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Fabrication and properties of reactively hot pressed ZrB_2–SiC ceramics

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Abstract

ZrB_2–SiC ceramics with relative densities >99% were fabricated by 'in situ' reactive hot pressing from ZrH_2, B_4C and Si. The reaction was studied using two processes, (1) powder reactions at temperatures from 1150 to 1400 °C and (2) reactive hot pressing between 1600 and 1900 °C. The products from the reaction of a $2ZrH_2$:$1B_4C$:1Si molar mixture were ZrB_2, SiC, ZrO_2 and ZrC. Modification of the composition to $2ZrH_2$:$1.07B_4C$:1.16Si resulted in the elimination of the undesired ZrO_2 and ZrC phases. The final composition was approximately ZrB_2–27 vol% SiC with no undesired phases detected by X-ray diffraction, and only low concentrations of B_4C detected by scanning electron microscopy. Elimination of the undesired phases was accomplished by removing surface oxides through chemical reactions at elevated temperatures. Reactively hot pressed samples consisting of ZrB_2 with 27 vol% SiC had a Young's modulus of 508 GPa, a flexure strength of 720 MPa, a fracture toughness of 3.5 MPa $m^{1/2}$ and a Vickers' hardness of 22.8 GPa.

Keywords: Reactive hot pressing; Borides; SiC; Microstructure-final; Mechanical properties

1. Introduction

Transitional metal borides and carbides are considered candidates for structural applications exceeding 2250 °C due to their high melting temperatures.[1] The high percentage of covalent bonding in zirconium diboride (ZrB_2) results in a high melting temperature (3050 °C), high strength (565 MPa) and resistance to chemical attack.[2,3] The high strength, combined with high room temperature thermal conductivity (~60 W/m K^2), indicate the potential for good thermal shock resistance. The high electrical conductivity of ZrB_2 (10^8 S/m) is sufficient for electrical discharge machining (EDM) allowing for relatively low cost machining of complex components.[2] Though resistant to chemical attack, oxidation at temperatures greater than 650 °C may be a problem for applications in atmospheric conditions.[4,5] Improvements to the oxidation resistance of ZrB_2 can be accomplished with the addition of 10–30 vol% silicon carbide (SiC) particulates as a second phase.[6–9] In addition to the improved oxidation resistance, the SiC particulates increase the strength and fracture toughness of ZrB_2 ceramics at room temperature.[3,9] Significant decreases in the strength at temperatures exceeding 1200 °C have been reported for ZrB_2–SiC materials.[10–14] One possible cause of this loss in strength is the existence of grain boundary phases, most likely glassy oxides, that result in limited creep resistance and reduced strengths at elevated temperatures.

Densification of ZrB_2–SiC ceramics typically requires temperatures of 1900 °C or higher and applied pressures of 20 MPa or more.[14] Sintering aids including $MoSi_2$, Ni, TiB_2, B_4C, Si_3N_4, Al_2O_3 and Y_2O_3 have been added to enhance the sinterability of ZrB_2-based ceramics.[10,11] Chamberlain et al. achieved fully dense conventionally hot pressed ZrB_2 with 20 and 30 vol% SiC with strengths (four-point bend flexure) greater than 1 GPa and toughness values in the range of 4.4–5.3 MPa $m^{1/2}$.[3] The processing of these materials included high energy attrition milling of the starting powders that led to the incorporation of residual WC into the final ceramic, which may have contributed to the enhanced mechanical properties.

Displacement reactions have also been used to fabricate boride ceramics. A potential advantage to reactive processing is the potential elimination of the oxides, normally found at the grain boundaries, which could provide higher strengths at tem-

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peratures greater than 1200 °C, a temperature where ZrB_2–SiC ceramics have shown a sharp decrease in strength in previous studies.[10–14] Reaction synthesis of TiB_2–(β)SiC ceramics has been accomplished by reactive hot pressing of TiH_2, B_4C and Si.[15] Zhang et al. investigated the reaction of stoichiometric amounts Zr, B_4C and Si to form ZrB_2 and 25 vol% α-SiC.[16] The reactively hot pressed ZrB_2–25 vol% SiC had a flexural strength (three-point bending) of 506 MPa and a fracture toughness of 4.0 MPa $m^{1/2}$, which are both significantly lower than the highest reported values for ZrB_2–SiC hot pressed from commercially available ZrB_2 and SiC powders.[3] The current study investigates the fabrication of ZrB_2–SiC ceramics using reactive hot pressing. A ternary displacement reaction with ZrH_2, Si and B_4C was used to produce ZrB_2–SiC composites. The adiabatic temperature of the displacement reaction with ZrH_2 was 1310 °C compared to 2870 °C if zirconium metal were used, indicating a more controllable reaction. This paper reports the processing conditions, mechanical strength, elasticity, hardness and toughness for ZrB2–SiC produced by reactive hot pressing and compares the results to other recent reports of similar materials produced from commercially available ZrB_2 and SiC powders. This study reports strengths comparable to previously reported strengths for conventional, hot pressed ZrB2–SiC materials. Furthermore, mechanisms which form ZrO_2 and ZrC contaminants in similar materials have been identified, allowing for the possible elimination of these contaminant phases.

