

# Mechanical property improvements in Nicalon SiC fibre reinforced silicon nitride ceramics by oxide coating of Si<sub>3</sub>N<sub>4</sub> starting powders

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Received 24 June 2003; revised 5 May 2004; accepted 7 May 2004

## Abstract

Ceramic matrix composites are attractive as candidate materials for high-temperature applications offering some advantages compared to monolithic ceramics and high-temperature metal alloys. SiC fibre reinforced silicon nitride is one such composite system. However, the processing route is critical to the production of a reliable composite. In this study, silicon nitride matrix densification was improved and sintering temperature was lowered by coating of Si<sub>3</sub>N<sub>4</sub> particles with oxides deposited from hydrolysed metal alkoxides. The solution containing oxide coated Si<sub>3</sub>N<sub>4</sub> powders was used as a slurry to infiltrate Nicalon SiC fibre tows. Following previous studies, the fibres were heat-treated in carbon monoxide to improve mechanical and surface properties. Infiltrated green bodies were hot-pressed at elevated temperatures to produce dense composites. The results showed that particle coating accelerated densification kinetics, eliminated pores and reduced the required hot-pressing temperature. There was also less fibre degradation as a result of the lower temperature of densification. Bending strength and fracture toughness of the composites were measured and fractography was conducted using scanning electron microscope. Composites manufactured using coated Si<sub>3</sub>N<sub>4</sub> powders showed improved properties, specifically matrix stiffening and delayed crack initiation under load.

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*Keywords:* A. Ceramic matrix composites (CMCs); B. Fibre/matrix bond; B. Mechanical properties; E. Sintering; Oxide coating

## 1. Introduction

Ceramic matrix composites (CMCs) are candidate structural materials for high-temperature applications because of their higher temperature capability compared with metal alloys, and higher fracture toughness compared with monolithic ceramics [1–7]. For this reason, CMCs are considered in particular to have potential in advanced aero-engines [8,9]. Among these CMCs, both carbon fibre and silicon carbide fibre reinforced silicon nitride composites are promising and have received considerable attention in the literature [10–12]. Successful toughening of CMCs depends upon the ability of reinforcing fibres to arrest crack propagation. One might imagine that the presence of high-strength fibres, which are well bonded to the matrix, might also greatly improve strength. However, what is required

more urgently is an increase in toughness. This depends upon the mechanisms of energy absorption such as fibre debonding and frictional pullout, and a balance must be achieved between load transfer across the fibre–matrix interface and fibre debonding and slip in the region of the propagating crack [2,6]. Therefore, the mechanical performance of CMCs is very sensitive to the properties of the fibre–matrix interface.

SiC-based fibres have a better resistance to oxidation than other ceramic fibres. However, the tensile strength of Nicalon fibres decreases dramatically with an associated significant weight loss as the temperature is raised beyond 1200 °C. The large amount of oxygen in the fibres (10–14%) is responsible for their degradation at high temperature. It is necessary to reduce the oxygen content or to improve refractoriness properties of the fibres to prevent the thermal degradation of fibres during composite fabrication. Recently, Hi-Nicalon with a low oxygen content (0.5% or less) was developed by Japan Nippon Carbon. With

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the oxygen content being decreased, silicon carbide fibre reinforced silicon nitride composites (Hi-Nicalon/SiC) are expected to be used at above 1400 °C [13,14].

Further studies suggest the fibre structure contained 1–3 nm silicon carbide microcrystals with clusters of polyaromatic carbon, and silica with evidence of oxycarbide phase. Many researchers have investigated the effect of high-temperature heat treatment on fibre strength retention in various environments [13–17]. It has been found that fibres heat treated in inert environments (Ar, N<sub>2</sub> and vacuum) showed outgasing of decomposition products. On the other hand partial pressure of carbon monoxide provided maximum strength retention [15–17]. Moreover Demir and Thompson [15] not only achieved a 50% strength increase but also deposited a thin carbon coating on the Nicalon fibres after high pressure CO heat treatment. This was an important development for using Nicalon SiC fibres to reinforce ceramic matrices at higher temperatures since strength increase and carbon coating of the reinforcing fibres enhance mechanical properties of CMCs. Also improvements in fibre properties and matrix properties are very important since crack initiation and crack propagation are sensitive to the porosity of the ceramic matrix.

When Nicalon SiC fibres are used to reinforce silicon nitride ceramics, low temperature densification of the matrix is important since fibre degradation occurs at higher temperatures (above 1200 °C). Therefore the sintering temperature should be kept as low as possible for Nicalon SiC fibre reinforced Si<sub>3</sub>N<sub>4</sub> ceramic green bodies. In order to reduce sintering temperature, well-established techniques for coating pigment particles with hydrated oxide or hydroxide films have recently been extended to the ceramic fields [18–20], and it is recognised that the production of coated particles using a hydrolytic method is, in principle, preferable to the simple production of mechanically mixed powders. It is clear that sintering additive particle size and homogeneity of dispersion within the silicon nitride are both factors favouring the densification of the silicon nitride. Sintering of coated powders has been reported to be faster, and higher sintered densities and strength may be obtained under conditions using in situ precipitation of the sintering additive by comparison with those obtained from conventionally mixed powders [20]. Therefore in the present study, oxide coated and mixed Si<sub>3</sub>N<sub>4</sub> powders and in situ carbon coated Nicalon SiC fibres [15] were used to fabricate

two types of continuous SiC fibre reinforced ceramic composites.

