Mechanical properties and microstructure in sintered and HIPed SiC particle/Si_3N_4 composites

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Pressureless sintered (PLS) and gas-pressure sintered (GPS) Si_3N_4, PLS and GPS SiC particle/Si_3N_4 composites, and PLS + HIP and GPS + HIP SiC particle/Si_3N_4 composites were produced. Investigation of their mechanical properties showed that PLS + HIP and GPS + HIP composites, containing SiC particles in the beta-silicon nitride grains, yield higher bending strength, although its fracture toughness remains at the same level. This is attributed to the fact that the added SiC particles inhibit excessive growth of beta-Si_3N_4 grains without changing the fracture behaviour. However, this investigation also found precipitation during the reaction between SiC and nitrogen in gas pressure sintering, resulting in a low Young's modulus and low density in the GPS composite.

1. Introduction

Material strengthening methods available today include the use of fibre and whisker reinforcement [1–3] and particle dispersion [3–6]. The results of various studies have contributed to improve the mechanical properties of ceramics. Although methods of strengthening ceramics have been studied extensively, cracks caused by thermal shock and contact stress in engine operation can result in catastrophic failure. The fracture toughness and strength of silicon nitride needs to be further improved when used in automotive engines.

The mechanical properties of Si_3N_4, which is a candidate material for engine application, have been improved through microstructural control achieved with a sophisticated sintering and hot isostatic pressing process [6]. Naturally, this sintering process is utilized to fabricate ceramic composites with enhanced mechanical properties [7, 8]. In the literature [5, 8], SiC particle/silicon nitride composites have been studied using hot pressing and sintering and hot isostatic pressing (HIPing) methods, and high strength has been reported. However, the sintering behaviour of these materials in relation to the sintering conditions has not yet been clearly described.

In the present work, SiC particle/Si_3N_4 composites were produced by HIPing following pressureless sintering (PLS) and gas-pressure sintering (GPS). The mechanical properties and composite microstructures were then examined using scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

2. Experimental procedure

Commercially produced silicon nitride powder and SiC particles (10% by volume) were mixed with 10 wt % yttria[+] and 5 wt % alumina[++] in a ball mill using ethanol as a solvent. The properties of the powders used in this experiment are listed in Table I. After ball milling, the slurry was dried in a rotary evaporator and then sieved to a particle size smaller than 210 μm. The SiC particle/Si_3N_4 mixture was then isostatically cold pressed at 400 MPa. The compacts were subjected to pressure less sintering (PLS) at a maximum temperature of 1700 °C under 0.1 and 0.9 MPa nitrogen for 3 h gas pressure sintering (GPS), and then HIPed (post-HIPed) in a graphite crucible for 1 h at 1850 °C under 100 MPa nitrogen. Six materials were produced.

The 5 mm × 5 mm × 40 mm PLS and GPS, then post-HIPed bars were ground into 4 mm × 3 mm × 40 mm specimens for bend testing and 4 mm × 1 mm × 40 mm specimens for measuring the

TABLE I Properties of starting powders

		Si_3N_4 E10	SiC beta-SiC
Chemical composition	N	> 38.4	–
	O	1.50	0.33
	C	0.3	0.47
	Al	< 0.001	0.03
(wt %)	Ca	< 0.001	–
	Fe	< 0.001	0.05
Crystal structure		Alpha-Si_3N_4 > 95%	Beta-SiC
Average particle diameter (μm)		0.5	0.28
Specific density (10^3 kg m^{-3})		3.18	3.21
Specific surface area (m^2 g^{-1})		11.3	15.1

[+]Yttria oxide, > 99.9%, average diameter 0.4 μm. [++]Alumina, A16SG, average diameter 0.4 μm.

