High-strength zirconium diboride-based ceramic composites consolidated by low-temperature hot pressing

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Received 26 March 2012
Accepted for publication 17 July 2012
Published 5 September 2012
Online at stacks.iop.org/STAM/13/045007

Abstract
Two compositions of ZrB₂-based ceramic composites containing Si₃N₄, Al₂O₃ and Y₂O₃ have been hot-pressed at different temperatures between 1673 and 1773 K for 60 min in vacuum. The densification behavior of the composites was examined during the sintering process. The microstructures of the composites were characterized by scanning electron microscopy, and the crystalline phases were identified by x-ray diffraction. The effects of Al₂O₃ and Y₂O₃ additives on the densification behavior and flexural strength were assessed. A relative density of ∼95% was obtained after sintering at 1723 K or higher temperatures. The microstructures of the composites consisted of (Zr, Y)B₂, α-Si₃N₄ and Y₃(Al, Si)₅O₁₂ phases. The room-temperature flexural strength increased with the amount of additives and approached 1 GPa.

Keywords: zirconium diboride, silicon nitride, oxide additives, low-temperature densification, high strength

1. Introduction
Zirconium diboride (ZrB₂) belongs to the family of refractory diborides of transition metals from the fourth to sixth groups of the periodic table. Most of these diborides have melting points above 3273 K, high thermal and electrical conductivities, chemical inertness against molten metals and good thermal shock resistance, making them potential candidates for a variety of high-temperature structural applications [1–3]. However, the densification of ZrB₂ powder requires very high temperatures (>2373 K) and external pressure because of strong covalent bonds and low self-diffusivity in ZrB₂ [4–6]. In addition, high-temperature structural applications of single-phase materials are limited by their poor oxidation and ablation resistance.

The composite approach has been successfully adopted to improve the densification, mechanical properties and oxidation and/or ablation resistance of single-phase ceramics. It is well known that the addition of SiC to ZrB₂ results in a composite with improved strength and resistance to oxidation, thermal shock and ablation [6–10]. The improvement of oxidation and ablation resistance is attributed to the formation of a coherent passivating oxide scale on the surface. The addition of SiC also produces an intergranular liquid phase that aids the densification of ZrB₂. The presence of SiC limits the grain growth of ZrB₂ during densification, thereby increasing the strength. Chamberlain et al [11] obtained highly dense ZrB₂-based ceramics with a fine and homogeneous microstructure by hot pressing an attrition-milled mixture of ZrB₂ and SiC powders at 2173 K, and the maximum strength was ∼1 GPa for the ZrB₂ ceramics containing 12 wt% or more of SiC.

Recently, silicides (MoSi₂, ZrSi₂) [12–15] have been used to aid in the densification of ZrB₂ at temperatures between 1723 and 2123 K, which are lower than those used for the ZrB₂-based ceramics with SiC. For example,
dense compacts were obtained from ZrB$_2$-based composites containing MoSi$_2$ by pressureless sintering or hot pressing between 2023 and 2123 K [12, 13]. For ZrB$_2$-based composites containing ZrSi$_2$, highly dense samples were obtained by pressureless sintering or hot pressing between 1723 and 1923 K [14, 15]. Unfortunately, the strengths of the resulting materials were not superior to those of single-phase ZrB$_2$ ceramics or ZrB$_2$-based composites containing SiC [12–14]. On the other hand, dense Si$_3$N$_4$ and/or SiC ceramic compacts were consolidated by hot pressing at 2023 K or above when Y$_2$O$_3$ and Al$_2$O$_3$ were added, as a result of the formation of a liquid oxynitride phase at grain boundaries during the sintering [16–18]. The Si$_3$N$_4$ ceramics with Y$_2$O$_3$ and Al$_2$O$_3$ additives had high bending strengths at room temperature and high temperatures, excellent oxidation resistance and high fracture toughness [19, 20]. Furthermore, the amount and composition of the formed oxynitride liquid phase determined the densification and mechanical properties of the ceramics. The sinterability and mechanical properties are expected to improve upon addition of Y$_2$O$_3$ and Al$_2$O$_3$ in ZrB$_2$-based composites as well; however, little has been published on this topic. Therefore, it is important to attempt the sintering of dense ZrB$_2$-based composites at low temperatures, through a selection of appropriate compositions, to obtain material with high strength and improved oxidation resistance.

