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Interfacial characterization of Nicalon SiC fibre reinforced oxynitride glass matrix composites

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Nicalon SiC and Hi-Nicalon SiC fibre oxynitride glass and glass–ceramic composites were prepared and the interface between the fibres and matrix characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) spectroscopy. It was found that the formation and thicknesses of interfacial layers were primarily determined by the type of fibre reinforcement, but the role of these interfaces in influencing composite properties was dependent on the thermal properties of the matrix. For Nicalon SiC composites, the carbon-rich layer did not promote fibre debonding and toughening unless the matrix had a smaller thermal expansion coefficient than the fibres. For Hi-Nicalon SiC composites, the absence of oxygen in the fibre significantly encouraged chemical reaction between fibre and matrix, resulting in no strengthening or toughening.

1. Introduction

Continuous SiC fibre reinforced oxide glass and glass–ceramic matrix composites have demonstrated a significant increase both in bending strength and fracture toughness compared with monolithic silicate materials [1–3]. Strengthening mechanisms in these materials can be mainly attributed to load transfer together with improvements in failure stress and failure strain of the matrix [4], and the energy-dissipating processes responsible for increasing fracture toughness include crack deflection and crack hindering, fibre bridging and fibre pull out [5–7]. It has been well established that the fracture behaviour of a composite is mainly determined by the nature of the interface between the fibres and the matrix [8, 9]. A strong interfacial bond will not facilitate toughening, but a weak interfacial bond can lead to crack deflection, crack bridging and fibre pull out, resulting in enhanced toughness. In all SiC fibre–oxide glass or glass–ceramic composites, it has been observed that the carbon-rich layer formed during high temperature processing provided a weak interfacial bond, which was able to act as a debond layer and promote toughening [10]. This carbon-rich layer is believed to be an important parameter in controlling the final properties of these composites.

SiC fibre reinforced oxynitride glass matrix composites are a new family of composite materials. It is expected that these materials are potential candidates for higher temperature applications than current fibre reinforced oxide glass materials [11]. In a previous paper, preparation, property measurement and fracture behaviour of both Nicalon SiC and Hi-Nicalon SiC fibre reinforced oxynitride glass and glass–ceramic composites have been reported [11]. The present study aims to characterize the nature of the interface between the fibres and matrix further in these new materials using SEM and TEM with compositional analysis by EDX. The mechanism of interface formation, its function in these materials and other phenomena affected by the nature of the interface will be discussed.

2. Experimental procedure

2.1. Materials

The raw materials used for preparing composites were oxynitride glass powders. Powdered Y–Si–Al–O–N (YN) and Li–Si–Al–O–N (LN) glasses with compositions $Y_{44}Si_{81}Al_{48}O_{240}N_{40}$ and $Li_{40}Si_{80}Al_{40}O_{216}N_{16}$, respectively, were prepared by melting mixed oxide and nitride powders in a graphite crucible in an inductively heated graphite furnace under a flow of nitrogen gas at 1550–1650 °C for 30 min. SiO_2 (BDH Chemicals Ltd), Al_2O_3 (A16, Alcoa Chemie, GMBH), Si_3N_4 (LC10-HC, Starck, Berlin), Y_2O_3 (99.9% Rare Earth Products), $LiAlO_2$ and Li_2SiO_3 (presynthesized) were used as the starting powders for glass melting. The as-prepared glass was crushed and ground to a fine powder of 5–20 μm size and made into a slurry with a mixture of 30% isopropanol and 70% polyvinyl alcohol (PVA) solution. Nicalon SiC (NL-207) and

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Hi-Nicalon SiC fibre yarn from Nippon Carbon were incorporated into the glass matrix by slurry infiltration followed by hot-pressing as described previously [11]. 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.

Consolidation of the green bodies was carried out by hot-pressing at temperatures of 1330 °C and pressures of 14 MPa for 15 min using graphite dies. Crystallization of the glass matrix into a glass–ceramic form was achieved by holding at a temperature of 1080 °C for 50 min during the cooling cycle of the hot-press.

