**High temperature flexural strength and oxidation behavior of
hot-pressed B₄C-ZrB₂ ceramics with various ZrB₂ contents at
1000-1600°C in air**

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Abstract

High temperature flexural and oxidation behavior of hot-pressed B_4C - ZrB_2 ceramics with various ZrB_2 addition amounts were measured and analyzed in the temperature range of 1000 to 1600°C in ambient air atmosphere. The high temperature flexural strength is strong function of temperature. With the temperature increasing, the high temperature flexural strength decreases. The oxidation behavior was investigated in detailed, and the oxidation mechanism was summarized. The purpose of this study is aim to give fundamental understanding of the high temperature behavior of B_4C based ceramics.

Keyword

B_4C ; ZrB_2 ; High temperature mechanical properties; oxidation.

1. Introduction

Boron carbide (B_4C) based ceramics exhibit unique properties such as a high melting point ($2450^\circ C$), low density (2.52 g/cm^3), high elastic modulus, high hardness, good resistant to chemical agents and high temperature, and high neutron absorption capability [1-5]. Therefore, B_4C based ceramics have been widely used in cutting tools, wear resistant parts, nuclear reactors, armor materials and functional elements of cathode assemblies, working in conditions of high-rate heating or cooling and heterogeneous thermal tension [6-8], at high temperature ranging between 1200 and $1700^\circ C$ [9, 10].

However, the fabrication of monolithic B_4C ceramic is a challenging task and obtaining a sufficient density requires high sintering temperature and long dwell time [11, 12]. Such conditions lead to significant grain growth which causes drop of mechanical properties, mainly toughness and flexural strength. Previous studies on B_4C based ceramics have shown improved sinterability and mechanical properties with the addition of a second phase, such as metallic (Al [13], Ni and Cr [14]) and non-metallic additives like oxides (Al_2O_3 [15] and Y_2O_3 [16]), carbides (SiC [17] and WC [18]), nitrides (AlN [19] and BN [20]), borides (TiB_2 [21], CrB_2 [22]), etc. These additives are proved to improve the sinterability of boron carbide efficiently. In our previous work [23], a novel additive, ZrB_2 , was added to improve the sinterability and mechanical properties. The as-prepared B_4C - ZrB_2 ceramics were found to exhibit good sinterability and mechanical properties, and the effects of ZrB_2 content on the flexural strength, fracture toughness and thermal shock resistance were studied systematically.

Besides, B_4C based ceramics also show promising potentials for high temperature materials working at temperatures ranging between 1200 and $1700^\circ C$ [9, 10]. It is well known that the high temperature bending strength is one of the most important issues evaluating the

mechanical properties of B_4C based ceramics when using at elevated temperatures [24, 25]. In most previous studies, B_4C based ceramics were either evaluated at room temperature [26, 27], or tested at high temperatures in vacuum or inert environments [28, 29]. However, engineering applications of B_4C based ceramics always work at high temperature in an oxidizing atmosphere. The mechanical properties obtained at room temperature or high temperature in vacuum or inert environments can not reflect the real temperature-dependent responses of B_4C based ceramics under real engineering service conditions. To our authors' best knowledge, there has been no report on the high temperature strength of B_4C based ceramics in oxidizing environments till now. In our previous work [30], the high temperature flexural strength of B_4C -30 vol.% ZrB_2 ceramic up to 1600°C in ambient air was measured and investigated. However, the intrinsic relationships between the ZrB_2 content and the high temperature high temperature flexural strength, have not been clearly analyzed.

In the present study, B_4C - ZrB_2 ceramics with 10, 20 and 30 vol.% ZrB_2 additives were prepared using hot-pressing from fine particles. The high temperature flexural strength of these hot-pressed B_4C - ZrB_2 ceramics were tested at the temperature of 1000, 1200, 1400 and 1600°C in air, and the significant effects of ZrB_2 content on the high temperature flexural strength of B_4C - ZrB_2 ceramics were studied systematically. The aim of this work is to give some fundamental data and understanding of B_4C based ceramics at elevated temperatures in air.

2. Experimental procedure

In our previous study [23], commercial B_4C particles with an average size of 2 μm and ZrB_2 particles with an average size of 1 μm were used for preparing B_4C - ZrB_2 ceramics were used. In this present study, fine B_4C particles (1 μm ; > 99%; Mudanjiang Jingangzuan Boron

Carbide Co. Ltd., China) and fine ZrB_2 particles ($0.7\ \mu\text{m}$; $> 99.5\%$; Beijing Zhongjinyan Micro-powder Co. Ltd., China) were chosen as raw materials.

