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Preparation of Si_3N_4–SiC composites by microwave route

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Abstract. **Si_3N_4–SiC composites have been microwave sintered using *b*-Si_3N_4 and *b*-SiC as starting materials. Si_3N_4 rich compositions (95 and 90 vol.% Si_3N_4) have been sintered above 96% of theoretical density without using any sintering additives in 40 min. A monotonic decrease in relative density is observed with increase in SiC proportion in the composite. Decrease in relative density has manifested in the reduction of fracture toughness and microhardness values of the composite with increase in SiC content although the good sintering of matrix Si_3N_4 limits the decrease of fracture toughness. Highest value of fracture toughness of 6·1 MPa $m^{1/2}$ is observed in 10 vol.% SiC composite. Crack propagation appears to be transgranular in the Si_3N_4 matrix and the toughening of the composites is through crack deflection around hard SiC particles in addition to its debonding from the matrix.**

Keywords. **Ceramics; composites; microwave processing; microwave sintering.**

1. Introduction

Silicon nitride (Si_3N_4)–silicon carbide (SiC) composites are structural ceramic materials with immense potential for high temperature applications. They possess very desirable properties such as high hardness, high strength and high fracture toughness. Both Si_3N_4 and SiC themselves exhibit good chemical stability and high temperature shock resistance (Baril *et al* 1993; Pezzotti 1993; Hirano *et al* 1996; Fukasawa and Goto 1998). When composited the creep resistance has also been reported to improve (Niihara *et al* 1990; Hirano *et al* 1996; Rendtel *et al* 1998; Yamada and Kamiya 1999). Possibilities of making engine components using Si_3N_4–SiC composites have been discussed in the literature. Si_3N_4–SiC composites can be designed and sintered using particle size combinations so that the resulting material is either conducting or insulating. Such composites can be used in place of Si_3N_4–$MoSi_2$ composites to make glow plugs for diesel engines (Pezzotti 1993; Yamada and Kamiya 1999). Due to such high potential for application, the study of this composite has attracted much attention in the literature (Lange 1973; Buljan *et al* 1987; Niihara *et al* 1990). SiC of different forms such as particulates, platelets, whiskers and polytypic combinations have all been used in various proportions to make Si_3N_4–SiC composites and their mechanical properties have been examined (Lange 1973; Buljan *et al* 1987; Niihara *et al* 1990; Baril *et al* 1993; Pezzotti 1993; Pezzotti *et al* 1993; Hirano *et al* 1996; Fukasawa and Goto 1998; Herrmann *et al* 1998; Rendtel *et al* 1998; Yamada and Kamiya 1999; Yang *et al* 1999). It has been found that the fracture toughnesses of these composites are attributable to a number of mechanisms including particulate debonding, crack deflection and modulus transfer. Several of these properties have been carefully examined, critically assessed and reviewed by Hermann *et al* (1998).

Sintering of Si_3N_4–SiC composites is a crucial step in the preparation of the Si_3N_4–SiC composites. So far this has been accomplished using only conventional procedures. These procedures require high temperatures of the order of 1700°C and up to 8 h of sintering time when Si_3N_4 and SiC are used as starting materials (Yang *et al* 1999). Preparation of composites has been accomplished using metalorganic precursors which decompose into amorphous powders. Compositions of the amorphous powders can be adjusted to yield the desired proportions of Si_3N_4 and SiC in the resulting composites (Bill and Aldinger 1995; Bao and Edirisinghe 1999; Gozzi *et al* 2001). Nevertheless, these procedures inherit all the well known limitations of ceramic processing such as requirement of high temperatures, long sintering times, sintering additives, high pressures etc, for making Si_3N_4–SiC composites. There is a keen necessity for developing an efficient alternative method of sintering the composites. In this paper we report a new microwave method for the preparation of Si_3N_4–SiC composites and their room temperature mechanical properties.