## 2. Experimental

Nicalon SiC fibre, NL-207 (Nippon Carbon Japan) was CO heat-treated in preparation for use as reinforcement. A high purity  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> powder (H.C. Starck-Berlin, Grade LC12N) containing 96%  $\alpha$ -phase with a mean grain size of 500 nm was used. Silicon nitride powder, in amounts corresponding to an overall MgO + Al<sub>2</sub>O<sub>3</sub>/(Si<sub>3</sub>N<sub>4</sub> + MgO + Al<sub>2</sub>O<sub>3</sub>) concentration of 5 wt%, was added to the MgO + Al<sub>2</sub>O<sub>3</sub> alcohoxides solution. After magnetic stirring for 24 h the silicon nitride powders had become coated. Details of the method are given elsewhere [18,21]. Incorporation of continuous heat-treated fibres into the matrix was performed using slurry infiltration (Fig. 1). Si<sub>3</sub>N<sub>4</sub> matrix slurry was prepared either from coated powders or mixed powders. The hydrolysed and coated powder gel was used directly for slurry infiltration. The mixed powders slurry was prepared by PVA water solution and then infiltrated through the fibre. The fibre yarn was fed through a slurry tank, and the slurry impregnated fibres were wound on to a hexagonal drum, and then partially dried as illustrated in Fig. 1. The infiltrated material was then cut into short segments, which were stacked together for cold-pressing into the green body. Consolidation of the green bodies was carried out by hot-pressing using a specially machined graphite die. The inside BN layer was used to avoid reaction between carbon and the glass matrix and the outside C layer created a CO atmosphere.

Bending strength and fracture toughness of the composites were determined by three-point bending. Bar shaped specimens were cut from hot-pressed samples, ground and polished into 3 × 4 × 45 mm bars for bend strength measurement, and 2 × 4 × 45 mm notched sample for fracture toughness measurement. A 30 mm span was used for both tests. The notch length was half of the sample height (2 mm) and cut by a thin diamond saw. All tests were carried out using an Instron universal testing machine (2–20 kN) using a cross-head speed of 0.1 mm/min using machine. Load–displacement curves during bending and fracture toughness tests were recorded using a computer/data-logging system. At least three specimens were tested

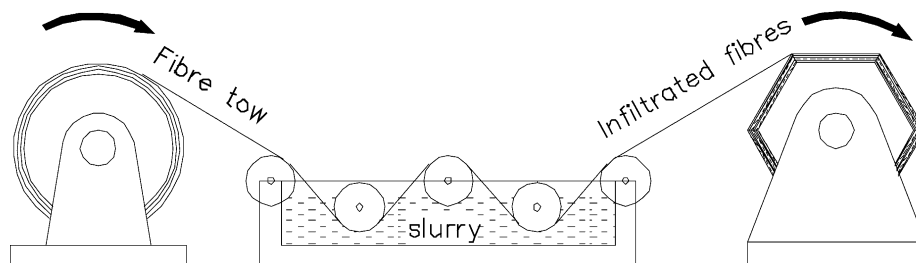


Fig. 1. Schematic representation of the slurry infiltration.

for each material. Polished sections of the composites and fracture surfaces were examined using a SEM, HITACHI S-2400. Product phase compositions were determined by X-ray diffraction using a Hagg-Guinier camera and Cu  $K\alpha_1$  radiation.

### 3. Results and discussion

#### 3.1. Pressureless sintering of oxide coated and mixed $Si_3N_4$ powders

The effect of oxide coated  $Si_3N_4$  powders on densification behaviour of pressureless sintered monolithic silicon nitride ceramics were investigated before composite fabrication. Sequential MgO and  $Al_2O_3$  coating was used since the previous study showed that low temperature and rapid densification was achieved with coating by these additives [21]. The powder processing was carried out using an additive mix of 3 wt% MgO + 2 wt%  $Al_2O_3$  for coating or mixed method. It is assumed that particle coating provided a uniform oxide layer around the silicon nitride powders. Mixed oxide additives were distributed randomly within the  $Si_3N_4$  powders. This decreased total contact surface area between oxide additives and  $Si_3N_4$  particles. It is expected that this situation will retard eutectic reaction during sintering. Cold isostatic pressed  $Si_3N_4$  samples prepared for each method were pressureless sintered at temperatures of 1350 and 1600 °C for 60 min as shown in Table 1. Densities and  $\alpha$ - $Si_3N_4$  to  $\beta$ - $Si_3N_4$  transformation as a function of temperature are plotted in Fig. 2 for these samples.

An immediate conclusion from the results is that the amount of densification achieved for the coated powder is significantly better than that for the mixed powders. Theoretical densities for these samples can be estimated as being in the range 3.15–3.16  $g\ cm^{-3}$  based on the presence of ~10 wt% of grain boundary material and the hot-pressed results [18]. The observed maximum sintered densities of 3.15  $g\ cm^{-3}$  (Table 1) are in good agreement with these calculations as also are SEM micrographs (Figs. 3 and 4) that showed negligible levels of porosity.