In this study, ZrB$_2$-based ceramic composites containing 13 wt% Si$_3$N$_4$ and variable amounts of Y$_2$O$_3$ and Al$_2$O$_3$ were hot-pressed at different temperatures between 1673 and 1773 K under a pressure of 20 MPa for 60 min in vacuum. The densification behavior, microstructure and room-temperature flexural strength of the resulting composites were examined. We also discuss the dependences of the densification behavior and flexural strength on the amount of additives.

### 2. Experimental procedures

The starting powders were ZrB$_2$ (median diameter $d_{50} = 2.12 \mu$m, Grade F, Japan New Metals), α-Si$_3$N$_4$ ($d_{50} = 0.48 \mu$m, SN-E10, Ube Industries, Japan) Y$_2$O$_3$ (High Purity Chemicals Co. Ltd., Japan) and α-Al$_2$O$_3$ (AKP-20, Sumitomo Chemical Co. Ltd., Japan). Two compositions of ZrB$_2$-based powders were hot-pressed into ceramic compacts: sample ZS10 contained 13% Si$_3$N$_4$, 4% Al$_2$O$_3$ and 6% Y$_2$O$_3$, whereas the corresponding values for sample ZS15 were 13, 6 and 9% (Table 1; all compositions in this article are given in weight percent). Assuming that Al$_2$O$_3$ and Y$_2$O$_3$ converted to Y$_2$Al$_2$O$_5$ after sintering, the resulting composites contained 77.1% ZrB$_2$, 12.9% Si$_3$N$_4$ and 10% Y$_2$Al$_2$O$_5$ for ZS10, and 71.9% ZrB$_2$, 13.1% Si$_3$N$_4$ and 15% Y$_2$Al$_2$O$_5$ for ZS15.

The starting powders were wet-ball milled for 24 h in SiC media using alcohol as a solvent, and the resulting slurry was then dried. Before sintering, the dried powders were sieved through a 60-mesh metallic sieve. Figure 1 shows scanning electron microscopy (SEM) images of the as-received ZrB$_2$ and Si$_3$N$_4$ powders and the milled powder mixture. The ZrB$_2$ powder had spherical particles (figure 1(a)) with a bimodal size distribution; the Si$_3$N$_4$ particles were also spherical, but

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**Table 1.** Properties of ZrB$_2$-based composites hot-pressed at 1723 K and 20 MPa for 60 min.

| Sample | ZrB$_2$ (wt%) | Si$_3$N$_4$ (wt%) | Al$_2$O$_3$ (wt%) | Y$_2$O$_3$ (wt%) | Bulk density ($\text{g cm}^{-3}$) | Real density ($\text{g cm}^{-3}$) | Relative density (%) | Size of ZrB$_2$ grains ($\mu$m) | Flexural strength ($\sigma_f$ (MPa)) |
|--------|---------------|-------------------|-------------------|-----------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| ZS10   | 77.15         | 12.85             | 4                  | 6               | 5.09                 | 5.37                 | 94.8                 | 1.3 ± 0.6             | 921 ± 140             |
| ZS15   | 71.90         | 13.10             | 6                  | 9               | 5.02                 | 5.28                 | 95.1                 | 1.5 ± 0.8             | 964 ± 10              |

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**Figure 1.** SEM images of the as-received (a) ZrB$_2$, (b) Si$_3$N$_4$, and (c) milled ZrB$_2$–Si$_3$N$_4$–Al$_2$O$_3$–Y$_2$O$_3$ powder mixture.
smaller (figure 1(b)). After the ball milling (figure 1(c)), the average particle size was significantly reduced, although several large (∼1.8 μm) ZrB₂ particles were still observed.