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Young's modulus. A four-point bending test (inner span of 10 and outer span of 30 mm) at a crosshead speed of 0.5 mm min^{-1} was used to measure bending strength of ten specimens. The results were analysed using a Weibull statistical technique [9]. The fracture toughness of ten specimens was measured by the single-edge precracked beam (SEPB) method [10], Young's modulus of five specimens by resonance, and hardness of 15 measurements by a Vicker's indentor with a 300 g weight,

3. Results and discussion

The mechanical properties of six materials (PLS-Si_3N_4 (A), PLS composite (B), PLS + HIP composite (C), GPS-Si_3N_4 (D), GPS composite (E), and GPS + HIP composite (F)) are summarized in Tables II and III. In the case of PLS materials, the density of composite B is the same level as other PLS materials (A, C). On the other hand, GPS-composite E exhibited the lowest density in these materials. The addition of SiC particles is thought to decrease the sinterability of

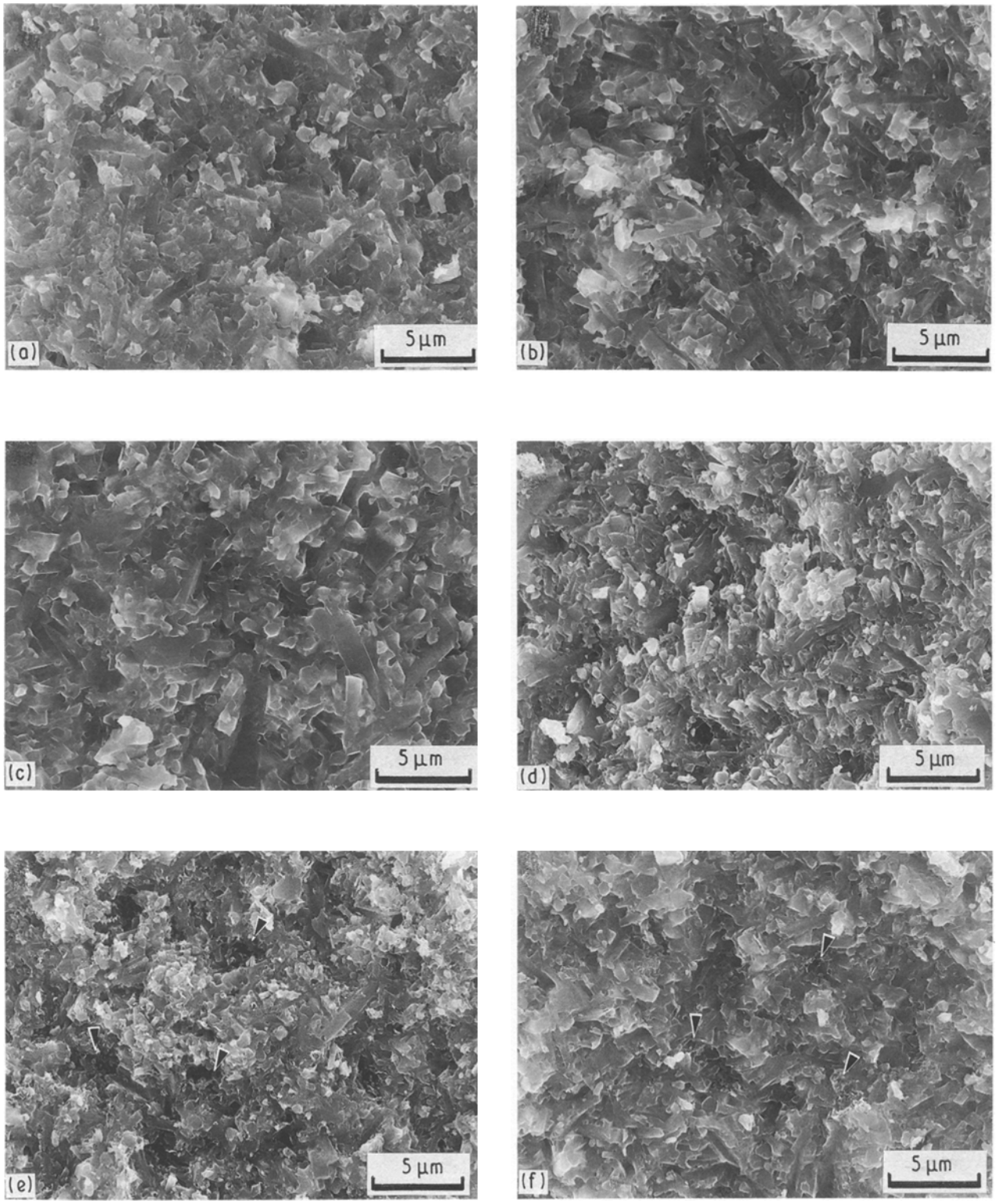

Figure 1 Scanning electron micrographs of the specimens (a) PLS-Si_3N_4 (A), (b) PLS composite (B), (c) PLS + HIP composite (C), (d) GPS Si_3N_4 (D), (e) GPS composite (E), (f) GPS + HIP composite (F). Arrows indicate precipitation.

TABLE II Materials properties (pressureless sintering)

Properties	PLS		PLS + HIP,
	Si_3N_4, A	Composite B	Composite C
Density ($g\,cm^{-3}$)	3.28	3.30	3.30
Crystal phase	β-Si_3N_4	β-Si_3N_4 β-SiC	β-Si_3N_4 β-SiC
Young's modulus (GPa)	294	307	307
Bending strength (MPa)	826 ± 75	728 ± 100	948 ± 174
Weibull modulus	12.7	8.1	6.3
Fracture toughness ($MPam^{1/2}$)	5.6 ± 0.3	5.3 ± 0.3	5.2 ± 0.3
C_f (μm)	14.6	16.8	9.5

TABLE III Materials properties (gas pressure sintering)

Properties	GPS		GPS + HIP,
	Si_3N_4,D	Composite E	Composite F
Density ($g\,cm^{-3}$)	3.25	3.02	3.26
Crystal phase	β-Si_3N_4	β-Si_3N_4 β-SiC	β-Si_3N_4 β-SiC
Young's modulus (GPa)	284	235	293
