Nitridation of whisker-reinforced reaction bonded silicon nitride ceramics

M. D. PUGH*, L.GAVORET
Department of Mining & Metallurgical Engineering, McGill University, Montreal, Quebec, Canada
E-mail: mecheng@vak2.concordia.ca

Ceramic matrix composites were fabricated from silicon carbide whisker-reinforced reaction bonded silicon nitride. Optimal dispersion of the SiC whiskers in the silicon powder slip was achieved by milling and pH control; a pH range of 4–5 giving the best results. Only a slight drop in green density was observed for a 30 wt% addition of SiC whiskers. The effects of the whisker additions on the nitridation kinetics of reaction bonding were investigated and the additions were found to increase the induction period before nitridation and to slightly decrease the nitridation rate but green density and temperature were still found to be the main factors controlling nitridation. Modulus of Rupture measurements for the composites showed a decrease in strength compared to the monolithic material. © *2000 Kluwer Academic Publishers*

1. Introduction

In the last two decades improved processing has resulted in significant improvements in the strength of engineering ceramics but this in itself has not overcome the main limitation to the use of these materials in mechanical engineering applications namely that of catastrophic failure. By reinforcing ceramic matrices with fibres, the ceramist is trying to control crack propagation within the material and thus reduce the likelihood of sudden, catastrophic failure. The toughening mechanisms that hinder crack movement in composites include load transfer, crack-fibre interaction (crack deflection), fibre pullout and crack-bridging and it is these effects that are desired in the ceramic matrix composite (CMC) [1]. Successful Si_3N_4 and Al_2O_3 matrix composites containing SiC whiskers have been produced using hot-pressing techniques, but these processes tend to be either limited to uni-directional pressing (hot-pressing) or are expensive (hot-isostatic pressing). Other techniques which hold more promise from a manufacturing viewpoint include pressureless sintering and reaction bonding.

The main difficulty in pressureless sintering of CMC's is the large bulk shrinkage ($\geq 40\%$) inherent in this process. As the composite shrinks during densification, interference occurs between whiskers or fibres, causing a bridging effect which inhibits further shrinkage and results in a porous and relatively weak microstructure. One way to avoid this problem is to align the whiskers prior to sintering. In previous work [2] this was achieved by extruding a mixture of Si_3N_4-whiskers and Si_3N_4-powder with an organic binder which was burnt out prior to sintering. This resulted in a significant toughening (13 MPa·m$^{1/2}$) compared to the monolithic material (8.1 MPa·m$^{1/2}$) but only in the plane perpendicular to the whisker orientation. As one would expect, the toughness parallel to the whiskers fell to 6 MPa·m$^{1/2}$.

Another way to solve this whisker-bridging problem is to avoid processes requiring densification and their associated shrinkages. Reaction bonding of silicon powder to form Si_3N_4 (RBSN) requires relatively low temperatures (compared to sintering of Si_3N_4) and has negligible shrinkage; the main drawback to this route is the resultant porosity of $\approx 23\%$ [3]. In this study, SiC whiskers were used as the reinforcing phase and the effects of these additions on the nitridation of silicon compacts has been investigated.

2. Experimental

A high purity silicon powder† ($\sim 7\,\mu$m diameter) was mixed with SiC whiskers‡ ($\approx 1\,\mu$m diameter and 15–50 μm in length) and a nitriding additive (high purity iron powder $\approx 6\,\mu$m) by attrition milling in distilled water with sintered silicon nitride media (5 mm diameter). Iron was added due to the presence of approximately 0.5 wt% oxygen on the starting silicon powder surface which rose to a maximum of 1.2 wt% after aqueous milling. This surface silica is known to hinder the onset of nitridation [4]. The viscosity of the colloidal dispersion was measured after mixing using a cone-type

---

† Sicomill 4C, Superior Graphite.

‡ American Matrix Co.

