Low-temperature densification, microstructures and mechanical properties of ZrB$_2$–SiC composites with Cr$_3$C$_2$ additives

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In this study, the densification, microstructures and elastic and mechanical properties of hot-pressed ZrB$_2$–20 vol % SiC composites with 3–10 wt % Cr$_3$C$_2$ additives were examined. The effects of the Cr$_3$C$_2$ content on the densification, microstructures and elastic and mechanical properties are discussed. The elastic moduli of the composites were calculated using measured longitudinal and transverse soundwave velocities, and the hardness and fracture toughness of the composites were determined using indentation measurements. The results show that the elastic moduli and fracture toughness are constant and independent of the Cr$_3$C$_2$ content, with a shear modulus of ~200 GPa, Young’s modulus of ~450 GPa and toughness of ~4.7 MPa$^2$m$^{1/2}$. The hardness was measured as 18.2–20.9 GPa and was dependent on the Cr$_3$C$_2$ content. The flexural strengths of the composites were affected by the Cr$_3$C$_2$ content, with resulting strength values of 426–523 MPa.

Key-words: Zirconium compounds, Composites, Densification, Microstructure, Mechanical properties

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1. Introduction

Zirconium diboride (ZrB$_2$) is a refractory transition-metal diboride composed of the fourth to sixth groups of the periodic table. Many diborides of this type have melting points greater than 3000°C, high thermal and electrical conductivities, and better thermal shock resistance, making them potential candidates for several high-temperature structural applications.$^{1–3}$ The major problems associated with ZrB$_2$ ceramic materials include densification and high-temperature oxidation.$^{4,5}$ Because of ZrB$_2$ ceramic’s strong covalent bonds and low self-diffusivity,$^5$ its densification requires very high temperatures (>2100°C) and external pressure (>20 MPa). Single-phase ZrB$_2$ ceramics are easily oxidized in air, moreover, to form ZrO$_2$ and B$_2$O$_3$ at temperatures greater than ~800°C.$^{5,6}$

The composite approach has been successfully adopted to improve the densification and the oxidation resistance of single-phase ZrB$_2$ ceramics. It is known that the addition of SiC to ZrB$_2$ results in a composite with improved sinterability and higher oxidation resistance,$^{7–13}$ and this composite has recently become a strong potential candidate for a variety of high-temperature structural applications. The addition of SiC is believed to produce an intergranular liquid phase that aids the densification of ZrB$_2$.$^{7–12}$ The improvement of oxidation resistance due to the addition of SiC is thought to arise from the formation of a coherent passivating oxide scale on the surface.$^{11,13}$

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The presence of SiC also limits the grain growth of ZrB$_2$ during sintering,$^{3,8–10}$ leading to higher strength. Sintering temperatures of 1900°C or above are still required, however, to obtain highly dense ZrB$_2$–SiC composites. In an attempt to lower the densification temperature of ZrB$_2$–SiC composites further, MoSi$_2$ has been added to aid the densification of the composites.$^{14,15}$ These studies showed that densities exceeding 97% were obtained for 5 and 10 vol % SiC-containing ZrB$_2$ powders at 1800°C after the addition of 20 vol % MoSi$_2$. On the other hand, a density of 94.6% was obtained for 20 vol % SiC-containing ZrB$_2$ powder.

By contrast, an early study of TiB$_2$ ceramics with Cr$_3$C$_2$ additives obtained densities exceeding 95% for TiB$_2$ powders with 5 wt % Cr$_3$C$_2$ or greater by pressureless sintering at 1900°C for 1 h in Ar.$^{16}$ Very recently, Grigoriev et al.$^{17}$ examined the kinetics of sintering and phase interactions in the diffusion contact zones of ZrB$_2$ and Cr$_3$C$_2$. They found that when Cr$_3$C$_2$ is used as a sintering activator, the hot-pressing temperature of ZrB$_2$ was lowered from 2200 to 1500–1750°C, depending on the Cr$_3$C$_2$ content. However, the densification behavior and elastic and mechanical properties of the ZrB$_2$–SiC composites with Cr$_3$C$_2$ additives are not well understood. In this study, ZrB$_2$–20 vol % SiC-based composites with 3–10 wt % Cr$_3$C$_2$ additives were consolidated by hot-pressing at 1650°C for 1 h under 20 MPa in a vacuum. The densification and microstructures of the composites were examined. The elastic and mechanical properties of the obtained composites were measured at room temperature, and the effect of Cr$_3$C$_2$ addition on these properties was analyzed.
2. Experimental procedures

