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Silicon Nitride–Silicon Carbide Nanocomposites Prepared by Water Processing of Commercially Available Powders

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Abstract

Dispersion of nano-sized silicon carbide powders in silicon nitride was examined. Zeta potential was measured over a range of pH values and the aqueous dispersion of nano-sized silicon carbide powders in silicon nitride matrix was optimised. Ultrafine silicon carbide, 30–200 nm, which had agglomerated in organic media leading to a degradation in strength, was well dispersed and acted to reinforce silicon nitride matrix material. Densification of these nanocomposites was also examined. They were densified to 98–99% theoretical density by hot pressing, gas pressure sintering and pressureless sintering. Flexural strengths were measured and nanocomposites densified by the different routes were compared. Gas pressure-sintered nanocomposites had strengths comparable to the hot pressed materials. Gas pressure sintering was identified as a viable densification route for these materials as it does not have the size and shape limitations associated with hot pressing. © 1997 Elsevier Science Limited.

1 Introduction

Silicon nitride–silicon carbide composites have been prepared from silicon carbide fibres, platelets, whiskers and particulates. Although improvements in K_{IC} have been observed, these second-phase inclusions generally led to an overall degradation in strength.[1–3]

The emergence of superior silicon nitride–silicon carbide composites which contained nano-sized silicon carbide inclusions have renewed the efforts to develop materials with both improved strength and fracture toughness. These were fabricated by hot pressing amorphous Si–C–N powders formed from polymer precursors[4] or by hot-pressing carbon-coated commercial Si_3N_4 powder.[5] Detailed characterisation of these materials has been carried out and their properties are shown in Table 1. While these materials provide evidence to suggest that nano-sized silicon carbide reinforces silicon nitride to a very high degree, the mechanism by which it occurs is still very much in dispute and it has been suggested that the improvements in mechanical properties were as a result of very careful processing.[8]

The economic viability of these materials has also been questioned.[9] Hot pressing is far from an ideal method of densification because of the limited shapes which can be produced. Ceramics formed from polymer precursors are very expensive and it is difficult to justify such a high cost raw material.

The present authors addressed some of these questions and attempted to produce Si_3N_4–SiC nanocomposites using commercially available powders and following the established techniques for dispersion of micron-sized SiC inclusions as the second phase in Si_3N_4 matrix.[9,10] Ball milling and attrition milling were used with isopropanol as vehicle to form slurries which were dried by evaporation. Silicon carbide agglomerates were a common feature of these composites and strength improvements were not observed.

It was obvious from this investigation that SiC powder dispersion was critical to the fabrication of these materials. The first advocates of nanocomposites, Niihara[4] and Ishizaki,[5] were not adding nano-sized SiC powder but, rather forming SiC particles during hot pressing, and thus agglomeration of SiC or dispersion in Si_3N_4 had not posed problems. Although some work has been carried out using a mixed powder route,[9–11] as yet the Si_3N_4 materials originally prepared by Niihara and Ishizaki have not been reproduced by other laboratories.

Table 1. State of the art Si_3N_4–SiC nanocomposites

Niihara (1990/1991)[6]		*Ishizaki (1994)*[7]	
Hot pressed Si_3N_4–SiC nanocomposites from amorphous Si–C–N powders produced from precursors		Si_3N_4–SiC nanocomposites by carbon coating and hot pressing	
Maximum values: K_{IC}:	7 MPa m$^{0·5}$	Maximum values: K_{IC}:	6·7 MPa.m$^{0·5}$
$\sigma_{F\ r\ t}$:	1350 MPa	$\sigma_{F\ r\ t}$:	1300 MPa
$\sigma_{F\ 1200°C}$:	1000 MPa	$\sigma_{F\ 1000°C}$:	1230 MPa
$\sigma_{F\ 1500°C}$:	840 MPa	$\sigma_{F\ 1200°C}$:	1140 MPa

Extensive investigations have been carried out on a powder-mixing route for the dispersion of SiC in Al_2O_3 matrix.[8,12,13] Notably, reproducible Al_2O_3–SiC nanocomposites have been formed by processing with water and freeze-drying. Processing using water as opposed to organic solvents results in clear advantages for industrial-scale production of these materials.

The present work examines the possibility of a water-processing route for the preparation of Si_3N_4–SiC nanocomposites. It also compares hot pressing, gas pressure sintering and pressureless sintering of Si_3N_4–SiC nanocomposites and compares the mechanical properties obtained for materials densified by the three different techniques.