Present Address: Department of Mechanical Engineering, Concordia University, Montreal, Quebec, Canada.

viscometer.[§] Dispersion of the whiskers and optimisation of the solids loading was achieved by varying the pH of the slip using ammonium hydroxide (NH_4OH) or hydrochloric acid (HCl). A popular polymeric deflocculant (Darvan C—ammonium polymethacrylate) was initially tried but proved unsuitable for this system. From the dispersed slurry, compacts were made by two techniques: firstly, slip casting into plaster moulds and secondly, microwave drying the slurry and die-pressing the resulting powder/whisker mixture after granulation through a 212 μm sieve.

After drying at 130°C, nitridation of the Si-SiC$_w$ compacts was carried out using a thermo-gravimetric-microbalance[¶] (TGB) attached to a controlled atmosphere furnace. Due to the weight gain (67%) that accompanies the complete nitridation of silicon, it is possible to follow the extent and kinetics of the reaction by monitoring the sample weight. A thermo-gravimetric balance (TGB) furnace system was constructed to allow continuous sample weight measurement, whilst the sample was suspended in flowing nitrogen at temperatures up to 1450°C. The sample was contained in a slipcast alumina crucible that contained many holes to allow unrestricted gas flow to and from the compact. This "basket" was lowered and suspended in the hot zone on platinum wire. Alumina was used for the basket due to the reactivity of the silicon/silicon species with other materials (Pt, Mo, W, BN). Nitridation experiments were carried out in pre-purified nitrogen after evacuation, purging and backfilling. The force readings from the microbalance were collected on a PC and the weight change recorded as a function of time.

The presence of SiC whiskers was expected to have some effect on the extent and rate of nitridation. This aspect was investigated by measuring the weight gain for samples containing differing amounts of whiskers (0, 15 and 30 wt%). Density measurements were made using Archimedes's method (in mercury for green compacts and in water for nitrided compacts). α/β phase ratios were measured using x-ray powder diffraction [5]. Four point bending was carried out on a universal testing machine with a crosshead speed of 0.5 mm/min on $9 \times 2.5 \times 55$ mm bars which had been surface ground (240 grit diamond). Hardness tests were carried out on polished samples using a Vickers diamond indentor with a 20 kg load.

3. Results
3.1. Dispersion
One of the main aims of the work was to obtain both a good dispersion of SiC whiskers in the silicon powder and produce a low viscosity slip of relatively high solids loading. Viscosity measurements at 500 rpm showed that viscosity was dependent on the % of whiskers added but that a minimum viscosity could be obtained by controlling the pH of the slip.

Plots of viscosity versus pH for 4 different slurries ranging from 0 to 20 wt% whisker content, shown in Fig. 1, indicate that for a given solids loading, the vis-
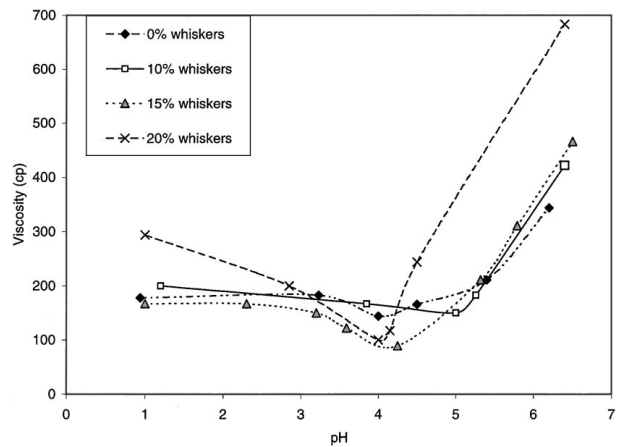
Figure 1 Viscosity vs pH for varying whisker content.

cosity of the slip decreases with increasing pH until a minimum viscosity is reached after which there is an increase in viscosity and an increase in the degree of whisker flocculation. The viscosity of the slurry containing more than 15% whiskers is more sensitive to a change in pH and flocculation occurs rapidly as the pH increases from the minimum value (pH 4).

Both the surface chemistry and the surface area of the colloidal particles play an important role in the dispersion behaviour. The silica layer around the particles and whiskers can easily form a silanol which could lead to aggregation of the colloidal particles. The higher surface area-to-volume ratio of the whiskers would promote this and coupled with the physical entanglement that is more likely with whiskers, flocculation of the slurry containing a high percentage of whiskers occurs more rapidly as pH changes from the minimum value.