2. Experimental

b-Si_3N_4 (Aldrich) and microwave prepared *b*-SiC (Ramesh *et al* 1994) were mixed in different volume proportions. Well mixed powders of Si_3N_4 and SiC were

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pelletized using 2% PVA as binder. Pellets were embedded in an insulated, thin SiC pit which was used as a secondary heater in microwave field. The assembly was placed inside a quartz setup with gas passing facility. The whole setup was then placed inside a monomode microwave reactor cavity (MES, France). Microwave sintering of the composites was performed in the ambience of flowing N_2. Pellets were irradiated with microwaves of 2·45 GHz frequency at 800 W of microwave power (MES, France). Temperature was measured using a shielded Pt/Rh thermocouple kept in close proximity to the sample and bringing it into contact with the pellet immediately (in under 2 s) after interrupting the microwave irradiation. Since the thermocouple was placed close to the pellet which was already heated nearly to the temperature of the pellet itself, the error in temperature measurement was very low and no more than – 10 to – 15°C. Density of the sintered pellets was measured using Archimedes method. Distilled water was used as displacement liquid. Pellets were dried at 120°C and then weighed to get dry weight (D). Pellets were then immersed in distilled water and evacuated in a vacuum desiccator. Bubbles started coming out from the pellets indicating water getting into the pores. Evacuation was stopped once bubbling was stopped. It was noticed that there was no bubbling from samples of high relative densities at the end of 3 min whereas it continued bubbling in samples with lower relative densities. Pellets were then suspended in water and suspended weight was noted (S). Finally, the sample was wiped with wet cotton to remove water from the surface and weighed to get wet weight (W). Bulk density, true density and apparent porosity of the samples were calculated as follows (Angadi *et al* 2002):

$$\text{Bulk density} = D/(W-S),$$

$$\text{True density} = D/(D-S),$$

$$\text{Apparent porosity} = [(W-D)/(W-S)] \times 100\%.$$

Phase analysis of the pellets was performed using X-ray diffraction (XRD, Siemens D-5005, Germany). Morphology of the sintered and fractured surfaces was studied using Scanning Electron Microscope (SEM, JEOL JSM-5600LV, Japan). Indentation method (Zwick 3212, Germany) was used to determine Vickers hardness and fracture toughness (K_{IC}) of the material. Anstis *et al* (1981) formula was used to evaluate the K_{IC} values. Vickers hardness was measured using a load of 100 g for 15 s and K_{IC} was evaluated after initiating cracks using a load of 10 kg for 15 s. Cracks were found to emanate from the corners of the diamond indenter.

3. Results and discussion

Compositions of the five different composites investigated here are listed in table 1 along with their measured properties in which SNC-95 represents a composite of 95 vol.% Si_3N_4 and 5 vol.% SiC. In figure 1, the XRD patterns of sintered composites are presented together. The peaks in the XRD were found to be only those due to *b*-Si_3N_4 and *b*-SiC. *b*-SiC used for the preparation of composite was itself prepared by microwaves by a process described elsewhere (Ramesh *et al* 1994). The highest temperature reached during sintering in all the cases was found to be 1375°C. Sintering was performed in the ambience of oxygen free nitrogen and there was no evidence of the formation of SiO_2 in the XRD. Theoretical densities were calculated assuming the volume-weighted densities of SiC and Si_3N_4. The densities of the sintered pellets evaluated, bulk and true densities along with relative densities with respect to theoretical are given in table 1. The estimated open porosities are also listed in table 1. Si_3N_4 rich compositions like SNC-95 exhibit high relative densities but sintered densities of SiC rich samples are low by comparison and decrease systematically indicating increased porosities. But all the sintered densities are much greater than what is generally obtained in conventional sintering performed without additives or use of pressure (Kodama *et al* 1990). It is known that SiC and Si_3N_4 particles do not sinter well at the interfaces and as a result elimination of porosity is difficult in SiC rich samples (Rendtel *et al* 1998).