The powder mixtures of B_4C -10 vol.% ZrB_2 , B_4C -20 vol.% ZrB_2 and B_4C -30 vol.% ZrB_2 were ball-milled in ethanol for 8 h with zirconia ball media in a planetary mill (QM-3SP2, Nanjing University Instrument Plant, China) at 240 rpm (revolutions per minute). After ball-milling, ethanol was removed by a rotating evaporator (RE-52A, Shanghai Yarong Biotech Co. Ltd., China) at 80°C to minimize segregation. The as-received B_4C - ZrB_2 powder mixtures were sieved through a 200 mesh and then uniaxially hot-pressed in a BN coated graphite die at 1950°C for 60 min under vacuum and 30 MPa applied pressure (ZT-70-23Y, Shanghai Chenxin Furnace Co. Ltd., China). Detailed fabrication procedure has been declared previously [23]. For simplicity, the hot-pressed B_4C -10 vol.% ZrB_2 , B_4C -20 vol.% ZrB_2 and B_4C -30 vol.% ZrB_2 and B_4C -40 vol.% ZrB_2 samples were named as BZ10, BZ20 and BZ30, respectively. The detailed label, composition and hot-pressing conditions are listed in Table 1.

(Table 1 here)

The bulk density was measured by Archimedes' method in deionized water; the theoretical density was calculated by applying the law of mixture, and the relative density was calculated based on the ratio of bulk density to theoretical density.

Room temperature flexural strength (σ) was measured using three-point bending test (WDW-100, Changchun Fangrui Technology Co. Ltd., China) on $36\ \text{mm} \times 4\ \text{mm} \times 3\ \text{mm}$ (length $\times$ width $\times$ thickness) testing bars, using a loading span of 30 mm with a crosshead speed of 0.5 mm/min at room temperature. Room temperature fracture toughness (K_{IC}) was evaluated using single-edge notched bend (SENB) on $22\ \text{mm} \times 4\ \text{mm} \times 2\ \text{mm}$ (length $\times$ height $\times$ width) beams, with a notched depth and width of 2 and 0.2 mm, respectively, using a span of 16 mm and a crosshead speed of 0.05 mm/min. All testing bars were fabricated with the tensile surface

perpendicular to the hot-pressing direction. A minimum number of five specimens were tested for flexural strength and fracture toughness.

High temperature flexural strength of the B_4C - ZrB_2 ceramics was conducted on a high temperature flexural strength testing system assembled in our laboratory, as shown in Fig. 1. This testing system is consisted of a universal testing machine, a high temperature Muffle furnace using $MoSi_2$ heating elements, a set of SiC ceramic fixture and indenter, and a Pt-Rh/Pt thermocouple. During the testing, the B_4C - ZrB_2 ceramic specimen with a geometry of $36\text{ mm} \times 4\text{ mm} \times 3\text{ mm}$ (length $\times$ width $\times$ thickness) was put on the SiC bottom fixture (30 mm span) and exposed in ambient air atmosphere. Then the high temperature Muffle furnace was heated to the target temperature (1000, 1200, 1400 and 1600°C) using $MoSi_2$ heating elements with a heating rate of $10^\circ\text{C}/\text{min}$. The testing specimen was soaked at the target testing temperature for 10 min to reach a thermal equilibrium. Then, At last, the flexural strength testing was carried out. The initial load was set as 20 N, and the loading rate of the SiC indenter was set as 0.5 mm/min ($25\text{N}/\text{min}$). A minimum number of five specimens were tested at each testing temperature.

(Figure 1 here)

The crystalline phases were characterized using a X-ray diffraction (XRD, Holland, $CuK\alpha=1.5418\text{ \AA}$). The microstructure of the B_4C - ZrB_2 ceramic was observed using a scanning electron microscope (SEM, S-4800, Hitachi, Japan) equipped with an X-ray EDS analyzer attachment (EDAX Inc., USA). The average particle size was determined using intercept method upon SEM images.

