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Fracture behaviour of SiC fibre-reinforced nitrogen glass matrix composites

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Both Nicalon and Hi-Nicalon SiC fibre-reinforced nitrogen glass composites were prepared by slurry infiltration and hot-pressing, and the interfacial features, fracture behaviour and mechanical properties of these composites were investigated. It was found that the interfacial characteristics were mainly dictated by the thermal expansion properties of the matrix and the type of SiC fibre. Yttrium sialon glass has a higher thermal expansion coefficient than SiC fibres, so a radial compressive stress on the fibre due to thermal mismatch caused a larger interfacial frictional stress between fibre and matrix. As a result, the composite failed in a brittle manner with no effective strengthening and toughening. Strong reaction between the Hi-Nicalon SiC fibre and matrix also resulted in relatively poor performance of these composites. In contrast, lithium sialon glass provided a matrix for these composites with significantly improved mechanical properties.

1. Introduction

Glass and ceramic matrix composites form a technologically important class of materials because of their potential use for structural applications at elevated temperatures. Over the last twenty years, considerable attention has been paid to the reinforcement of oxide glasses and ceramics by fibres or whiskers, and it has been confirmed that both the bending strength and the fracture toughness of these materials can be greatly enhanced under suitable conditions [1–4].

Nitrogen glasses have been systematically investigated since the mid-1970s, and the glass compositions, glass-forming regions and their properties are now well known [5–8]. This type of glass is important not only because it appears in nitrogen ceramics as the grain-boundary phase, but also because of its own intrinsic properties. As far as mechanical properties are concerned, nitrogen glass has a higher microhardness and Young's modulus than equivalent oxide glass; more importantly, its higher glass transition temperature with increasing nitrogen content enables it to withstand higher temperatures. Therefore, these glasses represent an attractive research area for the development of composite materials.

This paper presents some recent results for SiC fibre-reinforced nitrogen glass composites, including preparation of the samples, analysis of interfacial features and a description of the fracture behaviour. The conditions which must be satisfied to achieve improvements in the mechanical properties of these composites are also discussed. Nitrogen glasses were used as precursors for both glassy and glass-ceramic matrices depending on the compositions and sintering conditions. For comparison, both Nicalon SiC and Hi-Nicalon SiC fibres were used as reinforcements.

TABLE I Typical properties of Nicalon and Hi-Nicalon SiC fibres

		Hi-Nicalon	Nicalon
Fibre diameter (μm)		14	14
Number of filaments (fil./yarn)		500	500
Tensile strength (GPa)		2.8	3.0
Tensile modulus (GPa)		270	220
Density ($kg\,m^{-3}$)		2740	2550
Composition (wt %)	Si	63.7	56.5
	C	35.8	31.2
	O	0.5	12.3

2. Experimental procedure

2.1. Melting of nitrogen glasses

Nitrogen glasses were melted in a graphite crucible in an inductively-heated graphite furnace under a flow of nitrogen gas at 1550–1650 °C for 30 min. To prepare Y–Si–Al–O–N (YN) glass, SiO_2 (BDH Chemicals Ltd), Al_2O_3 (A16-Alcoa Chemie GmbH), Si_3N_4 (LC10-HC Starck Berlin) and Y_2O_3 (99.9% Rare Earth Products) were used as the starting powders, but for Li–Si–Al–O–N (LN) glass, Li_2O and Al_2O_3 were introduced in the form of presynthesized $LiAlO_2$ and Li_2SiO_3 powders to reduce weight loss of both lithium and nitrogen as a result of thermal decomposition during melting (Table II). The powders, weighed out in batches of about 50 g, were ball mixed in isopropanol. After drying, the mixture was pressed into compacts, and then embedded in BN powder in graphite crucibles for melting.

The bulk glass after melting was crushed and ground to a fine powder of size 3–20 μm.

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TABLE II Compositions of nitrogen glasses (at %)

	Li	Y	Si	Al	O	N
YN		9.7	17.9	10.6	53.0	8.8
LN	10.2		20.4	10.2	55.1	4.1

2.2. Preparation of composites

2.2.1. *Chopped SiC fibre/nitrogen glass green bodies*

To explore the sintering performance of SiC fibre/nitrogen glass samples, chopped fibres were first tried. Powdered glass was made into a slurry with a mixture of 30% isopropanol and 70% PVA solution. SiC fibre yarn (NL-207) from Nippon Carbon was cut into short lengths of about 2–3 mm and the chopped fibres added to the slurry during continuous blending with a laboratory blender. Mixing of slurry and fibres in this way became progressively more difficult as the fibre content increased. For this reason, the chopped fibres and slurry were mixed in an agate mortar by gentle grinding and in this way, a homogeneous mixture of matrix and fibre was obtained. The mixture was kept agitated while the solvent was removed by infrared radiant heating until it was partially stiff in consistency. In this condition, it was put into a steel die assembly and cold pressed to give a pellet form, and then was fully dried.