SEM images of HF etched (deep etching) surfaces are shown in figure 2 for all the samples. It is evident from the figure that Si_3N_4 particles in contact sinter into surprisingly large monoliths in microwaves whereas SiC particles are found unaffected. Some SiC particles appear

Table 1. Density and mechanical properties of microwave-sintered composites.

Composite	Theoretical density (g/cc)	True density (g/cc)	Relative density (%)	Bulk density (g/cc)	Apparent porosity (%)	Fracture toughness (MPa m$^{1/2}$)	Vickers hardness (GPa)
SNC-95	3·429	3·356	97·8	3·255	3·06	5·2 (± 0·2)	16·5 (± 0·1)
SNC-90	3·418	3·290	96·2	3·150	4·28	6·1 (± 0·2)	16·8 (± 0·1)
SNC-85	3·407	3·247	95·3	3·084	5·03	5·5 (± 0·4)	17·1 (± 0·2)
SNC-80	3·396	3·179	93·6	2·973	6·46	4·7 (± 0·4)	15·8 (± 0·4)
SNC-75	3·385	3·050	90·1	2·747	9·91	4·0 (± 0·4)	14·6 (± 0·4)

embedded in Si_3N_4 monoliths. The prevalence of enclosed porosity is also evident. In SNC-75 where we expect inter-Si_3N_4 particle contacts to be reduced, Si_3N_4 sinters into a labyrinth with interspersed SiC particles.

The fractured surfaces were also examined using SEM (figure 3). Fracture has occurred by transgranular propagation of cracks in the monolithic Si_3N_4 matrix. During the crack propagation process SiC particles have also got debonded and the crack does not appear to have propagated through SiC. This is because the particulate (darker in contrast) embedded in the matrix of Si_3N_4 are seen unaffected. We feel that during debonding of SiC particles, the direction of the crack propagation has got deflected. The crack initiation could have occurred at points on the surface where the concentration of SiC particles is high (Kodama *et al* 1990) because SiC–Si_3N_4 interparticle bonding is weak. There is only a moderate decrease (~ 12%) in both microhardness and fracture toughness values as SiC concentration is increased (table 1). However, the relative densities have decreased significantly in SiC rich sample (by almost 8%). We consider this as a result of two compensating factors: (i) degradation of fracture toughness due to the decrease in density (Kodama *et al* 1990) and (ii) increase in fracture tough-