Bending strength (MPa)	814 ± 97	651 ± 80	909 ± 108
Weibull modulus	9.2	13.8	9.11
Fracture toughness ($MPam^{1/2}$)	6.5 ± 0.3	5.2 ± 0.2	5.5 ± 0.2
C_f (μm)	20.2	20.3	11.6

the composites in gas-pressure sintering (GPS-Composite, E), resulting in the lowest density due to their porous microstructure. Density was then recovered through HIPing after gas pressure-sintering (GPS + HIP composite, F). The same trend is shown in Young's modulus. Young's modulus of the GPS composite (E) is the lowest level in all the materials; similarly, it was also recovered by a post-HIPing process.

The fracture toughness values, K_{IC}, of the HIP composites C and F were also at the same level as those of the PLS (B) and GPS (E) composites, respectively, but smaller than those of matrices A and D. Fracture toughness of the composites C and F were no higher than the values reported in the literature for small particle-added composites [5, 8]. This suggests that the addition of SiC particles may not directly affect the fracture behaviour of the HIP composites.

On the other hand, the bending strength results (PLS + HIP composite (C) and GPS + HIP composite (F)) show a considerable improvement due to both the addition of SiC particles [4] and post-HIPing [8, 10]. Although the bending strength is lower than these in the literature, it changes with the first sintering temperature. Post-HIPing densifies the materials and minimizes critical flaw size for fracture, thereby increasing their strength without significantly altering the microstructural characteristics governing fracture. Tables II and III show the calculated C_f from

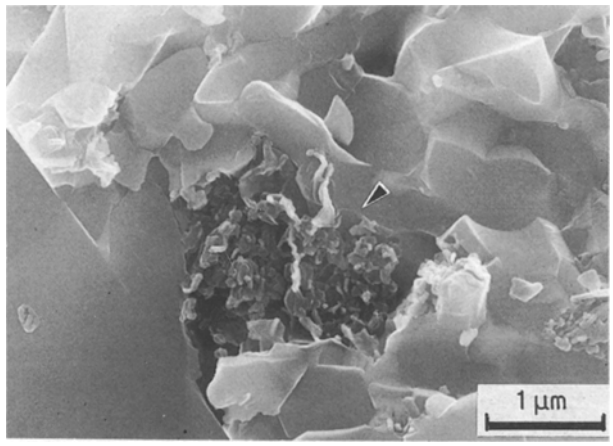

Figure 2 Precipitation (arrowed) and pore in GPS + HIP composite.

the equation

$$C_f = (1/\pi) \cdot (K_{IC}/\sigma_f)^2. \quad (1)$$

Thus, a combination of SiC particle addition and the HIPing process yields a higher strength as a result of minimizing the critical flaw size for fracture, in spite of the differences in the first sintering methods.

