phase of ZrAlC is Zr2Al3C5 in the pure ZrAlC ceramic and all other composite ceramics. The minor phases of Zr2Al3C5 and Zr3Al4C6 are detected in the composite ceramics. For the 9ZAC/1ZB sample with the composition of 90 vol.% ZrAlC and 10 vol.% ZrB2, two main phases of Zr2Al3C5 and Zr2Al4C5 coexist in the

![Fig. 1. XRD patterns of samples with different compositions of ZrAlC and ZrB2 volume contents.](image-url)
composite ceramics. In addition, Al$_4$C$_3$ is detected in all the samples containing ZrAlC.

The open porosity and aspect ratio of the ZrAlC grains of samples with various compositions of ZrB$_2$ and ZrAlC volume content are listed in Table 1. The open porosity of ZrB$_2$ ceramic sintered at 1800°C is approximately 10%, while the ZrAlC ceramic and all composite ceramics have much lower open porosities of around 0.04–0.21%, indicating that the densification of the composite ceramics is easier to achieve owing to the existence of ZrAlC which is densified at 1700°C. The aspect ratio of the ZrAlC grains in pure ZrAlC ceramic is 4.25 ± 0.94. As the ZrAlC content decreases from 90 to 70 vol.%, the aspect ratio first increases from 4.15 ± 1.17 for 9ZAC/1ZB to 4.75 ± 0.96 for 8ZAC/2ZB, and then apparently decreases to 3.87 ± 0.85 for 7ZAC/3ZB. Furthermore, as the ZrAlC volume content decreases from 40 to 10%, the aspect ratio gradually decreases from the largest value of 5.34 ± 0.85 for 4ZAC/6ZB to the smallest value of 3.75 ± 0.65 for 1ZAC/9ZB.

The mechanical properties of the samples are listed in Table 1. The relative density of pure ZrB$_2$ ceramic with 10% open porosity is only 84%, and its fracture toughness was not tested owing to the high density of pores distributed on its surface. The value 2.5 ± 0.4 MPa m$^{1/2}$/ is shown in Table 1) refers to the fracture toughness of pure ZrB$_2$ ceramic with approximately 96% relative density.\(^{13}\) Meanwhile, the obtained Vickers hardness and Young’s modulus of the pure ZrB$_2$ ceramic listed in Table 1 cannot be used to make a comparison for analysis. The pure dense ZrB$_2$ ceramic has been reported to show a high Vickers hardness of approximately 23 GPa and a high Young’s modulus of 489 GPa.\(^{17}\) As seen in Table 1, both the Vickers hardness and Young’s modulus of the composite ceramic samples increase slightly with an increase in the ZrB$_2$ volume content. These values are closer to the reported values of pure dense ZrB$_2$ ceramic, which means that they are positively related to ZrB$_2$ volume content. The pure ZrAlC ceramic exhibits a fracture toughness of 4.6 ± 0.4 MPa m$^{1/2}$/, while the 9ZAC/1ZB and 8ZAC/2ZB composite ceramics exhibit close toughness values of 4.7 ± 0.2 and 5.0 ± 0.2 MPa m$^{1/2}$/, respectively. The 7ZAC/3ZB sample exhibits a toughness value of 4.3 ± 0.2 MPa m$^{1/2}$/, which is 20% greater than that (3.5 ± 0.2 MPa m$^{1/2}$/) of the 4ZAC/6ZB sample. Furthermore, as the ZrB$_2$ volume content continues to increase, the fracture toughness of the composite ceramic samples decreases slightly, and the 1ZCA/9ZB sample exhibits a toughness similar to that of pure dense ZrB$_2$ ceramic. In addition, when the ZrAlC volume content is greater than 70%, the fracture toughness of the composite ceramics is similar to that of pure ZrAlC ceramic. When ZrAlC volume content is less than 70%, the fracture toughness of the composite ceramics first decreases dramatically and then gradually to a value closer to that of pure ZrB$_2$ ceramic as the ZrAlC volume content decreases. Considering the comprehensive effects of the composition and the aspect ratio of the ZrAlC grains and combining this with data from our previous studies,\(^{16,18,19}\) the ZrAlC aspect ratio is not believed to directly influence fracture toughness because a larger aspect ratio of ZrAlC grain does not mean a greater length of Zr–Al–C grain in actual size, which leads to brittle crack propagation stop for effective toughening.