2 Experimental Procedure

2.1 Materials used

Silicon nitride matrix material was prepared prior to addition of nano-sized silicon carbide powders. The processing of this matrix had previously been optimised and used as part of extensive investigations into Si_3N_4–SiC composite materials by pressureless sintering.[14] Si_3N_4 (H. C. Starck, Germany, LC12SX) and sintering additives (5·5 wt% Y_2O_3, H. C. Starck, Grade C and 3 wt% Al_2O_3 Taimei, Japan, Taimicron TM-DR) were ball milled for 72 h, dried by hot plate–magnetic stirrer and the dried powder mix was brushed through a 212 μm sieve. Relatively high flexural strengths have been obtained for this matrix densified by pressureless sintering ($>$650 MPa)[3] and it was therefore used as a starting point for Si_3N_4–SiC nanocomposite production.

2.2 Commercial nano-sized silicon carbide powders

Two commercially available silicon carbide powders were mixed with pre-prepared silicon nitride matrix material. Detailed characterisation of Ibiden β-SiC-Betarundum, and Norton α-SiC-FCP40 was carried out and the average grain size, specific surface area and density of these powders are given in Table 2. Of the two powders, the Norton has the lower average particle size and higher specific surface area. The density of the powders was the same at 3·15 g cm^{-3}.

2.3 Dispersion

The zeta potential of the commercial SiC powders, Si_3N_4 powder and Si_3N_4 pre-prepared matrix was measured for a range of pH values using a Coulter Delsa 440. Based on these measurements and on processing trials, the processing route outlined in the flowchart shown in Fig. 1 was established to fabricate reproducible Si_3N_4–SiC nanocomposite powders.

Appropriate amounts (5–10 vol%) of nano-sized SiC powder were dispersed ultrasonically in water/ammonia solution at pH$\sim$11 for 1 h and then milled for 1 h in an attrition mill with silicon nitride milling media, spindle and pot. Si_3N_4 pre-prepared matrix was added to the attrition mill and the slurry was milled for a further 3 h. The mill was kept at $<$20°C to ensure pH$\sim$11 was maintained throughout the milling procedure.

After milling, the aqueous slurry was freeze-dried (Finn Aqua Lyovac GT2 Freeze Dryer, France). Freeze-drying is a process which removes water from frozen material. Ice sublimes directly to water vapour avoiding the liquid state. This takes place under vacuum where the product is generally frozen between -10 and -70°C. Water vapour is extracted by way of a low temperature condenser. Pre-freezing should be at a speed of 0·1 to 2°C per min and in this case was carried out using liquid nitrogen.

2.4 Densification

The freeze-dried powder was densified by three different sintering routes:

1. Hot pressing at 1750°C for 1 h at 40 MPa in nitrogen.
2. Pressureless sintering at 1850°C for 2 h in flowing nitrogen. Compacts for pressureless sintering were formed by CIP-ing the freeze-dried powders in latex moulds at 170 MPa. They were sintered in alumina crucibles in a tightly packed 50:50 Si_3N_4:BN powder bed.

Table 2. Characterisation of commercial silicon carbide powders

Powder	*Average grain size* [μm] (50%)	*Specific surface area* BET [$m^2 g^{-1}$]	*Density* [$g\,cm^{-3}$] *gas Pycnometry*	*Crystal form*
Norton FCP40 NLC	0·20	30	3·15	α
Ibiden-betarundum	0·27	19·5	3·15	β

3. Gas pressure sintering (GPS) was also carried out on CIP-ed compacts in a similar powder bed to that used for pressureless sintering. A low pressure sintering step at 1800°C for 2 h was followed by a high pressure step at 1850°C for 1 h. Nitrogen gas (0·3 MPa) and argon gas (0·3 MPa) were injected into the furnace chamber at room temperature before the GPS cycle had commenced. All further pressure increases during the GPS cycle were achieved using argon gas. The furnace was heated at 10°C min^{-1} and pressure increased gradually with temperature until, at 1800°C, a further injection of argon gas brought the pressure for the low pressure, sintering step to 2 MPa. After 2 h at 1800°C 2 MPa^{-1}, temperature and pressure were increased to 1850°C and 40 MPa, respectively, for 1 h.