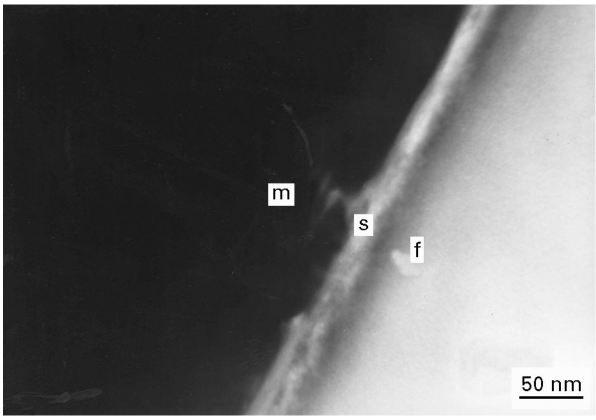

Figure 1 Bright-field TEM micrograph of the Nicalon SiC fibre–YN glass composite: (f) fibre, (m) matrix, (s) carbon-rich layer.

2.2. Microstructural and microchemical characterization

Observation of fracture surfaces and transverse cross-sections perpendicular to the fibre direction was carried out using a S4-80DV Camscan SEM. A JEOL-2010 TEM was employed for the fibre–matrix interface examination. Specimens for TEM were cut from hot-pressed samples, mechanically ground and polished to 0.1 mm in thickness, dimpled to 0.03 mm in thickness, and subsequently ion thinned (argon ions, 6 kV) to perforation. Chemical analysis was done using EDX with a Be window.

3. Results and discussion

3.1. Interfacial characterization

The interfacial regions of the composites were directly observed by TEM and compositions analysed by EDX. Three samples were designed containing different fibres and matrices. These were Nicalon SiC fibre–YN glass, Nicalon SiC–LN glass–ceramic and Hi-Nicalon SiC fibre–LN glass–ceramic composites, respectively. Nicalon SiC fibre consists of a mixture of very fine β-SiC crystals, SiO_2 and some free carbon. As Hi-Nicalon contains much less oxygen than normal Nicalon (Nicalon contains 12 wt % oxygen, but Hi-Nicalon contains only 0.5 wt % oxygen), it was expected to be stable up to higher temperatures. The LN glass–ceramic sample had a much lower thermal expansion coefficient, α, than the YN glass sample. With such fibres and matrices, comparison can be made in terms of physical and chemical compatibility of fibres and matrices.

Fig. 1 shows bright-field images of the interfacial area in a SiC fibre–YN oxynitride glass matrix composite fabricated at 1330 °C for 15 min. An amorphous, thin carbon-rich interface was identified. The thickness of this layer was about 20–40 nm, which is thinner than normally reported. On the matrix side of the carbon-rich layer, EDX analysis (Fig. 2) at an interfacial point further into the matrix showed that there was a slight increase in silicon content. The carbon interface apparently did not facilitate fibre debonding from the matrix; on the contrary, the fibre was tightly gripped by the glass matrix (Fig. 3).