3. Results and Discussion

The relative densities of the sintered ceramics are summarized in Table 1. The relative

density of BZ10, BZ20 and B30 are 99.7, 99.8 and >99.9%, respectively. As known, monolithic B_4C ceramic is hard to achieve full densification at a lower sintering temperature. The addition of ZrB_2 additive has been proved to significantly improve the sinterability of B_4C at a lower temperature in previous paper [23]. In this study, all as-prepared B_4C - ZrB_2 ceramics achieved nearly full densification. The hot pressing temperature for these nearly fully dense B_4C - ZrB_2 ceramics is $1950^{\circ}C$, which is much lower than that of monolithic B_4C ceramic (usually $>2100^{\circ}C$) [5].

The microstructure and EDS point analysis results of the polished surfaces of the as-prepared B_4C - ZrB_2 ceramics are presented in Fig. 2. All B_4C - ZrB_2 ceramics are fully dense, and no residual pore is detected. Black B_4C matrix (plot 1 by EDS) with homogeneously dispersed gray ZrB_2 particles (plot 2 by EDS) can be easily differential in all B_4C - ZrB_2 ceramics. It is well known that high temperature makes ceramic particles have obvious grain growth. The addition of ZrB_2 particles significantly inhibits the grain growth behavior [23]. With the increment of ZrB_2 content, more gray ZrB_2 particles disperse in dark B_4C matrix are observed. After hot-pressing, both B_4C and ZrB_2 particles exhibit obvious grain growth behavior. The examination of microstructure after hot-pressing reveals a particle size of about 8-10 μm for B_4C particles and about 6-8 μm for ZrB_2 particles, respectively. The ceramic particle size decreases with the increasing of ZrB_2 content. When the ZrB_2 content is 10 vol.%, the particle size for B_4C and ZrB_2 grains are approximate 10 and 8 μm , respectively. When the ZrB_2 content is 20 vol.%, the particle size for B_4C and ZrB_2 grains are both approximate 5 μm . However, the average particle size does not have significant increase when the ZrB_2 content is above 20 vol.%. When the ZrB_2 content is 30 vol.%, the particle size for B_4C and ZrB_2 grains are also both about 5 μm .

(Figure 2 here)

Room temperature flexural strength and fracture toughness were measured for the three B₄C-ZrB₂ ceramics, as listed in Table 1. The room temperature flexural strength appears to decrease as the ZrB₂ content increases. The room temperature flexural strength of BZ10, BZ20 and BZ30 ceramics are 685.5±17.7, 647.3±15.6 and 604.3±12.5 MPa, respectively. The strength is found to be much higher than our previous reported results (523.4 ± 22.3, 492.8 ± 23.5 and 417.5 ± 18.7, respectively [23]). The reason is that the average grain size of B₄C and ZrB₂ used in this study are smaller than those reported previously. Fine particles have beneficial effect on the strength improvement of B₄C-ZrB₂ ceramics. The fracture toughness of BZ10, BZ20 and BZ30 ceramics are 6.2±0.8, 6.5±0.7 and 6.6±0.6 MPa m^{1/2}, respectively, which are nearly as same as previous reported results (6.3 ± 0.6, 6.6 ± 0.4 and 7.0 ± 0.7 MPa m^{1/2}, respectively [23]).

High temperature flexural strength of BZ10, BZ20 and BZ30 ceramics testing at 1000, 1200, 1400 and 1600°C in air are shown in Fig. 3. And the flexural strength of B₄C-ZrB₂ ceramics at 1000, 1200, 1400 and 1600°C are listed in Table 2. With the testing temperature increasing, the high temperature flexural strength for all B₄C-ZrB₂ ceramics decrease linearly. At the temperature of 1000°C, the flexural strength of BZ10, BZ20 and BZ30 ceramics are 273.8±16.5, 375.4±21.4 and 576.3±19.2 MPa, respectively, reducing by approximate 60.1, 42.1 and 4.6%, respectively, comparing with room temperature flexural strength. It is found that the BZ10 ceramic exhibits the most serious strength drop, whereas the BZ30 ceramic exhibits the minimum strength drop. Although the room temperature flexural strength of B₄C-ZrB₂ ceramics decrease with ZrB₂ content increasing, the high temperature flexural strength of B₄C-ZrB₂ ceramics increase with ZrB₂ content increasing at 1000°C. The reason for this may be attribute to the anti-oxidation behavior of B₄C-ZrB₂ ceramics is improved significantly with the increase of ZrB₂ content, which will be discussed in the follow section in detail. Similar trends are also

detected at 1200, 1400 and 1600°C. The flexural strength of BZ10, BZ20 and BZ30 ceramics at 1200°C are 231.3±15.3, 305.4±20.3 and 451.5±21.8 MPa, respectively. The flexural strength of BZ10, BZ20 and BZ30 ceramics at 1400°C are 201.3±15.3, 267.4±20.2 and 287.5±19.6 MPa, respectively. And the flexural strength of BZ10, BZ20 and BZ30 ceramics at 1600°C are 167.4±12.2, 189.6±21.6 and 202.5±23.9 MPa, respectively.