Generally, a good dispersion of whiskers was obtained in the pH range of 4 to 5. The relative density of green slipcast compacts made from slips of minimum viscosity decreased slightly with increasing whisker content but even with 20 wt% whiskers the value only dropped by 4% from that of a pure silicon compact (53%).

Microstructural analysis of the green compacts indicated that good dispersion of the SiC whiskers occurred when they were prepared from minimum viscosity (deflocculated) slips. Flocs (whisker bundles) became more common in the 20% whisker slips at pH > 5. It is apparent that careful slip control is required to produce well-dispersed, homogeneous compacts.

Slipcasting was found to be the best method for achieving a uniform green compact from the dispersed whisker-silicon powder mixture. The other method investigated (die-pressing of dried powder/whiskers mixtures) gave lower green densities and for this reason more emphasis was placed on slipcasting.

3.2. Kinetics
The effect of the silicon carbide whiskers on the nitridation of the silicon compacts was measured by lowering the samples into the hot zone and monitoring the ensuing weight change with time, at a constant temperature. The microbalance can also be used to show a decrease in nitridation rate and hence indicate the time for a temperature rise; this gives a step-ramp heating profile similar

T A B L E I Nitridation kinetic data

$T/°C$	Δt_1 (hrs)			k_{II} (%Si conv./min)		
	0% whisk	15% whisk	30% whisk	0% whisk	15% whisk	30% whisk
1340	1.35	1.7	1.7	0.4	0.4	0.4
1365	1.3	0.8	1.5	0.9	0.8	0.3
1390	0.4	0.4	0.5	3.4	1.8	1.6
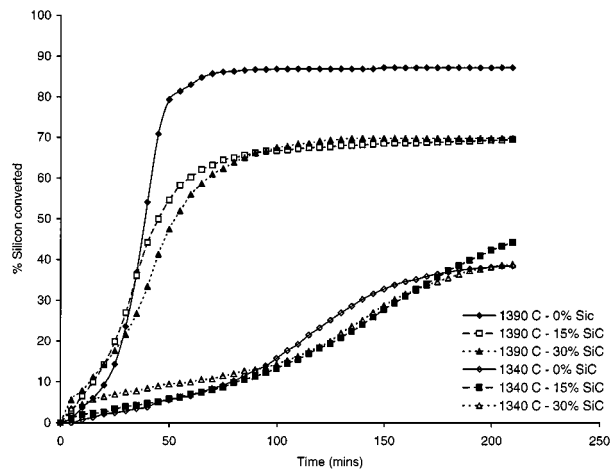
Figure 2 Thermo-gravimetric curves for the nitridation of (a) 0%, (b) 15%, and (c) 30% SiC$_w$—compacts.

to that commonly used in commercial reaction-bonding and as used in Section 3.3.

Thermo-gravimetric curves were obtained, with examples shown in Fig. 2. These data were further analysed by differentiation to determine induction periods (Δt_1, the time taken before rapid weight gain started) and linear rate constants (k_{II}, the slope at the point of inflection).

The graphs show that, as expected, the % silicon converted is markedly dependent on temperature for all whisker contents (0–30 wt%). Table I gives the nitridation rate parameters and these indicate that the induction period (Δt_1) decreases with increasing temperature, i.e. nitridation starts sooner at the higher temperatures. In this stage of the process, removal or disruption of the surface silica layer on the silicon particles has to occur to allow nitrogen access to the silicon. This reaction, as well as the actual nitridation, is very temperature dependent thus the decrease in Δt_1 with increasing temperature. The mechanism of surface silica removal has not yet been firmly established but the formation of gaseous SiO at higher temperatures in reducing conditions can occur; SiO_2 can react with silicon to form gaseous SiO and in this way be eliminated during the nitridation process. In the present case, deliberate additions of small quantities of iron, which have been shown to assist in the disruption of this silica film by devitrification [4], lead to the direct exposure of the underlying silicon and subsequent nucleation and growth can then occur.

As shown in Table I, with increasing temperature, the linear rate constant increases. The gas state reaction during the formation of α-Si$_3$N$_4$ is coupled with the

diffusion of nitrogen into the pores generated by silicon evaporation. Increasing the temperature has the effect of accelerating this evaporation-condensation process and also of increasing the nitrogen diffusion rate and therefore directly increases the rate constants.