The polished surface morphologies of the SEM images of the samples are shown in Fig. 2. Two distinct phases showing different grain shapes and sizes are observed in Figs. 2(b)–2(h). Combining this with XRD and EDS results (not shown), the columnar grains in gray color are identified as ZrAlC (Zr$_2$Al$_4$C$_5$, Zr$_3$Al$_4$C$_6$ and Zr$_2$Al$_3$C$_5$) grains, the bright particles with equiaxed or polygonal shapes are ZrB$_2$ grains, and the black-contrast regions are corresponding to Al$_4$C$_3$ phase. As shown in Figs. 2(a)–2(h), the ZrB$_2$ grain size in the ZrAlC-rich samples is smaller than that in the ZrB$_2$-rich samples, while the ZrAlC grain size in 9ZAC/1ZB and 8ZAC/2ZB samples is similar to that in the pure ZrAlC ceramic and evidently larger than those in the other composite ceramics (Figs. 2(d)–2(h)). This may explain why the fracture toughness of 9ZAC/1ZB and 8ZAC/2ZB samples is similar to that of pure ZrAlC ceramic and is evidently higher than those of other composite ceramic samples with a lower ZrAlC volume content: normally, a larger ZrAlC grain results in prevention and stop of fast brittle crack propagation for toughening the ceramics.

As shown in Figs. 3(a)–3(h), all ZAC and ZAC/ZB samples are almost densified, and pores are barely observed. Plenty of large pores are observed on the fracture surface of the pure ZrB$_2$ ceramic in Fig. 3(i), which agrees

| Samples | Open porosity (%) | Aspect ratio of Zr–Al–C grains | Vickers hardness (GPa) | Young’s modulus (GPa) | Fracture toughness (MPa m$^{1/2}$/) |
|---------|------------------|-------------------------------|-----------------------|----------------------|---------------------------------|
| ZAC     | 0.15             | 4.25 ± 0.94                   | 11.1 ± 0.3            | 315 ± 20             | 4.6 ± 0.4                      |
| 9ZAC/1ZB| 0.14             | 4.15 ± 1.17                   | 11.5 ± 0.3            | 330 ± 30             | 4.7 ± 0.2                      |
| 8ZAC/2ZB| 0.11             | 4.75 ± 0.96                   | 12.7 ± 0.5            | 355 ± 25             | 5.0 ± 0.2                      |
| 7ZAC/3ZB| 0.04             | 3.87 ± 0.85                   | 14.0 ± 0.4            | 375 ± 25             | 4.3 ± 0.2                      |
| 4ZAC/6ZB| 0.21             | 5.34 ± 0.85                   | 15.5 ± 0.5            | 385 ± 20             | 3.5 ± 0.2                      |
| 3ZAC/7ZB| 0.16             | 4.52 ± 0.72                   | 16.2 ± 0.4            | 405 ± 25             | 3.3 ± 0.2                      |
| 2ZAC/8ZB| 0.08             | 4.05 ± 0.95                   | 16.6 ± 0.5            | 430 ± 25             | 2.9 ± 0.2                      |
| 1ZAC/9ZB| 0.12             | 3.75 ± 0.65                   | 17.6 ± 0.4            | 450 ± 20             | 2.6 ± 0.1                      |
| ZB      | 10.09            | —                | 12.2 ± 0.6            | 360 ± 25             | 2.5 ± 0.4\(^{13}\)          |
with its 10% open porosity and 84% relative density. From Figs. 3(a) and 3(i) it is clear that the fracture mode is a trans-granular fracture in both ZrAlC and ZrB₂ grains of the pure ZrAlC and ZrB₂ ceramics, which exhibit flat fracture surfaces. The fracture surfaces of the composite ceramic samples [Figs. 3(b)–3(h)] are relatively rough and
exhibit an evident combination fraction mode of inter- and trans-granular fractures, especially for 9ZAC/1ZB, 8ZAC/2ZB, 7ZAC/3ZB, 4ZAC/6ZB and 3ZAC/7ZB samples.