The obtained powder mixtures were hot-pressed (NEW-HP5, Nissin Giken Co. Ltd., Japan) in graphite dies as 21 × 25 × 3.5 mm³ tablets. To study the effect of temperature on the densification, the ZS10 powder was processed at 1673, 1723 and 1773 K, whereas the ZS15 sample was sintered only at 1723 K. The powders were heated in vacuum at a rate of ∼15 K min⁻¹ under a pressure of 20 MPa. The temperature of the sample was monitored by a two-color optical pyrometer through a hole in the die. After hot pressing for 60 min, the load was removed, the sample was cooled at ∼15 K min⁻¹ to 773 K and the electric power was switched off. During the sintering process, we recorded the sample height along the pressing direction to monitor the densification behavior.

The final densities, ρ, of the sintered samples were measured by the Archimedes method using distilled water as the immersion medium. The theoretical densities were calculated according to the rule of mixtures, taking densities as the immersion medium. The theoretical densities were measured by the Archimedes method using distilled water as the immersion medium. The density of ZS10 samples is shown in figure 2. The density vs sintering temperature for the ZS10 composite.

3. Results and discussion
3.1. Densification and microstructure

Figure 2 shows typical shrinkage curves of the composites recorded during hot-pressing. The shrinkage depends on the amount of additive and initiates at ∼1493 and ∼1453 K for ZS10 and ZS15 samples, respectively. The shrinkage rates exhibit a maximum (figure 2(b)) that shifts toward lower temperatures with increasing amount of additive. Densification did not complete during the temperature rise and stopped after ∼40 and ∼15 min of holding at 1723 K for ZS10 and ZS15, respectively. Thus, increasing the amount of additive significantly accelerated the densification.

The effect of sintering temperature on the relative density of ZS10 samples is shown in figure 3. The density increases significantly from 1673 to 1723 K and is almost constant at ∼95% between 1723 and 1773 K. The same value was measured for ZS15 samples consolidated at 1723 K (table 1). Thus, although increasing the amount of additive significantly accelerated the densification, it could not reach 100%. Monteverde and Bellosi [22] reported a relative density exceeding 98% in a ZrB₂ powder containing 2.5% Si₃N₄, hot-pressed at 1973 K and 30 MPa for 15 min in vacuum; although this value is higher than ours, it was obtained at a significantly higher temperature.

Figure 4 shows typical SEM images of the hot-pressed ZrB₂-based ceramic composites. Three phases can be distinguished according to the image contrast. EDS mapping (figure 5) reveals that Zr, B and Y elements are concentrated in the brighter phase, the gray phase is dominated by Y, Al, Si and O, whereas the dark contrast phase is rich in Si and N. XRD patterns (figure 6) show that the ZrB₂ phase is mostly crystalline; trace amounts of the α-Si₃N₄ and Y₃Al₅O₁₂ secondary phases are present, whereas the β-Si₃N₄, Y₂O₃ and Al₂O₃ phases could not be detected. Combining the XRD and EDS results, we attribute the light gray phase in the
Figure 4. SEM images of ZrB$_2$-based composites hot-pressed at 1723 K and 20 MPa for 60 min: (a, c) ZS10 and (b, d) ZS15. Symbols: Z: (Zr, Y)B$_2$, S: Si$_3$N$_4$, and Y: Y$_3$(Al, Si)$_5$O$_{12}$.

SEM images to (Zr, Y)B$_2$ (marked by Z in figure 4(d)), the intermediate gray phase to Y$_3$(Al, Si)$_5$O$_{12}$ (Y in figure 4(d)) and the darkest phase to Si$_3$N$_4$ (S in figure 4(d)). In a previous study of ZrB$_2$ with 2.5% of Si$_3$N$_4$ additive, consolidated by hot pressing at 1973 K in vacuum, a BN phase was detected at grain boundaries owing to the reaction of B$_2$O$_3$ with Si$_3$N$_4$ during the sintering [22]. This reaction is thermodynamically favored at high temperatures because of the strongly negative Gibbs free energy, e.g. $-304$ kJ mol$^{-1}$ at 1773 K. Although a similar reaction is expected for our ZrB$_2$-based composites containing 13% Si$_3$N$_4$, we could not detect the BN phase by SEM and XRD.