2.1 Composite materials

ZrB₂ (d₀ = 2.1 μm, Grade F, Japan New Metals, Osaka), α-SiC (d₀ = 0.5 μm, UF-15, H.C. Starck, Berlin, Germany) and Cr₇C₃ (325 mesh, 98% purity, Mitsuwa Chemicals Co. Ltd., Osaka) powders were used as the starting powders in this study. Four ZrB₂–20 vol% SiC composites with 3, 5, 7 and 10 wt% Cr₇C₃ additives were prepared to examine the effect of Cr₇C₃ content on the densification and the mechanical properties. Hereafter, the four ZrB₂–SiC composites with Cr₇C₃ additives are denoted as ZSCRC03, ZSCRC05, ZSCRC07 and ZSCRC10 (Table 1), respectively. The four powder mixtures were ball-milled using SiC milling media and ethanol for 24 h, and the resulting slurries were then dried.

The obtained powder mixtures were hot-pressed using an apparatus comprising a high-frequency induction furnace in a BN-coated graphite die in tablets 21 mm × 25 mm × 3.0 mm in size. The powder compacts were heated in a vacuum to 1650°C at a heating rate of ~15 °C/min. When the die temperature reached 1650°C, a uniaxial pressure of 20 MPa was applied. After hot-pressing at 1650°C for 60 min, the pressure load was removed, and the temperature was decreased to 500°C at a cooling rate of ~15 °C/min, and the sample was then cooled to room temperature in the furnace. The densities of the hot-pressed composites were measured using the Archimedes method with distilled water as the medium.

2.2 Characterizations

X-ray diffraction (XRD) was used to identify any crystalline phases present in the prepared composites. The microstructure of the composites was characterized by field emission scanning electron microscopy (FE-SEM). The grain size, d, of ZrB₂ and SiC in the composites was determined by measuring the average linear intercept length, dᵢn, of the grains in FE-SEM images of the composites, using the relationship \( d = 1.56dᵢn \). The shear modulus, G, Young’s modulus, E, bulk modulus, B, and Poisson’s ratio, ν, of the composites were calculated using longitudinal and transverse soundwave velocities measured in the specimens with ultrasonic equipment (TDS 3052B, Tektronix Inc. Beaverton, OR, USA). The detailed calculations are reported elsewhere. The hardness, Hᵥ, and the fracture toughness, KᵥC, of the composites were determined using indentation crack size measurement.

Indentation tests were performed on the polished surfaces of the specimens by loading a Vickers indenter for 15 s at room temperature. The corresponding diagonals of the indentation and the crack sizes were measured using an optical microscope attached to the indenter. An indentation load of 98 N was applied, and ten indentations were made for each measurement. The fracture toughness of the composites was calculated from the Anstis equation.

Specimens averaging 25 mm × 2.5 mm × 2 mm in size were cut from the hot-pressed plates using a diamond grinder. The surfaces of the specimens were ground with an 800-grit diamond wheel, after which one of the large surfaces was polished with diamond paste down to 1.0 μm. The flexural strength was measured using a four-point bending test fixture (inner span 10 mm and outer span 20 mm) at room temperature. The polished surface of the specimen was used as the tensile surface for the bending test. The bending test was performed using an Autograph testing system (AG-X/R, AG-100KND, Shimadzu, Kyoto, Japan) with a crosshead speed of 0.5 mm/min. At least five specimens were utilized for each measurement. After testing, the fracture surface was examined using an FE-SEM.