2.2.2. *Continuous SiC fibre/nitrogen glass green bodies*

Incorporation of continuous SiC fibres into the glass matrix was done by slurry infiltration. Before use, the fibres were heat treated at 400 °C to burn off the organic coatings on the surfaces. The fibre yarn was fed through a slurry tank and then the slurry-impregnated fibre was wound on to a drum in an aligned manner, and then partially dried. It was then cut into short segments and stacked together for cold-pressing into the green body.

2.2.3. *Hot pressing*

Consolidation of the green bodies was carried out by hot pressing using graphite dies. To create a carbon monoxide atmosphere, the samples were surrounded by two layers; an inside layer of BN powder and an outside carbon layer. The sample was heated to 600 °C very slowly to ensure that all the organic bonder was burned off, and the maximum pressure was applied to the sample only when the required consolidation temperature had been reached in order to prevent the fibre being cut by the glass particles.

2.3. Mechanical property measurement

Three-point bend testing was used to measure the bending strength, σ, and the fracture toughness, K_{IC}, of the composites. Specimens were cut from hot-pressed samples, ground, and polished into 3 mm × 4 mm × 40 mm bars for strength measurement, and 2 mm × 4 mm × 40 mm for toughness measurement. A notch of 0.2 mm width and about 2 mm depth at the central position of the specimen was made by a special diamond saw and all the tests were carried out in an Instron machine. The load was applied at a rate of 0.2 mm min^{-1}, and the bend span was 30 mm.

2.4. Interfacial frictional stress measurement

The fibre/matrix interfacial frictional stress, τ, was determined by indentation using the microindentation technique reported by Marshall [9]. The value of τ was calculated from the formula

$$\tau = \frac{F^2}{4\pi^2 u r^3 E_f} \tag{1}$$

where $F = 2a^2 H_f$ and $u = (b - a)\cot 68°$, F is the force, u is the fibre displacement, a is half the diagonal length of the indentation on the fibre, and b is half the diagonal length in the matrix surrounding the fibre; r, E_f and H_f are the radius, Young's modulus and hardness of the fibres respectively.

2.5. Phase identification and microstructural examination

Phase identification of the glass and the glass-ceramic matrix were carried out by X-ray Hägg Guinier cameras. The microstructures of the composites were examined using both an Olympus BHSM light microscope and an S4-80DV Camscan scanning electron microscope (SEM).

3. Results and discussion

3.1. SiC fibre/YN glass composites

Yttrium sialon glass was selected as the matrix for producing composites because its large glass forming region with relatively high nitrogen content provides a wide range of choice for glass compositions; its slow devitrification rate at high temperatures makes it easy to obtain pure glass after melting and its relatively high transition temperature and relatively small thermal expansion coefficient compared with other rare-earth element-doped nitrogen glasses fits the compatibility requirements of the composites reasonably well. Previous studies of the sintering performance of this glass powder showed that a total density of over 97% could be reached by hot pressing the glass powder at temperatures slightly higher than the glass transition temperature of 1000–1050 °C. When fibres are incorporated into this glass, the lowest temperature at which a fully dense material can be obtained is 1200 °C.

Both chopped and continuous SiC fibre/YN glass composites were prepared. Hot-pressing conditions of 1200 °C at 14 MPa for 5–15 min gave samples of almost full density. Optical microscopy observations on polished surfaces showed that the fibres were well distributed within the matrix (Fig. 1), and no big voids were seen. The properties of these composites were examined by three-point bend testing, and it was found that all samples were weak and brittle. Scanning electron micrographs of the fracture surface showed no fibre pull-out, but sticking between fibre and matrix was not observed (Figs 2 and 3), indicating that under the above sintering conditions, reaction between fibres and matrix is negligible. On the polished section, it can been seen that the fibres were tightly gripped by the matrix (Fig. 4).