Further details of this GPS/mixed gas procedure for successful densification of Si_3N_4–SiC materials are detailed in previous publications by the authors.[9,10]

Nanocomposites with 5 and 10 vol% nano-sized SiC were prepared. Pre-prepared matrix Si_3N_4 was milled in water for 3 h without SiC, freeze-dried and sintered together with the composites.

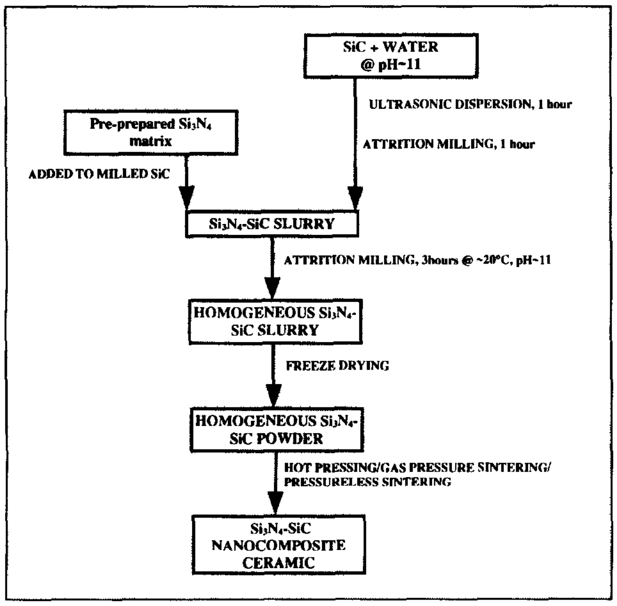

Fig. 1. Water processing of SiC–Si_3N_4 nanocomposites.

2.5 Characterisation

The dense nanocomposite materials were characterised. Fired density was measured by upward displacement of water applying the principle of Archimedes. The phases present in all samples were identified using a Philips 'X'Pert' diffractometer (CuK_α radiation).

Test bars, 3 × 4 × 50 mm were cut, ground-polished and chamfered, and flexural strength was estimated from 3-point bend tests (span, 16 mm; crosshead speed, 0·1 mm min^{-1}). Because of the importance and influence of the surface finish of test bars on measured strength, grinding and polishing was completely mechanised and a standard process used to prepare all bars tested.

3 Results and Discussion

3.1 Dispersion

Reproducible Al_2O_3–SiC nanocomposites have been formed by processing with water and freeze-drying. O'Sullivan *et al.*[13] dispersed SiC ultrasonically before adding to an Al_2O_3/water slurry. A pH ~ 6 was maintained. At this pH, the Al_2O_3 particles have an overall positive charge and the SiC particles an overall negative charge. SiC repels SiC and attracts Al_2O_3. The aqueous slurries were freeze-dried and Al_2O_3–SiC nanocomposites with strengths of ~800 MPa were formed by hot-pressing of the freeze-dried powder product.

Dispersion of SiC in Si_3N_4 differs from the Al_2O_3–SiC case in that both matrix and inclusion powders have a SiO_2 layer and effectively, dispersion involves mixing SiO_2 with SiO_2. The approach used for Al_2O_3–SiC is not directly applicable as both SiC and Si_3N_4 particles would have a similar overall charge at each pH.

The zeta potential of both commercial SiC powders, Ibiden β-SiC-Betarundum and Norton α-SiC FCP 40 was measured and is shown in Fig. 2. The carbide powders showed a minimum zeta potential at pH ≈ 11. At this pH, the SiC particles have an overall negative charge and therefore repel each other.

Zeta potential data for silicon nitride powder and pre-prepared silicon nitride matrix are shown in Fig. 3. The sintering aids have little effect on