3. Results and discussion

3.1 Densification

The densities of the hot-pressed composites were determined using the Archimedes method to be 5.33 g/cm³ for ZSCRC03, 5.35 g/cm³ for ZSCRC05, 5.34 g/cm³ for ZSCRC07 and 5.36 g/cm³ for ZSCRC10; the corresponding relative densities were ~96.4, 96.5, 96.2 and 96.3%, respectively. It is seen that densities exceeding 96% are obtained at 1650°C for 60 min at 20 MPa in a vacuum for the four powder mixtures independent of the Cr₇C₃ content. Previous studies of ZrB₂–SiC composites without additives showed that densification of the composites via hot-pressing or spark plasma sintering required a temperature of 1900°C or higher. Obviously, the addition of Cr₇C₃ substantially improved the sinterability of ZrB₂–SiC composites. In order to compare the effect of additives on densification, data reported elsewhere for ZrB₂–SiC composites with and without various additives consolidated via hot-pressing are summarized in Table 2. It is seen that the sinterability of ZrB₂–SiC composites was improved by the addition of carbides, nitrides and transition metal disilicides, and that the improvement was strongly dependent on the additives used. Densities exceeding 99%
were obtained at 1900°C for 60 min at 30 MPa in Ar for ZrB2–20 vol% SiC composites with 5 vol% VC or WC. For ZrB2–30 vol% SiC composites with 2 wt% B2C, full densification was achieved by hot-pressing at 1950°C and 32 MPa for 10 min in Ar. The addition of 3 vol% Y2O3 or Yb2O3, moreover, makes it possible to achieve almost fully dense ZrB2–20 vol% SiC (RD: >99%) compacts at 1900°C and 30 MPa for 60 min in Ar. Compared with carbides and the rare-earth oxides, the addition of AlN, Si3N4 or MoSi2 could further improve the sinterability of ZrB2–SiC composites. It is reported that hot-pressing of ZrB2–20 vol% SiC composites with 4 vol% Si3N4 required 1870°C for 10 min at a pressure of 30 MPa. Similarly, hot-pressing of ZrB2–20 vol% SiC composites with 5–10 vol% AlN required 1850°C for 60 min at a pressure of 30 MPa. For ZrB2–20 vol% SiC composites with 20 vol% MoSi2, moreover, a density of ~95% was obtained by hot-pressing at 1800°C for 30 min under 30 MPa in a vacuum. The improvement of densification due to the additives is attributable to the removal of oxygen impurities present in the starting powder and to the formation of an intergranular liquid phase that favors the process of grain rearrangement and improves the packing density of the particles.

A recent study of the ZrB2–Cr3C2 system revealed that the addition of Cr3C2 to ZrB2 reduced the densification temperature from 2200 to 1500–1750°C, depending on the Cr3C2 content. The same study showed that an intensive contact interaction between ZrB2 and Cr3C2 grains occurred at ~1310°C, accompanied by the formation of a diffusion zone due to the diffusion of Cr and C from Cr3C2 into ZrB2. In addition, two possible eutectic phases of Cr3C2–Cr and ZrB2–Cr are formed within the diffusion zone. Their melting points are ~1530°C for Cr3C2–Cr and ~1550°C for ZrB2–Cr. In this study, therefore, the lower temperature densification of the ZrB2–20 vol% SiC composites with Cr3C2 additives is presumably associated with the formation of the eutectic liquid phase and with increased diffusion in the phase contact zones. It is known, furthermore, that ZrO2 film, which inhibits densification in non-oxide ceramic systems, is commonly present on the surfaces of the starting ZrB2 particles. An interaction of ZrO2 and Cr3C2 should occur, during sintering resulting in the elimination of oxygen impurities (ZrO2) present on the surfaces of the starting ZrB2 particles and reducing the sintering temperature as a result.