2. Experimental procedure

Commercially available ZrH_2, Si and B_4C powders (Table 1) were used as precursors. In this study, three different batch compositions were prepared (Table 2). The stoichiometric composition (S) was prepared along with an intermediate composition (I) and a final composition (F). The stoichiometric formulation had a ZrH_2:B_4C:Si molar ratio of 2:1:1, based on the stoichiometry of Reaction 1. The I composition contained excess B_4C and Si compared to the S composition giving it a molar ratio of $2ZrH_2$:$1.94B_4C$:1.42Si. Composition F contained excesses of 0.7 mol% B_4C and 2.3 mol% Si and had a reduction of ZrH_2 content of 3 mol% compared to the S composition resulting in a molar ratio of $2ZrH_2$:$1.09B_4C$:1.16Si.

$$2ZrH_2 + B_4C + Si \rightarrow 2ZrB_2 + SiC + 2H_2 \quad (1)$$

Precursor powders were ball milled in ethanol for 48 h using SiC milling media in a high-density polyethylene (HDPE) bottle. Rotary evaporation was used to separate the milled powder from the slurry, following by sieving (to 75 μm), to minimize powder segregation and agglomeration.

Two methods were used to react the precursor powders, powder reactions and reactive hot pressing. Powder reaction studies were carried out using pellets ∼10 mm in diameter and ∼3 mm in height that were isostatically pressed using a pressure of 300 MPa. During the reaction, the bottoms of the pellets were in contact with the graphite crucible, but the sides and tops of the pellets had no contact with the crucible. The graphite crucible was covered loosely with graphite foil. Pellets of each composition (S, I and F) were heated at 10 °C/min to 1400 °C in flowing argon. Pellets were held at 1400 °C for 120 min and then cooled at ∼25 °C/min to room temperature. Additional pellets of the S composition were heated to 1150, 1300 and 1450 °C to characterize the intermediate reactions.

Based on the powder reaction studies, samples were fabricated from the S and F compositions by hot pressing (Allaria, Type GE, Torino, Italy). An isostatically pressed green billet was loaded into a BN coated graphite hot press die and heated at ∼10 °C/min in vacuum (∼75 m Torr). The samples were heated to 1400 °C and held for 60 min for reaction. After the hold, a 30 MPa pressure was applied and maintained while ramping at 10 °C/min to 1890 °C. The samples were pressed for an additional 10 min at 1890 °C for densification. Round billets, with a thickness of 10 mm and a diameter of 32 mm, were fabricated to determine the product phases and density. Rectangular billets with a thickness of 6 mm, a width of 48 mm, and a length of 32 mm were hot pressed (Thermal Technologies, HP20-3060, Santa Rosa, CA) to obtain mechanical test bars. An alternative hot press schedule (Fig. 1) was used to allow for the removal of volatile gases during the processing of the larger billets. Billets

Table 1
Size, grade and manufacturer of starting powders

Starting powder	Particle size (μm) (D50)	Grade/manufacturer	Purity (from manufacture assay)
ZrH_2	2	Grade C, Chemetall, Frankfurt, Germany	95% ZrH_2, 2% HfH_2, 0.5% Si, 0.25% Mg, 0.15% Ti, 0.1% Al, 0.07% Fe, 0.01% Ca
B_4C	0.8	Grade HS, H.C. Starck, Newton, MA	0.44% N, 1.34% O, 0.03% Fe, 0.05% Si, 0.01% Al
Si	3.5	Grade AX5, H.C. Starck, Newton, MA	High purity (99.995%)

Table 2
Batch compositions reacted to form ZrB_2–SiC ceramics

	Stoichiometric (S)			Intermediate (I)			Final (F)		
	Wt%	Vol%	Mol%	Wt%	Vol%	Mol%	Wt%	Vol%	Mol%
ZrH_2	69.1	49.5	50.0	57.1	37.0	39.2	66.7	46.7	47.0
B_4C	20.5	32.6	25.0	32.9	47.4	38.1	21.6	33.6	25.7
Si	10.4	17.9	25.0	10.0	15.6	27.8	11.7	19.7	27.3

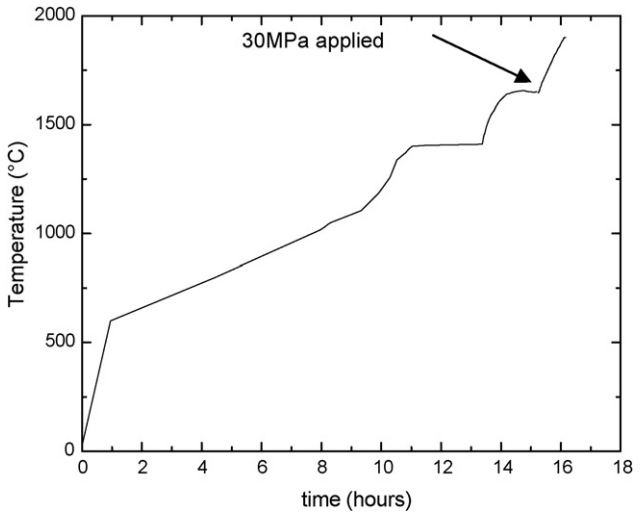

Fig. 1. The temperature profile for reactive hot pressing of large billets, which required 16 h to reach 1890 °C.

prepared for mechanical testing were machined into flexure bars (45 mm × 4 mm × 3 mm) with a 600 grit finish.