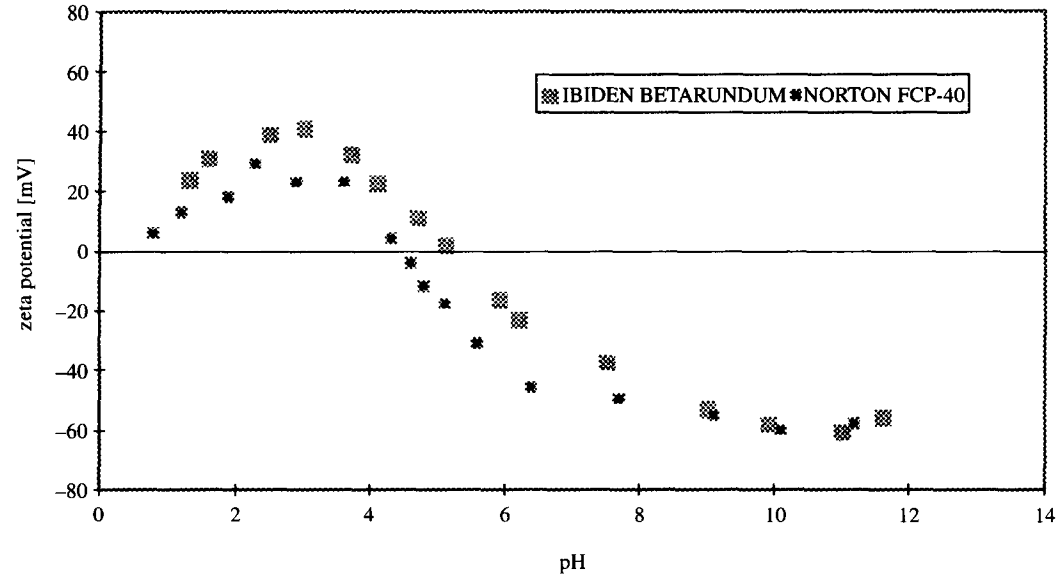

Fig. 2. Zeta potential of commercially available nano-sized silicon carbide powders.

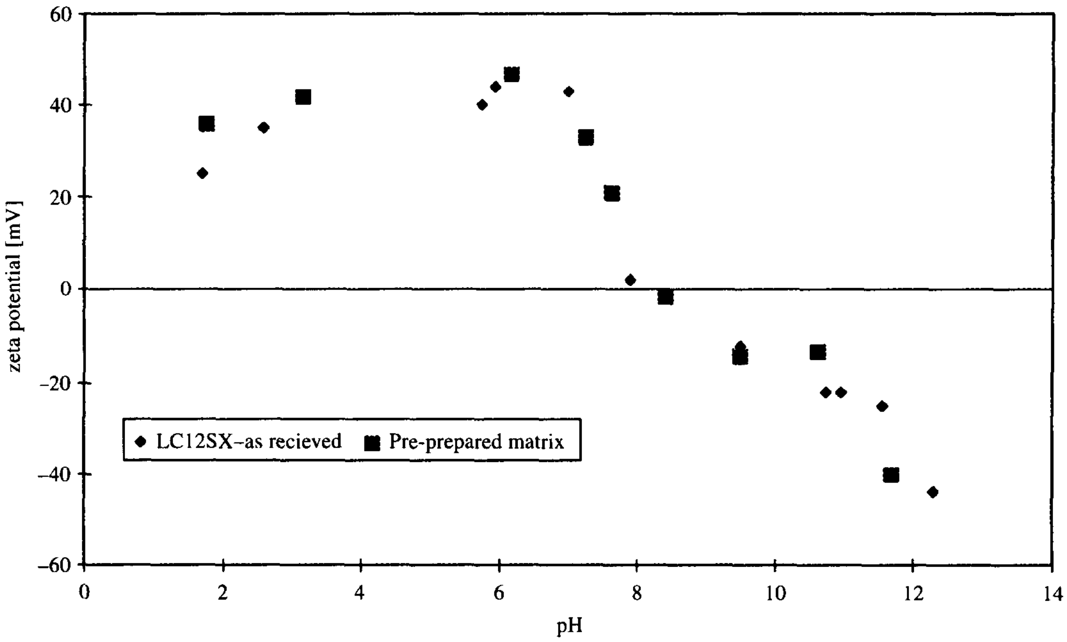

Fig. 3. Zeta potential of LC12 SX Si_3N_4 powder as received and pre-prepared Si_3N_4 matrix (LC12SX + 3 wt% Al_2O_3 + 5·5 wt% Y_2O_3) ball milled in isopropanol.

powder behaviour as the zeta potential data points were similar with and without additives. As with SiC, minimum values for zeta potential were observed for Si_3N_4 at pH $\approx$11. Because particles of both materials have an overall negative charge in aqueous media at this pH, particle agglomeration is prevented and a good dispersion of SiC in Si_3N_4 can be expected with intense mechanical agitation.