The eutectic liquid phase formed between the ZrB2 and Cr3C2 interfaces vanishes during sintering, however, due to the formation of new high refractory phases by the interaction of ZrB2 and Cr3C2 according to the following reaction:

\[ \text{ZrB}_2(s) + \text{Cr}_3\text{C}_2(s) \rightarrow \text{ZrB}_2(\text{residual}) + \text{ZrC}(s) + \text{CrB}(s) \]  

where ZrB2 (residual) is the residual ZrB2 phase after the interactions between ZrB2 and Cr3C2 at the ZrB2/Cr3C2 grains-boundary contact zones. The formation of ZrC and CrB led to formation of a liquid phase disappearing upon further phase interactions with formation of new high refractory compounds of ZrC and CrB. After the formation of the ZrC and CrB phases, the main densification mechanism transferred from the contact melting between the ZrB2 and Cr3C2 interfaces to the diffusion in the final stage. This transition of the densification mechanism makes it difficult to achieve a theoretical density of 100% at 1650°C for the ZrB2–20 vol% SiC-based composites with Cr3C2 additives investigated in this study. Thus, it might be expected that increasing the sintering temperature would be more effective than extending the holding time for further improving densification of the composites investigated in this study because of the formation of ZrC and CrB with a high-melting point.

### Table 2. Comparison of the final densities of hot-pressed ZrB2–SiC composites with and without various additives

| Compositions | Additives | Hot-pressing conditions | Final density (%) | References |
|--------------|-----------|-------------------------|------------------|------------|
| ZrB2–20 vol% SiC | No additive | 2000°C/60 min/20 MPa/vacuum | >97 | 12 |
| ZrB2–20 vol% SiC–(3–10) wt% Cr3C2 | Cr3C2 | 1650°C/60 min/20 MPa/vacuum | >96 | Present work |
| ZrB2–20 vol% SiC–4 vol% Si3N4 | Si3N4 | 1870°C/10 min/30 MPa/vacuum | 98 | 25 |
| ZrB2–20 vol% SiC–5 vol% VC | VC | 1900°C/60 min/30 MPa/argon | >99 | 21 |
| ZrB2–20 vol% SiC–20 vol% MoSi2 | MoSi2 | 1800°C/30 min/30 MPa/vacuum | 94.6 | 14, 15 |
| ZrB2–20 vol% SiC–3 vol% Y2O3 | Y2O3 | 1900°C/60 min/30 MPa/vacuum | 99.1 | 24 |
| ZrB2–20 vol% SiC–3 vol% Yb2O3 | Yb2O3 | 1900°C/60 min/30 MPa/argon | 99.7 | 24 |
| ZrB2–20 vol% SiC–5 vol% WC | WC | 1900°C/60 min/30 MPa/argon | >99 | 22 |
| ZrB2–20 vol% SiC–(5–10) vol% AlN | AlN | 1850°C/60 min/30 MPa/argon | >97 | 26 |
| ZrB2–30 vol% SiC–2 wt% B4C | B4C | 1950°C/10 min/32 MPa/argon | 100 | 23 |

3.2 Microstructural characterization

Figure 1 displays the XRD patterns of the ball-milled powder mixture and the hot-pressed composites. Before hot-pressing [Fig. 1(a)], only the ZrB2, SiC and Cr3C2 phases were detected. Among these detectable phases, ZrB2 is the primary phase, while SiC is the secondary phase and Cr3C2 is the minor phase. After hot-pressing [Figs. 1(b)–1(e)], new ZrC and CrB phases were detected in addition to ZrB2 and SiC, with no detectable Cr3C2 phase. The ZrB2 phase is presented as the primary phase, SiC with ZrC as the secondary phase and CrB as the minor phase. The presence of the ZrC and CrB phases indicates that the reactions of ZrB2 with Cr3C2 occurred during sintering. In addition, the peak intensities of the ZrB2 phase decreased as the amount of Cr3C2 additives increased.
because of the interactions of ZrB₂ with Cr₃C₂ during sintering, while the peaks of the ZrC and CrB phases intensified. This result suggests that the ZrB₂ phase content decreased with increase in Cr₃C₂ additives, while the ZrC and CrB content increased. Reaction behavior in a ZrB₂–Cr₃C₂ system has previously been reported elsewhere. Grigoriev et al.¹⁷) showed that when ZrB₂ ceramics with Cr₃C₂ additives were sintered between 1500 and 1750°C, new high-temperature refractory compounds of ZrC and CrB were formed by consuming the eutectic liquid phases in the diffusion zone produced at the ZrB₂/Cr₃C₂ grain boundaries, due to an intense diffusion of C and Cr from Cr₃C₂ to ZrB₂. The phase compositions determined by XRD for the hot-pressed composites are summarized in Table 1.