The phases produced by the reactions were characterized using X-ray diffraction (Scintag, XDS 2000, Cupertino, CA). The reaction samples were crushed and ground using an agate mortar and zirconia pestle. Spectra were obtained by scanning from 3° to 90° 2θ at 0.03° per step with a 1 s count time. The bulk reactive hot pressed parts were also evaluated using X-ray diffraction analysis of a 2 mm thick cross section diced from the middle of the 32 mm round billet.

Scanning electron microscopy (SEM; Leica Cambridge, S360, UK) with energy dispersive spectroscopy (EDS; Oxford Instruments, INCA 300, UK) was used to characterize the microstructure and chemical composition of hot pressed samples. The specimens were polished to a 0.25 μm finish and were mechanically etched using colloidal silica. An accelerating voltage of 6 kV was used for phase identification to allow for adequate phase contrast. The final SiC content in the ZrB_2–SiC samples prepared by reactive hot pressing of the S and F compositions was determined by areal analysis using Image J (National Institutes of Health, USA) of micrographs from areas randomly selected within the samples.

Density values were calculated from Archimedes' measurements using deionized water as the immersion medium. The samples were submerged in a water bath and placed in vacuum (8000 Pa) for 24 h for infiltration. Hardness was measured by Vickers' indentation on polished surfaces using a 1 kg load with a hold of 20 s. Four-point bend flexure strength was calculated by averaging the strength of ten 3 mm × 4 mm × 45 mm chamfered flexure bars (type 'B'; ASTM C 1161). The flexure fixture had a 40 mm outer span and a 20 mm inner span, and testing was conducted at a loading rate of 0.5 mm/min. Young's modulus was measured using the resonance frequency method (ASTM C 1198-01) with the samples suspended by thread connected to electrical transducers. Direct crack fracture toughness values were calculated using two equations in order to compare the current data to previous literature values. The Anstis Eq. (2)[17] is a common equation used to determine the toughness of ceramics. The Japanese Industrial Standard JIS R 1607 Eq. (3) was also used to calculate the toughness values comparable to previously reported values of reactively hot pressed ZrB_2–SiC materials.[16] The reported fracture toughness values are the average of ten Vickers's indentations using a 5 kg load for 20 s, sufficient to produce radial cracks from the corners of the indent.

$$K_{\mathrm{DCM}} = 0.016\left(\frac{E}{H}\right)^{1/2}\frac{P}{c_{\mathrm{I}}^{3/2}} \tag{2}$$

$$K_{\mathrm{DCM}} = 0.026\left(\frac{E\cdot P}{C^3}\right)^{1/2} a \tag{3}$$

where E is the Young's modulus (Pa), P the indentation load (gf), H the hardness (Pa), $c_{\mathrm{I}} = C$ the radial half crack length (m) and a is the indentation half crack length (m).

3. Results and discussion

X-ray diffraction analysis confirmed that ZrB_2 was formed in the stoichiometric samples heated to temperatures between 1150 and 1450 °C (Fig. 2a). Less intense peaks at 28.2°, 30.2°, 32.6°, 35.7° and 38.5° 2θ indicated that additional phases had formed including β-SiC, ZrC and ZrO_2 (Fig. 2b). Samples heated and held at 1150 °C reacted to form ZrB_2, ZrC and SiC, with traces of unreacted silicon (2θ = 28.7°, Fig. 2b). A mass loss of 1.3% was observed for this specimen, which was attributed to the decomposition of ZrH_2 to Zr and the resulting loss of H_2. A mass loss of 1.49% is predicted for Reaction 1.

For the S composition, the products included the expected ZrB_2 and SiC phases (according to Reaction 1) with some minor secondary products including ZrC, ZrO_2 and Si. The presence of ZrC and Si in the final composition indicated that the precursors were deficient in boron compared to Reaction 1. The boron deficiency probably resulted from the presence of oxide impurities (as B_2O_3) on the surface of the B_4C powder. Because it is a more reactive metal than Si, any free Zr will preferentially react with B, C or O species present to form a Zr compound and leave unreacted Si. In addition, ZrC is not stable in the presence of boron or B_4C as Reaction 4 is favorable at 1150 °C ($\Delta G^{\circ}_{\mathrm{rxn}} = -350$ kJ) as shown in Fig. 3. Thus, ZrB_2 and SiC should form if additional B_4C were added to the system (i.e., the I and F compositions). Because of the boron (B_4C) deficiency in the S formulation, ZrB_2 and ZrC form and are stable with silicon as indicated by the positive change in Gibbs' free energy of Reactions 5 and 6 at 1150 °C (Fig. 3).

$$2\mathrm{ZrC} + 3\mathrm{Si} + \mathrm{B_4C} \rightarrow 2\mathrm{ZrB_2} + 3\mathrm{SiC} \tag{4}$$

$$\mathrm{ZrC} + \mathrm{Si} \rightarrow \mathrm{SiC} + \mathrm{Zr} \tag{5}$$

$$2\mathrm{ZrB_2} + \mathrm{Si} \rightarrow \mathrm{SiB_4} + 2\mathrm{Zr} \tag{6}$$