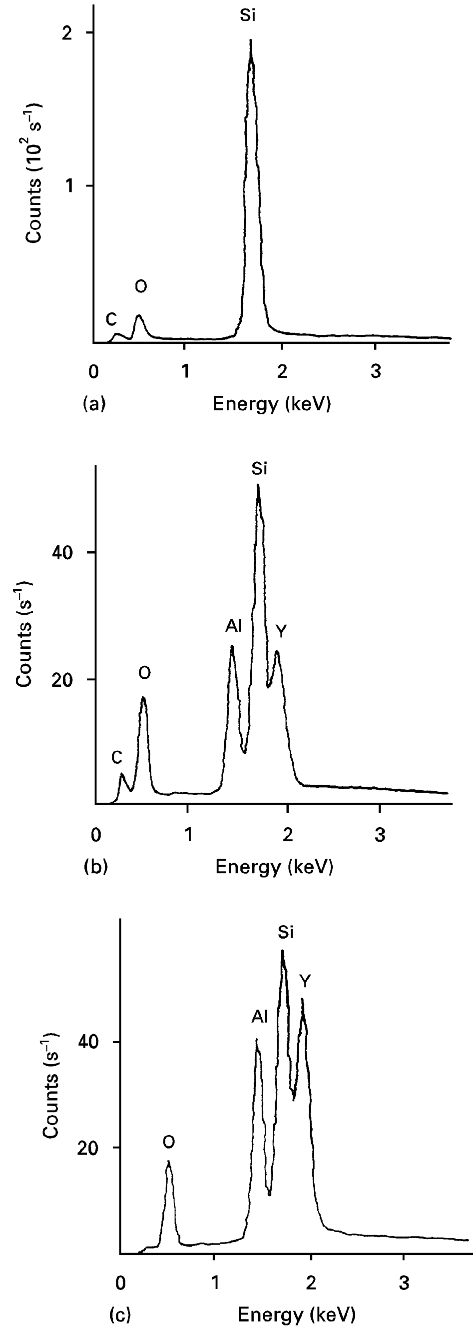

Figure 2 EDX spectra of the Nicalon SiC fibre–YN glass composite at different regions: (a) fibre region, (b) interface region between the fibre and the matrix, and (c) glass matrix region.

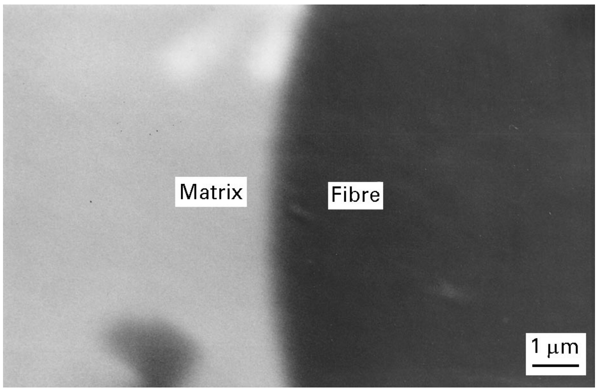

Figure 3 SEM micrograph of a polished cross-section of the Nicalon SiC fibre–YN glass sample.

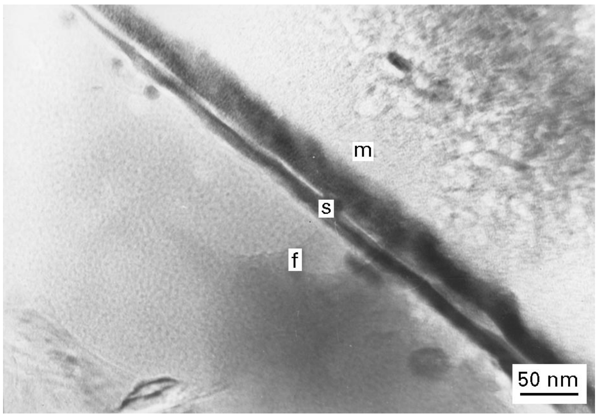

Figure 4 Bright-field TEM micrograph of the Nicalon SiC fibre–LN glass composite: (f) fibre (m) matrix, (s) thermal debonding between fibre and matrix.

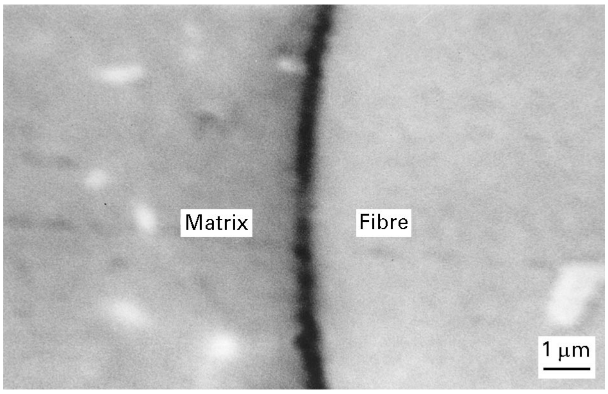

Figure 5 SEM micrograph of a polished cross-section of the Nicalon SiC fibre–LN glass sample.

The interfacial region in SiC fibre–LN oxynitride glass–ceramic composites was easily distinguishable from that of the SiC–YN sample. Fibre debonding did occur in this material, leaving a small gap between the fibre and the matrix (Figs 4 and 5). Because of fibre debonding, a carbon-rich layer was not visible as it had probably peeled off during ion-thinning. However, EDX analysis (Fig. 6) of the matrix immediately adjacent to the gap demonstrated an obvious increase in oxygen and silicon content.