Table 1  
Densities of  $Si_3N_4$  pressureless sintered with 2 wt%  $Al_2O_3$  + 3 wt% MgO at various temperatures for 60 min

Temperature (°C)	Coated powder			Mixed powder		
	Density ( $g\ cm^{-3}$ )	%TD	% $\beta$	Density ( $g\ cm^{-3}$ )	%TD	% $\beta$
1350	2.37	75.3	5	2.31	73.3	5
1400	2.80	88.9	7	2.68	85.1	5
1450	3.12	99.1	15	2.98	94.6	14
1500	3.15	100	28	3.02	95.8	24
1550	3.15	100	58	3.01	95.5	56
1600	3.12	99.1	77	2.99	94.9	75

Each  $Si_3N_4$  particle initially has a silica layer (3.5 wt%) on its surface. MgO or MgO +  $Al_2O_3$  oxides coating of  $Si_3N_4$  powders are both possible. Therefore ternary (MgO +  $SiO_2$  +  $Al_2O_3$ ) eutectic reactions occur during sintering when the silicon nitride powders are coated by (MgO +  $Al_2O_3$ ). Densities of oxides coated and mixed  $Si_3N_4$  ceramic samples are both increasing with time but coated powders reach theoretical density (TD) at 1450 °C whereas mixed powders do not reach TD even at 1600 °C. This shows that particle coating of  $Si_3N_4$  powders lowers sintering temperatures, by at least 200 °C. The low temperature densification of matrix ceramic will surely inhibit thermal degradation of fibres when fibre–matrix incorporation is carried out.

The level of additive is similar in both cases (~10 wt%), but it might have been expected that the lower eutectic temperature in the MgO– $Al_2O_3$ – $SiO_2$  system (~1358 °C) compared with the MgO– $SiO_2$  system (1518 °C) would result in a significant lowering of the optimum sintering temperature for achieving full density. Coating studies using mixed solutions of Mg- and Al-alkoxides showed a tendency for mutual polymerisation, rather than co-depositing homogeneously on the silicon nitride powder. Improved coating was achieved by sequential deposition, and this also afforded better control of the total thickness of the deposited layer. A particular advantage of the coated powders was that they could be sintered to >99% density at temperature as low as 1450 °C. Fig. 2 shows that significant densification starts at 1400 °C just above ternary eutectic temperatures (1358 °C), and full densification is achieved at 1450 °C and remained constant for oxide coated samples. The plot of mixed oxide is parallel to the curve of coated powder but the densities of each sample are lower than coated powder.

X-ray phase analysis showed that pressureless sintered, coated and mixed oxide materials were composed of mixtures of  $\alpha$ - $Si_3N_4$  and  $\beta$ - $Si_3N_4$ . Fig. 2 shows that the  $\beta$ : $\alpha$ - $Si_3N_4$  ratio increases with increasing pressureless sintering temperature at 1500 and 600 °C for both samples

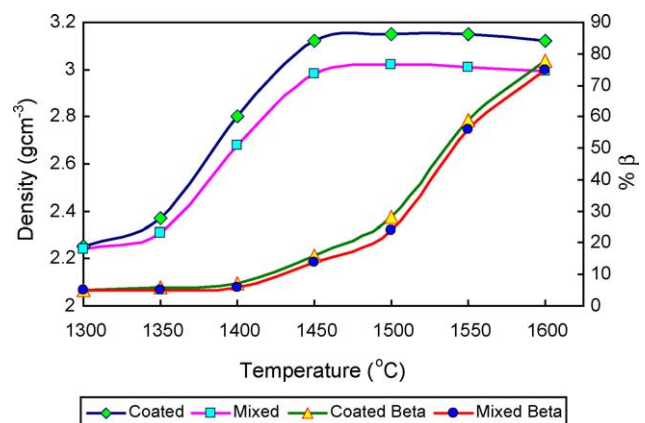


Fig. 2. Density and % $\beta$  ratio as a function of temperature for  $Si_3N_4$  pressureless sintered with 2%  $Al_2O_3$  + 3% MgO for 60 min.

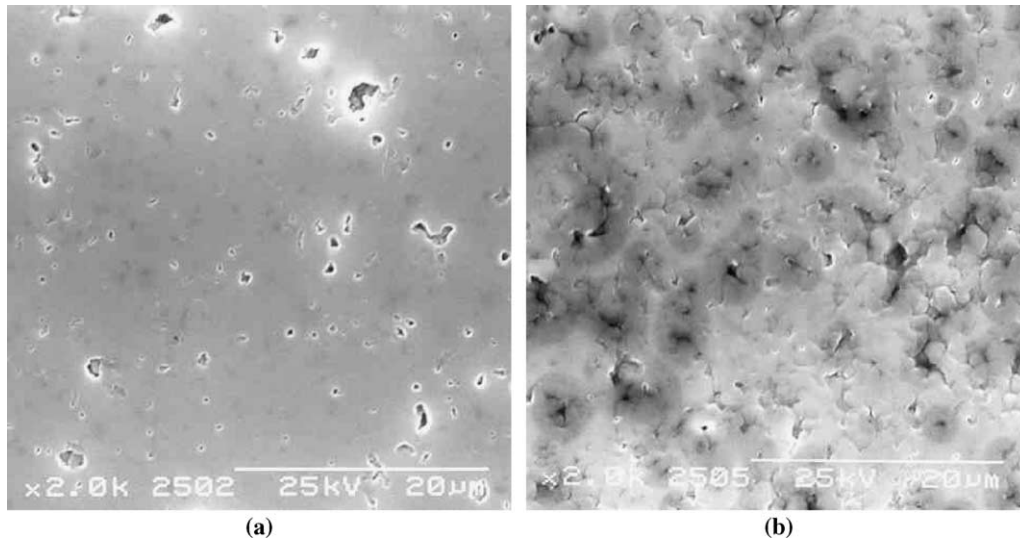


Fig. 3. SEM images of polished surfaces of (a) coated and (b) mixed Si<sub>3</sub>N<sub>4</sub> powders, pressureless sintered at 1400 °C for 60 min.

but the coated samples shows little bit higher than mixed oxide samples. When densification occurs at 1400 °C, there is some  $\alpha \rightarrow \beta$ -Si<sub>3</sub>N<sub>4</sub> phase transformation. The amount of  $\beta$ -phase can be increased if the sintering time is increased, but in this study, the sintering time was held constant. At temperatures below 1400 °C, the achievement of high density was restricted by the absence of liquid phase and the presence of MgAl<sub>2</sub>O<sub>4</sub> in grain boundaries.

