Structure and oxidation behavior of high temperature ZrB$_2$–SiBCN ceramics with polyborosilazane as a sintering additive

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The polyborosilazane (PBSZ) was employed as the sintering additive and the dense ZrB$_2$ ultra-high temperature ceramic samples were fabricated by hot pressing at 1900°C. The relative density of sintered ceramics is 96.4%. The PBSZ was converted to amorphous SiBCN ceramics after sintering. Mass transfer process was significantly improved in the amorphous region among the ZrB$_2$ grains. Densification temperature was reduced. The mechanical properties and high temperature oxidation resistance were also enhanced. The bending strength and fracture toughness of the ZrB$_2$ ceramics were $241 \pm 10$ MPa and $4.47 \pm 0.5$ MPa m$^{1/2}$, respectively. The crack was deflected along the grain boundaries. During high-temperature oxidation process, the grain boundary at SiBCN ceramic was oxidized into borosilicate glass and the low viscous glass was extruded out and spread over the surface quickly. The continuous oxide coating formed on the ZrB$_2$ ceramics surface prevented further oxidation.

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Ceramics of borides, carbides and nitrides are referred as Ultra-High Temperature Ceramics (UHTCs) due to their high melting points, which makes them as potential candidates for use at extremely high temperature. ZrB$_2$ is considered as the most promising material due to its unique features, such as high melting point (exceeds 3200°C), high hardness, excellent corrosion resistance against slags and molten iron, good thermal shock resistance and excellent oxidation/ablation resistance at elevated temperatures. However, the extremely high melting point leads to difficulties for the densification of the ZrB$_2$ ceramics, which limits the application of the material. Sintering additives, such as SiC,$^{3-5}$ B$_4$C,$^{4}$ Nb$^{5,6}$ and so on, had been selected in order to obtain fully dense ZrB$_2$ materials. While SiC is considered the most promising second phase (reference here), ZrB$_2$-based ceramics containing about 20 vol% SiC particles show great potential for use at hot sections of supersonic aircraft.$^7$ The oxidation behavior of the ZrB$_2$–SiC ceramic composites has attracted a great deal of interest, and the improvement by the introduction of SiC can be ascribed to the formation of protective silica-rich glass when exposed to oxygen under elevated temperatures. However, SiO$_2$ and B$_2$O$_3$, which result from the oxidation of SiC and ZrB$_2$, respectively, are not produced at the same time. ZrB$_2$ is not well protected until the formation of borosilicate glass. An early-forming borosilicate glass coating is thus crucial to protect ZrB$_2$ from being oxidized.

Polymer precursor has been used as sintering additive in preparing ZrB$_2$ ceramics. Dense ZrB$_2$ ceramics can be acquired with the polymer-to-ceramic conversion. ZrB$_2$ powders coated by Polycarbolisilane (PCS) which can convert to SiC grains and amorphous carbon at 1000°C can be sintered to form dense ceramics at a relatively low temperature of 1800°C (pressed for 60 min at 20 MPa). For comparison, the ZrB$_2$ powder without PCS coating was highly porous with a relative density of 78% under the same HP conditions.$^8$ In contrast to the pure ZrB$_2$ sintered in the same condition, although the ZrB$_2$ ceramics can be prepared by the methods mentioned above, the oxidation resistance property is not effectively improved. It is thus very important to find a new polymer precursor as sintering additive, which not only enhances densification during sintering but also improve oxidation resistance of ZrB$_2$ ceramics at high temperature.

Recently, amorphous SiBCN ceramics prepared by polyborosilazane (PBSZ) have been reported to possess excellent chemical stability at temperatures above 2000°C$^9$ and good oxidation resistance.$^{10,11}$ Polymer-derived SiBCN has a high activity during pyrolysis process, and its oxidation product, borosilicate glass, possesses good oxidation resistance. Its polymer precursor can thus be expected as a good candidate as sintering additive for ZrB$_2$ ceramics. However, to the best knowledge of the authors, no work has been published in the open literature using PBSZ as sintering additive to prepare ZrB$_2$. In the present work, dense ZrB$_2$ ceramics are prepared with PBSZ as the sintering additive. The mechanical properties and oxidation behavior of the ZrB$_2$ ceramics are studied.