At higher temperatures, the formation of β-Si$_3$N$_4$ occurs. It has been suggested [6] that this reaction happens in the liquid state. The nitrogen diffuses through a liquid, often FeSi$_2$ or down the large channels which exist in the z-direction of the β-Si$_3$N$_4$ structure [3, 7].

The data indicate that at low temperatures (1340°C) there is a slight increase in induction time for whisker-containing samples. This is due to several factors: firstly, the SiC whiskers are also prone to surface oxidation and will be covered in a surface silica film (even though a small amount of fine iron powder was milled in with the starting material to facilitate the silica breakdown). Thus it will take longer for the appropriate nitriding conditions (P$_{N2}$, P$_{Si}$, P$_{SiO}$) to be attained within the whisker reinforced compacts. Secondly, the SiC whiskers provide nucleation sites for silicon nitride formed from the gaseous phase. These nuclei would not be favourable growth sites compared to those on silicon surfaces due to the absence of available silicon for further nitridation and thus lead to a reduction in the number of "effective" nuclei and hence a reduction in the growth rate of the RBSN. However this step, involving formation of Si$_3$N$_4$ on the SiC, is important in providing material to bond the SiC whiskers into the growing Si$_3$N$_4$ matrix as shown in Fig. 3.

The rate constant (k_{II}) for the period Δt_2, when most of the conversion takes place, is again very temperature dependent, increasing markedly with increasing temperature as expected and also decreasing with increasing whisker content especially at higher temperatures. This slower conversion may be due to the reason stated above, where the growth of nuclei on the SiC whiskers is curtailed by the absence of underlying silicon (the SiC being stable in these conditions).