Microstructural studies were carried out using scanning electron microscopy. Typical microstructures for pressureless sintered materials are given in Figs. 3 and 4. As shown in Fig. 3a almost half of the densification is completed in the coated powders at 1400 °C whereas in the mixed powders, significant densification is not achieved (Fig. 3b) since sufficient liquid phase does not occur at 1400 °C. The mixed oxide materials include some heterogeneities of a pore-clustered nature indicative of the absence of sintering

additive in these regions in Fig. 4b. This kind of heterogeneity is not visible in the coated powder materials (Fig. 4a) at 1450 °C. The microstructure of coated sample sintered at 1450 °C confirms that liquid phase sintering is achieved and all pores are eliminated. This low temperature densification is quite ideal for Nicalon fibre incorporation due to the low temperature densification which prevents fibre degradation during hot-pressing.

In the previous study [15], it was shown that CO gas pressure heat-treatment of Nicalon fibres for 30 min at 1600 °C gave the most improved fibre properties for use in CMCs. Demir and Thompson [12] used these heat-treated fibres to reinforce  $\beta$ -sialon matrices. Significant strength increase was achieved with heat-treated fibres compared with as received fibres. Although fibre properties were improved by CO heat-treatment, densification temperature of Si<sub>3</sub>N<sub>4</sub> matrices and grain boundary glass needed to be

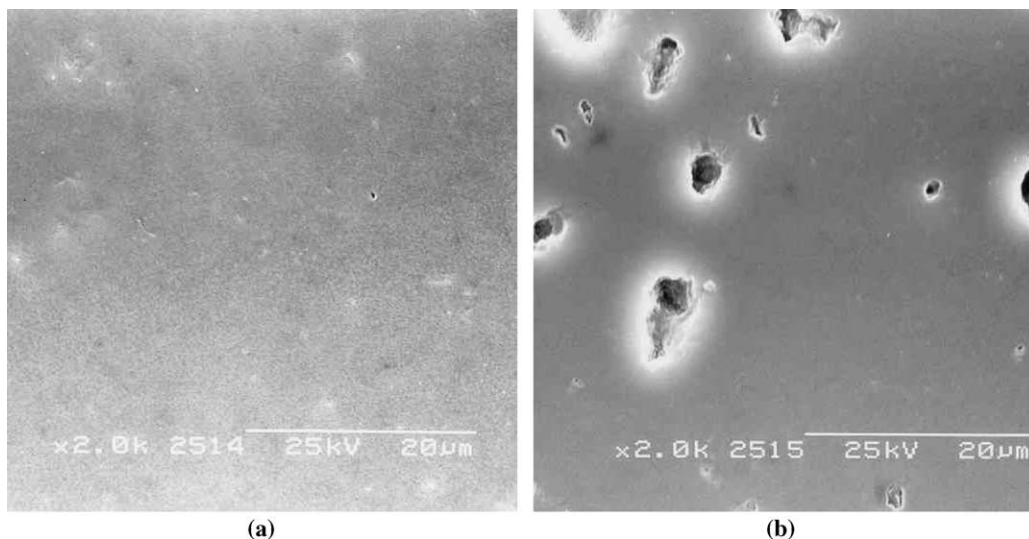


Fig. 4. SEM images of polished surfaces of (a) coated and (b) mixed Si<sub>3</sub>N<sub>4</sub> powders, pressureless sintered at 1450 °C for 60 min.



decreased further. When conventional powder mixing is used to sinter  $\text{Si}_3\text{N}_4$  ceramics, large amount of oxide additives (over 20 wt%) are required to lower densification temperature. However, this causes high amount of grain boundary glass, which reduces the potential for high-temperature applications of composites since glass-softening

delayed formation of eutectic reaction during hot-pressing. Since three-oxide components are well contacted, the kinetics of eutectic reaction is accelerated as shown in Fig. 5. As soon as eutectic point (1358) is overtaken, liquid phase occurs and densification starts at 1400 °C as a result of instant liquid phase formation.

