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Microstructure and mechanical properties of barium aluminosilicate glass-ceramic matrix composites reinforced with SiC whiskers

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BAS glass-ceramic composites reinforced with different volume fractions (0, 10, 20, 30, 40 vol%) of SiC whiskers were successfully fabricated by a hot-pressing method. The microstructure, whisker/matrix interface structure, phase constitution and mechanical properties of the composites have been systematically studied by means of SEM, TEM, XRD techniques as well as three-point bending tests. It was demonstrated that the incorporation of SiC whiskers could significantly increase the flexural strength and fracture toughness of BAS glass-ceramic matrixes. The celsian seeds can effectively promote the hexacelsian-to-celsian transformation in $BaAl_2Si_2O_8$. The active Al_2O_3 added to the BAS matrix obviously reduced the amount of SiO_2 in the matrix and formed needle-like mullite. The high temperature strengths of the composites were also investigated.

1. Introduction

The need for structural materials which can withstand temperatures above 1200 °C has attracted an interest in ceramics and ceramic matrix composites. Glass-ceramics are of particular interest because of their high melting temperature, low thermal expansion, oxidation resistance and low dielectric constant.

Barium aluminosilicate (BAS) has one of the highest melting temperature (1760 °C) among the glass-ceramic materials [1] and the monoclinic form exhibits a low thermal expansion coefficient (2.29×10^{-6}/°C from 22 °C to 1000 °C) [2]. Therefore BAS is attracting considerable interest for diverse applications such as structural components, electronic packaging and matrix for ceramic-matrix composites. However, like most glass-ceramic materials, BAS glass-ceramics exhibit relatively low mechanical properties, which limit its use in many structural applications. SiC whiskers have been commonly used in the reinforcement of glass-ceramics, and resulted in strong, tough and refractory ceramic composites [3–7]. But, up to now, the reports about BAS glass-ceramic matrix composites are very few. Many researchers focused their efforts on LAS glass-ceramic matrix composites [3, 4, 8–10]. But, the mechanical properties of LAS matrix composites at 1100 °C decrease greatly compared to the room properties [8, 9].

The objective of this work is to study the fracture behavior of hot-pressed BAS composites reinforced with SiC whiskers. The phase constitutions, microstructure and whisker/matrix interfacial structure were investigated by means of XRD, SEM and TEM techniques. The strengthening and toughening mechanisms have also been discussed.

2. Experimental procedure

The materials used in this study were BAS glass-ceramics reinforced with SiC whiskers (from 10 to 40 vol% SiCw). The BAS glass matrix powders were synthesized though hydrolysis of alkoxides [11]. The chemical compositions of the BAS matrix powders are showed in Table I.

As shown in Table I, 22 wt% active Al_2O_3 were added to their gel-glass powders to reduce the amount of excessive SiO_2 in the matrix of the composite and form mullite phases. In addition, 20 wt% celsian Barium aluminosilicat (BAS) seeds were also incorporated into the BAS matrixes to promote the hexacelsian to celsian phase transformation in $BaAl_2Si_2O_8$. The seeds were obtained through a crystallization treatment of BAS glass powders with 3 wt% LiO_2 [11]. The β-SiC whisker used in this study supplied by Shanghai institute of ceramics, China, has a diameter of 0.5–1.0 μm and a length of 30–100 μm. The glass-ceramic powders and SiC whiskers (0–40 vol%) were mechanically mixed in ethyl alcohol using ZrO_2 balls. After milling, the mix was dried in flat bed and aggregates were dispersed by hand as required. The dried blends were then hot-pressed in graphite dies for 30 min at 1370 °C. To

TABLE I Chemical compositions of BAS matrix powders (wt%)

Composition			Active	Celsian
BaO	Al_2O_3	SiO_2	Al_2O_3	BAS seeds
37	26	37	22	20

improve the formation of mullite, the composites were heat-treated in nitrogen atmosphere for 2 h at 1300 °C. The final specimen density of the composite was measured by the Archimedes method.