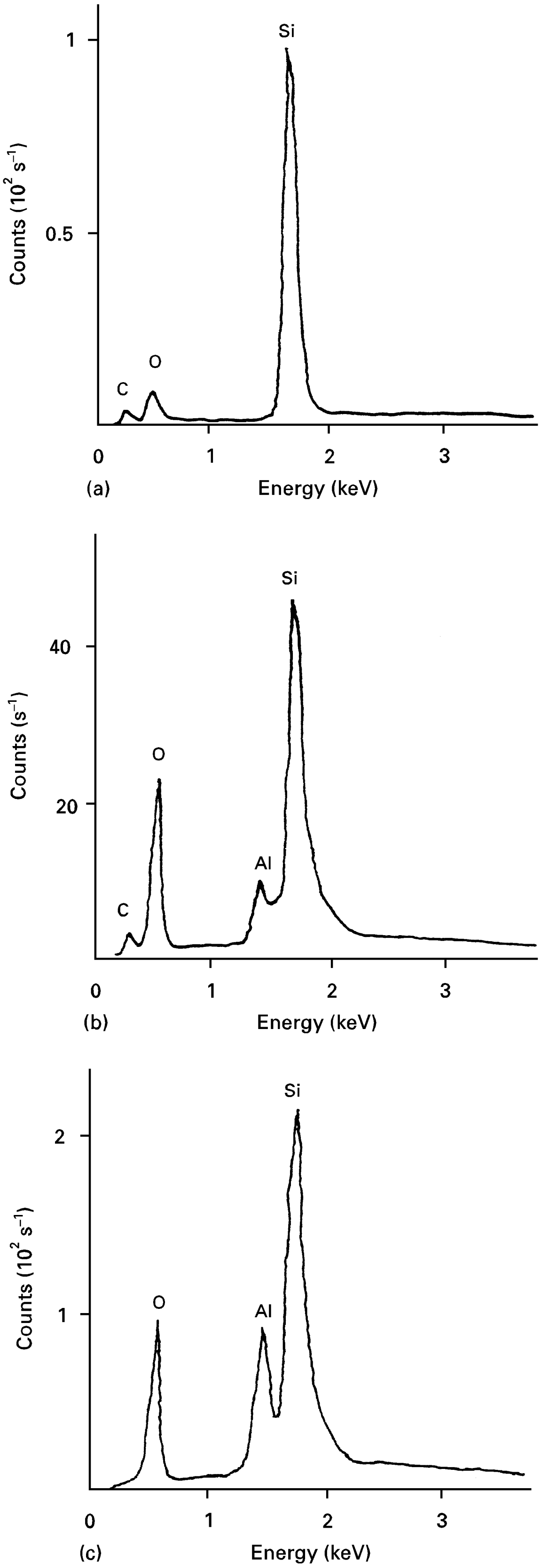

Figure 6 EDX spectra from different areas of the Nicalon SiC fibre–LN glass composites: (a) fibre region, (b) matrix region adjacent to the gap, and (c) glass matrix region.

TEM micrographs of the Hi-Nicalon fibre–LN oxynitride glass–ceramic sample provided a totally different type of interface compared with those described above. This was typical of a reaction-produced interface (Figs 7 and 8). The thickness of the reaction layer

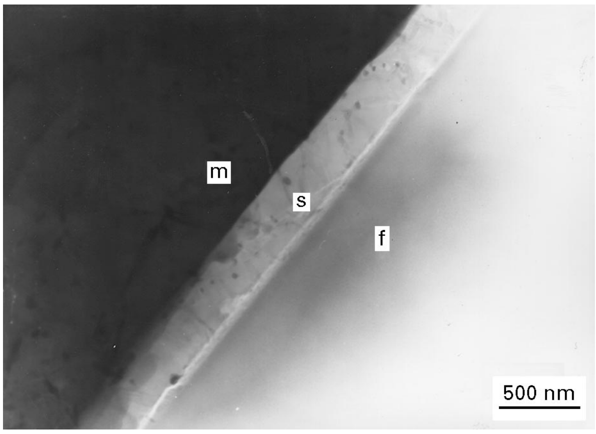

Figure 7 Bright-field TEM micrograph of the Hi-Nicalon SiC fibre–LN glass composite: (f) fibre, (m) matrix, (s) silicon and oxygen-rich reaction layer.