The poor mechanical properties of SiC fibre/YN glass composites could be ascribed to thermal mismatch between the fibre and the matrix. The thermal expansion coefficient of SiC fibre is about $3.4 \times 10^{-6}\,°\mathrm{C}^{-1}$, but for YN glass, it is about $6 \times 10^{-6}\,°\mathrm{C}^{-1}$, which is much larger. During cooling from high temperatures, significant radial compressive stresses build up because the matrix shrinks more round the fibres. The magnitude of this stress can be calculated from the formula [10]

$$\sigma_r = \frac{-qE_f E_m[(\alpha_f - \alpha_m)\Delta T + A/r]}{E_f(1 + \nu_m) + E_m(1 - \nu_f)} \tag{2}$$

where ΔT is the temperature change during cooling, q is an adjustable parameter (normally taken as unity), A is the amplitude of fibre roughness, r is the fibre radius, E_f and E_m are the elastic moduli and ν_f and ν_m are the Poisson's ratios of the fibre and matrix, respectively. When values of $E_f = 220\,\mathrm{GPa}$, $E_m = 140\,\mathrm{GPa}$, $\nu_f = \nu_m = 0.3$, $A = 0.012\,\mu\mathrm{m}$, $r = 15\,\mu\mathrm{m}$, $\alpha_m = 6 \times 10^{-6}\,°\mathrm{C}^{-1}$, $\alpha_f = 3.4 \times 10^{-6}\,°\mathrm{C}^{-1}$ and $\Delta T = 950\,°\mathrm{C}$ [11] are substituted into Equation 2, the calculated radial compressive stress on the fibre is about 84 MPa. This large stress would lead to a large interfacial frictional stress between fibre and matrix given by

$$\tau = \mu\sigma_r \tag{3}$$

where μ is the coefficient of friction, generally between 0.1 and 0.6. This theoretical calculation has been tested

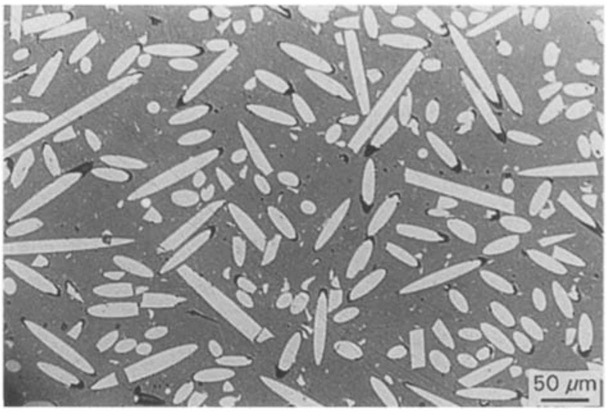

Figure 1 A polished section in the pressing plane of a 30 vol % chopped SiC fibre/YN glass composite hot pressed at 1200 °C, 14 MPa for 15 min.

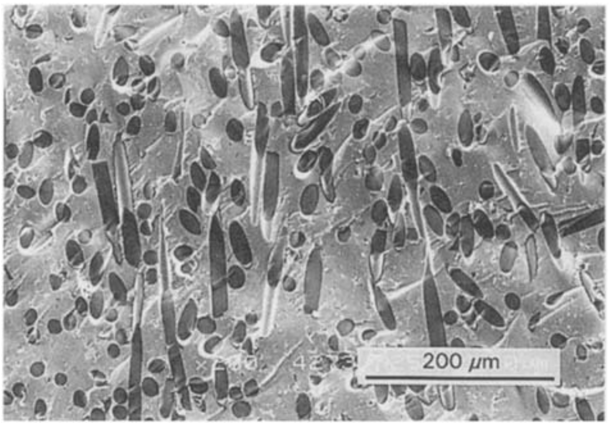

Figure 2 Fracture surface of a chopped SiC fibre/YN glass composite hot pressed at 1200 °C, 14 MPa for 15 min.

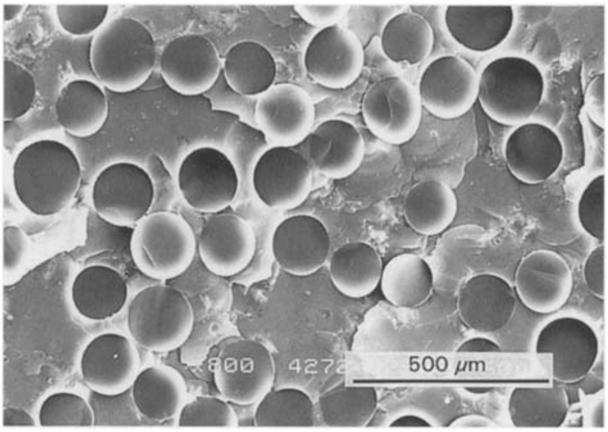

Figure 3 Fracture surfaces of continuous SiC fibre/YN glass composites hot pressed at 1200 °C for 15 min.