(Figure 3 here)

In order to explain the changes of the high temperature flexural strength, the oxidation behavior of B₄C-ZrB₂ ceramics were investigated. During the high temperature oxidation in air, the B₄C-ZrB₂ ceramic specimen exposes to air and undergoes severe oxidation, resulting in microstructure evolution on the outer surface of the ceramic. There are severe chemical reactions between the oxidation atmosphere (ambient air) and the B₄C-ZrB₂ ceramics. At elevated temperature, there are three main kinds of oxidants, i.e., O₂, H₂O and CO₂, in present case. H₂O and CO₂ are not taken into account for the sake of simplicity. Therefore, the main expected reactions during oxidation process are as follows:

The Gibbs free energy for Reactions (1) and (2) are calculated as a function of temperature (0 to 2000°C), as plotted in Fig. 4. In standard state, both Reactions 1 and 2 are favorable ($\Delta G < 0$) at elevated temperatures. Comparing the Gibbs free energy of Reactions 1 and 2, Reaction 1 is easier to happen than Reaction 2. As known, the oxidation behavior of ceramics

depends on the protective oxide scale formed on the surface of the ceramic matrix. The main oxidation products of B_4C - ZrB_2 ceramics are B_2O_3 , ZrO_2 and CO, or CO_2 . The product of CO and CO_2 is gas, and diffuse into air. The oxidation behavior of B_4C - ZrB_2 ceramics and the determination of whether the oxide products can form a dense adherent scale are very important. This is largely dependent on the volatilization of the oxide products. Similar oxidation behavior has been reported in the oxidation studying of ZrB_2 -SiC ceramics by Zhang *et al* [31, 32].

(Figure 4 here)

The oxidation behaviors of B_4C - ZrB_2 ceramics in the temperature range 1000-1600°C are discussed apart at each testing temperature:

(I) 1000°C:

When the testing temperature is 1000°C, the Gibbs free energy of both Reaction 1 and Reaction 2 are below zero ($\Delta G < 0$), indicating both Reactions 1 and 2 are favor at this temperature. The oxide product are consisted of B_2O_3 (l), ZrO_2 (s) and CO or CO_2 (g). The gases (CO or CO_2) always blow off into the environment. Reaction 5 from ZrO_2 (s) to ZrO_2 (g) need a very high temperature owing to the vapor pressure of ZrO_2 is relatively low. So Reaction 5 usually does not occur in the temperature range of 1000-1600°C. At 1000 °C, the oxide product of B_2O_3 (l) can not volatilize (the volatilization temperature usually above 1100°C needed for Reaction 4). Therefore, the oxide surface of the B_4C - ZrB_2 ceramics is believed to be covered with a layer of mainly B_2O_3 (l) and little ZrO_2 (s) (Reactions 1 and 2). Fig. 5 presents the microstructure of the oxide surfaces of the B_4C - ZrB_2 ceramics after testing at 1000°C. Slight surface oxidation of the B_4C - ZrB_2 ceramics is detected. B_4C grains are oxidized to B_2O_3 (l) and CO_2 , and ZrB_2 grains begin to oxidize to B_2O_3 (l) and ZrO_2 (s) identified based on EDS spectra (not shown here). As shown in Fig. 5, diamond shaped recrystallized ZrO_2 grains covered with a thin glass phase layer of B_2O_3 are found on the specimen's surface. The grain

size of the recrystallized ZrO_2 grains increases as the amount of ZrB_2 addition increases from 10 vol.% to 30 vol.%. There is no obvious crack found on the oxide surface. The oxide products are consisted of mainly B_2O_3 (l) and little ZrO_2 (s), inducing an appearance of compressive stress zone beneath the oxide surface layer owing to the little difference of thermal expansion coefficient, which is favorable to inhibit the crack initiation and propagation among the ceramics.