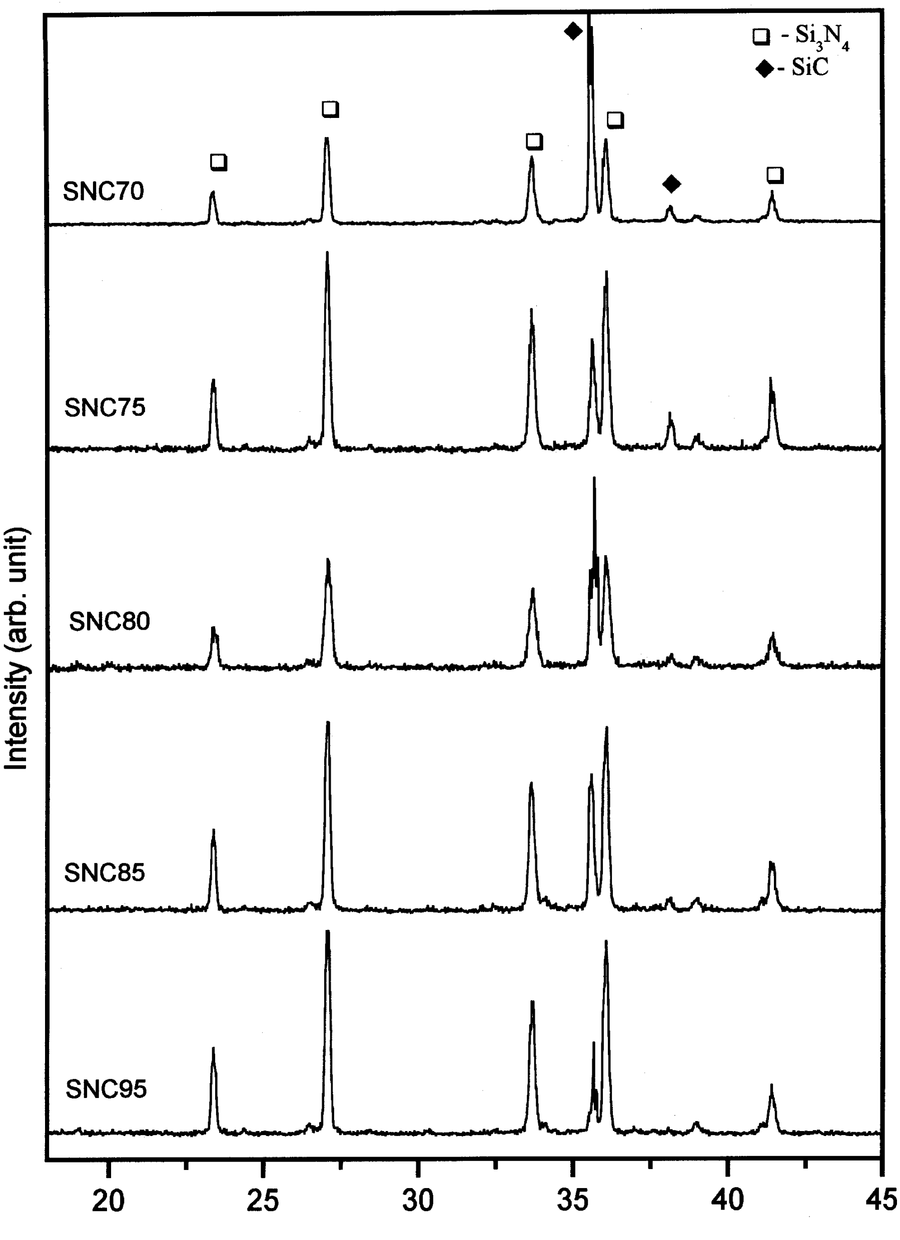

Figure 1. XRD patterns of microwave sintered Si_3N_4–SiC composites.

ness due to good sintering of Si_3N_4 and role of SiC (debonding and crack deflection). The severe loss in fracture toughness or strength due to low relative density (enclosed porosity) of the composite has been compensated by the presence of hard particles of SiC.

What is remarkable about the formation of these composites is that the sintering times required are just 40 min whereas in conventional heating it takes 4–8 h. Similarly the maximum temperature of sintering which is about 1700°C (Rendtel *et al* 1998) in conventional processes is