3.3. Complete nitridation
In further experiments, compacts of varying green density, both with and without whiskers, were nitrided following a temperature schedule which had been previously determined on the TGB by raising the temperature when a significant decrease in the rate of weight change of the sample was recorded. Fig. 4 shows the conversion rates for 0% and 18% SiC whisker-containing materials with two green densities. There are no significant differences in behaviour except that the composite materials reach 50% conversion sooner than the silicon-only compacts but they all reach ≈90% conversion at the same time. For the complete nitridation experiments, the nitridation schedule began at 1250°C in a similar fashion to a typical commercial nitridation (the main reason being to prevent overheating and melting of silicon in the interior due to the exothermic nature of the nitridation reaction). At this temperature, the gas phase reactions between SiO, Si and N$_2$ are favoured and promote the formation of fine α-Si$_3$N$_4$ [3, 6, 8] and it is believed that these reactions are responsible for the initial weight gains observed however these early
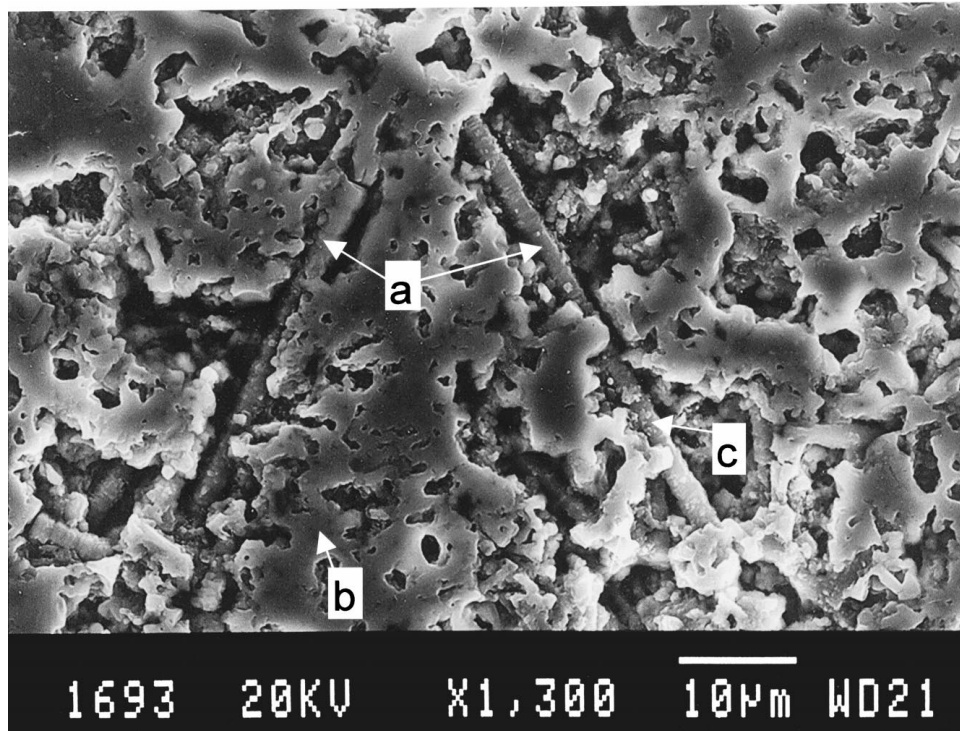
(i)
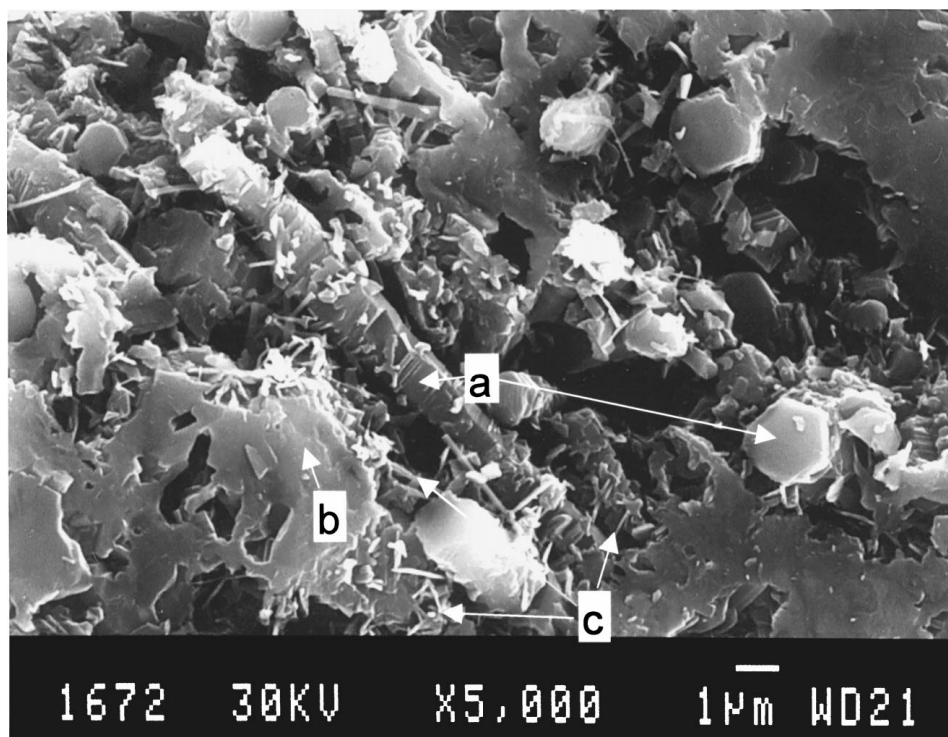
(ii)

Figure 3(i and ii) Microstructure of SiC-whisker reinforced RBSN (SEM) at low (i) and higher (ii) magnification showing (a) the SiC whiskers, (b) the α-Si_3N_4 matte and (c) α-Si_3N_4 whiskers.

reaction products can "seal" the silicon surface, slowing down further reaction (in this case the increase in temperature changes the reaction rate due to increased volatilization and diffusion of silicon[3]). In the kinetic studies (e.g. Fig. 3) the samples are brought to temperature very quickly and thus avoid this low temperature stage. (As shown in Fig. 5, in a similar way to pure silicon reaction-bonding, the nitrided density of the whisker-containing compacts is strongly dependent on green density, with the whisker additions having little effect.