Flexural strength and fracture toughness were measured in air at 25 °C (for fracture toughness) and at over a temperature range of 25–1200 °C (for flexural strength). All flexural bars were fabricated with the surface perpendicular to the hot-pressing direction. Flexural strength measurements were performed on bar specimens (3 mm × 4 mm × 36 mm) using a three-point bending fixture with a span of 30 mm. Fracture toughness measurements were performed on single-edge-notch bar specimens (SENB) with span of 16 mm and a half-thickness notch was made using diamond wafering blade.

Fracture surfaces of the composites were examined using HITACHI S-570 scanning electron microcopy (SEM). The phase content was determined by X-ray diffraction (XRD). The microstructure of the composites was characterized by transmission electron microscopy (TEM). Thin foil specimens taken normally to the hot-pressing axis were prepared by dimpling and subsequent ion-beam thinning.

3. Results and discussion

3.1. Microstructural characterization

All of the composites were densified to 99% of theoretical density, indicating that the used hot-pressing sintering technique can obtain nearly full density SiCw/BAS composites. SEM observations revealed that the distribution of whiskers was homogeneous with a preferred long-axes orientation perpendicular to the hot-pressing direction.

XRD results of the composites are summarized in Table II and Fig. 1. It reveals that celsian is the predominant crystalline phase in BAS matrix, indicating that the seeds effectively promote the hexacelsian to celsian $BaAl_2Si_2O_8$ transformation during hot-pressing sinter.

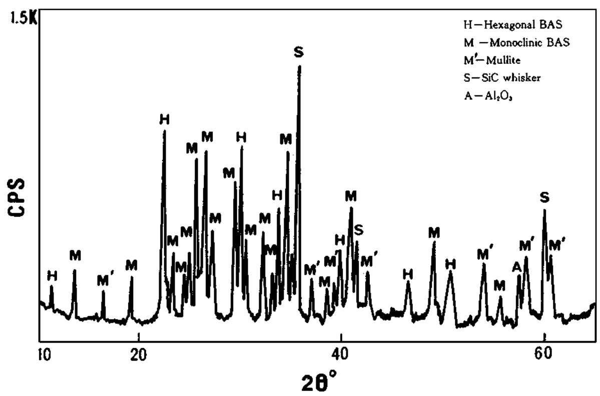

Figure 1 XRD results of BAS composite with 30 vol% SiC whiskers.

TABLE II Summary of XRD analyses of SiCw/BAS composites

Material	XRD phases
BAS matrix	Celsian(65%), Hexacelsian(10%), Mullite(25%)
10 vol% SiCw/BAS-B	β-SiC, Celsian(59%), Hexacelsian(17%), Mullite(24%)
20 vol% SiCw/BAS-B	β-SiC, Celsian(54%), Hexacelsian(20%), Mullite(26%)
30 vol% SiCw/BAS-B	β-SiC, Celsian(53%), Hexacelsian(25%), Mullite(22%)
40 vol% SiCw/BAS-B	β-SiC, Celsian(47%), Hexacelsian(30%), Mullite(23%)

No non-crystalline compounds were found, which undoubtedly contributes to the reaction between the addition of Al_2O_3 and excessive SiO_2 during the heat-treatment. This can be confirmed by the production of mullite, as shown in Fig. 1.

Typical microstructures of the BAS matrix are shown in Fig. 2. The formation of a mullite phase (Noted M in Fig. 2) is confirmed and no amorphous phase are found in the BAS matrix. Fig. 3 demonstrates the SiCw-BAS interfacial structure of the composites. Although the bright-field image shows that the whiskers are well bonded with the matrix grains, a thin interfacial amorphous layer can be found using the dark field image taken with diffusely scattered electrons (Fig. 3b). It may be caused by the the high SiO_2 contents of SiC whisker surfaces because the result of AES analysis proved the amount of oxygen at the as-received SiC whisker surfaces was very high (28.34 at%) [11]. At room or low temperature, the presence of the amorphous phase at the whisker/matrix interface evidently increases the bonding strength and hence inhibited the pullout of whisker, resulting in a lower fracture toughness. [12–14] On the other hand, at high temperature, the softening of interfacial amorphous layer decreases the interfacial friction stress between whiskers and grains, resulting in easier whisker pullout. Therefore, the contribution to the toughness increasement due to whisker pullout and bridging could also be reduced.