The presence of the solid solution (Zr, Y)B$_2$ in the composites suggests that Y has dissolved in the ZrB$_2$ phase during the sintering process. There is a eutectic point at $\sim$1636 K in the Y–Zr system [23]. Thus, Y could form a liquid phase with Zr at $\sim$1636 K or above and dissolve in the ZrB$_2$ phase to produce the solid solution (Zr, Y)B$_2$ during the sintering. The calculated lattice parameter, $a$, of (Zr, Y)B$_2$ is 0.3177 nm for ZS10 and 0.3173 nm for ZS15 composites. Thus, the introduction of Y atoms into ZrB$_2$ increased the lattice parameter because of the larger atomic radius of Y (0.18 nm) than Zr (0.16 nm). On the other hand, the presence of the Y$_3$(Al, Si)$_5$O$_{12}$ phase and the disappearance of Y$_2$O$_3$ and Al$_2$O$_3$ phases indicated that the Y$_3$(Al, Si)$_5$O$_{12}$ phase was formed by the reaction of Y$_2$O$_3$ with Al$_2$O$_3$ and SiO$_2$, which existed on the surface of the Si$_3$N$_4$ powder during the sintering process. The Y$_3$(Al, Si)$_5$O$_{12}$ XRD peaks were stronger for the ZS15 than ZS10 samples in accordance with the larger amount of additives. In a previous study of Si$_3$N$_4$ containing 6% Y$_2$O$_3$ and 3% Al$_2$O$_3$, the Y$_3$Al$_5$O$_{12}$ phase was formed between 1523 and 1723 K [17]. In addition, the absence of the $\beta$-Si$_3$N$_4$ phase suggests that the $\alpha \rightarrow \beta$ phase transformation of Si$_3$N$_4$ did not proceed during the sintering. Honma and Ukyo [17] reported that this transformation starts at 1823 K and completes only at 2023 K (4 h sintering). Thus, the nonobservation of the $\alpha \rightarrow \beta$ phase transformation in Si$_3$N$_4$ may be attributed to the lower sintering temperature (1723 K) used in this study.
Both studied composites had a homogeneous microstructure with fine $\alpha$-Si$_3$N$_4$ and Y$_3$(Al$_2$,Si$_3$)O$_{12}$ grains randomly dispersed in the (Zr, Y)$_2$B$_2$ matrix (figures 4(a), and (b)). Most of the (Zr, Y)$_2$B$_2$ grains are isometric, but some rod-like ZrB$_2$ grains are also observed. The formed Y$_3$(Al$_2$,Si)$_3$O$_{12}$ particles had irregular shapes and were located between the (Zr, Y)$_2$B$_2$ and/or Si$_3$N$_4$ grains (figures 4(c) and (d)). Although elongated Si$_3$N$_4$ grains are common in a liquid-phase-sintered Si$_3$N$_4$ ceramic with Y$_2$O$_3$ and Al$_2$O$_3$ additives, very few Si$_3$N$_4$ rods were observed in the studied materials. This result implies that the $\alpha$-Si$_3$N$_4$ grain growth mechanism was suppressed by the low sintering temperature, despite the high amount of additives. The (Zr, Y)$_2$B$_2$ grains became coarser when the amount of additive increased from 10 to 15% (table 1). However, the average grain diameters were about three times smaller than in the ZrB$_2$-based ceramics with a SiC additive, which were hot-pressed at 2273 K for 60 min [6]. It is evident that the grain growth is significantly inhibited at low sintering temperatures, because the grain boundary migration is a thermally activated process.