To elucidate the mechanism of the composition-dependent fracture toughness, the crack propagation features in the SEM images of all sintered ceramic samples (Fig. 4) are examined. Trans-granular fractures are clearly observed in the pure ZrAlC and ZrB2 samples. In the composite ceramic samples, the crack path is zigzagged and prolonged owing to the combination of trans- and inter-granular fractures, indicating that these interactions lead to shorter crack paths for toughening the composite ceramics.20) This is evident in Figs. 4(b)–4(e) and agrees well with the results of the fracture morphologies shown in Figs. 3(b)–3(f). Furthermore, crack deflection and bridging are caused by the layered-structured ZrAlC grains, as shown in Figs. 4(b)–4(e). For the samples with similar compositions, a longer crack propagation path results in a higher fracture toughness.

The TEM and HRTEM images of the 3ZAC/7ZB sample are shown in Fig. 5. An obvious and a clear interface is seen between the layered-structured ZrAlC grain and equiaxed ZrB2 grain because the in-situ-reaction synthesized ZrAlC grains from the raw powders cover the ZrB2 grains during the sintering process.

3.2 Oxidation behavior

Although the ZrAlC compounds with Si solid solute exhibit good oxidation resistance up to 1600°C due to the formation of aluminosilicate glass filling up pores and cracks at high temperatures,8) it was found that the B2O3 resulted from ZrB2 reacted with the Al2O3 around 1000°C to prevent the formation of protective aluminosilicate glass. In that case, the pore structure resulted from gas release of carbon oxides during the high-temperature oxidation of ZrAlC compounds provides an invading path for oxygen to cause further deep oxidation, which is a significant obstacle to preventing composite ceramics from severe oxidation. In this work, only the results of the ZrB2-rich ZrB2/ZrAlC composite ceramic samples are shown for analysis and discussion.

Figure 6 indicates the oxidation mass gain of the ZrB2 ceramic and ZrB2/ZrAlC composite ceramics after 30 min of oxidation at various temperatures from 800 to 1500°C. The oxidation mass gain of the samples evidently increases.

Fig. 4. Propagation path of ZrB2/ZrAlC composite ceramics with different compositions: (a) ZAC, (b) 9ZAC/1ZB, (c) 8ZAC/2ZB, (d) 7ZAC/3ZB, (e) 4ZAC/6ZB, (f) 3ZAC/7ZB, (g) 2ZAC/8ZB, (h) 1ZAC/9ZB, (i) ZB.

Fig. 5. TEM and HRTEM images of 3ZAC/7ZB sample.
above an oxidation temperature of 1000°C. After oxidation at 1200°C, the oxidation mass gain of the composite ceramics increases as the ZrAlC volume content increases. After oxidation at 1400 and 1500°C, the composite ceramics with 10 and 20 vol.% show a similar oxidation mass gain, which evidently increases when the ZrAlC volume content increases from 20 to 40%. Furthermore, only the 4ZAC/6ZB sample exhibits apparently larger oxidation mass gains than that of pure ZrB2 ceramic after oxidation at 1200°C and higher temperatures.

Figure 7 shows the XRD patterns of the ZrB2 ceramic and the composite ceramic samples after 30 min of oxidation at various temperatures from 800 to 1500°C. It is apparent that the peaks corresponding to ZrB2 disappear when the oxidation temperature is 1000°C, indicating that ZrB2 grains on the surface of the samples are completely

Fig. 6. Oxidation mass gain of ZrB2 ceramic and ZrB2/ZrAlC composite ceramics after 30 min oxidation at various temperatures from 800 to 1500°C.