3.2. Mechanical properties of SiCw/BAS composites

The room temperature flexural strengths of SiCw/BAS composites are shown in Table III and Fig. 4a. It could be seen that the flexural strength of the composites increases with increasing SiC whiskers content. The strength of 30% SiCw/BAS-B composite increases 128% compared to the BAS matrix, indicating that SiC whiskers provide good strengthening effect. Further increasing the volume of SiC whisker to 40 vol%, the

TABLE III Room temperature mechanical properties of SiCw/BAS glass-ceramic matrix composites

	SiC whisker content vol%				
Material	0	10	20	30	40
Flexural strength, MPa	156	170	272	356	408
Fracture toughness, $MPam^{1/2}$	1.40	1.98	3.07	4.06	4.30

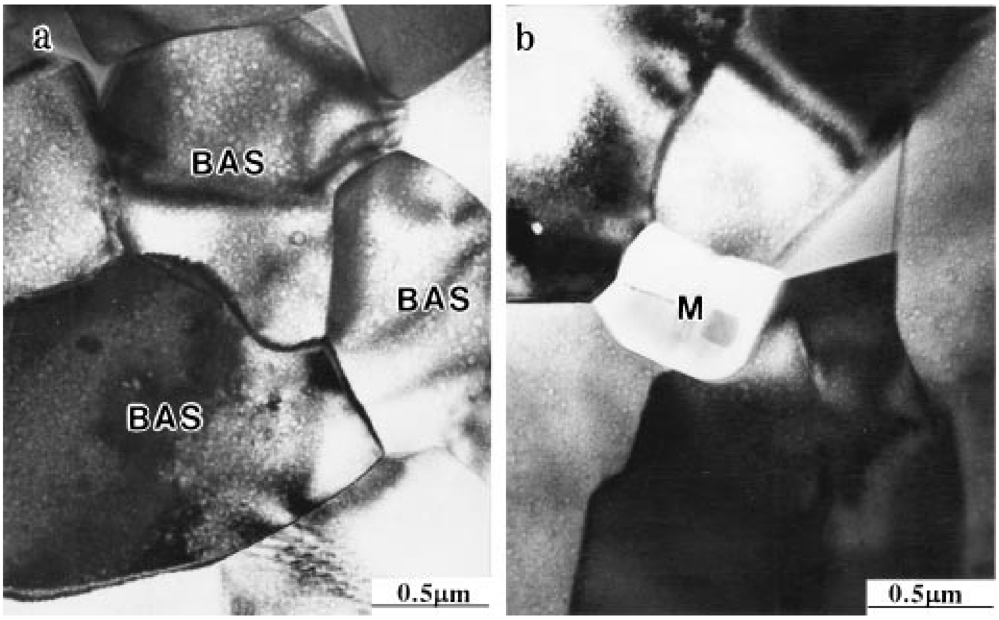

Figure 2 Transmission electron micrographs of matrix in SiCw-BAS composites. (a) Micrograph of $BaAl_2Si_2O_8$ grains. (b) Micrograph showing the existence of a vast amount of mullite.