Table 2

Compression of hot-pressing SiC-fibre/coated and mixed  $\text{Si}_3\text{N}_4$  composite with 2%  $\text{Al}_2\text{O}_3$  + 3%  $\text{MgO}$  at various temperatures

Temperature (°C)	Time (min)	Pressure (MPa)	SiC-fibre/coated $\text{Si}_3\text{N}_4$			SiC-fibre/mixed $\text{Si}_3\text{N}_4$		
			Density ( $\text{g cm}^{-3}$ )	%TD	% $\beta$	Density ( $\text{g cm}^{-3}$ )	%TD	% $\beta$
1300	30	20	1.97	67.0	5	1.95	66.3	5
1350	30	20	2.00	68.0	5	1.97	67.0	5
1400	30	20	2.43	82.6	7	2.12	72.1	5
1450	30	20	2.76	93.9	13	2.35	79.9	12
1500	30	20	2.86	97.3	25	2.56	89.8	24
1550	30	20	2.92	99.3	54	2.74	93.2	51
1600	30	20	2.91	99.0	73	2.82	95.9	70

temperature is far lower than targeted application of SiC fibre reinforced  $\text{Si}_3\text{N}_4$  composites. Hence, it is essential to use minimum amount of oxide additives and minimum densification temperature to increase refractoriness of the matrix and to prevent Nicalon SiC fibre degradation during hot-pressing. Tatli [18] revealed that oxide coating of silicon nitride starting powders accelerated eutectic reactions, dropped densification temperature and decreased amount of sintering aid. It has been thought that this sintering property of oxide coated  $\text{Si}_3\text{N}_4$  matrix will surely prevent fibre degradation and improve matrix refractoriness due to the lower grain boundary glass.

### 3.2. Fabrication of hot-pressed $\text{Si}_3\text{N}_4$ matrix composites

The heat-treated Nicalon fibres were incorporated into oxide coated and mixed  $\text{Si}_3\text{N}_4$  matrices to show coating effect on densification and matrix refractoriness. Roller-tank slurry infiltration was carried out to infiltrate both coated and mixed powder into Nicalon fibres. It is assumed that 3.5 wt%  $\text{SiO}_2$  is present on the  $\text{Si}_3\text{N}_4$  particles. Therefore, only  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$  additives were used to coat or mix with the  $\text{Si}_3\text{N}_4$  starting powders before fibre infiltration. Hot-pressing of their green bodies was carried out at elevated temperatures. The densification behaviour of hot-pressed composites is given in both Table 2 and Fig. 5. Higher densification was obtained with the oxide coated  $\text{Si}_3\text{N}_4$  matrix. The particle coating affected densification rate of CMCs as in monolithic  $\text{Si}_3\text{N}_4$  ceramics, although the compositions and hot-pressing conditions were the same. This was because of increasing contact surface of oxide components, which were sequentially coated individual  $\text{Si}_3\text{N}_4$  particles by  $\text{SiO}_2$ ,  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$ , respectively. On the other hand, conventional mixing of oxide additives did not lead to inherent contact between the additives, which

When each matrix is compared, as shown from Table 2 and Fig. 5,  $2.43 \text{ g cm}^{-3}$  density, 82.6% of TD can be reached at 1400 °C for the coated matrix, which is a reasonably low temperature for fibre degradation. With conventionally mixed matrix, eutectic reaction is just initiated and only 72.1% TD is obtained. After this point, the density of coated matrix composites increases sharply and reaches 93.9% TD at 1450 °C. Large density differences occur between coated and mixed matrix especially at lower temperatures since densification starts at low temperature and promote rapidly due to the higher reaction kinetic of the oxide coated matrix. The best densification (99% theoretical density) was achieved between 1550 and 1600 °C for coated matrix composites but for mixed composites at the same temperature, 96% TD cannot be taken over. If the large amount of porosity

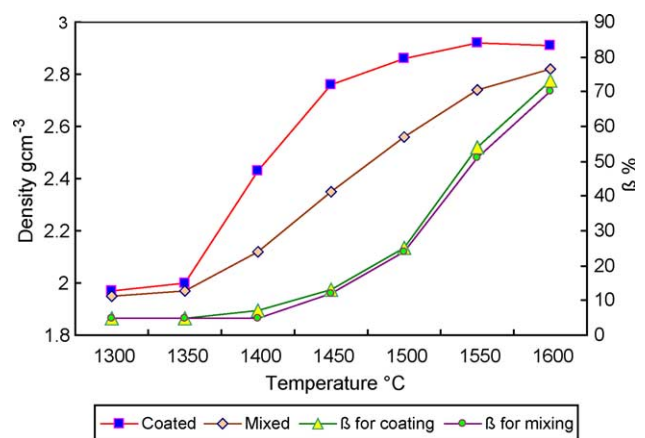


Fig. 5. Densification behaviour of hot-pressed oxide mixed and coated  $\text{Si}_3\text{N}_4$  matrix composites.

is left in the matrix at the sintering temperature, oxygen and free carbon in Nicalon fibres react together and carbon monoxide is produced which causes fibre degradation.

fibres and high porous matrix lowered composite strength and fracture toughness in the conventional mixed matrix composites compared to the coated matrix composites over the whole temperature ranges investigated.

Table 3  
Bending strength of the SiC fibre reinforced coated and mixed Si<sub>3</sub>N<sub>4</sub> composites

Temperature (°C)	Coated matrix composites			Mixed matrix composites		
	TD (%)	Bending strength (MPa)	Fracture toughness (MPa m <sup>1/2</sup> )	TD (%)	Bending strength (MPa)	Fracture toughness (MPa m <sup>1/2</sup> )
1300	67.0	NA	NA	66.3	NA	NA
1350	68.0	NA	NA	67.0	NA	NA
1400	82.6	308 ± 35	6.18	72.1	NA	NA
1450	93.9	504 ± 21	9.85	79.9	241 ± 28	5.58
1500	97.3	606 ± 33	11.24	89.8	403 ± 32	7.53
1550	99.3	693 ± 18	13.38	93.2	495 ± 13	9.67
1600	99.0	677 ± 25	13.35	95.9	558 ± 20	11.02