**Figure 2** presents backscattered FE-SEM micrographs of the microstructures of the four composites. The general microstructures of the four composites are similar in morphology. The composite microstructures consist of equiaxed ZrB₂ (grey contrast), fine SiC (dark contrast), ZrC (white-grey contrast) and irregular CrB (dark-grey contrast) grains. In addition, the ZrB₂ and SiC grains became gradually finer with increase in the amount of Cr₃C₂ (Table 1), with a grain size range of 2.18–2.76 and of 1.12–1.45 µm, respectively. By comparison, an earlier study of hot-pressed ZrB₂–20 vol% SiC with 5 vol% Yb₂O₃ additives showed that ZrB₂ and SiC grains in the starting powder grew from 2 and 0.7 µm, respectively, to ~10 and ~3.9 µm after hot-pressing at 1850°C for 60 min under 30 MPa in a vacuum.²⁷) After spark plasma sintering at 1900°C for a holding time of 4 min, the ZrB₂ and SiC grains were significantly coarsened,²⁷) with a grain size of ~4.5 and ~2.1 µm, respectively. This comparison indicates that the addition of Cr₃C₂ inhibits the coarseness of the ZrB₂ and SiC grains during sintering. Presumably, the grain growth-inhibiting effect due to the addition of Cr₃C₂ is associated with the following three factors: (i) a lower densification temperature, (ii) elimination of oxygen impurities which promote grain growth in non-oxide ceramic systems, and (iii) formation of new ZrC and CrB phases which limit grain growth. The microstructures of the composites were also observed in the secondary-electron image; typical FE-SEM micrographs are shown in **Fig. 3**. Trace quantities of pores were found in the four composites, and the pores were mainly present in the
multi-grain pockets consisting of ZrB$_2$, SiC, ZrC and/or CrB grains (indicated by the arrows in Fig. 3). The presence of the pores in the multi-grain pockets may be associated with the rapidly vanishing eutectic liquid phase formed between the ZrB$_2$ and Cr$_3$C$_2$ interfaces during sintering.$^{17}$ The disappearance of the eutectic liquid phase led to difficult densification at 1650°C, causing the pores to remain in the multi-grain pockets after sintering. Further SEM observations of the microstructures of the four composites show the presence of long-range defects in them [Figs. 4(a) and 4(b)]. These defects’ sizes were determined to be 35–60 μm for ZSCRC03, 30–75 μm for ZSCRC05, 50–85 μm for ZSCRC07 and 40–80 μm for ZSCRC10. Under higher-magnification FE-SEM observation, it is seen that the defects contain many larger pores [indicated by the arrows in Figs. 4(c) and 4(d)]. In addition, the backscattered FE-SEM images of the defects (Fig. 5) show the presence of a large amount of the CrB (dark-grey contrast) and/or ZrC (white contrast) phases in the defect zones, compared to the non-defect zones (Fig. 2). These observations indicate that the long-range defects were large pore-containing agglomerates of the sintering phases formed during sintering. These large porous agglomerates of the sintering phases were probably traces of the blocks of the eutectic liquid phase, produced due to the interactions between the ZrB$_2$ and Cr$_3$C$_2$ during sintering. The consumption of the eutectic liquid phases during sintering by the formation of a large amount of CrB and ZrC makes densification difficult at 1650°C, and large porous agglomerates of the sintering phases are formed as a result.