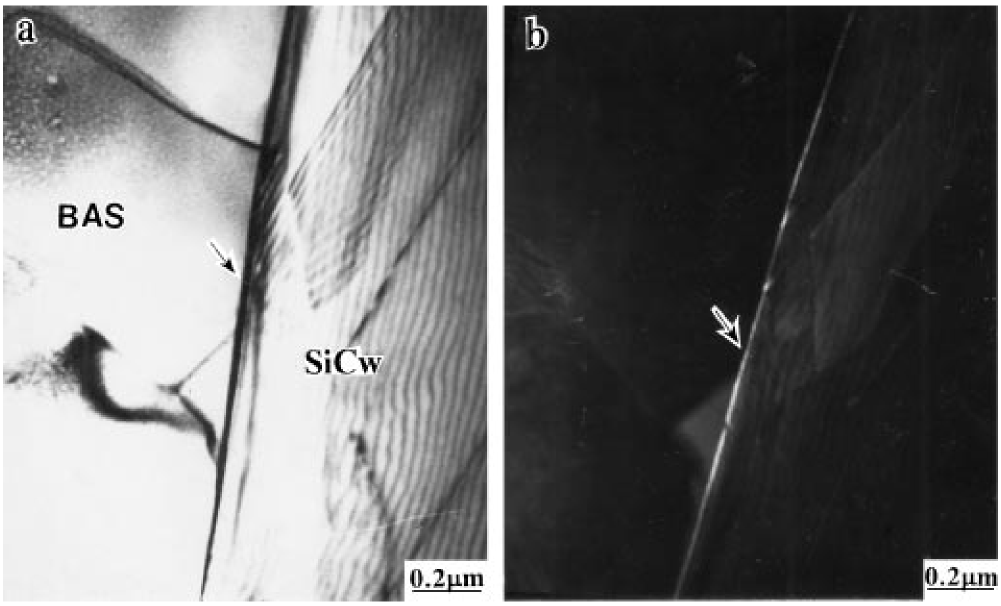

Figure 3 TEM micrographs of the SiCw-BAS interface. (a) Bright-field image showing that the BAS grains have a good bond with the SiC whiskers. (b) Dark-field image formed with diffusely scattered electron showing a thin layer of amorphous phase at the interface.

decrease of the strengthening effect may be due to the higher hexacelsian phase contents in the composites with higher SiCw contents. It will be discussed in next section.

The increase of the strength is contributed to the load transforming effect from matrix to whisker. Though there is a thin amorphous layer at the interface between the whisker and matrix, the results of mechanical properties indicate that the amorphous layer does not destroy the whiskers strengthening effect at room temperature. In addition, the thermal mismatch stress between the matrix and whisker is harmful to the strength of the composite ($\alpha_{SiCw} = 5.0 \times 10^{-6}\,^{\circ}C^{-1}$, $\alpha_{Hexacelsian} = 8 \times 10^{-6}\,^{\circ}C^{-1}$, $\alpha_{Celsian} = 2.3 \times 10^{-6}\,^{\circ}C^{-1}$). The strengthening effect is the mixed results as stated above.

Fracture toughness of SiCw/BAS composites at room temperature as a function of SiCw content is illustrated in Fig. 4b, indicating that the toughness of BAS matrices is very low, 1.40 MPa $m^{1/2}$. Incorporation of SiC whiskers greatly increases the fracture toughness of the composites and the fracture toughness of the composite increases with increasing SiCw content. The fracture toughness of the composite reinforced with 30 vol% SiCw increases by 2.66 MPa $m^{1/2}$ compared with the pure glass-ceramic matrix.

The fracture surfaces of the composites obtained after flexural strength tests are shown in Fig. 5. They appeared to be quite rough with lots of pulled-out whiskers and residual holes due to whisker pull-out on the fracture surface, indicating the stronger reaction between the propagating crack and the whiskers during

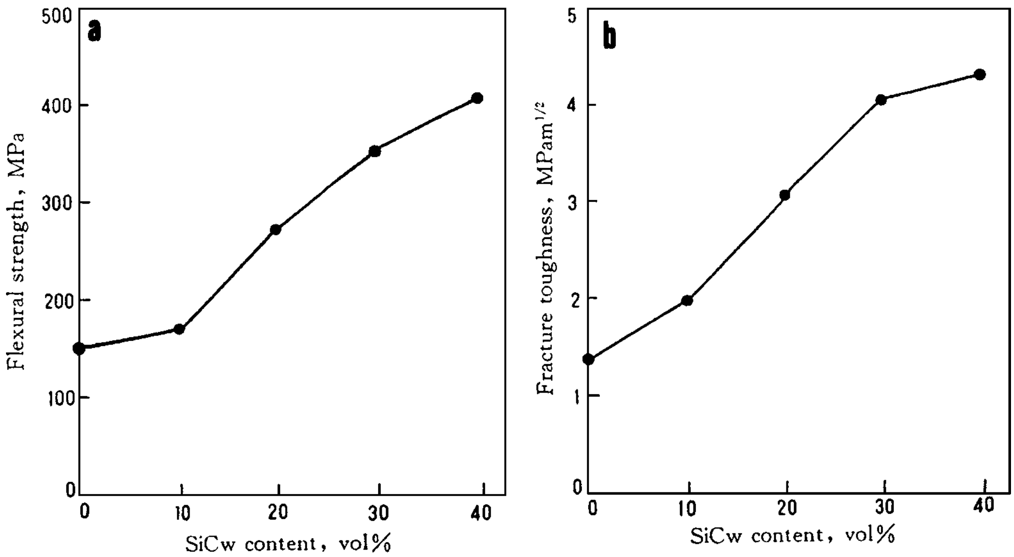

Figure 4 Room temperature mechanical properties of SiCw/BAS composites as a functions of SiC content. (a) Flexural strength. (b) Fracture toughness.