### 3.3. Mechanical properties of hot-pressed Si<sub>3</sub>N<sub>4</sub> matrix composites

Bending strength and fracture toughness test results are given in Table 3. Compared with conventional mixing, oxide coated matrix composites reached higher bending strength and fracture toughness values. Mechanical property measurements of some low temperature hot-pressed samples would not be determined due to low densities (below 75% TD). As the hot-pressed densities increased, bending strength and fracture toughness of both composites increased. Samples of the coated matrix composite had remarkable strength at lower temperatures than conventional mixed matrix composites since higher densities resulted for using oxide coated Si<sub>3</sub>N<sub>4</sub> matrix powders. When the densification was delayed, SiC Nicalon fibres started to degrade since the free carbon and oxygen in the fibres found opportunity to react and emit CO due to exposure of the fibres from the pores. High porosity lowers matrix strength and therefore depending on matrix strength composite strength decreases as well. Hence, combination of degraded

Maximum strength (693 MPa) and maximum toughness (13.38 MPa m<sup>1/2</sup>) were obtained with a hot-pressing temperature of 1550 °C and TD of 99.3% for oxide coated matrix whereas. At the same temperatures values of 495 MPa and 9.67 MPa m<sup>1/2</sup> were obtained for conventional mixed matrix composites. This suggests that high dense matrix delays crack initiation, and non-degraded fibre prevents crack propagation. Thus, better mechanical properties can be obtained by oxide coating of starting Si<sub>3</sub>N<sub>4</sub> powders. Not only oxide coated Si<sub>3</sub>N<sub>4</sub> powders but also heat-treated SiC Nicalon fibres were used in this study. CO gas pressure heat-treatment provided strength increase and carbon coating for the SiC Nicalon fibres, the details explained elsewhere [15]. Because of physical and mechanical improvement in both matrix and fibre, their combination in this study gives better results compared with previous work [12].

Load–displacement curves illustrate further the difference in behaviours between the SiC fibre reinforced Si<sub>3</sub>N<sub>4</sub> matrix composites during bending and fracture toughness tests (Fig. 6). As shown in Fig. 6a, whilst the mixed matrix

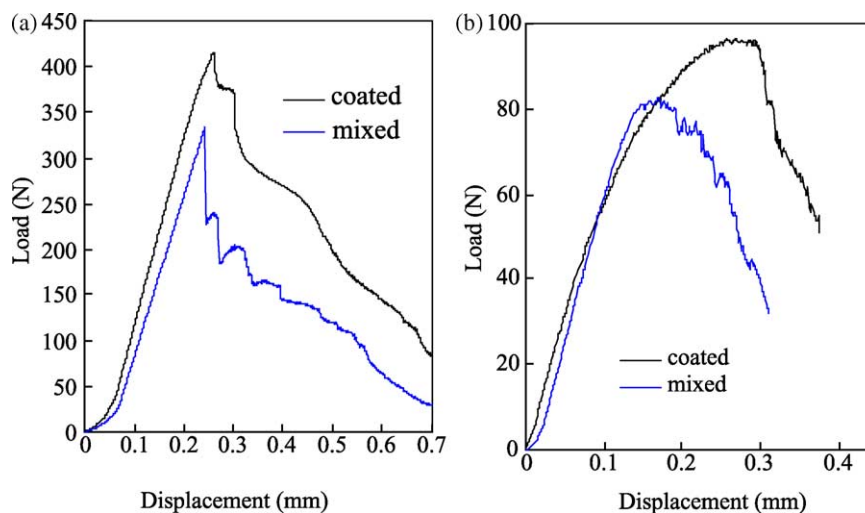


Fig. 6. Mechanical testing of the composites hot-pressed at 1550 °C. (a) Bending strength, (b) fracture toughness.

composites failed at low load values, the coated matrix composites failed at higher load values for bending strength. Furthermore, there is more evidence of a ‘graceful’ failure in the coated matrix composites whereas in the mixed composites, failure is more catastrophic.

Typical load–displacement plots during fracture toughness tests on each composite are shown in Fig. 6b. The coated matrix composite again shows more of a gradual failure reaching higher loads. For the mixed matrix, displacement before the peak load is shorter and the displacement after the peak load is greater in mixed composite than coated. This makes mixed composites more brittle. The crack initiated from the notch propagates gradually after certain load for the coated composite if the load is transferred to the fibres. Otherwise composites behave like monolithic ceramic and slope of the increasing load becomes steep. The instant crack initiation and propagation results in early failure as in mixed matrix composites due to the high stress concentration at the crack tip. In the coated matrix, since fibres are not degraded and matrix is fully densified instant failure has not been observed. When the crack starts to propagate crack bridging mechanism occurs and the crack is deflected.

Crack deflection provides some energy absorption occurring at crack tips. Since applied load can be transferred to the fibres, toughening is successfully achieved for the coated matrix. Increasing in displacement over 70 N loads in Fig. 6b indicates that the crack is propagating slowly but instant failure does not take place in spite of gradual load increase. This shows that fibre pullout occurs and the crack is hindered. As a result of crack bridging and deflection catastrophic failure has not been occurred and  $\text{Si}_3\text{N}_4$  matrices have been toughened by using oxide coated  $\text{Si}_3\text{N}_4$  matrix and carbon coated SiC Nicalon fibres.