Drying of these aqueous slurries also needed careful consideration. Any heat or evaporation technique would inevitably lead to a change in the pH and therefore to the overall charge on the particles and their subsequent behaviour. For this reason, freeze-drying of the slurries was considered to be the best option. The particles could be frozen into their well dispersed positions.

In addition, the resultant powders from the freeze-drying process are free-flowing and highly compressible, requiring no further treatment prior to compaction and sintering.

A processing route was thus established for the dispersion of nano-sized commercial SiC powders in Si_3N_4 matrix using water processing as outlined in the flowchart of Fig. 1.

3.2 Densification

Sintering was carried out by three different routes. Initially, the materials were hot-pressed to verify the good dispersion expected from the processing route used. Hot pressing at 1750°C for 1 h at 40 MPa in nitrogen yielded dense composites with <0·1% open porosity.

Pressureless sintering was carried out at a range of temperatures from 1700°C, but temperatures as high as 1850°C were necessary to obtain relative densities of 98–99%, comparable with those obtained through hot-pressing.

Gas pressure sintering was previously studied in detail for these materials but using a non-aqueous (organic liquid) processing route.[9,10] GPS is considered an extremely viable densification alternative to hot pressing. It involves a two-step sintering cycle which can lead to the complete densification of pre-formed compacts but does not require glass or metal encapsulation. During the first step, a low pressure step, the compacts are sintered sufficiently to reduce porosity to <5%. At these porosity levels, higher pressures can be applied without the expensive and often unreliable encapsulation techniques necessary for HIP-ing. During the second high pressure step, the remaining porosity is eliminated.

Densification of Si_3N_4–SiC composites by GPS poses a dilemma in that a nitrogen atmosphere is essential during sintering to prevent the decomposition of Si_3N_4. However, at certain nitrogen pressures and temperatures, the decomposition of silicon carbide under nitrogen occurs[3,9,15] in the presence of a silica-rich liquid according to:

$$2SiC + SiO_2 + 2N_2 = Si_3N_4 + CO \qquad (1)$$

or

$$3SiC + 3SiO_2 + 2N_2 = Si_3N_4 + 3SiO_2 + 3CO \qquad (2)$$

To retain the SiC without Si_3N_4 decomposition during GPS of these composites, a nitrogen/argon gas mixture was used and relative densities of 98–99% were obtained for SiC–Si_3N_4 nanocomposites with <0·1% open porosity.

The presence of nano-sized silicon carbide did not inhibit densification. Unlike Si_3N_4–SiC composites with micron-sized inclusions,[14] composites with ultrafine SiC, even up to 15 vol%, densified readily when conditions similar to those used to densify monolithic Si_3N_4 were employed.

3.3 Characterisation

X-ray diffraction analysis was carried out on all samples. The $\alpha \rightarrow \beta$-Si_3N_4 transformation was complete in all cases. The added silicon carbide remained unchanged during densification and the SiC peaks grew in intensity as the volume percentage addition was increased. β-Si_3N_4 only was present in monolithic silicon nitride and β-Si_3N_4 with α/β SiC were present in the nanocomposite specimens when densified by hot-pressing, gas pressure sintering or pressureless sintering.

SiC was well dispersed in the Si_3N_4 matrix. Figure 4 shows an SEM micrograph of a typical fracture face for these composites (5 vol% Ibiden β-SiC). Fracture sites were generally at surface flaws, usually at the chamfers which were not polished to the same mirror finish as the faces under tension. TEM confirmed that no SiC agglomeration had occurred and both intragranular and intergranular SiC was observed during preliminary TEM observations.

Figure 5 compares the strength of hot pressed and gas pressure sintered water processed monolithic Si_3N_4 with Si_3N_4 nanocomposites containing 5 vol% α- and β-SiC. The average strengths for monolithic hot-pressed and gas pressure sintered Si_3N_4 are 930 and 910 MPa, respectively. At 5 vol% SiC additions, significant improvements in strength were observed and strengths of >1GPa were obtained for the nanocomposite materials. With either hot pressed or gas pressure sintered nanocomposites, higher average strengths were obtained for the nanocomposite with β-SiC inclusions.