3.3 Elastic and mechanical properties

3.3.1 Elastic moduli, hardness and fracture toughness

Table 3 summarizes the elastic properties of the hot-pressed composites. The shear modulus, Young’s modulus, bulk modulus and Poisson’s ratio obtained for these composites remain nearly constant, regardless of the Cr$_3$C$_2$ content. The Poisson’s ratio value for each of the four composites is the same. The weak compositional dependence of the elastic properties indicates that the addition of 3–10 wt % Cr$_3$C$_2$ had no significant effect on the elastic properties, because the elastic moduli of the materials are insensitive to the amount of additives$^{19}$ but strongly dependent upon the pore volume.$^{28}$ The elastic moduli of the composites are comparable to those of ZrB$_2$–SiC composites (10–30 vol % SiC) and ZrB$_2$–ZrC–SiC composites.$^{28}$–30

The hardness and fracture toughness of the composites

![Fig. 4](image_url) Typical examples of FE-SEM images of defects in (a, c) ZSCRC05 and (b, d) ZSCRC10: (a, b) low-magnification, and (c, d) higher-magnification.

![Fig. 5](image_url) Higher-magnification backscattered FE-SEM images of defects in composites: (a) ZSCRC05 and (b) ZSCRC10.

| Materials | $G$ (GPa) | $E$ (GPa) | $B$ (GPa) | $H$ (GPa) | $K_I$ (MPa m$^{1/2}$) | $\sigma_f$ (MPa) |
|-----------|-----------|-----------|-----------|-----------|----------------|---------------|
| ZSCRC03   | 202       | 452       | 198       | 18.7 ± 1.1 | 4.7 ± 0.5       | 477.8 ± 21.6  |
| ZSCRC05   | 200       | 449       | 197       | 19.8 ± 1.0 | 4.7 ± 0.6       | 523.3 ± 88.3  |
| ZSCRC07   | 203       | 454       | 199       | 18.2 ± 1.1 | 4.5 ± 0.8       | 426.2 ± 24.7  |
| ZSCRC10   | 205       | 460       | 202       | 20.9 ± 1.2 | 4.9 ± 0.4       | 447.1 ± 71.8  |
were determined by indentation crack size measurements, and the obtained values are listed in Table 3. The hardness of the composites gradually increased with increase in the Cr$_3$C$_2$ content within a hardness range of 18.2–20.9 GPa. These hardness values are lower than those of ZrB$_2$–SiC (10–30 vol % SiC) composites ($H_v = 24$ GPa), but they are higher than those of ZrB$_2$–20 vol % SiC composites with Yb$_2$O$_3$ additives ($H_v = 17$ GPa) and comparable to those of ZrB$_2$–ZrC–SiC composites ($H_v = 19$–22 GPa). On the other hand, the fracture toughness values of the composites were measured at 4.5–4.9 MPa m$^{1/2}$, showing only a slight sensitivity to the Cr$_3$C$_2$ content; this insensitivity suggests that the presence of ZrC and CrB did not substantially affect the fracture toughness of the composites. The fracture toughness of the hot-pressed single-phase ZrB$_2$ was reported to be 2.3 to 3.1 MPa m$^{1/2}$. Also, the fracture toughness values for the hot-pressed ZrB$_2$–SiC (10–30 vol % SiC) composites were reported to be between 4.1 and 5.3 MPa m$^{1/2}$. The fracture toughness values of the composites obtained in this study are therefore higher than those of single-phase ZrB$_2$ ceramics and comparable to those of ZrB$_2$–SiC composites, but lower than those of ZrB$_2$–ZrC–SiC composites ($K_{IC} = 4.6$–6.1 MPa m$^{1/2}$).

3.3.2 Flexural strength

The room-temperature flexural strengths measured for the composites are also summarized in Table 3. Unlike the elastic moduli and the fracture toughness, the flexural strengths obtained from the four composites are significantly dependent on the Cr$_3$C$_2$ content. The ranges of the flexural strength values were measured as 425 to 523 MPa. The maximum strength value of 523 MPa was observed in ZSRCRC05. This value is comparable to those of the ZrB$_2$ ceramics or ZrB$_2$–20 vol % SiC composites consolidated by hot-pressing.