SEM images of fracture surfaces of Nicalon SiC fibre reinforced coated and mixed  $\text{Si}_3\text{N}_4$  matrix composites are shown in Fig. 7. All sample surfaces showed massive fibre-pullout indicating reinforcement has achieved. Fibrous failure consists of debonding at the fibre–matrix interface, fibre pullout and fibre bridging. This type of failure mechanism is attributed to a weak interface and the presence of a carbon layer at the fibre–matrix interface clearly shown in Fig. 7c. This carbon layer is strong enough to transfer the load from the matrix to the fibre, however, weak enough to debond preferentially prior to fibre failure and ahead of an advancing matrix crack. The carbon layer,

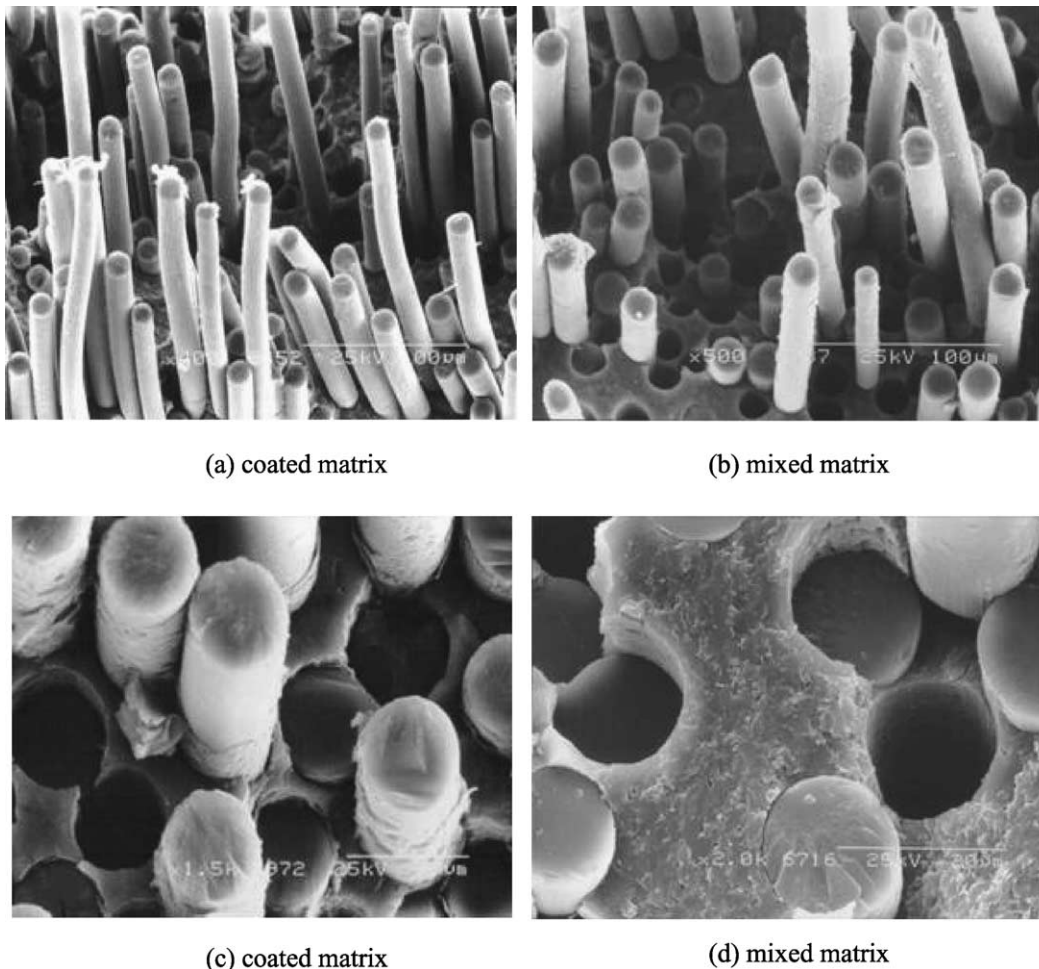


Fig. 7. High and low magnification of fibre pullout at the fracture surfaces of the  $\text{Si}_3\text{N}_4$  matrix composites hot-pressed at 1550 °C.

therefore, increases flaw tolerance by allowing the debonding to occur prior to crack propagation through the fibres or by deflecting matrix cracks. The carbon layer is sacrificed during debonding which is an indication of sufficiently low interfacial bond strength between the fibre and the matrix. All these characteristics together signify the damage tolerance and high toughness nature of the composites. Hence, a high flexural strength and fracture toughness values are obtained for both composites. However, coated matrix composites are superior to mixed matrix composites due to the high density and fibre refractoriness resulting from low temperature and instant densification. As shown in Fig. 7c fibre coating gives weak interface providing fibre pullout since modulus transfer is carried out. Whilst oxide coating provides high dense or pore-free matrix as shown in Fig. 7c, conventional mixing of oxide additives causes lower densification and fine porosity as apparent from SEM examinations (Fig. 7d). A fully dense matrix delays crack initiation and crack propagation at higher loads giving higher bending strengths. Even though heat-treated fibres (in situ carbon coated) are used for all composites, sufficient fibre pullout is not observed for mixed matrix composites since densification is not completed (Fig. 7b–d). Hence, these results are coherent with the observation that if  $\text{Si}_3\text{N}_4$  powders are coated from the participation of metal alkoxides rather than using conventional oxide mixing, and the heat-treated fibres are used as reinforcements their composite strength and toughness can be increased.