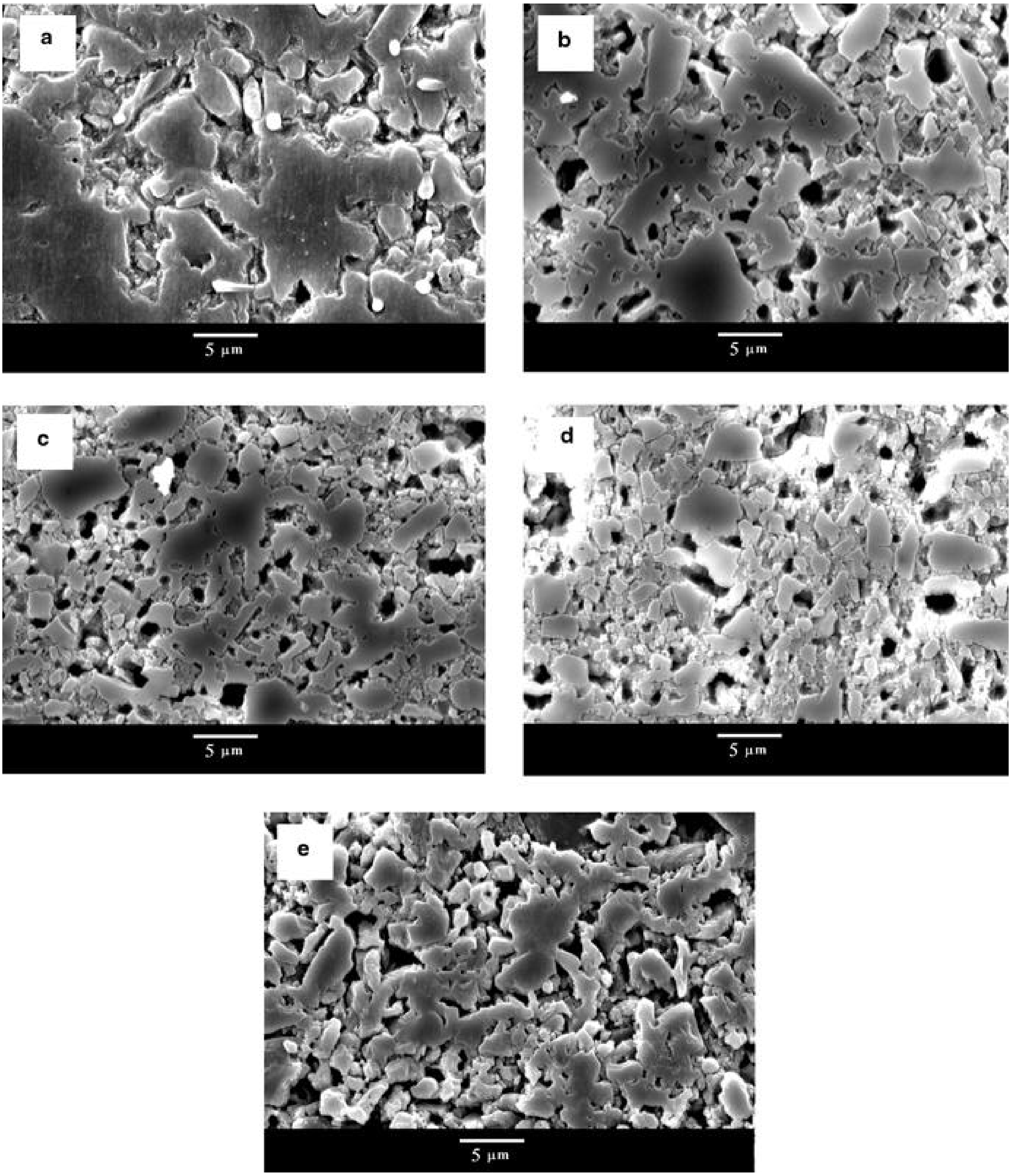

Figure 2. SEM pictures of microwave sintered and etched surface of Si_3N_4–SiC composites: **a**. SNC-95, **b**. SNC-90, **c**. SNC-85, **d**. SNC-80 and **e**. SNC-75.

only 1375°C in the microwave process. While in the conventional processes a variety of sintering aids like Al_2O_3, Y_2O_3 etc are used, in the present microwave processing no sintering aids have been added. This has resulted in relative densities being significantly lower than when sintering aids are used which therefore, causes significant loss of fracture toughness. However, figure 2 suggests that Si_3N_4 sintering itself is so extensive that the matrix behaves like a Si_3N_4 monolith. We, therefore, feel that by the use of modest sintering aids in microwave processing may actually help in realizing densities and toughnesses much higher than in the present work.