ZrB$_2$ (China New Metal Materials Technology Co., Ltd., particle size ~700 nm, purity ≥99 mass %) and polymeric polyborosilazane precursor powders (synthesized according to the reports of Riedel$^{15}$ with made by oneself, purity ≥95 mass %) were used as the starting materials. ZrB$_2$ powder was mixed with 2.64 mass% polyborosilazane precursor powder. The mixed powder was hot-pressed at 1900°C for 1 h at a pressure of 30 MPa, in a graphite die covered with BN-coated carbon paper. After loading, the furnace was heated to target temperature at an average ramp rate of 30°C/min in argon. The load was removed when the die temperature dropped below 1750°C.

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The bulk density and porosity of the sintered specimens was determined by Archimedes’ principle. The microstructures were observed using a scanning electron microscope (SEM, Model-CamScan-3400, Cambridge, England), which was equipped with an EDS detector (INCAINCAPentaFET-x3, Oxford, England). Linear-intercept technique was used to determine the grain size of composites by counting a minimum of 70 grains. The fracture toughness ($K_{IC}$) was measured by the indentation method on polished sections with a load of 196N, which was calculated from the length of a crack formed around the indentations. The flexural strength was measured using a three-point bending test (SANS, Sans Testing Machine, Shen Zhen, China) with a span of 30 mm. Five samples with a dimension of $36 \, \text{mm} \times 4 \, \text{mm} \times 3 \, \text{mm}$ were used for the test.

XRD results of the hot-pressed ZrB$_2$–SiBCN ceramics showed only ZrB$_2$ phase (see Fig. 1). It was reported that $\beta$-Si$_3$N$_4$ and $\beta$-SiC were observed in quaternary phase SiBCN ceramic at $T \geq 1700^\circ\text{C}$, as a result of the crystallization and subsequent decomposition of the metastable SiBCN phase. However, neither $\beta$-SiC nor $\beta$-Si$_3$N$_4$ phase was observed. The quantity of PBSZ introduced (2.64 mass %) was very limited and even though part of the resulting SiBCN phase may have crystallized and decomposed, the signal from the product was too small to be detected.

Figure 2 shows a fracture surfaces SEM micrograph of hot-pressure sintered ZrB$_2$–SiBCN ceramics. As shown in the micrographs, the grain sizes of matrix ZrB$_2$ range from 3 to 7 mm. Because of the high processing temperature ($1900^\circ\text{C}$), the in situ formation of SiBCN from PBSZ resulted in a uniform distribution of SiBCN in the dense ZrB$_2$ matrix and no abnormal particles growth of ZrB$_2$ was observed. The amorphous SiBCN distributed on the ZrB$_2$ grain boundaries leads to a high activity that improves the densification process. The amorphous SiBCN derived from PBSZ pyrolysis was not discernible in the microstructure. Based on this observation, it was assumed that SiBCN has been used as a sintering additive. The presence of amorphous SiBCN in the final microstructure has resulted in an enhanced strength and hardness.

Figure 3 shows a SEM (BSE) image and EDS analysis of the ZrB$_2$–SiBCN polished surface. The SiBCN pyrolysis products formed in the grain interfaces, while some of SiBCN itself forms the amorphous regions. The amorphous SiBCN among the interfaces is not visible on the SEM pictures but will appear after the oxidation process. The dark-grey and light-grey regions were analyzed with energy spectrum in the SEM micrograph of ZrB$_2$–SiBCN ceramics. The results indicate that dark-grey regions contain SiBCN phase and ZrB$_2$ phase, and the light-grey regions only contain ZrB$_2$ phase as shown Fig. 3. The ZrB$_2$ phase

![Fig. 1. The XRD pattern of a ZrB$_2$–SiBCN Ceramics with a 2.64 mass % PBSZ addition after sintering at 1900°C.](image1)

![Fig. 2. SEM micrograph of pressure sintered ZrB$_2$–SiBCN Ceramics with Fracture surfaces.](image2)

![Fig. 3. The SEM (BSE) image and EDS analysis of the ZrB$_2$–SiBCN polished surface.](image3)
was found in the dark-grey probably due to the large detection depth of energy spectrum.

The physical and mechanical properties of the ZrB$_2$–SiBCN ceramics sintered at 1900°C are summarized in Table 1. An almost fully dense ZrB$_2$ ceramic was HP sintered at 1900°C for 1 h with only a 2.64 mass% PBSZ addition. The relative density was 96.4%. The bending strength of the material at room temperature (RT) was 241 ± 10 MPa and the fracture toughness was 4.47 ± 0.5 MPa m$^{1/2}$. The fracture toughness of the sintered ceramic was higher than those results of monolithic ZrB$_2$ (2.3–3.5 MPa m$^{1/2}$) and is similar to the values reported for SiC particle reinforced ZrB$_2$ composite (4.0–4.5 MPa m$^{1/2}$). Because of the high processing temperature (1900°C), the formation of SiBCN from PBSZ resulted in a uniform distribution of SiBCN in the dense ZrB$_2$ matrix. The amorphous SiBCN distributed within the ZrB$_2$ grain boundary regions resulted in a high activity that improve the densification process. Based on this observation, it can be inferred that the presence of amorphous SiBCN in the final microstructure lead to an enhanced strength and hardness.