Both SEM and TEM were employed to explore the relationship between the mechanical properties and the specimen microstructures. Fig. 1a–f are scanning electron micrographs showing the microstructures of the PLS (A–C) and GPS (D–F) materials. Beta-Si_3N_4 grains in PLS Si_3N_4 (A) and PLS composite (B) were the same size and beta-Si_3N_4 grains in the HIP composites (C) developed larger than (A) and (B). In GPS series, GPS + HIP composite (F) shows the largest grain size; however, scanning electron micrographs also indicated that the decomposition of SiC was observed as predicted in the literature [7, 11, 12] (Fig. 2). SEM also revealed that precipitation (arrow) remained in the microstructure (GPS composite, E) resulting in low density and low Young's modulus. The microstructure in GPS + HIP composite (F) shows that pores were compressed by HIPing.

The transmission electron micrographs in Fig. 3a–f show the microstructural characteristics of PLS and GPS materials. Fig. 3a and b show the microstructure of PLS Si_3N_4 (A), and PLS composite (B), beta-Si_3N_4 grains are of varying sizes and are distributed within a glassy phase [8]. The PLS composite (B) in this figure shows SiC grains (under 0.2 μm diameter) trapped in beta-Si_3N_4 grains and distributed within the glassy phase. It has also been suggested that carbon contamination from Si_3N_4 and SiC particles (see Table I) influences the grain growth of beta-Si_3N_4 grains [8]. Fig. 3c shows the microstructure where some of the SiC particles smaller than 0.2 μm are trapped in the beta-Si_3N_4 grains, which also enlarged, and others which are distributed along the grain boundaries. This type of composite microstructure may produce a higher bending strength resulting from minimizing fracture origin [8].

Transmission electron micrographs in Fig. 3 shows the microstructure of GPS-Si_3N_4 (D), GPS composite