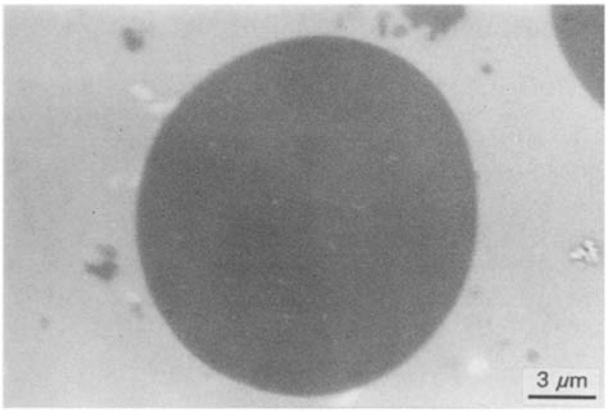

Figure 4 Scanning electron micrograph of polished surfaces of SiC fibre/YN glass composites.

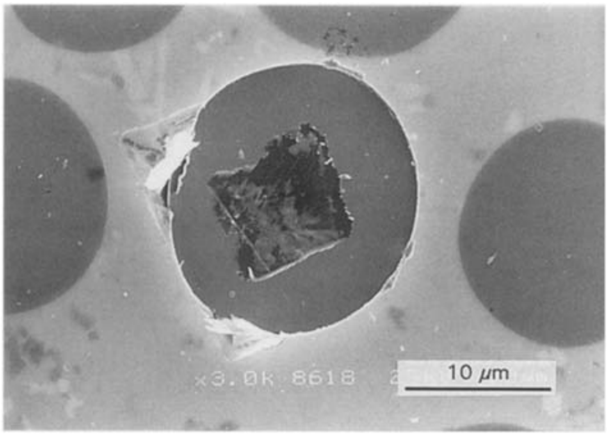

Figure 5 Scanning electron micrograph of a microindentation at forces of 1 N in a SiC fibre/YN glass composite.

by measuring the interfacial frictional stress between fibre and matrix. For SiC fibre/YN glass composites, this stress is as large as 10 MPa (equal to the value from Equation 3, where $\mu = 0.12$), being five times as large as that of SiC fibre/LN glass samples. This value of interfacial frictional stress can cause a gripping of the fibres by the matrix, or in other words, the fibre is not strong enough to tear itself from the matrix before it is broken on bending, so that the composites fail in a brittle manner.

3.2. SiC fibre/LN glass composites

Both experimental and theoretical analysis of the fracture behaviour of SiC fibre/YN glass composites indicated that the thermal incompatibility between fibre and matrix is the key parameter controlling the interfacial characteristics of the composites in the absence of chemical bonding. In this regard, it must be beneficial if the matrix material has a similar or slightly lower thermal expansion than the fibre, in order to achieve the required weak mechanical bond. Among all nitrogen glass systems studied, nitrogen-containing lithium aluminum silicate (LN) glass appears the most promising as a matrix because its thermal expansion coefficient is readily adjustable over a large range by controlling the nitrogen content and heat-treatment conditions.

To optimize processing conditions for the preparation of SiC fibre/LN glass composites in order to obtain tough materials, hot-pressing temperatures were initially varied (Tables III and IV). The first approach aimed to produce samples at a low temperature of 1200 °C, under a pressure of 14 MPa for 15 min, which are the optimized conditions for SiC fibre/YN glass composites. Scanning electron micrographs revealed that the sample did not densify well and some voids can be seen on the surface of polished sections, suggesting that the matrix was not sufficiently soft at such temperatures to flow around the fibre. A higher temperature of 1260 °C was used to reduce the porosity of the sample and, as a result, a relative density of 95% was achieved. Fully dense materials can be obtained at temperatures of 1330 °C (Fig. 6). For all the samples, 1080 °C was used to crystallize the glass matrix into a glass-ceramic form. From X-ray diffraction, β-spodumene ($LiAlSi_2O_6$) was identified as the main crystalline phase in the matrix. β-spodumene has a melting point of 1425 °C, and the introduction of nitrogen into glass increases its transition temperature, so this is a promising matrix for high-temperature composites.