The fracture surface was rough and the crack exhibits an intergranular feature. Figure 4 shows a crack propagation on the surface of ZrB$_2$–SiBCN ceramics. It was noticed that crack deflection was along the grain boundaries. Increased fracture toughness produced by amorphous SiBCN addition is attributed to the crack deflection that occurs near the amorphous SiBCN phase and at ZrB$_2$/SiBCN interfaces. Contribution of crack deflection to increasing fracture toughness depends on the total number of crack deflections and the crack deflection angle, i.e. crack propagation path. The increase in fracture toughness that accompanies crack deflection is also associated with the elastic and/or frictional bridging mechanism of grains.

The addition of SiBCN not only enhances the strength and toughness, but also improves the oxidation resistance. During the oxidation process, the SiBCN phase is converted to SiO$_2$, which forms a protective layer and prevents further oxidation of the ZrB$_2$ matrix. This protective layer acts as a barrier to oxygen diffusion, thereby reducing the rate of oxidation.

Table 1. Physical and Mechanical properties of the ZrB$_2$–SiBCN ceramics

| Property              | ZrB$_2$–SiBCN |
|-----------------------|---------------|
| Theoretical densities (g/cm$^3$) | 5.71          |
| Relative densities (%)  | 96.4          |
| Bending strength (MPa)  | 241 ± 10      |
| Fracture toughness (MPa m$^{1/2}$) | 4.47 ± 0.5    |

Fig. 4. SEM micrograph of pressure sintered ZrB$_2$–SiBCN Ceramics with crack propagation

Fig. 5. Surface morphology of specimens oxidized for 30 min and the oxidation temperatures are a) 1300°C, b) 1400°C, c) 1500°C and d) 1600°C.
high-temperature oxidation process, SiBCN was oxidized into borosilicate glass. When the resulting low viscous glass spread over the surface, a continuous coating could form and further oxidation could be prevented. However, the oxidation resistance property depends on the wettability and the thickness of the glass coating, which are greatly influenced by volatilization rate of borosilicate glass. Higher temperature results in a lower viscosity and better wettability for borosilicate glass. However, it also increases the volatilization rate of the glass, which is undesirable. The transition temperature from SiBCN ceramic to borosilicate glass is 1300°C followed by expansion and extension into grain boundaries. As shown in Fig. 5(a), the ZrB2 grains were surrounded by the borosilicate glass; it indicated that the amorphous SiBCN phase distributed among the grain interface uniformly in the specimens. At 1400°C, the glass started to cover the specimen surface due to the lower viscosity, and some ZrO2 particle were seen in Fig. 5(b). With the further increase in temperature, this tendency was more apparent at 1500°C. The specimen was almost fully covered by borosilicate glass, with just a few ZrO2 particles exposed on the surface. At 1600°C, however, the rate of volatilization becomes so high that all glass phase were gone, the oxidation resistance ability degraded and the ZrO2 phase can be observed clearly [Fig. 5(d)].

The PBSZ was firstly employed as ceramic sintering additive, and the homogeneous dense ZrB2 ceramic samples were successfully prepared. The polymer is pyrolyzed to amorphous SiBCN during ZrB2 sintering process. Significant improvement mass transfer process in amorphous regions among ZrB2 grains facilitated densification, and an almost full density was attained at a relative low temperature. Compared to sintering additive SiC, the polymer-derived amorphous SiBCN s more effective and only a small amount is required, which is of benefit especially to Ultra-High Temperature Ceramics with good properties. While the sintering process was improved, the mechanical properties such as fracture toughness and high temperature oxidation resistance were also enhanced. During high temperature oxidation process, amorphous SiBCN phase among ZrB2 grains is oxidized to borosilicate glass. The low viscous glass spreads over the material surface to form a continuous and dense coating in the sintering process, which is why a small amount of the additive remarkably improves high temperature oxidation resistance of the ZrB2 ceramics. The polymer-derived amorphous SiBCN not only works as an excellent sintering additive for the ZrB2 ceramics, but also can be expected for other non-oxide ceramics.

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