The XRD pattern of the S composition heated to 1300 °C revealed no silicon peaks, an apparent increase in the amount of SiC, a decrease in the amount of ZrC, and the formation of ZrO_2. The reduction in the amount of ZrC and Si, relative to the sample reacted at 1150 °C, may be due to reactions involving

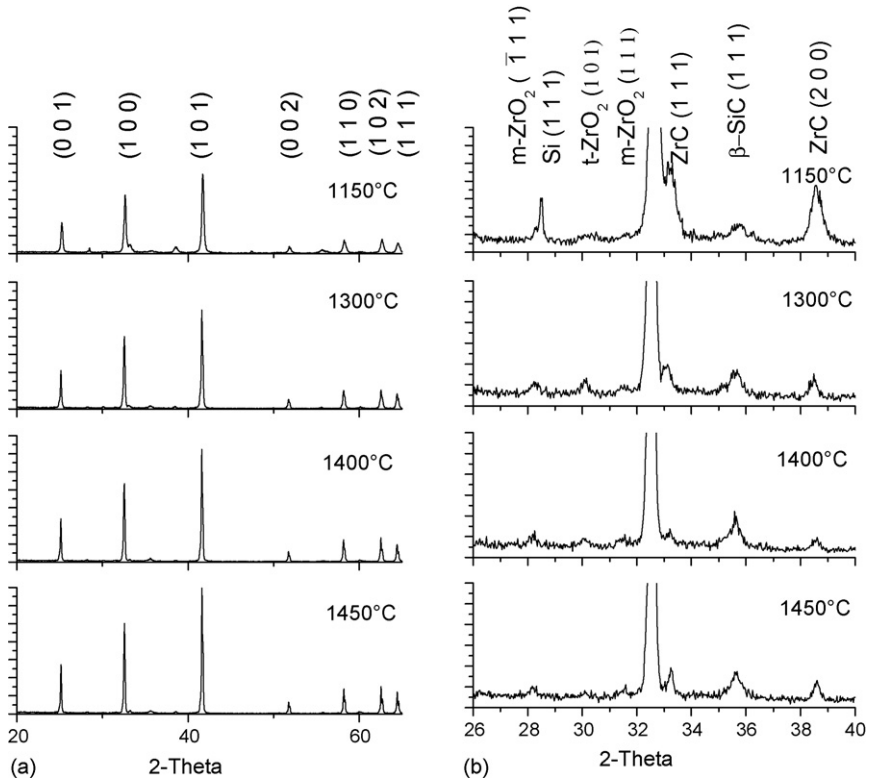

Fig. 2. X-ray diffraction patterns of S powder samples heated to 1150, 1300, 1400 and 1450 °C and held for 120 min showing (a) full patterns that confirm reaction products include the ZrB_2 phase and (b) magnification of the region between 26° and 40° confirming that β-SiC, ZrC and ZrO_2 are present.

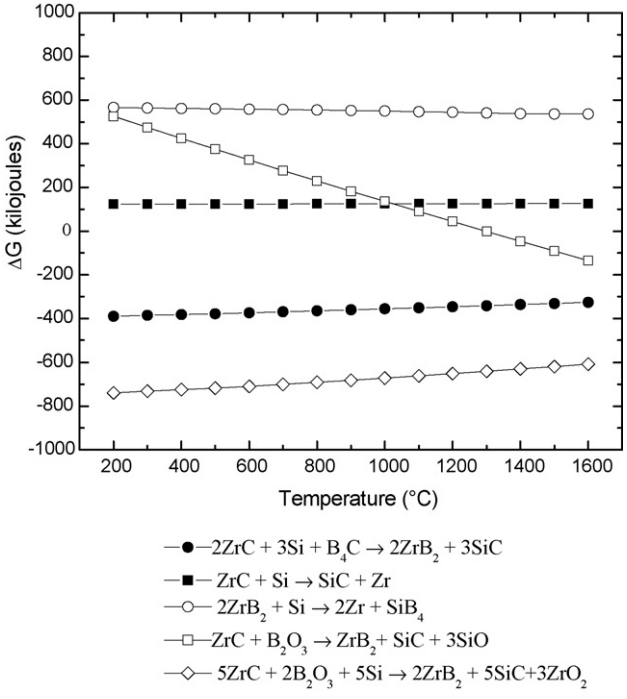

Fig. 3. Gibbs free energy as a function of temperature indicating favorable reactions for (●) Reaction 4 and (◊) Reaction 8 for temperatures between 200 and 1600 °C, a favorable reaction for (□) Reaction 7 above 1300 °C and unfavorable reactions for (■) Reaction 5 and (○) Reaction 6 at temperatures between 200 and 1600 °C.