The mechanical properties of pressureless sintered materials are generally lower than materials sintered with pressure. However, the same trends were evident as for pressure-assisted sintered nanocomposites. Inclusion of nano-sized SiC enhanced the mechanical properties of pressureless sintered Si_3N_4. The average flexural strength ($n = 7$) of water processed monolithic Si_3N_4 pressureless sintered at 1850°C was 660 MPa. Strength for nanocomposite containing 5 vol% Norton FCP 40 was slightly higher at 680 MPa but the average flexural strength of pressureless sintered nanocomposite with 5 vol% Ibiden Betarundum was 750 MPa. Again, β-SiC gave higher strengths than α-SiC.

Fig. 4. Fracture face of hot pressed Si_3N_4 5 vol% Ibiden Betarundum SiC.

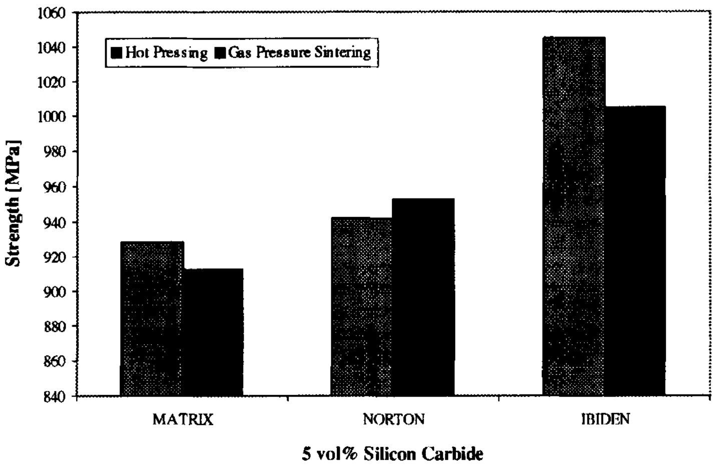

Fig. 5. Strength of hot pressed and gas pressure sintered Si_3N_4–SiC nanocomposites.

α-SiC is hexagonal which is the same crystallographic system as β-Si_3N_4, but β-SiC is cubic. If the SiC within β-Si_3N_4 grains is of a different crystal structure, then this may in some way influence the effect of the SiC particle within the grain. This is tentatively suggested at this stage and detailed TEM is required to investigate the effects of α- or β-SiC powder as reinforcement.

Increasing the volume fraction of silicon carbide led to further increases in the average strength. Figure 6 compares the strength of monolithic Si_3N_4 and nanocomposites containing 5, 7·5 and 10 vol% Norton FCP 40 α-SiC, densified by hot pressing. The average strength increased from 940 MPa with 5 vol% SiC to 1110 MPa with 7·5 vol% SiC present. At 10 vol%, the average strength, 1090 MPa, was very slightly lower. However, there was a wider range of values for this composite and strengths of up to 1275 MPa were obtained for individual specimens.

The optimum volume percentage addition of SiC is still not known. Nanocomposite with 15 vol% Norton SiC have been prepared and are currently being characterised. Materials containing higher volume percentage additions of Ibiden SiC are also under investigation.

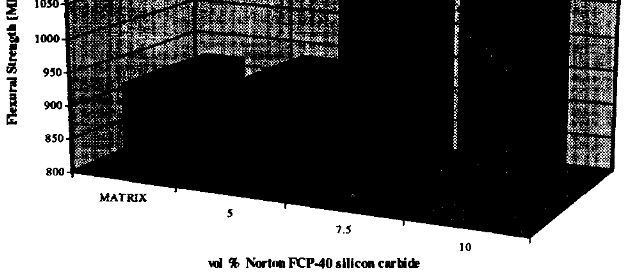

Fig. 6. Flexural strength of Si_3N_4 and Si_3N_4 containing 5, 7·5 and 10 vol% Norton FCP 40 α-SiC.

It is evident from this work that commercial ultrafine SiC powders can be well dispersed in Si_3N_4 to enhance its mechanical performance and, therefore, exploitation of these materials may be feasible since high strengths achieved in hot pressed silicon nitride nanocomposites can be reproduced by gas pressure sintering which requires unencapsulated pre-formed compacts thus alleviating the drawbacks associated with hot pressing.

4 Conclusions

Homogeneous Si_3N_4–SiC nanocomposites have been produced by water processing commercially available powders. It was found that addition of nano-sized SiC, even at 5 vol%, significantly improved the strength compared with monolithic silicon nitride. Near-complete densification has been achieved by pressureless sintering and gas pressure sintering, two economically viable sintering alternatives to hot-pressing and the high strengths achieved by hot pressing have been reproduced using gas pressure sintering.

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