Fig. 7. XRD patterns of (a) pure ZrB2 ceramic, (b) 1ZAC/9ZB, (c) 2ZAC/8ZB, (d) 3ZAC/7ZB and (e) 4ZAC/6ZB composite ceramics samples after 30 min oxidation at various temperatures.
oxidized into ZrO2 and B2O3 at 1000°C. At 800°C, the ZrAlC peaks disappear in the 1ZAC/9ZB and 2ZAC/8ZB samples, while they remain in the 3ZAC/7ZB and 4ZAC/6ZB samples, revealing a severe oxidation of ZrAlC at 800°C. After oxidation at 1000°C, all ZrB2/ZrAlC composite ceramic samples show clear peaks corresponding to Al18B4O33 and Al4B2O9. These aluminum borate compounds formed from the reaction of Al2O3 and B2O3, which are the oxidation products of ZrAlC and ZrB2.21,22 From 1200 to 1500°C only the Al18B4O33, Al4B2O9 and ZrO2 crystalline phases exist on the sample surface.

Distinct surface morphologies are observed in the SEM surface morphologies of the 2ZAC/8ZB composite ceramic after 30 min of oxidation at 1000 and 1200°C, as shown in Fig. 8. At 1000°C, the oxidized surface shows a lot of cracks spreading on the relatively flat surface while the oxidized surface at 1200°C exhibits a crack-free but very rough surface full of whiskers that correspond to the Al18B4O33 and Al4B2O9 grains.22,23 It is concluded that the Al18B4O33 and Al4B2O9 evidently form above 1000°C. The SEM surface morphology of sample oxidized at 800°C (not shown) shows a slightly oxidized surface with small amounts of pores and cracks. On the other hand, the oxidized surface at 1400°C is too rough to obtain a clear surface morphology by SEM, indicating a greatly severe oxidation.

To demonstrate the mechanism underlying the composition-dependent oxidation behavior, a comparative analysis is performed on the SEM surface and cross-sectional morphologies of pure ZrB2 ceramic and ZrAlC/ZrB2 composite ceramic samples after 30 min of oxidation at 1200°C, as shown in the Fig. 9. The oxidized surface of pure ZrB2 ceramic is relatively flat and full of holes [Figs. 9(a) and 9(b)], and the thickness of the oxidized layer is approximately 170 μm [Fig. 9(c)]. It is apparent that all of the composite ceramic samples exhibit a rough surface full of whiskers [Figs. 9(d) and 9(e), Figs. 9(g) and 9(h), Figs. 9(j) and 9(k), Figs. 9(m) and 9(n)], corresponding to the Al18B4O33 and Al4B2O9 grains.22,23 From the cross-sectional morphology of the 1ZAC/9ZB sample shown in Fig. 9(f), different from the pure ZrB2 sample [Fig. 9(c)], two oxidized layers are observed: a 90-μm-thick top fluffly and porous surface layer and a 50-μm-thick intermediate transition layer partially oxidized with a profile similar to that of the ceramic bulk body. According to the XRD results shown in Fig. 7, it can be concluded that the porous and fluffly top surface layer is composed of ZrO2, Al18B4O33 and Al4B2O9 whiskers. And detected B element from EDS result (not shown) indicates apparent existence of amorphous B2O3 on the surface. The relatively dense intermediate transition layer is partially oxidized ZrB2/ZrAlC composite layer containing ZrO2, Al2O3, B2O3 and probable Al18B4O33 and/or Al4B2O9. For the 2ZAC/8ZB sample, the thickness of the top fluffly and porous layer is approximately 110 μm [Fig. 9(i)], which is slightly higher than that of the 1ZAC/9ZB sample [Fig. 9(f)]. Furthermore, 3ZAC/7ZB [Fig. 9(j)] and 4ZAC/6ZB [Fig. 9(o)] samples have remarkably thicker fluffly and porous top layers that are more than two times the thicknesses of the layers in the 1ZAC/9ZB and 2ZAC/8ZB samples after oxidation. This indicates that in the sample with a higher ZrAlC volume content, a greater amount of Al2O3 is produced, which can react with B2O3 from ZrB2 during oxidation. This eventually leads to the formation of a larger number of Al18B4O33 and Al4B2O9 whiskers to construct a more porous top oxidized layer, providing numerous paths for oxygen to further invade deeper layer of composite ceramic and then cause the deeper oxidation and thus a thicker oxidized layer. According to the Al2O3–B2O3 phase diagram,21 on the other hand, the formation of liquid phase and Al–B–O solid phase above 1000°C depends on composition of base ZrB2/ZrAlC composites and would affect the oxidized surface. For 1ZAC/9ZB at 1200°C, a part of liquid B2O3 reacted with a small amount of Al2O3 to form Al–B–O, while a lot of aggregated liquid B2O3 evaporated to leave relatively pure Al–B–O to form big-size Al18B4O33 and Al4B2O9 whiskers on the oxidized surface, as shown in Fig. 9(e). For the case of 2ZAC/8ZB and 3ZAC/7ZB, the congruent mixture of solid Al–B–O and liquid B2O3 at 1200°C leads to the formation of amorphous B2O3 mixed with Al18B4O33 and Al4B2O9 whiskers on oxidized surface at low temperature, which could be seen in Figs. 9(h) and 9(k). Even though liquid B2O3 exists on the surface at oxidation temperature, the continuous gas release during oxidation of ZrAlC still cause paths for oxygen invading. For 4ZAC/6ZB at 1200°C, liquid B2O3 reacted with enough Al2O3 to form solid Al–B–O, thus amorphous B2O3.
is not clearly observed on the oxidized surface shown in Fig. 9(n). Compared to the oxidized surface of 1ZAC/9ZB in Fig. 9(e), Fig. 9(n) shows much smaller and thinner whiskers with a higher areal density on oxidized surface of 4ZAC/6ZB, which means more pores and thus causes thicker oxidized layer and larger mass gain during the oxidation.