What is more significant is that due to the volume expansion during the nitridation, the lower the volume fraction of silicon in the green material (or the higher the silicon carbide or other "inert" filler content) the higher the volume of porosity will be in the nitrided compact. This is shown in Fig. 6 where the volume % of porosity, SiC whiskers and Si_3N_4 in a completely
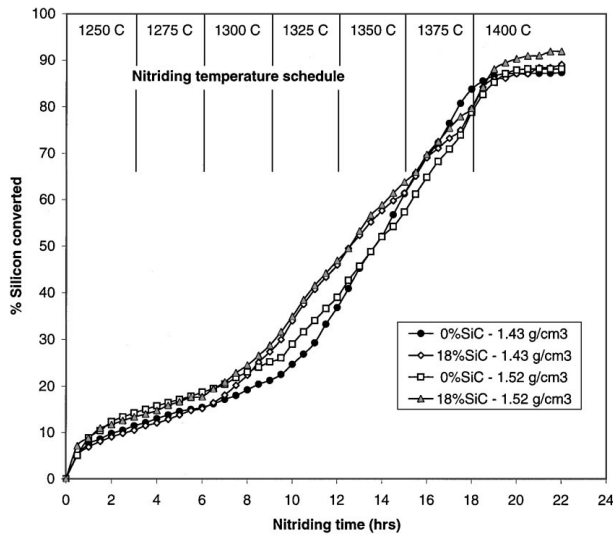
Figure 4 Nitridation schedule and % Silicon converted for compacts with (18 wt%) and without SiC whiskers.
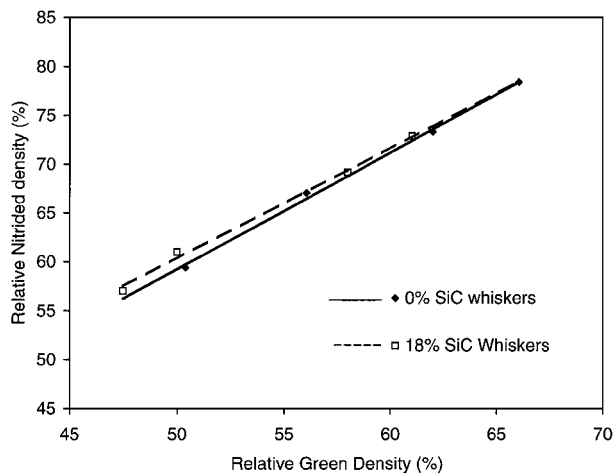

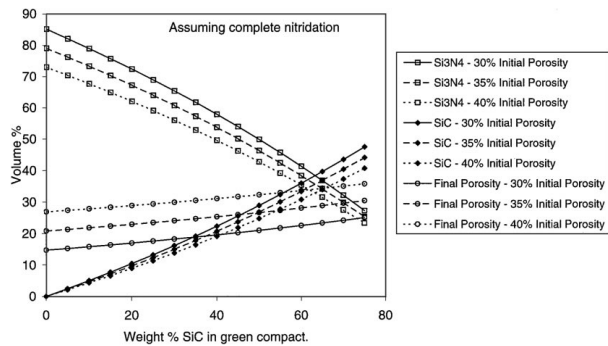*Figure 5* Effect of green density and whisker content on nitrided density.

Figure 6 Variation of volume % of final constituents with Initial SiC content and initial porosity.

nitrided compact are calculated as a function of initial SiC whisker content for three levels of porosity in the green compact. The 30 volume % porosity is an upper bound as green compacts with higher densities than this do not usually completely nitride due to premature closure of the interconnected pore structure limiting access of nitrogen. What can also be seen is that an initial SiC whisker content of 30 wt% results in only ≈15 vol% SiC in the nitrided material. In the present study, 30

wt% whiskers was chosen as the maximum reinforcement content in order to limit the residual porosity in the final material.