(Figure 5 here)

(II) 1200°C:

Fig. 6 presents the microstructure of the oxide surfaces of the $\text{B}_4\text{C-ZrB}_2$ ceramics after testing at 1200°C. Reactions 1, 2 and 3 happen. The oxide layer are consisted of B_2O_3 (l) and ZrO_2 (s). When the amount of ZrB_2 is 10 vol.%, the oxidation layer is mainly B_2O_3 (l) and a little ZrO_2 (s). The difference between the coefficients of thermal expansion of B_2O_3 and ZrO_2 induces the cracks among the oxide layer, as shown in Figs. 6 a and d. With the increasing of the amount of ZrB_2 , the difference between the coefficients of thermal expansion of B_2O_3 and ZrO_2 decreases correspondingly. Therefore the amount of cracks among the oxide layer also decreases, as detected in Figs. 6 b, e, c and f. When the addition of ZrB_2 is 30 vol.%, there is nearly no obvious thermal expansion induced cracks among the oxide layers. In addition, some liquid B_2O_3 begin to volatilize to the top of the oxide layer, and even begin to volatilize to gas B_2O_3 , resulting a smooth glass surface on the surface of the oxide layer.

(Figure 6 here)

(III) 1400°C:

When the testing temperature is further increased, the oxidation happened to the $\text{B}_4\text{C-ZrB}_2$ ceramics becomes much severer. There are more oxidation products covering the surface of the ceramics. Reactions 1, 2 and 3 are still the main oxidation reactions happened to the $\text{B}_4\text{C-ZrB}_2$

ceramics, and Reaction 4 starts to be much severer. Fig. 7 gives the microstructure of the oxide surfaces of the B_4C - ZrB_2 ceramics after testing at $1400^\circ C$. Owing to the severe volatilization from B_2O_3 (l) to B_2O_3 (g), the residual oxidation products on the surface of the B_4C - ZrB_2 ceramics are mainly consisted of recrystallized ZrO_2 grains and a little residual liquid B_2O_3 . From Figs. 7 a and d, recrystallized ZrO_2 grains with an average grain size of about $3\ \mu m$ are detected dispersed among the B_2O_3 glass matrix. It is also found that the volatilization from B_2O_3 (l) to B_2O_3 (g) becomes less obvious with the increasing of the amount of ZrB_2 addition. When the addition of ZrB_2 is 20 vol.%, the glass B_2O_3 still cover the surface of the ceramics even the volatilization from B_2O_3 (l) to B_2O_3 (g) at such high temperature, as shown in Figs. 7 b and e. Cracks induced from the difference between the coefficients of thermal expansion of B_2O_3 and ZrO_2 are also detected. However, when the addition of ZrB_2 is as high as 30 vol.%, more glass B_2O_3 cover the surface of the ceramic, and no obvious cracks are observed (Figs. 7 c and f).

(Figure 7 here)

(IV) $1600^\circ C$:

When the temperature is $1600^\circ C$, the oxidation phenomenon is very severe. Reactions 1, 2 and 3 happen. And Reaction 4 is much more obvious. And the oxide surface of the ceramic is mainly covered with a layer of glass products and a little recrystallized ZrO_2 grains. The microstructure of the oxide surfaces of the B_4C - ZrB_2 ceramics after testing at $1600^\circ C$ are presented in Fig. 8. The average of the recrystallized ZrO_2 grains are found to be larger than those of other testing temperatures (Figs. 8 a and d). With the addition of ZrB_2 increasing, more glass B_2O_3 cover the surface of the ceramic, and the recrystallized ZrO_2 grains locates beneath the glass layer owing to the volatilization of B_2O_3 (Figs. 8 b and e), only a corner of the recrystallized ZrO_2 grains are detected (Figs. 8 c and f).