B_2O_3 (an amorphous phase at room temperature not detectable by XRD) that become favorable in a flowing gas atmosphere that would keep the activity of SiO low (Reaction 7). The loss of SiO as a gaseous phase is consistent with the total mass loss of 1.5% observed at 1300 °C, compared to 1.3% (Fig. 4) for the sample reacted at 1150 °C and 1.49% predicted from Reaction

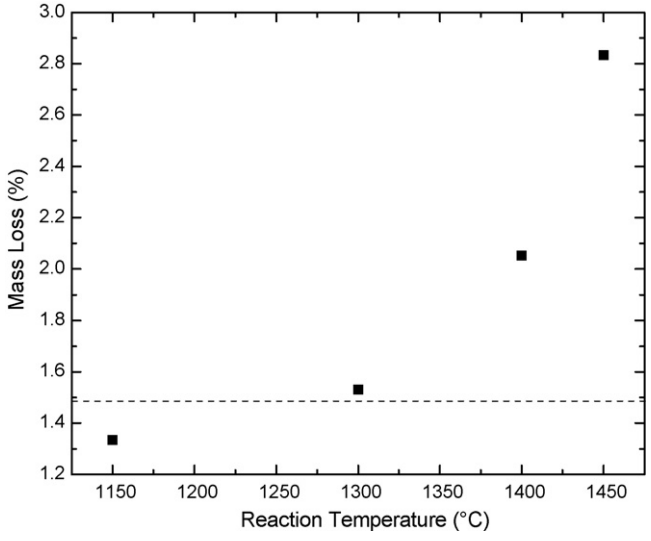

Fig. 4. Pellets of the stoichiometric (S) composition that were heated to temperatures between 1150 and 1450 °C showed higher mass loss at higher temperatures. The mass loss for the pellets that were heated at 1300, 1400 and 1450 °C was greater than the theoretical mass loss (horizontal line at 1.49%) from the loss of H_2 due to the decomposition of ZrH_2.

1. Reactions between ZrC and B_2O_3 could also result in the formation of ZrO_2 (Reaction 8). The XRD analysis and mass loss of the S composition heated to 1300 °C were consistent with the consumption of ZrC and B_2O_3 described by Reactions 7 and 8.

$$ZrC + B_2O_3 + 4Si \rightarrow ZrB_2 + SiC + 3SiO \quad (7)$$

$$5ZrC + 2B_2O_3 + 5Si \rightarrow 2ZrB_2 + 5SiC + 3ZrO_2 \quad (8)$$

Samples reacted at 1400 and 1450 °C had the same phases as observed at 1300 °C. Mass losses of 2.0% and 2.8% were measured (Fig. 4) for the samples reacted at 1400 and 1450 °C, respectively. The higher mass losses were attributed to volatilization of unreacted B_2O_3 and SiO, which was formed due to Reaction 7.

Ceramics produced by the reactive hot pressing of composition S had a density of 5.27 g/cm^3 (98% of the theoretical density of ZrB_2–25 vol% SiC). SEM micrographs revealed ZrB_2 with a grain size of ~6 μm containing SiC particles with an average size of ~3.5 μm that were uniformly dispersed in the ZrB_2 (Fig. 5). X-ray diffraction analysis showed the formation of ZrB_2, β-SiC, ZrC and ZrO_2 (Fig. 6), consistent with the phases observed in the powder samples. Evaluation of the SiC content by areal analysis of SEM images indicated a SiC content of only 22%, which is slightly lower than the 25% predicted by Reaction 1. The lower SiC content was attributed to the loss of Si due the formation of SiO (Reaction 7).

In order to eliminate the undesired ZrO_2 and ZrC phases, a second powder batch (I) was formulated with excess B_4C and Si. Excess B_4C supplied a sufficient amount of boron to react with all of the zirconium to minimize the formation of ZrC. This formulation also increased the zirconium to silicon molar ratio from 2:1 to 2:1.16 to accommodate Si loss due to SiO formation. Based on XRD analysis, the products of the reaction included ZrB_2, β-SiC and excess B_4C (Fig. 7). Neither ZrC nor ZrO_2 peaks were observed in the X-ray diffraction patterns.

The amount of B_4C present after hot pressing of composition I was determined by comparing the integrated peak areas for the

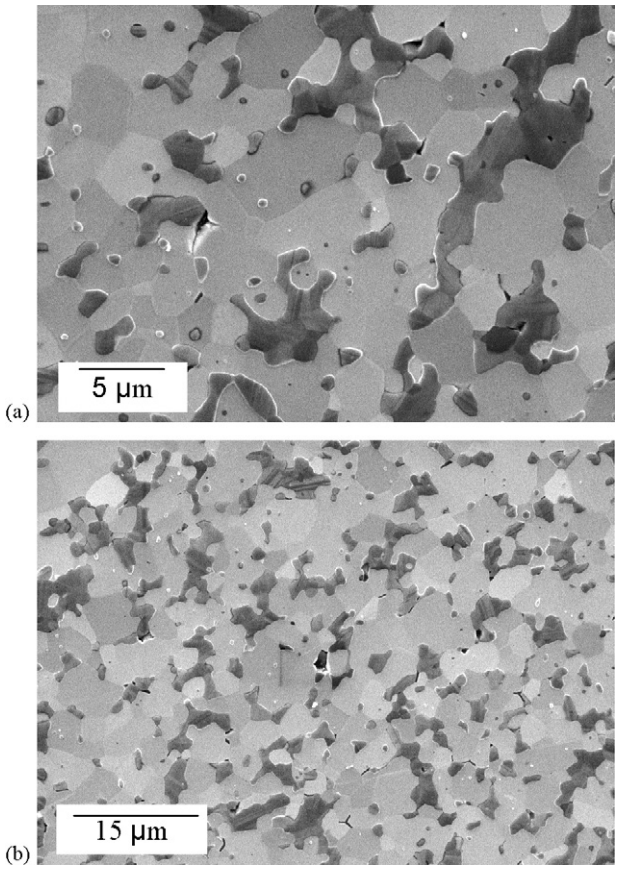

Fig. 5. SEM micrographs at (a) high and (b) low magnification showing the microstructure of ZrB_2–SiC produced by reactive hot pressing of the stoichiometric (S) powder mixture, the darker phase is SiC.