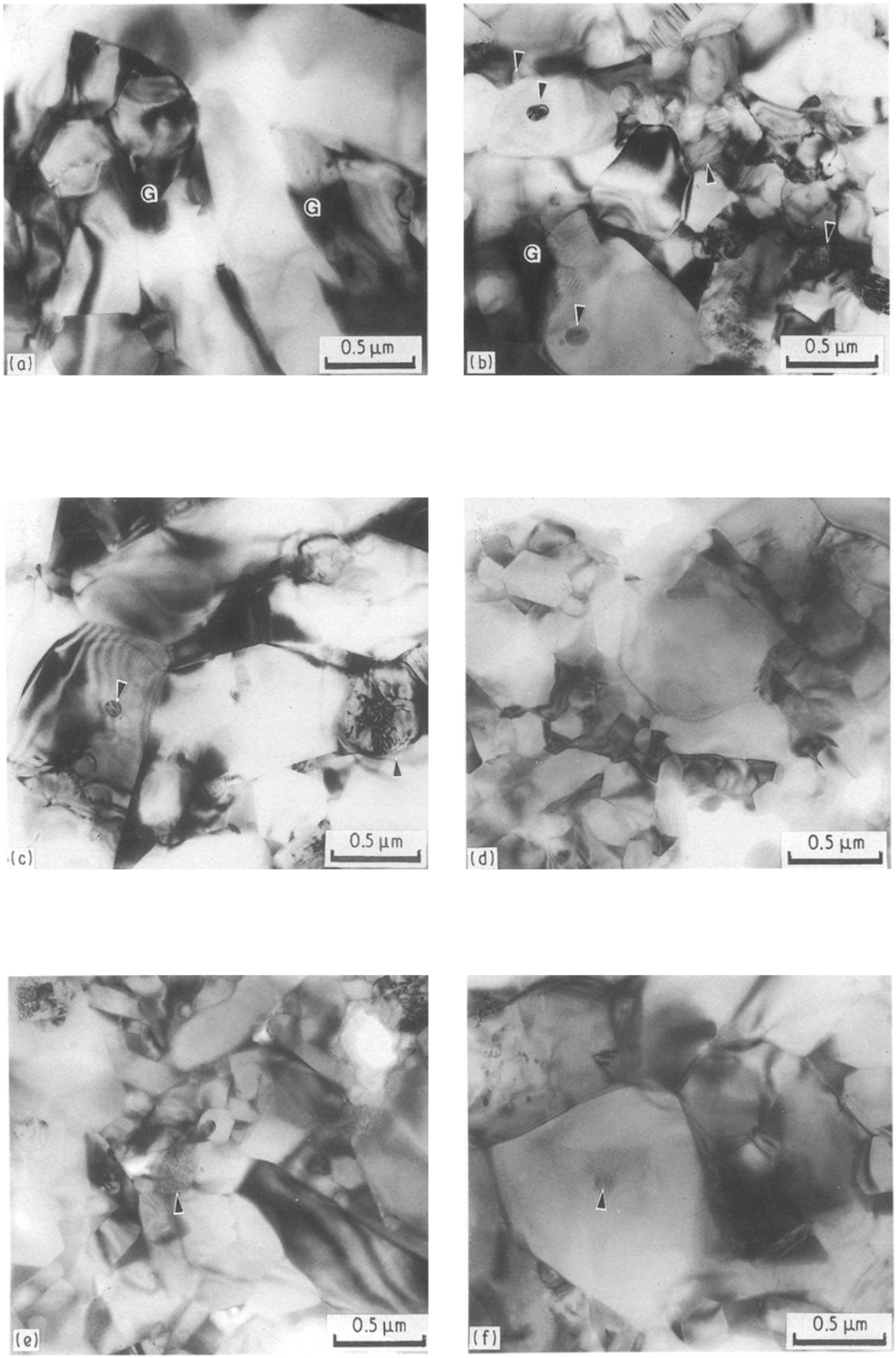

Figure 3 Transmission electron micrographs of the specimens. (a) PLS-Si_3N_4 (A), (b) PLS composite (B), (c) PLS + HIP composite (C), (d) GPS Si_3N_4 (D), (e) GPS composite (E), (f) GPS + HIP composite (F). G, glassy layer; arrows, SiC.

(E), and GPS + HIP composite (F). Beta-Si_3N_4 in composites D and E show the same morphologies of varying size, and distributed pores are detected in GPS composite, E. On the other hand, in GPS + HIP composite (F), beta-Si_3N_4 grains become similar in size and pores were diminished; as a result, its strength level recovered and increased to the same level as the PLS + HIP composite (C). Some of beta-SiC particles (< 0.2 μm) are also incorporated in the beta-Si_3N_4 grains, although others are already decomposed during the gas pressure sintering. These microstructural morphologies are different from that in PLS + HIP composite (C). Thus the sintering behaviour at the GPS influences the post-HIPing microstructure.

4. Conclusion

In the present study, a PLS and GPS silicon nitride, PLS and GPS SiC particle/Si_3N_4 composites, and PLS + HIP and GPS + HIP composites were produced. Investigation of their mechanical properties showed that PLS + HIP and GPS + HIP composites, containing SiC particles in the beta-silicon nitride grains, yield higher bending strength, although their fracture toughness remains at virtually the same level. This is attributed to the fact that the addition of SiC particles inhibits excessive growth of beta-Si_3N_4 grains resulting in a smaller flaw size for fracture. Fine SiC particles of less than 0.2 μm diameter are trapped within the beta-Si_3N_4 grains through hot-isostatic-processing which has the effect of reducing the crack size for fracture. This trend is the same in both series. However, this investigation also shows that added SiC is decomposed and reacted with nitrogen during gas pressure sintering, resulting in a low Young's modulus and low density in the GPS composite.

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