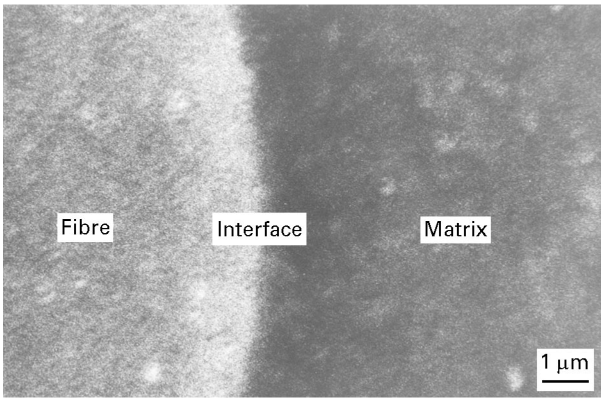

Figure 8 SEM micrograph of a polished cross-section of the Hi-Nicalon SiC fibre–LN glass sample.

was about 500 nm, and this was apparently part of the original matrix surface. EDX results (Fig. 9) showed that this reaction layer was a silicon-rich crystalline phase, with no sign of C, Al nor Li diffusion either from fibre to matrix or in the opposite direction.

3.2. Interface-forming mechanisms

Carbon-rich interfacial layers in Nicalon SiC fibre–oxide glass and glass–ceramic composites have been confirmed by several researchers, but the outside silica layer has received less attention in these materials [12–15]. It is commonly agreed that there is an increase in silicon content outside the carbon interface adjacent to the matrix. From this point of view, the present results are consistent with those previously reported. Hi-Nicalon composites have not been investigated to the same extent, and the present study provides new information on interfaces involving these fibres.

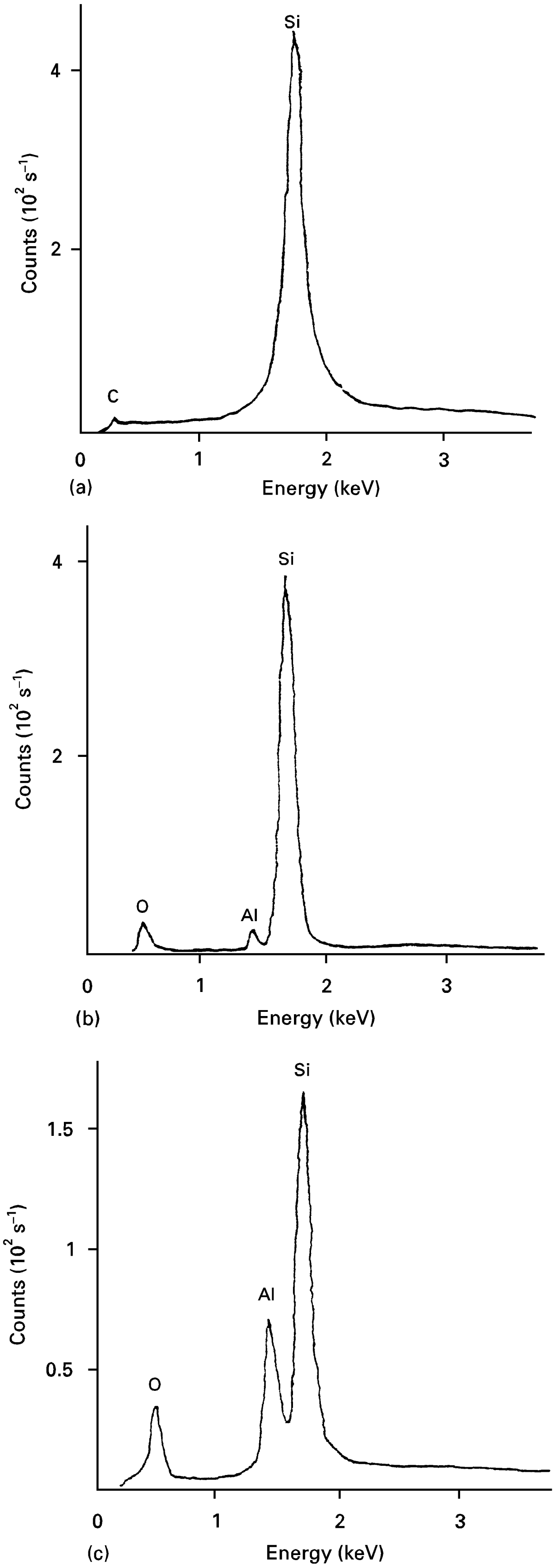

Figure 9 EDX spectra from different areas of the Hi-Nicalon SiC fibre–LN glass sample: (a) fibre region, (b) interfacial region, and (c) glass matrix region.