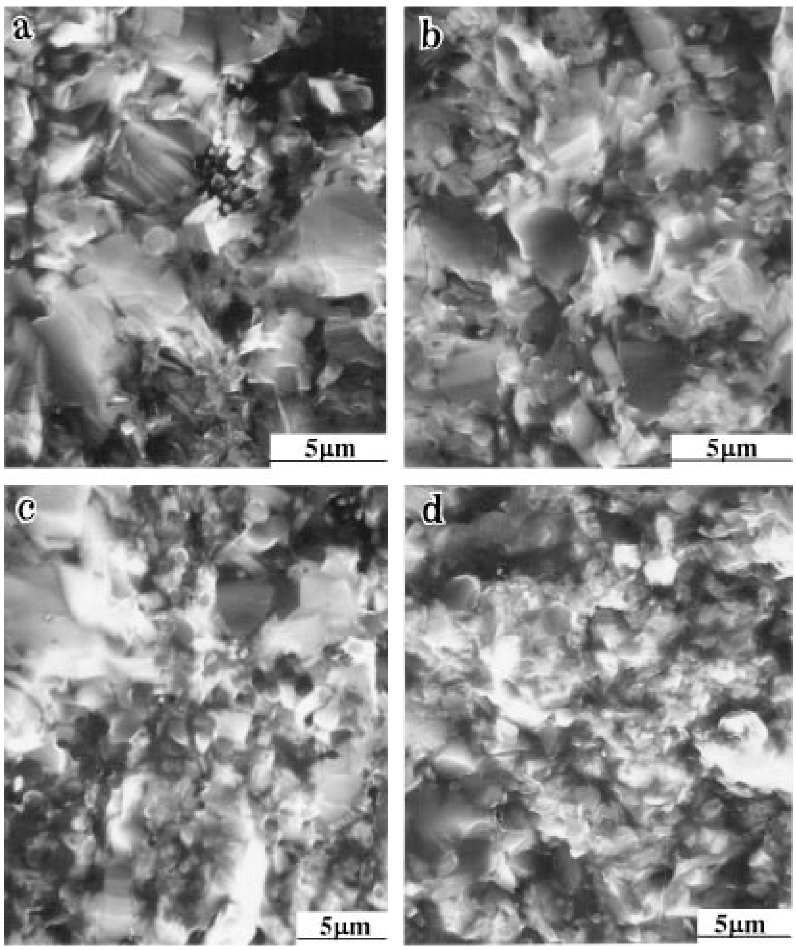

Figure 5 SEM photographs of bending fracture surfaces of SiCw/BAS composites. (a) 10 vol% SiCw/BAS composite. (b) 20 vol% SiCw/BAS composite. (c) 30 vol% SiCw/BAS composite. (d) 40 vol% SiCw/BAS composite.

fracturing. Fig. 5 also shows that, with increasing of whisker content, the fracture surface becomes more and more rough.

The strengthening and toughening effects of SiC whisker have been also found in other glass-ceramic [8–10] and ceramic matrix composites. Liang and Chen reported that the flexural strength and fracture toughness of 30 vol% SiCw/LAS composite increase by 100 MPa and 1.9 MPa $m^{1/2}$ compared with the pure glass-ceramic matrix, respectively [15].