More work was done to investigate the fracture behaviour of SiC fibre/LN glass composites as a function of hot-pressing temperature. All the samples hot pressed at temperatures in the range 1260–1540 °C demonstrated extensive fibre pull-out, and no sticking between fibre and matrix (Fig. 7). This suggests that the SiC fibre can survive at high temperature for extended periods, and also it can be concluded that the surface of the fibre is chemically unreactive towards the matrix. Scanning electron micrographs of

TABLE III Hot-pressing conditions and fracture behaviour of SiC-fibre composites in different glass matrices

Matrices	Hot-pressing conditions			Fibre pull-out
	T (°C)	*P* (MPa)	*t* (min)	
YN	1200	14	15	No
YN	1260	14	15	No
YN	1330	14	15	No
YN	1400	14	15	No
LN	1260	14	15	Good
	1080		50	
LN	1330	14	15	Good
	1080		50	
LN	1400	14	15	Good
	1080		50	
LN	1470	14	15	Good
	1080		50	
LN	1540	14	15	Good
	1080		50	

TABLE IV Hot-pressing conditions and fracture behaviour of Hi-nicalon fibre/LN glass-ceramic composites

Matrix	Hot-pressing conditions			Fibre pull-out
	T (°C)	*P* (MPa)	*t* (min)	
LN	1260	14	15	Poor
	1080		50	
LN	1330	14	15	Poor
	1080		50	
LN	1400	14	15	Poor
	1080		50	

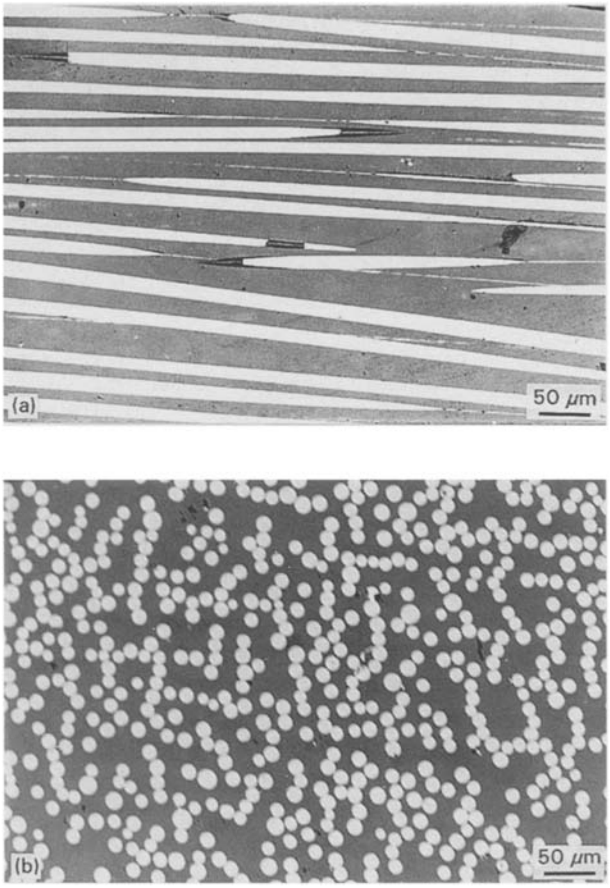

Figure 6 Polished sections in (a) the pressing plane and (b) perpendicular to the fibre direction of SiC fibre/LN glass composites.