Formation mechanisms for the carbon- and silicon-rich interfacial layers in SiC fibre–glass and glass–ceramic composites have been postulated but are not fully understood. It is normally accepted that oxidation of the SiC fibre surface is responsible for the interface layers [16]. Either O_2 or CO dissolved in the glass matrix or produced by chemical reaction are believed to oxidize the fibre according to the reactions

$$SiC + O_2 = SiO_2 + C \quad (1)$$

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

The above reactions are assumed to be kinetically rate limited by diffusion rates of oxygen, silicon and carbon through the surface layers. The reaction products, P, can be structurally represented as

$$\text{matrix}_1(P_{\mathrm{O}_2}, P_{\mathrm{CO}})\,|\,\text{SiC fibre} \rightarrow \text{matrix}_2$$

$$(P^{\mathrm{I}}_{\mathrm{O}_2}, P^{\mathrm{I}}_{\mathrm{CO}})\,|\,\mathrm{SiO}_2\,|\,\mathrm{C}\,|\,\text{SiC fibre}$$

This explanation appears satisfactory for explaining interface formation in oxide-based composites, but the principle does not seem to operate in the same way in SiC fibre–oxynitride glass and glass–ceramic materials. This is because in such matrices, oxidation of the oxynitride glass at processing temperatures is more favourable than oxidizing the SiC fibre at low oxygen activity, and moreover, there is no sign that the interfacial layer is part of the original fibre surface, which is the normal evidence for fibre oxidation. It is believed that the formation of a carbon-rich interfacial layer is related to fibre degradation, which leads to uncontrolled release of SiO and CO due to the excess carbon and oxygen in the fibre. Because SiO diffusion through the SiC fibre is more rapid than that of CO [17], a carbon-rich interface is formed near the fibre, but SiO dissolves in the glass matrix.

The mechanism of interface formation in Hi-Nicalon SiC–oxynitride glass–ceramic matrix composites is totally different from that discussed above. TEM observations showed that the interface in this material was clearly a portion of the matrix, indicating that it represented the reaction products between the fibre and the matrix. It is supposed that diffusion of silicon from the fibre to the matrix and oxygen from the matrix to the fibre are responsible for this interface formation. Due to the absence of oxygen on the surface of the fibre, there is no emission of SiO and CO, thus encouraging reaction between the fibre and the matrix.

3.3. Fracture behaviour

The fracture behaviour of fibre reinforced glass or ceramic composites is primarily determined by the interfacial characteristics. A weak bond between fibre and matrix is beneficial to crack deflection, fibre bridging and fibre pull out, hence increasing the fracture toughness of the material. An interfacial bond normally involves chemical and mechanical bonding, which are, respectively, controlled by chemical reaction and physical compatibility between the fibres and the matrix. Although these two types of bonding often occur simultaneously in composites, however, only one predominantly influences the mechanical properties of the final materials.

Nicalon SiC fibre–YN glass composites demonstrated brittle failure, with no fibre pull out on the fracture surface (Fig. 10). This was caused by compressive stresses on the fibre surface generated by the thermal expansion mismatch between the fibres and the matrix ($\alpha_{\mathrm{YN}} \approx 6 \times 10^{-6}\,{}^{\circ}\mathrm{C}^{-1}$, $\alpha_{\mathrm{SiC\ fibre}} \approx 3.4 \times 10^{-6}\,{}^{\circ}\mathrm{C}^{-1}$), which makes it difficult for the fibre to extract itself from the matrix even in the presence of a carbon-rich interface. Nicalon SiC–LN glass–ceramic composites showed extensive fibre pull out (Fig. 11), resulting from thermal debonding of the fibre from the matrix, caused by the fibre contracting more than the matrix on cooling ($\alpha_{\mathrm{LN}} \approx 1\text{–}2 \times 10^{-6}\,{}^{\circ}\mathrm{C}$, $\alpha_{\mathrm{SiC\ fibre}} \approx 3.4 \times 10^{-6}\,{}^{\circ}\mathrm{C}^{-1}$). Thermal debonding reduced the frictional stress between fibres and matrix, thereby enabling the fibre to slide away from the matrix easily. In the above two cases, mechanical bonding was the predominant factor controlling the fracture behaviour of the composites. In contrast, the Hi-Nicalon SiC fibre–LN glass–ceramic composites did not show strengthening and toughening due to the strong chemical bonding present between the fibres and the matrix (Fig. 12).