(Figure 8 here)

To sum up, the analysis reveals the presence of four distinct oxide layers. The outer layer is mainly composed of B_2O_3 liquid glass (some is volatilized to gas). At high temperatures, with the volatilization of B_2O_3 porous gas passageway is formed. Beneath this layer, a layer composing of recrystallized ZrO_2 , few B_2O_3 and some voids is found. The third layer is composed of recrystallized ZrO_2 and un-oxidized B_4C-ZrB_2 particles, and the fourth layer is the B_4C-ZrB_2 ceramic matrix. From the experimental results, the oxidation mechanism can be illustrated as shown in Figs. 9. The oxide products on the surface of the B_4C-ZrB_2 ceramic are composed of four distinct layers: 1) B_2O_3 glass layer with some porous oxygen passageways; 2) a layer composing of recrystallized ZrO_2 , few B_2O_3 and some voids; 3) a layer composing of recrystallized ZrO_2 and un-oxidized B_4C-ZrB_2 particles, and 4) the B_4C-ZrB_2 ceramic matrix. In order to protect the underlying layers, the outer B_2O_3 glass layer should exist and play its protection role of preventing oxygen from diffusing into the inner. Beside, we believe that a kind of silicide, as SiC , which can be oxidized to glass SiO_2 , is helpful for the improving of the high temperature oxidation resistance and high temperature mechanical properties of B_4C based ceramics. And this hypothesis will be studied in our future work. Combining the results from high temperature mechanical property measurement and oxidation analysis in this study, the B_4C-ZrB_2 ceramics are believed to have a good engineering application potential below $1600^\circ C$.

(Figure 9 here)

4. Conclusions

The high temperature flexural strength and oxidation behavior of hot-pressed B_4C-ZrB_2 ceramics with various ZrB_2 addition amounts were investigated in the $100-1600^\circ C$ temperature

range in detailed. The high temperature mechanical properties were discussed and the oxidation mechanism was investigated. The following conclusions were drawn from the results:

- (1) All B_4C - ZrB_2 ceramics are fully dense, and no residual pore is detected. The room temperature flexural strength appears to decrease as the ZrB_2 content increases. The room temperature flexural strength of BZ10, BZ20 and BZ30 ceramics are 685.5 ± 17.5 , 647.4 ± 15.6 and 604.3 ± 12.3 MPa, respectively.
- (2) With the testing temperature increasing, the high temperature flexural strength for all B_4C - ZrB_2 ceramics decrease linearly. At the temperature of 1000°C , the flexural strength of BZ10, BZ20 and BZ30 ceramics are 273.8 ± 16.5 , 375.4 ± 21.4 and 576.3 ± 19.2 MPa, respectively, reducing by approximate 60.1, 42.1 and 4.6%, respectively, comparing with room temperature flexural strength. The flexural strength of BZ10, BZ20 and BZ30 ceramics at 1200°C are 231.3 ± 15.3 , 305.4 ± 20.3 and 451.5 ± 21.8 MPa, respectively. The flexural strength of BZ10, BZ20 and BZ30 ceramics at 1400°C are 201.3 ± 15.3 , 267.4 ± 20.2 and 287.5 ± 19.6 MPa, respectively. And the flexural strength of BZ10, BZ20 and BZ30 ceramics at 1600°C are 167.4 ± 12.2 , 189.8 ± 21.1 and 202.5 ± 23.8 MPa, respectively.
- (3) The oxidation behavior of the B_4C - ZrB_2 ceramics with various ZrB_2 addition amounts was studied. The oxide products on the surface of the B_4C - ZrB_2 ceramic are composed of four distinct layers: 1) B_2O_3 glass layer with some porous oxygen passageways; 2) a layer composing of recrystallized ZrO_2 , few B_2O_3 and some voids; 3) a layer composing of recrystallized ZrO_2 and un-oxidized B_4C - ZrB_2 particles, and 4) the B_4C - ZrB_2 ceramic matrix.

The B_4C - ZrB_2 ceramics are believed to have a good engineering application potential below 1600°C .

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Table Caption

Table 1. Label, composition, relative density, and room temperature mechanical properties of the B_4C - ZrB_2 ceramics.

Table 2. Flexural strength of the B_4C - ZrB_2 ceramics at different temperatures.

Figure Captions

Fig. 1. Diagrammatic sketch of the high temperature flexural strength testing system.

Fig. 2. Microstructure and EDS analysis of the polished surfaces of B_4C - ZrB_2 ceramics: (a) BZ10, (b) BZ20, (c) BZ30, (d) EDS analysis.

Fig. 3. High temperature flexural strength of B_4C - ZrB_2 ceramics.

Fig. 4. Gibbs free energy calculations of Reactions 1 and 2.

Fig. 5. Microstructure of oxide surface of B_4C - ZrB_2 ceramics after testing at 1000°C: (a, d) BZ10, (b, e) BZ20, (c, f) BZ30.