SiC and/or Si$_3$N$_4$ ceramics with Y$_2$O$_3$ and Al$_2$O$_3$ additives typically require 1973 K or higher hot-pressing temperatures to yield highly dense compacts [16–20]. However, for ZrB$_2$-based composites containing Si$_3$N$_4$, Y$_2$O$_3$ and Al$_2$O$_3$, a relative density of $\sim$95% was obtained at 1723 K (table 1). The improvement in densification of SiC and/or Si$_3$N$_4$ upon addition of Y$_2$O$_3$ and Al$_2$O$_3$ is attributed to the presence of an intergranular liquid phase, which consists of an oxynitride formed by the additives together with SiO$_2$ in the Al$_2$O$_3$–Y$_2$O$_3$–SiO$_2$ system [16–18]. However, B$_2$O$_3$ and ZrO$_2$ films are often present on the surfaces of the starting ZrB$_2$ powder. A previous study [24] of TiB$_2$ showed that oxygen impurities present in the starting powder promote grain growth and inhibit densification in nonoxide ceramic systems. In particular, the presence of B$_2$O$_3$ significantly inhibited the densification of TiB$_2$ due to the evaporation of B$_2$O$_3$, which results from its low melting point (723 K) and high vapor pressure. Therefore, to improve the sinterability of ZrB$_2$ ceramics and ZrB$_2$-based composites containing SiC, which were consolidated by hot pressing of ZrB$_2$ and SiC powders without adding Y$_2$O$_3$ or Al$_2$O$_3$ [6, 9, 10]. The values in table 1 are comparable to those for fine and highly dense ZrB$_2$-based composites containing SiC, which were consolidated by hot pressing of an attrition-milled mixture of ZrB$_2$ and SiC powders at 2173 K [11]. The flexural strength is higher for ZS15 (higher amount of additives) than ZS10 samples, whereas the spread in its value is significantly lower. Note that in a previous study of hot-pressed ZrB$_2$–SiC ceramics [28], the room-temperature flexural strength increased with the amount of added Yb$_2$O$_3$.

Figure 7 shows the fracture surfaces of the hot-pressed composites. The low-magnification image suggests that the fracture origin is located at and/or near the surface (indicated by arrows in figure 7(a)). At high magnification, pores are clearly observed for both compositions, mostly at multigrain pockets (see arrows in figures 7(b) and (c)). Such pores at and/or near the surface might be the major cause of failure. The pores are larger in ZS10 than ZS15 samples, which might explain the lower flexural strength and larger scattering in the strength values in the former composite. Thus, despite the larger (Zr,Y)B$_2$ grains (table 1), the flexural strength is higher in ZS15 than ZS10 samples.

Figures 7(b) and (c) reveal a typical intragranular fracture for both composites, and a similar fracture mode was observed in the hot-pressed ZrB$_2$–SiC ceramics containing Yb$_2$O$_3$ [28]. For comparison, in single-phase ZrB$_2$ ceramics and ZrB$_2$-based composites containing SiC [6], the ZrB$_2$ phase showed a typical intergranular fracture. The intragranular fracture of ZrB$_2$ suggests that the intergranular bonding is stronger in the ZrB$_2$-based composites containing Si$_3$N$_4$, Y$_2$O$_3$ and Al$_2$O$_3$ than in the single-phase ZrB$_2$ ceramics and ZrB$_2$-based composites containing SiC but no oxides. Grain boundary strengthening can improve the mechanical properties of ceramics [29]. Therefore, we attribute the increase in the flexural strength on addition of Y$_2$O$_3$ and Al$_2$O$_3$, as well as the intragranular fracture mode, to the grain boundary strengthening.
Figure 7. Fracture surfaces of the (a, b) ZS10 and (c) ZS15 composites hot-pressed at 1723 K and 20 MPa for 60 min.

4. Summary

Relative densities of ∼95% were obtained in ZrB2-based ceramic composites containing Si3N4, Y2O3 and Al2O3 by hot pressing at 1723 K and 20 MPa for 60 min in vacuum. The addition of Y2O3 and Al2O3 aided the densification of ZrB2-based composites during low-temperature sintering. Only the α, but not the β Si3N4 phase was detected after sintering, indicating the suppression of the α → β phase transformation in Si3N4. The microstructures of the two studied composites consisted of isometric (Zr, Y)B2, α-Si3N4 and Y3(Al, Si)2O12 secondary-phase grains. The (Zr, Y)B2 grains became coarser and the room-temperature flexural strength increased with increasing amount of additives, approaching a value of 1 GPa. The intragranular fracture mode was observed for both studied composites.

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