B_4C peaks at 37.7° for the unreacted and reacted samples. The reacted and unreacted samples had relative intensity areas of 76 and 176° cps, respectively, indicating that ~60% of the B_4C was consumed during reaction. This calculation was used to formulate the final composition, which was subsequently reacted at 1400 °C for 2 h. X-ray diffraction analysis detected only ZrB_2 and β-SiC after reaction (Fig. 8).

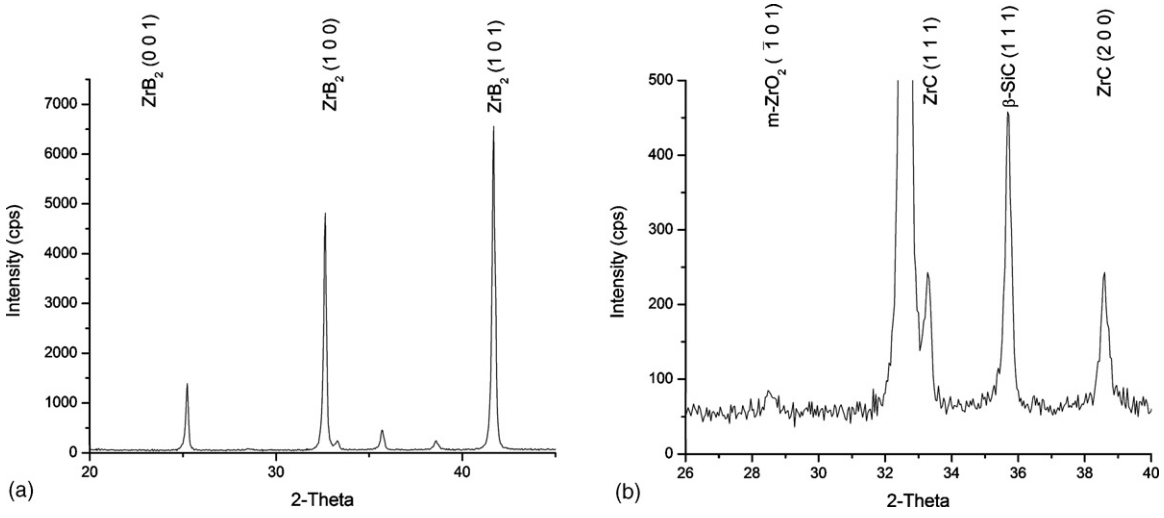

Fig. 6. X-ray diffraction patterns showing that ZrC and ZrO_2 are present after reactive hot pressing the stoichiometric (composition S) powder mixture.

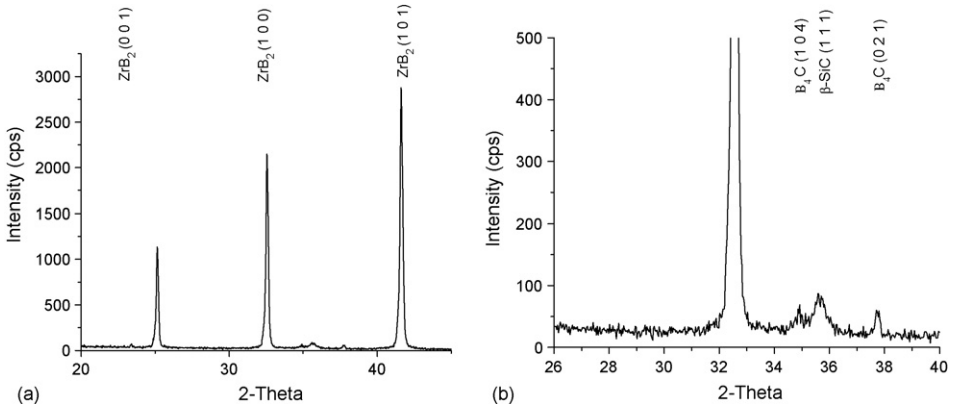

Fig. 7. X-ray diffraction patterns showing that ZrC and ZrO_2 were not detected for reaction mixtures containing excess B_4C and silicon (composition I).

As with the powder samples, XRD analysis (not shown) for the reactively hot pressed samples detected only ZrB_2 and β-SiC. SEM micrographs (Fig. 9) showed SiC dispersed in a ZrB_2 matrix with a slight excess of B_4C. The SiC particle size and the ZrB_2 grain size were estimated to be ∼1 and ∼2 μm, respectively. Areal analysis provided a SiC content of 27 ± 2 vol% and the measured density of the composite was 5.32 g/cm^3, indicating that a relative density of ∼100% was achieved by reactive hot pressing. The residual B_4C in the hot pressed specimen was less than 1 vol% and did not have a significant effect on the true density of the material. Based on areal analysis, composition F had a SiC content of ∼27 vol% after hot pressing. The slight increase in SiC content compared to the 25 vol% expected from the stoichiometry of Reaction 1 was due to the 2.3 mol% excess of silicon and 0.7% excess of B_4C compared to composition S. The higher SiC content, and the absence of ZrC and ZrO_2 peaks in the XRD pattern, indicate that the excess B_4C provided sufficient boron to fully react the Zr, Si and B_4C to produce only ZrB_2 and SiC.