For three other compositions, the strength values were lower than 500 MPa, and the minimum value of 425 MPa was obtained for ZSRCRC07. These strength values are lower than those reported for ZrB$_2$ ceramics or ZrB$_2$–20 vol % SiC composites.

FE-SEM observations were carried out on the fracture surfaces of specimens to examine the fracture origin of the various materials; typical micrographs are shown in Fig. 6. It is evident that the fracture origin is located at the defects in the surface [indicated by the arrows in Figs. 6(a) and 6(b)]. Under higher-magnification FE-SEM observation [Figs. 6(c) and 6(d)], it is clear that the defects contain a large number of porosities. Microstructural observation of the composites shows the presence, moreover, of large-range porous agglomerates in the sintering phases in the four composites (Fig. 4). The sizes of the agglomerates are, moreover, linked with the Cr$_3$C$_2$ content. The major cause of failure was presumably the presence of the large-range porous agglomerate defects in the sintering phases on the surface, the size of which defects governed the fracture strength of the composites. Because the formation of large agglomerates of the sintering phase which acted as critical defects, future investigations will seek to improve the fracture strength by eliminating or minimizing the large-range agglomerates present in the composites by further improving densification of the composites at higher sintering temperatures.

Figure 7 presents FE-SEM micrographs of the fracture surfaces for the four composites, showing that the fracture surfaces of all the samples have similar features. The fracture surfaces are somewhat rough, with protruding fine SiC grains and open sockets left by grain pull-out. The fracture surfaces of hot-pressed single-phase ZrB$_2$ or ZrB$_2$–SiC composites without Cr$_3$C$_2$ addition do not exhibit similar features, as their fracture surfaces are relatively flat. This difference indicates that the protruding grains are more pronounced for ZrB$_2$–SiC composites with Cr$_3$C$_2$ additives compared to ZrB$_2$–SiC composites alone, which suggests that the intergranular bonding is weaker for the former than for the latter. The weak intergranular bonding due to Cr$_3$C$_2$ additives may be associated with the following two factors: (i) formation of new CrB and ZrC
phases at the grain boundaries during sintering; and (ii) a complex residual stress state developed during cooling from the processing temperature accompanying the formation of the CrB and ZrC phases. Because the amount of the CrB and ZrC phases formed at the grain boundaries during sintering increased with increase in Cr$_3$C$_2$ additives (Fig. 1), the intergranular bonding seems to weaken as the amount of Cr$_3$C$_2$ increases. Presumably, the weaker intergranular bonding degrades the strengthening effect of SiC particles in ZrB$_2$–SiC composites with Cr$_3$C$_2$ additives, resulting in lower strength.

4. Conclusions

(1) The addition of Cr$_3$C$_2$ significantly improved the sinterability of ZrB$_2$–20 vol% SiC composites. Densities of ~96% were obtained by hot-pressing at 1650°C under a pressure of 20 MPa in a vacuum for a holding time of 1 h, regardless of the Cr$_3$C$_2$ content.

(2) The obtained composites comprised ZrB$_2$, SiC, CrB and ZrC phases, with no Cr$_3$C$_2$ phase. The addition of Cr$_3$C$_2$ significantly inhibited the growth of ZrB$_2$ and SiC grains during sintering.

(3) The Young’s modulus, shear modulus, bulk modulus and Poisson’s ratio of the composites remained constant, regardless of the Cr$_3$C$_2$ content.

(4) The hardness of the composites increased gradually with increase in the Cr$_3$C$_2$ content, but the fracture toughness of the composites remained constant.

(5) The flexural strength of the composites was in the range of 426–523 MPa, depending on the Cr$_3$C$_2$ content. The maximum strength value was obtained for ZSCRC05, while the minimum value was observed in ZSCRC07. Lower composite strength was associated with the presence of defects.

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