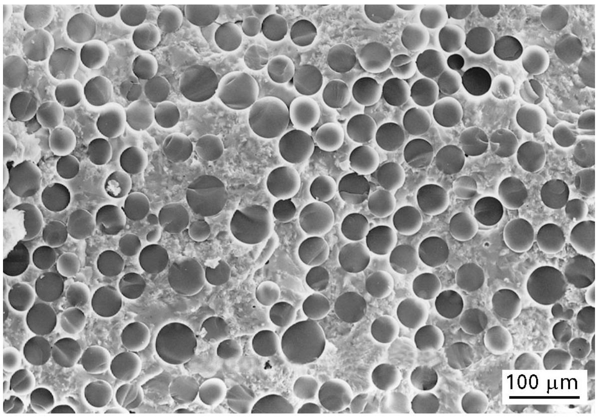

Figure 10 Fracture surface of the Nicalon SiC fibre–YN glass composite.

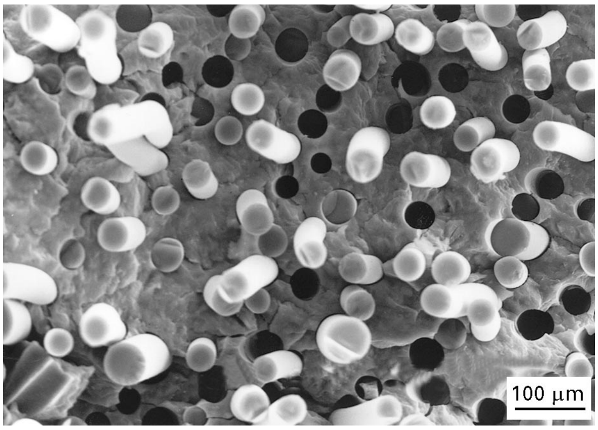

Figure 11 Fracture surface of the Nicalon SiC fibre–LN glass composite.

4. Conclusions

Interfacial regions of Nicalon- and Hi-Nicalon SiC fibre–oxynitride glass and glass–ceramic matrix composites demonstrated different features compared with those observed in comparable oxide glass and glass–ceramic composite materials. In these materials, the carbon-rich interface between the fibre and the matrix did not facilitate fibre debonding and toughening

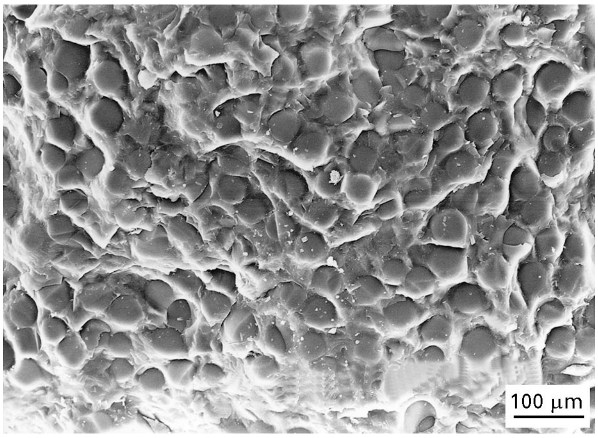

Figure 12 Fracture surface of the Hi-Nicalon SiC fibre–LN glass composite.

unless the matrix had a smaller thermal expansion coefficient than that of the fibres. A strong chemical bond between Hi-Nicalon SiC fibres and the oxynitride glass matrix was formed during high temperature processing, which resulted in neither strengthening nor toughening. In order to improve the interfacial chemistry, it is necessary that C- or SiC-coated Hi-SiC fibres should be used and in this case tough oxynitride glass and glass–ceramic composites would be expected to be produced.

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