A reduction in the size of both the ZrB_2 grains and the dispersed SiC particles was observed in going from the S to the F composition. The average grain size of the F composition was approximately the same as that of the starting ZrH_2 powder (∼2 μm). The larger average grain size of the S composition (∼6 μm) may indicate the presence of oxide phases in the grain boundaries that promoted grain growth during the hot pressing cycle. Both samples appeared to have a broad distribution of SiC particle sizes ranging from ∼0.5 to ∼10 μm. However, there was a lower mean SiC particle size in the F composition (∼1 μm) compared to the S composition (∼3.5 μm). The larger number of smaller SiC particles in the material produced from the F composition may have been more effective in pinning the grain growth than the smaller number of larger SiC particles observed in the material produced from the S composition.

The flexure strength, Vicker's hardness and Young's modulus of ceramics prepared from composition F were 720 ± 140 MPa, 22.6 ± 0.9 GPa and 508 ± 6 GPa, respectively. The hardness and elasticity values were similar to recently reported values for ZrB_2–30 vol% SiC processed by hot pressing commercially available ZrB_2 and SiC powders.[3] The minor differences between the elasticity and hardness values may be a result of the slightly lower SiC content, the presumed lower level of the oxide impurities, and the smaller grain size of the material produced by reactive hot pressing.

The Anstis and JIS R 1607 fracture toughness values were 3.5 and 4.1 MPa m$^{1/2}$, respectively. The toughness values were comparable to the results of Zhang et al.[16] who reported a JIS R1607 toughness value of 4.0 MPa m$^{1/2}$ for a material produced by reactive hot pressing. The Anstis fracture toughness value was significantly lower (∼34%) than the value of 5.3 MPa m$^{1/2}$ obtained by indentation strength in bending method that was

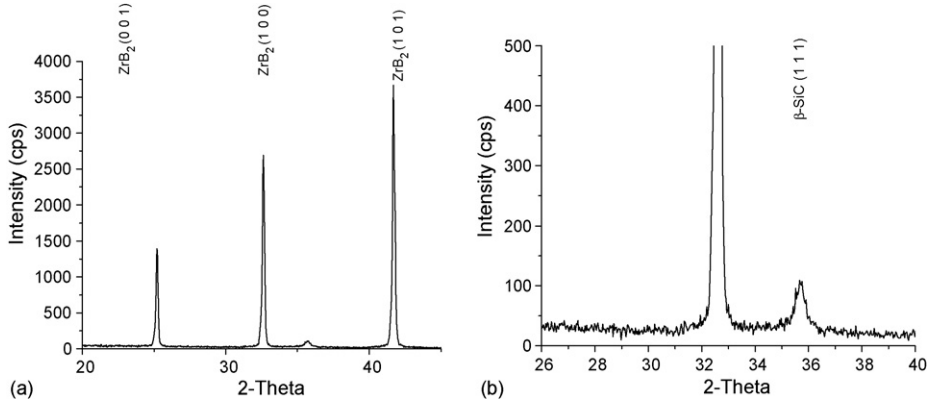

Fig. 8. X-ray diffraction patterns for composition F heated to 1400 °C detected only ZrB_2 and SiC.

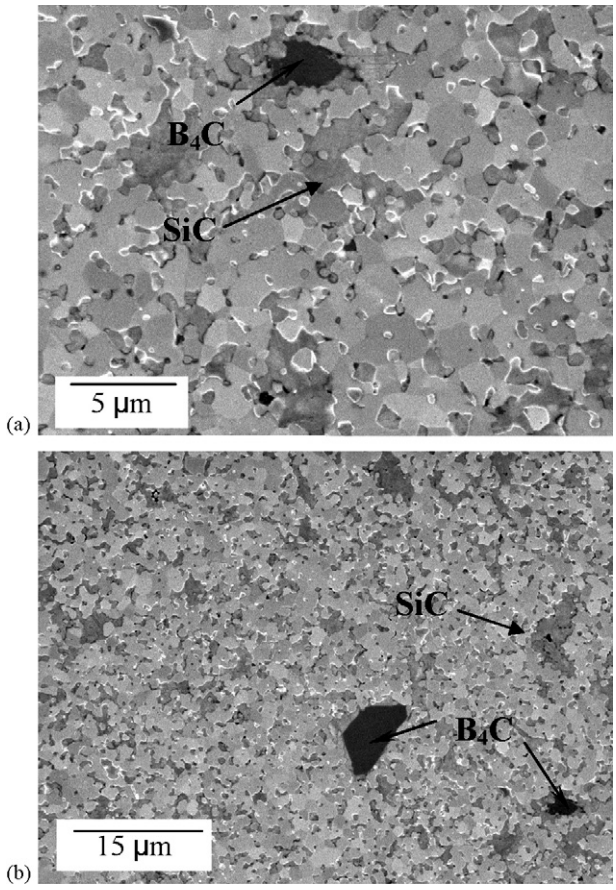

Fig. 9. SEM micrographs at (a) high and (b) low magnification showing the microstructure of ZrB_2–SiC ceramic fabricated by reactive hot pressing of composition F.