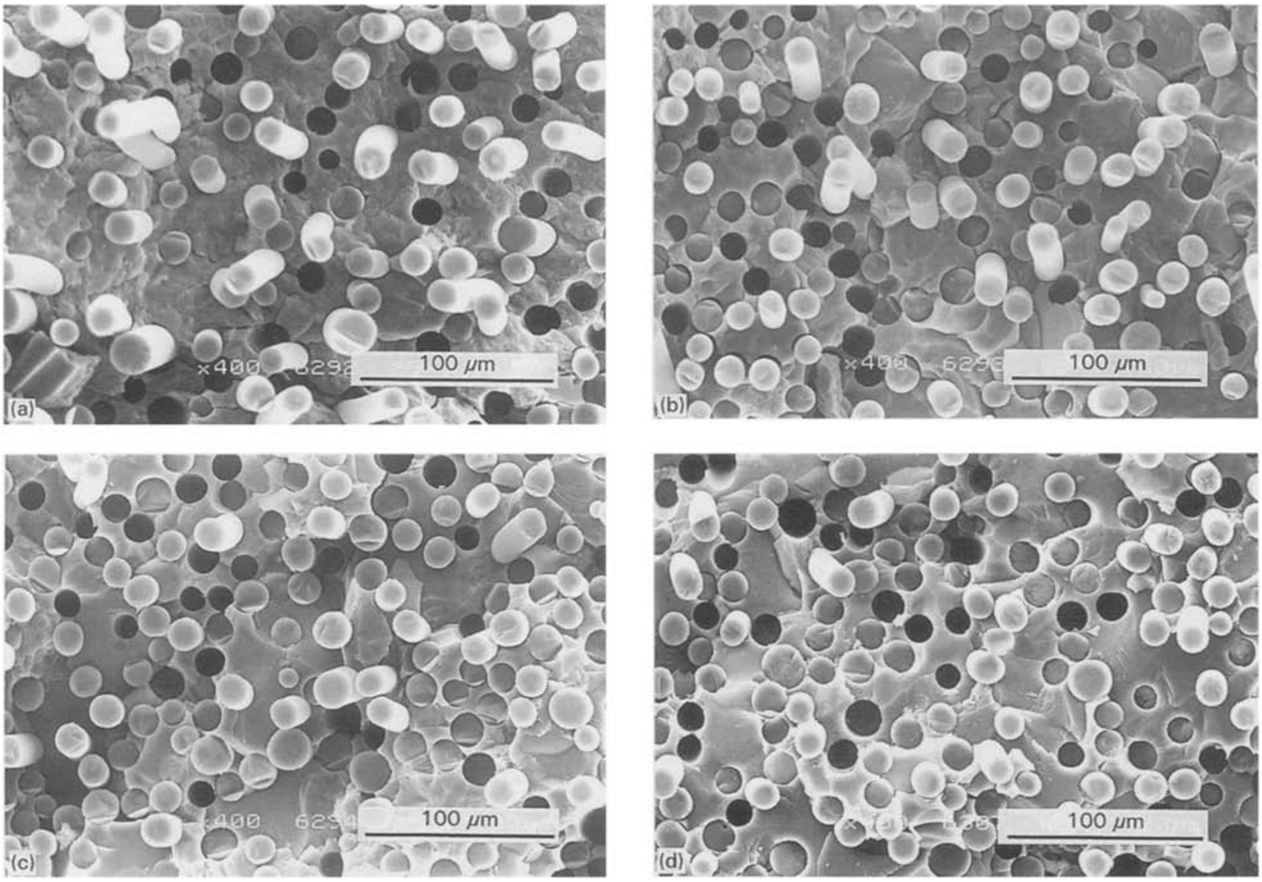

Figure 7 Fracture surfaces of SiC fibre/LN glass composites hot pressed for 15 min, under 14 MPa at (a) 1330 °C; (b) 1400 °C; (c) 1470 °C; (d) 1540 °C.

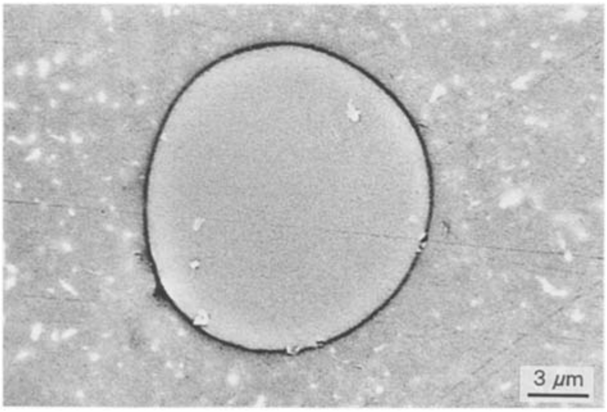

Figure 8 Scanning electron micrograph of a polished surface of a SiC fibre/LN glass composite.

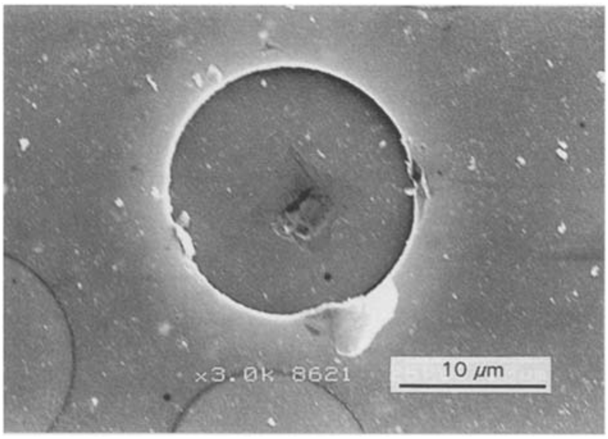

Figure 9 Scanning electron micrograph of microindentation at forces of 0.6 N in a SiC fibre/LN glass composite.

polished sections of this material showed that the fibres were not as tightly wrapped by the matrix as in the YN glass composite (Fig. 8). This is because the smaller thermal expansion coefficient of the LN glass matrix ($1\text{–}2 \times 10^{-6}\,°\mathrm{C}^{-1}$) compared with the fibres ($3.4 \times 10^{-6}\,°\mathrm{C}^{-1}$) makes it shrink less than the fibres on cooling. The interfacial frictional stress of 1.8 MPa obtained from this material indicated relatively weak mechanical bonding between matrix and fibre (Fig. 9).