Fig. 6. Microstructure of oxide surface of B_4C - ZrB_2 ceramics after testing at 1200°C: (a, d) BZ10, (b, e) BZ20, (c, f) BZ30.

Fig. 7. Microstructure of oxide surface of B_4C - ZrB_2 ceramics after testing at 1400°C: (a, d) BZ10, (b, e) BZ20, (c, f) BZ30.

Fig. 8. Microstructure of oxide surface of B_4C - ZrB_2 ceramics after testing at 1600°C: (a, d) BZ10, (b, e) BZ20, (c, f) BZ30.

Fig. 9. Schematic diagram of microstructure of the oxide layers.

Figures

High Temperature Flexural Strength Testing System

Fig. 1. Diagrammatic sketch of the high temperature flexural strength testing system.

Fig. 2. Microstructure and EDS analysis of the polished surfaces of B_4C - ZrB_2 ceramics: (a) BZ10, (b) BZ20, (c) BZ30, (d) EDS analysis.

Fig. 3. High temperature flexural strength of B₄C-ZrB₂ ceramics.

Fig. 4. Gibbs free energy calculations of Reactions 1 and 2.

Fig. 5. Microstructure of oxide surface of B_4C - ZrB_2 ceramics after testing at $1000^\circ C$: (a, d) BZ10, (b, e) BZ20, (c, f) BZ30.

Fig. 6. Microstructure of oxide surface of B_4C - ZrB_2 ceramics after testing at $1200^\circ C$: (a, d) BZ10, (b, e) BZ20, (c, f) BZ30.

Fig. 7. Microstructure of oxide surface of B_4C - ZrB_2 ceramics after testing at $1400^\circ C$: (a, d) BZ10, (b, e) BZ20, (c, f) BZ30.

Fig. 8. Microstructure of oxide surface of B_4C - ZrB_2 ceramics after testing at $1600^\circ C$: (a, d) BZ10, (b, e) BZ20, (c, f) BZ30.

Fig. 9. Schematic diagram of microstructure of the oxide layers.

Tables

Table 1. Label, composition, relative density, and room temperature mechanical properties of the B₄C-ZrB₂ ceramics.

Label	Composition (vol.%)	Relative density (%)	Flexural strength (MPa)	Mean Flexural strength (MPa)	Fracture toughness (MPa m ^{1/2})	Mean Fracture toughness (MPa m ^{1/2})
BZ10	80B ₄ C+10ZrB ₂	99.7	711.1	685.5±17.7	7.4	6.2±0.8
			701.4		6.6	
			669.3		6.1	
			678.8		5.7	
			666.7		5.0	
BZ20	80B ₄ C+20ZrB ₂	99.8	673.8	647.3±15.6	7.3	6.5±0.7
			655.1		6.8	
			640.7		6.6	
			637.2		6.6	
			629.8		5.1	
BZ30	80B ₄ C+30ZrB ₂	>99.9	617.5	604.3±12.5	7.2	6.6±0.6
			606.2		7.0	
			612.3		6.9	
			581.2		6.1	
			604.1		5.7	

Table 2. Flexural strength of the B₄C-ZrB₂ ceramics at different temperatures.

Temperature (°C)	BZ10		BZ20		BZ30	
	Flexural strength (MPa)	Mean Flexural strength (MPa)	Flexural strength (MPa)	Mean Flexural strength (MPa)	Flexural strength (MPa)	Mean Flexural strength (MPa)
1000°C	299.7	273.8±16.5	406.9	375.4±21.4	611.2	576.3±19.2
	277.2		378.1		575.5	
	276.3		375.2		574.8	
	266.8		377.5		567.4	
	249.1		339.7		552.6	
1200°C	251.7	231.3±15.3	337.4	305.4±20.3	488.8	451.5±21.8
	241.5		318.2		462.7	
	230.7		297.2		440.5	
	226.8		295.4		436.7	
	206.3		278.5		429.1	
1400°C	220.6	201.3±15.3	299.7	267.4±20.2	317.5	287.5±19.6
	212.7		276.8		291.3	
	206.2		266.1		287.4	
	186.3		254.3		285.6	
	180.5		240.5		255.7	
1600°C	188.7	167.4±12.2	224.7	189.6±21.6	241.8	202.5±23.9
	173.5		193.4		207.1	
	159.3		189.1		203.4	
	158.8		183.2		191.7	
	156.4		157.3		168.2	