reported for ZrB_2–30 vol% SiC produced by conventional hot pressing.[3]

The strength and toughness differences between the ZrB_2–SiC produced by hot pressing commercially available powders and the reaction processed ZrB_2–SiC were attributed to differences in the processing and the resulting microstructures of the materials. The B_4C particles in the material produced by reactive hot pressing (Fig. 9) were estimated to be ~14 μm in diameter. Using a Griffith type analysis, a strength of 720 MPa in this material is consistent with the presence of surface flaws between 12 and 14 μm in size, based on half spherical and half ellipsoid surface inclusions, respectively,[18] which is similar to the particle size of ~14 μm observed for the B_4C inclusions. Fig. 9 also showed that the specimens produced by reactive hot pressing had a wide distribution of SiC particle sizes. Larger SiC particles were up to ~10 μm, which may also act as critical flaws. Because of the relatively small volume fraction of B_4C particles and the presence of a larger number of SiC particles as large as 10 μm, a wide distribution of strengths is possible in these materials. The measured strengths varied from a minimum of 550 MPa to a maximum of 980 MPa. The flaw sizes associated with the minimum and maximum strengths are ~22 and ~7 μm. It may be possible to improve the strength of ZrB_2–SiC produced by reactive hot pressing by reducing the initial content of B_4C in the batch composition, which should result in the reduction of the number and in the size of the B_4C inclusions. Further strength improvements may be obtained by reducing the SiC particle size by using a finer Si precursor powder.

Previous reports have attributed the higher fracture toughness values for ZrB_2–SiC ceramics compared to ZrB_2 to crack deflection around the SiC grains during crack propagation.[3,9] An SEM investigation (not shown) was performed on numerous (20) radial cracks outlet from the corners of Vickers' indentations (5 kg, 20 s) in the reaction processed ZrB_2–SiC materials. The radial cracks did not preferentially deflect at the ZrB_2–SiC interfaces in the materials produced by reactive hot pressing as has been observed in materials produced from commercial powders. The difference in the behavior of the reaction and conventionally hot pressed ZrB_2–SiC may be an indication that the reactively hot pressed samples contain a significantly lower volume of oxide impurities at the grain boundaries. This hypothesis will require further investigation by transmission electron microscopy. However, it would be expected that minimizing the amount of the grain boundary phases might result in a lower fracture energy and lower fracture toughness (Griffith relationship) at ZrB_2–ZrB_2 interfaces. Assuming intergranular fracture behavior, the reduction of crack deflection at the SiC–ZrB_2 interface can be explained using the He and Hutchinson crack deflection theory.[19] Reducing the amount of oxide phase present in the grain boundaries may increase the fracture energy ratio of the SiC–ZrB_2 interface and the initial crack path, enough to exceed the critical crack deflection criteria resulting in the loss of crack deflecting behavior.

4. Conclusions

Fully dense ZrB_2–27 vol% SiC ceramics were fabricated by reactive hot pressing at 1890 °C for 10 min. Reacting a stoichiometric ZrH_2, B_4C and Si mixture (2:1:1 molar ratio) should have produced ZrB_2 containing 25 vol% SiC. However, the reaction resulted in the formation of ZrO_2 and ZrC, in addition to ZrB_2 and SiC, which was the result of a deficiency of available boron in the reaction mixture. The boron deficiency and the formation of ZrO_2 were attributed to the presence of B_2O_3 in the reactants. At temperatures of 1350 °C and higher, the ZrC, Si and B_2O_3 reacted resulting in the loss of silicon in the form of SiO, which reduced the SiC content of the resulting composite to ~22 vol% compared to 25 vol% expected based on the reaction stoichiometry. The formation of ZrC and ZrO_2 was minimized by using a powder mixture that was rich in B_4C and Si (2:1.09:1.16 molar ratio) compared to the stoichiometric mixture (2:1:1 molar ratio). The excess B_4C provided sufficient boron to react with all of the zirconium to produce ZrB_2, thus eliminating the formation of ZrC. In addition, excess Si was added based on the lower-than-expected SiC content. Reactive hot pressing of the B_4C-rich composition produced ZrB_2 with 27 vol% SiC and less than 1 vol% excess B_4C. Reactively hot pressed samples with excess B_4C also appeared to decrease the ZrB_2 grain size from ~5 to ~2 μm and the mean SiC particle size from ~3.5 to ~1 μm compared to samples reactively hot pressed with a stoichiometric powder mixture.

The flexure strength, fracture toughness, Young's modulus and Vicker's hardness were measured on dense ZrB_2–27 vol% SiC samples. The flexural strength (720 MPa) was lower than that reported for ZrB_2–SiC ceramics hot pressed using commercially available powders, but greater than reaction hot pressed materials previously reported in the literature. Strength increases may be possible, if the amount of residual B_4C were reduced or the SiC particle size were decreased in the final ceramics. The fracture toughness (3.5 MPa $m^{1/2}$) was comparable to previously reported reaction processed samples, but lower than conventional hot pressed materials, possibly due to a reduction in the amount of oxide phases at the grain boundaries.

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