4. Conclusion

ZrB$_2$/ZrAlC composite ceramics, with various ZrAlC and ZrB$_2$ volume contents, were synthesized from ZrB$_2$, Zr, Al and graphite powders by using SPS. The main conclusions with regard to the composition-dependent microstructure, mechanical properties and oxidation behavior are as follows:

1. The ZrB$_2$ grain size is smaller in ZrAlC-rich composite ceramics than in ZrB$_2$-rich composite ceramics. The ZrAlC grain size in pure ZrAlC ceramic is similar to that in 9ZAC/1ZB and 8ZAC/2ZB composite ceramics, which have evidently much larger Zr-Al-C grains than do other composite ceramic samples.

2. Both the Vickers hardness and Young’s modulus of the composite ceramics increase slightly with an increase in the ZrB$_2$ volume content. The fracture roughness of ZrAlC-rich ($\geq$ 70 vol.%) composite ceramics is equivalent to that of pure ZrAlC ceramic. As the ZrAlC volume content decreases, the ZrB$_2$-rich ($\geq$ 60 vol.%) composite ceramics exhibit a remarkably lower fracture roughness, gradually decreasing and coming close to the value of pure dense ZrB$_2$ ceramic.
(3) The fracture mode is a trans-granular fracture for pure ZrAlC and ZrB2 ceramics, while the composite ceramics exhibit a combination fracture mode of inter- and trans-granular fracture especially in ZrAlC-rich samples. The layered-structured ZrAlC grains cause crack deflection and bridging.

(4) The oxidation mass gain of the samples evidently increases above an oxidation temperature of 1000°C. At 1200°C, the oxidation mass gain of composite ceramics increases with an increase in the ZrAlC volume content. When oxidation is carried out at 1400 and 1500°C, the composite ceramics with 10 and 20 vol.% ZrAlC content show a similar oxidation mass gain, and with increasing ZrAlC volume content from 20 to 40% the oxidation mass gain evidently increases. Only the 4ZAC/6ZB sample exhibits apparently larger oxidation mass gain than does the pure ZrB2 ceramic after oxidation at temperatures of 1200°C and higher.

(5) Oxidation of composite ceramics at 1000°C leads to the formation of Al12B4O33 and Al6B2O13, which result from the oxidation products of Al2O3 and B2O3. After oxidation at 1200°C, the composite ceramics exhibit a fluffy and porous top oxidized layer composed of whiskers of Al12B4O33 and Al6B2O13 grains, whose thickness increases with an increase in the ZrAlC volume content.

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