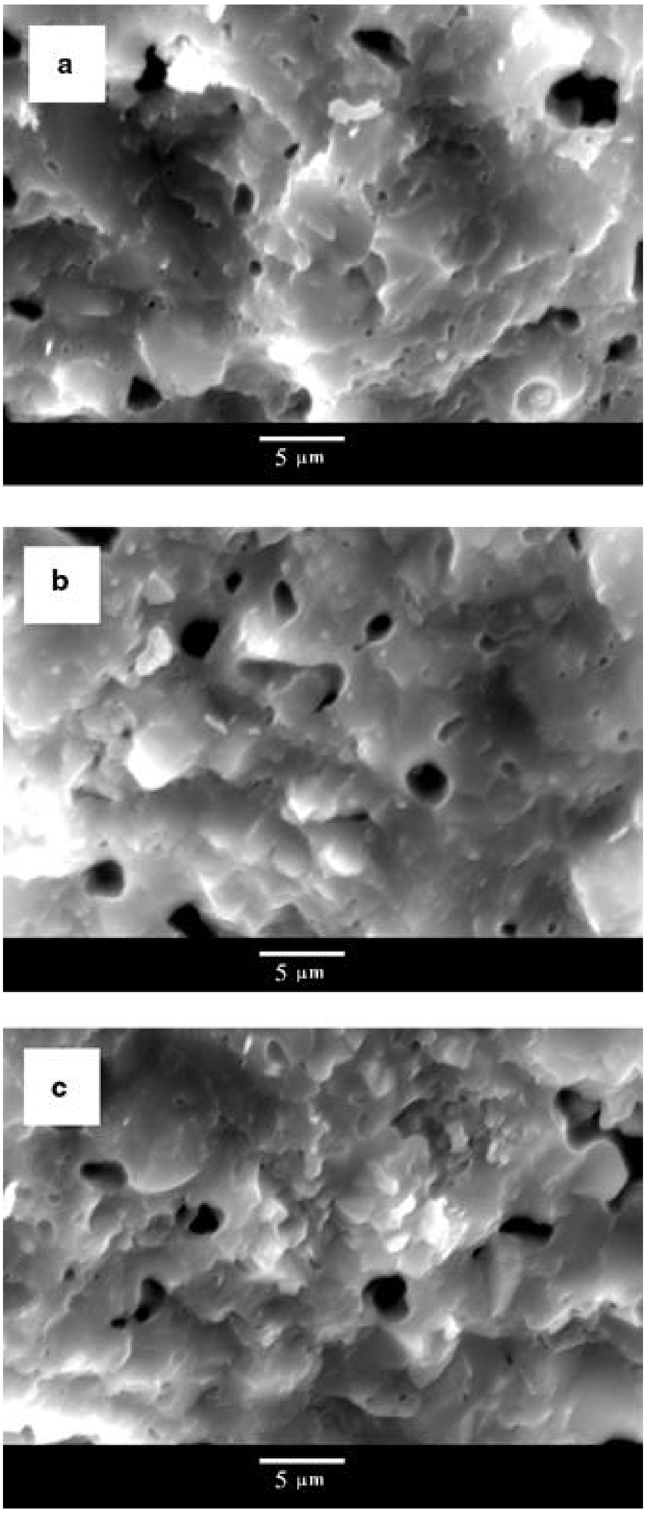

Figure 3. SEM pictures of freshly cleaved surface of microwave sintered Si_3N_4–SiC composites: **a**. SNC-90, **b**. SNC-85 and **c**. SNC-75.

Some preliminary conductivity studies have been performed on these sintered samples. While SNC-95, SNC-90 and SNC-85 were clearly insulators (conductivity of the order of 10^{-9} S/cm), SNC-80 exhibited a conductivity of $\sim 10^{-3}$ S/cm. However, behaviour of SNC-75 was found to be ambiguous. Such behaviour is expected because with 20 vol.% of SiC, we would expect SiC to cross the lower limit for percolation and hence makes the pellet conducting. But for rapid growth of Si_3N_4 into monoliths appear to keep SiC particles physically separated. Further investigations are in progress in which different methods of preparation are adopted. One, using SiC of distinctly smaller particle sizes in comparison to the size of Si_3N_4 particles and two, forming SiC *in situ* by using a ($Si_3N_4 + SiO_2 + C$) mixture where the initial carbothermal reduction and carbidation yields SiC particles of very small sizes.

4. Conclusions

Si_3N_4–SiC composites have been microwave sintered to very high densities in very short durations without the use of any additives or pressure. Relative densities of the composites have been found to decrease with increase in SiC content. Crack deflection and debonding appear to be the toughening mechanisms responsible for the observed increase in fracture toughness.

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