The reaction between the crack and the microstructure of the composites can be demonstrated more cleanly by examining the crack propagation produced by a Vickers indentation, as shown in Fig. 6. It can be seen that the propagating cracks tend to deflect along the whisker/matrix interface, and crack bridging and

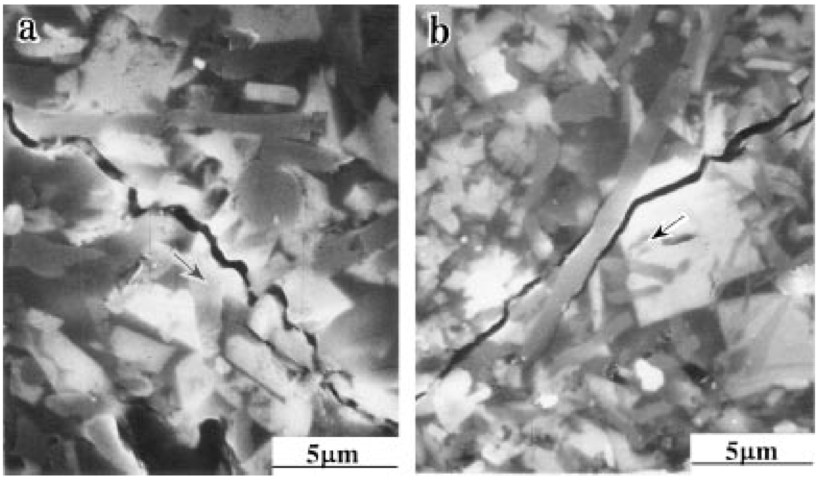

Figure 6 SEM photographs of indentation crack paths in SiCw/BAS composites: (a) crack deflected by whiskers. (b) crack deflection and bridging by a whisker.

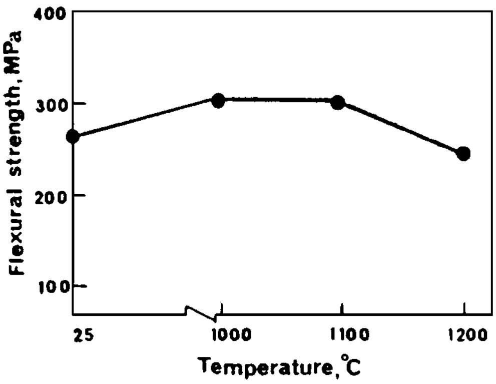

Figure 7 Variation of the strength of 20 vol%SiCw/BAS composite with temperature.

whisker pull-out were commonly observed in the wake of the extending cracks. This resulted in a rough fracture path. Whisker pull-out and bridging undoubtedly increase the fracture toughness of the composite, which is consist with the results of mechanical properties.

Fig. 7 shows the variation of the strength of the 20 vol% fraction whiskers reinforced BAS glass-ceramic as a function of temperature. The strength increases with temperature as the temperature increases from 25 °C to 1000 °C. It then decreases gradually but still maintains a strength of 240 MPa at 1200 °C, which is 88% of the strength of the composite at room temperature. On the contrary, the strength of LAS glass-ceramic matrix composites at 1100 °C decrease greatly compared to the room temperature properties [3–7, 15], indicating that BAS glass-ceramic has great potential as the matrix for composites applied at high temperature.

The reason for the deterioration of the strength of the BAS composite with increasing temperature may be explained as follows. The apparent increase in strength at 1000 °C is contributed to the crack blunting effects due to the small amount of residual glass in the BAS matrix. With the further increase in temperature, the presence of glass in the composites results in an elastic–plastic type of matrix and hence destroys the ability of the matrix to transfer the load to whiskers, resulting in the decrease in strength at a higher temperature. In addition, the interface oxidation at higher temperature also degrades the mechanical properties of the BAS composites. The high temperature fracture behavior of SiCw/BAS composite will be investigated in detail.

4. Conclusions

(1). Incorporation of active Al_2O_3 can obviously reduce the amount of SiO_2 in matrix via the reaction between the addition of Al_2O_3 and excessive SiO_2 during the heat-treatment. The seeds can effecitively promote the hexacelsian to celsian-phase transformation in $BaAl_2Si_2O_8$.

(2). The whisker and matrix grain are separated by a thin amorphous layer, which is harmful to the high temperature mechanical properties of the composites.

(3). The flexural strength and fracture toughness values of BAS glass-ceramics can be effectively improved by the addition of SiC whiskers. The main toughening mechanisms are crack deflection, whisker bridging and pulling-out.

(4). The BAS composite has good high temperature mechanical properties and the flexural strength of 20 vol% SiCw/BAS-B composite at 1200 °C only drops off 12% compared to that at room temperature.

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