Table V gives the results of mechanical property measurements on SiC fibre/LN glass composites. These materials possess reasonable bending strength and fracture toughness. It is clear that 1330 °C gives the composite higher strength than other temperatures; when the hot-pressing temperature is over 1400 °C, the strength decreases sharply. Short hot-pressing times and low pressures at the optimized temperature are beneficial for making strong and tough products, but these effects are not significant. Obviously the decrease in strength of the composite hot pressed at high temperature is caused by fibre degradation.

3.3. Hi-Nicalon SiC fibre/LN glass composites

Hi-Nicalon SiC fibre is a relatively new product of Nippon Carbon and tests have showed that this fibre

TABLE V Hot-pressing conditions and properties of SiC fibre/LN glass-ceramic composites

	Hot-pressing conditions			Fibre content	Density	Properties	
	T (°C)	P (MPa)	t (min)	(vol %)	(g cm^{-3})	(MPa)	K_{IC} (MPa m$^{1/2}$)
1	1260	14	15	36	2.29	305	7.65
	1080		50				
2	1330	14	15	36	2.45	315	9.60
	1080		50				
3	1400	14	15	36	2.48	205	4.04
	1080		50				
4	1330	6	15	36	2.44	337	6.45
	1080		50				
5	1330	10	15	36	2.44	323	7.35
	1080		50				
6	1330	6	5	36	2.36	327	9.00
	1080		50				
7	1330.	6	45	36	2.42	384	7.55
	1080		50				

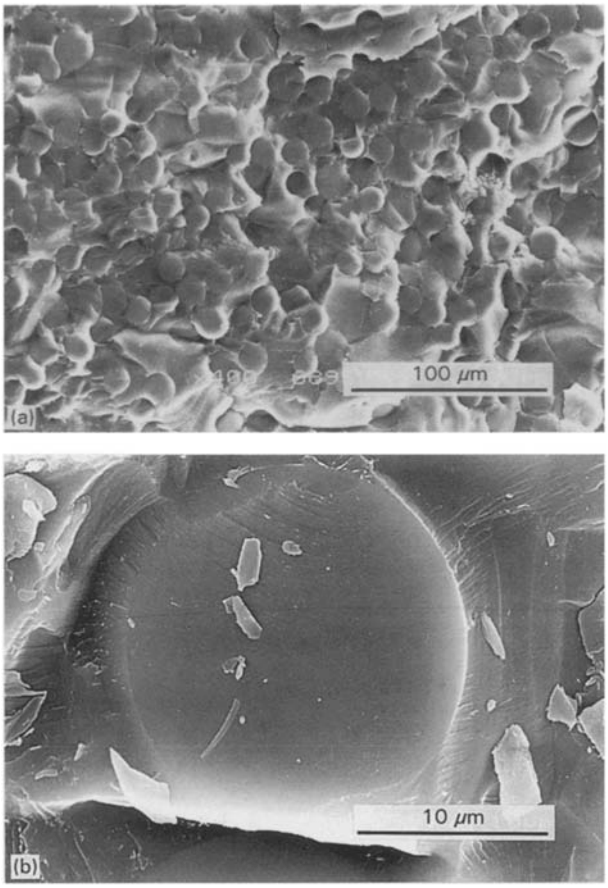

Figure 10 Fracture surfaces of Hi-Nicalon SiC fibre/LN glass-ceramic composites hot pressed at 1330 °C, at 14 MPa for 15 min.

can bear higher temperatures than the standard grade of SiC fibre. Degradation cannot take place as easily at processing temperatures because of the extremely low oxygen content inside the fibre. It was suggested that Hi-Nicalon SiC fibre/LN glass composites could retain excellent thermal and chemical stability up to relatively high temperatures, but incorporation of this fibre into an LN glass matrix did not offer encouraging results. SEM observation revealed that reaction obviously took place between the fibres and the matrix at sintering temperatures varying from 1260–1400 °C as indicated by fibres sticking to the matrix on the fracture surface of the sample (Figs 10 and 11); moreover, no fibre pull-out was observed. Indentation tests showed that the bonding between fibre and matrix was so strong that no fibre sliding occurred even when the load was increased to the extent that damage occurred to the surface of the fibre (Fig. 12). The strong interfacial bond did not impede an incoming crack, and as a result, the composites failed in a brittle or semi-brittle manner.