One factor that may be important in nitriding of these whisker compacts is the ability to nitride at higher temperatures or at faster rates. In normal reaction bonding of silicon, temperatures have to be increased very slowly so as to prevent large scale melting of the silicon ($T_m = 1410°C$) leading to large pores and unreacted silicon. This problem is exacerbated by the exothermic nature of the nitridation reaction and commercial firings can take several days to complete. In compacts containing high percentages of whiskers (30%), this problem was reduced, possibly due to a containment effect of the whiskers preventing the formation of large pockets of liquid or their role as heat sinks or moderators (due to the higher thermal conductivity of the pure silicon carbide whiskers), providing a more uniform temperature distribution especially in the sample interior where overheating is more likely. This overheating (and liquid formation) can limit further nitridation by blocking off access of nitrogen to the interior and hence reduce the rate at which the ambient temperature can be increased. This aspect of nitriding a composite RBSN was not explored further in the present study but may indicate a method of decreasing production times which can be quite lengthy in reaction bonding of commercial products.

The typical microstructure of an RBSN-SiC$_w$ composite (see Fig. 3) shows the SiC whiskers, the α-Si$_3$N$_4$ matte and fine β-Si$_3$N$_4$ whiskers as indicated. Approximately 30% of the Si$_3$N$_4$ formed was in the β phase as detected by X-ray analysis.

3.4. Mechanical properties

RBSN bars containing 0, 15 and 30 wt% SiC were fabricated, ground and tested in 4 point bending. The average Modulus of Rupture (MoR) values are shown below (Table II):

All the samples were characterised by having similar nitrided densities (≈72% theoretical) and these relatively low densities are in part responsible for the low strengths measured. The unreinforced material is similar in strength to some commercial materials (160 MPa) but not as high as that expected. The MOR decreases with increasing whisker content, dropping by 70 MPa on the addition of 30 wt% SiC whiskers. Scanning Electron Microscopy (SEM) showed that in all types of samples, both with and without whiskers, fracture initiation occurred at large pores and sometimes at low density regions. Large whisker clumps which would have acted as critical defects were not observed, providing additional confirmation of the successful dispersion of the whiskers in the slip. The decrease in fracture strength upon whisker reinforcement in CMC's is not

TABLE II Modulus of rupture values as a function of SiC content

	0% SiC	15% SiC	30% SiC
MoR/MPa	190	140	120

uncommon and in the present case is attributed to a decrease in the structural homogeneity of the material and the presence of low strength interfaces. Microstructural examination showed that some whiskers were fully incorporated into the silicon nitride matrix whilst others were not. Some whiskers are partially bonded into the matrix with the remainder of the whisker unattached with possibly some nitride growth on the surface. These types of inhomogeneities in the structure are the most likely reason for the decrease in strength.

4. Conclusions

Silicon Carbide whiskers can be successfully dispersed in an aqueous\silicon powder slip by milling and pH control. Deflocculation occurs at minimum viscosity in the pH range 4 to 5.

Addition of 30 wt% SiC whiskers results in $\approx$4% decrease in green density.

The induction period for nitridation increases and the nitridation rate decreases with increasing whisker content at low reaction temperatures but in general the whisker additions have only a small effect on the nitridation kinetics when compared to other factors such as temperature and green density.

Fracture strength decreases with increasing whisker content; from 190 MPa with no whiskers to 120 MPa with 30 wt% whiskers for samples with 28% porosity.

Although nitridation is slower for whisker-containing samples, it is not a major problem as temperatures can be increased more rapidly during the nitriding cycle without melt-out.

References

1. D. B. MARSHALL and J. E. RITTER, *Bull. Am. Ceram. Soc.* **66**(2) (1987) 309.
2. D. MUSCAT, M. PUGH and R. A. L. DREW, "Ceramic Transactions, Vol. 19: Advanced Composite Materials," edited by M. Sacks (Am. Ceram. Soc., Westerville, OH, 1991) p. 137.
3. A. J. MOULSON, *J. Mat. Sci.* **14** (1979) 1017.
4. S. M. BOYER, D. SANG and A. J. MOULSON, "Nitrogen Ceramics," edited by. F. L. RILEY (Noordhoff, Leyden, 1977) p. 297.
5. A. BENNET, *Mat. Sci and Tech.* **2** (1986) 895.
6. M. JENNINGS, *J. Mat. Sci.* **18** (1983) 951.
7. S. M. BOYER and A. J. MOULSON, *ibid.* **11** (1976) 1288.
8. P. LONGLAND and A. J. MOULSON, *ibid.* **13** (1978) 2279.