#### 4. Conclusion

Particle coating of  $\text{Si}_3\text{N}_4$  powders reduces the required sintering temperatures for the hot-pressing of  $\text{SiC}/\text{Si}_3\text{N}_4$  composites by at least  $150^\circ\text{C}$  compared to composites based on mixed powders. Consolidation of hot-pressed samples is carried out between  $1450$  and  $1550^\circ\text{C}$  which is quite low for  $\text{Si}_3\text{N}_4$  matrix composites. Low temperature densification with short duration keeps fibre strength resulting in high strength and toughness for the oxide coated composites. Since oxide coating accelerates eutectic reaction, less oxide additives are needed for hot-pressing. The reduction in oxide additive reduces the amount of grain boundary glass and increases refractoriness of the composites as well. The use of a heat-treated fibre provides the necessary weak interface, so preventing catastrophic failure and increasing toughness. Strength increase in matrix by oxide coating of  $\text{Si}_3\text{N}_4$  starting powders is achieved since uniform distribution of oxide additives decreases densification temperature and amount of porosity.

#### References

- [1] Naslain R. CVI composites. In: Warren R, editor. Ceramic matrix composites. London: Chapman & Hall; 1992, 199.
- [2] Chiang YC. On fiber debonding and matrix cracking in fiber-reinforced ceramics. *Comp Sci Technol* 2001;61(12):1743–56.
- [3] McDonald KR, Dryden JR, Majumdar A, Zok FW. Thermal conductance of delamination cracks in a fiber-reinforced ceramic composite. *J Am Ceram Soc* 2000;83(3):553–62.
- [4] Song GM, Zhou Y, Sun Y. Modeling of fiber toughening in fiber-reinforced ceramic composites. *Ceram Int* 1999;25(3):257–60.
- [5] Hinoki T, Yang W, Nozawa T, Shibayama T, Katoh Y, Kohyama A. Improvement of mechanical properties of  $\text{SiC}/\text{SiC}$  composites by various surface treatments of fibers. *J Nucl Mater* 2001;289(1–2):23–9.
- [6] Chandra N, Ghonem H. Interfacial mechanics of push-out tests: theory and experiments. *Composites Part A: Appl Sci Manuf* 2001; 32(3–4):575–84.
- [7] Ismar H, Streicher F. Modelling and simulation of the mechanical behavior of ceramic matrix composites as shown by the example of  $\text{SiC}/\text{SiC}$ . *Comput Mater Sci* 1999;16(1–4):17–24.
- [8] Ohnabe H, Masaki S, Onozuka M, Miyahara K, Sasa T. Potential application of ceramic matrix composites to aero-engine components. *Composites Part A: Appl Sci Manuf* 1999;30(4):489–96.
- [9] Kaya H. The application of ceramic–matrix composites to the automotive ceramic gas turbine. *Comput Sci Technol* 1999; 59(6):861–72.
- [10] Ueno K, Inoue T. Preparation and properties of  $\text{SiC}$  fibre reinforced  $\text{SiAlON}$  ceramic composite. *Ceram Int* 1997;23(2):165–70.
- [11] Kitaoka S, Kawashima N, Suzuki T, Sugita Y, Shinohara N, Higuchi T. Fabrication of continuous- $\text{SiC}$ -fiber-reinforced  $\text{SiAlON}$ -based ceramic composites by reactive melt infiltration. *J Am Ceram Soc* 2001;84(9):1945–51.
- [12] Demir A, Thompson DP. High-performance  $\text{SiC}$ -fibre reinforced  $\beta$ -sialon CMCs prepared from heat treated Nicalon fibres. *J Eur Ceram Soc* 2001;21:639–47.
- [13] Ichikawa T. Recent developments of the  $\text{SiC}$  fiber Nicalon and its composites, including properties of the  $\text{SiC}$  fiber Hi-Nicalon for ultra high temperature. *Comput Sci Technol* 1994;51:135–44.
- [14] Takeda M, Sakamoto J, Imai Y, Ichikawa H. Thermal stability of the low-oxygen-content silicon carbide fiber, Hi-Nicalon™. *Comput Sci Technol* 1999;59(6):813–9.
- [15] Demir A, Thompson DP. Improvements in refractoriness and properties of Nicalon fibres by high-temperature heat treatment. *J Mater Sci* 2001;36:2931–5.
- [16] Mah T, Hetch NL, McCullen DE, Hoinigman JR, Kim HM, Katz AP, Lipsitt HA. Thermal stability of  $\text{SiC}$  fibres (Nicalon). *J Mater Sci* 1984;18:119–201.
- [17] Jaskowiak MH, DiCarlo JA. Pressure effects on the thermal stability of silicon carbide fibres. *J Am Ceram Soc* 1989;72(2):192–7.
- [18] Tatli Z. Silicon nitride and silicon carbide fabrication using coated powders. PhD Thesis, University of Newcastle upon Tyne; 2002.
- [19] Show TM, Pethica BA. Preparation and sintering of homogeneous silicon nitride green compacts. *J Am Ceram Soc* 1986;69:88–93.
- [20] Wang CM, Riley FL. Alumina coating of silicon nitride powders. *J Eur Ceram Soc* 1992;10:83–93.
- [21] Tatli Z, Thompson DP, Errington RJ. Densification of mixed-oxide coated silicon nitride powders. *Key Eng Mater* 1997;V. 132–136: 994–7.