From a comparison of the fracture behaviour of SiC fibre/YN glass, SiC fibre/LN glass and Hi-Nicalon SiC fibre/LN glass composites, the performance of SiC fibres can be easily understood. According to the results of several researchers [11–14], thermal degradation of SiC fibre starts at temperatures of 1200 °C mainly due to the release of CO and SiO from inside the fibre. On the surface of the fibre, an interfacial layer consisting of an inside carbon-rich layer and an outside SiO_2 layer is formed as the products of oxidation. The reactions occurring can be represented as follows:

$$SiO_xC_y \rightarrow SiO + CO \quad (1)$$

$$SiC + 2CO \rightarrow SiO_2 + 3C \quad (2)$$

$$SiC + O_2 \rightarrow SiO + CO \quad (3)$$

$$SiC + O_2 \rightarrow SiO_2 + C \quad (4)$$

$$SiO + 1/2O_2 \rightarrow SiO_2 \quad (5)$$

The thickness of the reaction layer is dependent on the processing conditions, i.e. sintering temperature, time and atmosphere. These reactions reduce the *in situ* strength of the fibre, finally affecting the mechanical properties of the composites; however, on the other hand, the reaction products are beneficial for the fracture performance of the materials. Firstly, they constitute a protective layer against the reaction between fibre and matrix; secondly, and of greater importance, the carbon-rich layer acts as a debonding layer because of its low fracture resistance [15]. In fact, the behaviour of the interfacial layer in these composites is influenced by several parameters, for example: chemical bonding, radial compressive stresses and thickness of the reaction layer, all of which have

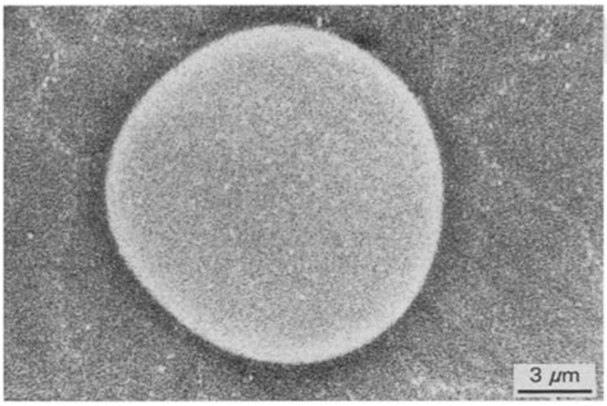

Figure 11 Scanning electron micrograph of a polished surface of a Hi-Nicalon SiC fibre/LN glass composite.

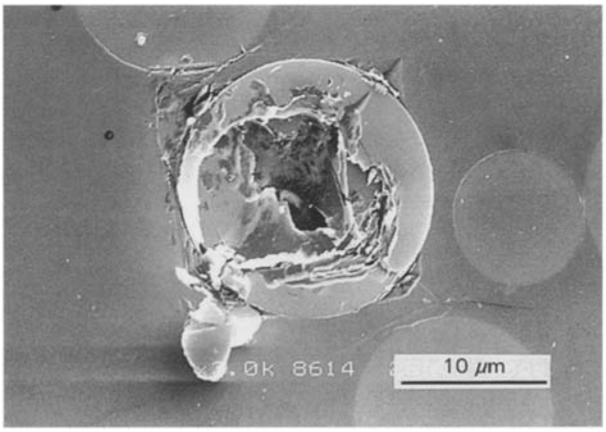

Figure 12 Scanning electron micrograph of a microindentation at forces of 1.5 N in a Hi-Nicalon SiC fibre/LN glass composite.

influence on the characteristics of the interface, controlling the extra expenditure of energy in the fracture process, including debonding of fibres from the matrix, crack deflection, crack bridging, fibre fracture and fibre pull-out, thereby determining the ultimate properties of a given composite. The present work has shown that SiC fibre/LN glass composites exhibit a good combination of all these parameters.

4. Conclusion

Different nitrogen glasses were evaluated as matrices for the preparation of composites and both Nicalon SiC and Hi-Nicalon SiC fibres were incorporated into these matrices. The performance of fibres and matrices was studied both physically and chemically in terms of obtaining an acceptable interface leading to enhanced fracture toughness of the composites. Yttrium sialon glass and related oxynitride glasses with similar thermal properties are not good candidates as matrices for SiC fibres because the thermal mismatch between the fibre and the matrix can produce large compressive stresses on the fibre, causing strong gripping of the fibre by the matrix, and finally brittle failure of the composites. Lithium sialon glass shows most promise as a matrix for SiC fibre for the production of composites and both strengthening and toughening took place in the final products. Hi-Nicalon SiC fibre was not found to be as satisfactory because it reacted with the matrix at even moderate processing temperatures.

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