JOURNAL OF MATERIALS SCIENCE 30 (1995) 1009–1017

# SiC fibre-reinforced lithium aluminosilicate matrix composites fabricated by the Sol–Gel process

K. S. KIM and H. M. JANG*
*Department of Materials Science and Engineering, and Advanced Ceramics Processing Science Laboratory, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea*
Y. K. BAIK
*Advanced Technology and Research Center, Agency for Defence Development, Yusung 305-600, Republic of Korea*

SiC fibre-reinforced lithium aluminosilicate (LAS) matrix composites were fabricated by (i) the hydrolysis–condensation reaction of relevant metal alkoxides, and (ii) the non-aqueous condensation route using diphenylsilanediol. Optimum reaction conditions of LAS sol formation for thin coating applications in the hydrolysis–condensation route were derived from rheological measurements. The SiC fibre–LAS composite fabricated by the hydrolysis–condensation route shows a uniform microstructure. The debonding/fibre pullout was more pronounced in the niobium-doped composites. The fracture toughness, $K_{1c}$, also increased from 11 MPa $m^{1/2}$ for the undoped composite to 16 MPa $m^{1/2}$ for the 5 wt% Nb-doped composite, suggesting that the fibre pullout contributes significantly to the toughening of SiC fibre–LAS composites. The crystallization of matrix at high temperatures (after hot pressing at 800 °C) eroded SiC fibres internally. This was attributed to the diffusion of aluminium atoms into the fibre, forming aluminium carbide above 1200 °C.

## 1. Introduction

SiC fibre-reinforced glass-ceramic composites have been found to combine excellent strength, toughness, and the potential for high-temperature oxidation resistance [1, 2]. It has been demonstrated that SiC fibre-reinforced lithium aluminosilicate (LAS) glass-ceramic system is capable of achieving excellent mechanical properties at temperatures of up to 1000 °C [1]. Glass-ceramics provide the unique capability to densify a composite in a low viscosity glassy state and then subsequently crystallize the matrix to achieve high-temperature stability.

In the fabrication of a glass-ceramic composite, however, hot-pressing of a stacked tape containing slurry-impregnated SiC yarn must be carried out at a sufficiently high temperature (well above 1000 °C) where the viscosity is low enough to permit the glass to flow into the interstices between individual fibres within a yarn bundle. The application of external pressure at a high temperature ($\sim$1300 °C in the conventional processing of SiC fibre LAS matrix composite [1]) is apt to result in excessive fibre/matrix interaction and consequent embrittlement of the composite in the fabrication of complex-shaped structure. This is especially true for the matrix transfer moulding [2] in which an external glass matrix is transferred at a high temperature into the mould cavity to fill the void spaces around the reinforcement structure. One possible solution to the above-mentioned problems is a replacement of slurry-impregnated SiC yarn by a bundle of SiC fibres coated with a chemically derived gel layer. The coated gel layer, in principle, removes problems associated with a direct bonding between SiC fibres during the hot-pressing stage and, therefore, maximizes the efficiency of load transfer during the crack propagation. Furthermore, the gel-derived matrix could significantly reduce the densification temperature.

In view of these facts, the main purpose of this study was to develop a sol–gel route (hydrolysis–condensation of metal alkoxides) for the fabrication of SiC fibre-reinforced LAS composite having high fracture toughness at a hot-pressing temperature well below 1000 °C. For this purpose, we first attempted to find suitable rheological conditions for a uniform coating of LAS sol on SiC fibres as a preliminary step for the fabrication of SiC fibre-reinforced LAS matrix composite having a uniform microstructure.

---

* Author to whom all correspondence should be addressed.

0022–2461 © *1995 Chapman & Hall*

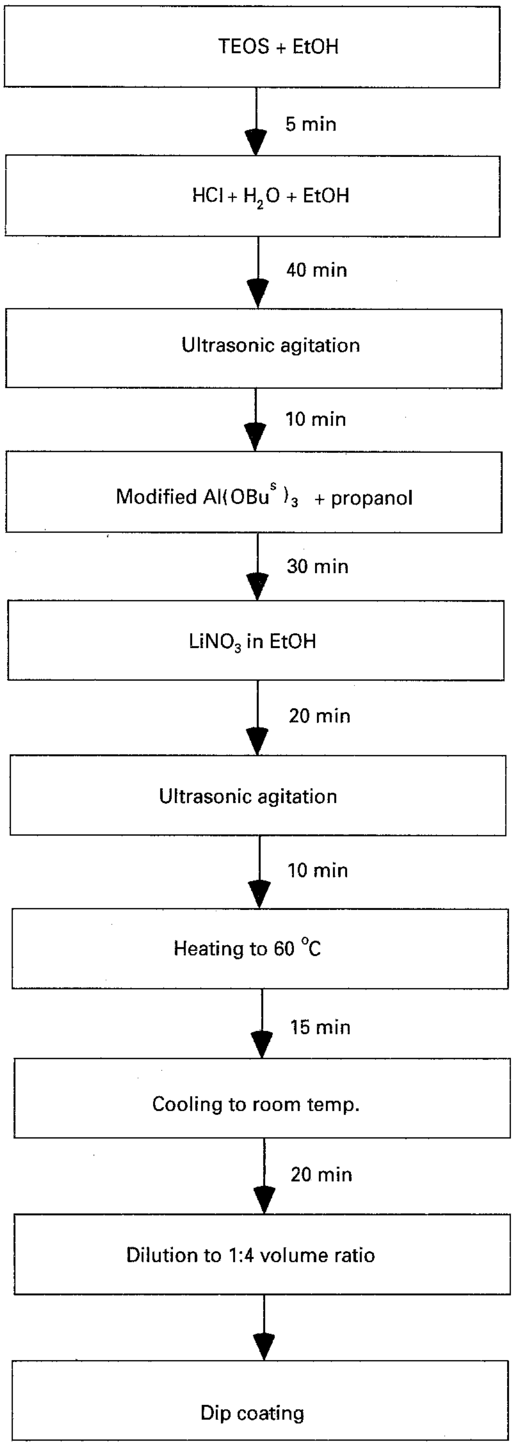


*Figure 1* Experimental procedure used for the preparation of LAS using the hydrolysis–condensation route.

## 2. Experimental procedure

LAS sol for the coating was synthesized using the hydrolysis–condensation reaction of tetraethylorthosilicate (TEOS), aluminium tri-sec-butoxide [$Al(OBu^s)_3$], and lithium-salt ($LiNO_3$) with $H_2O$ in alcohol medium. Unless specified elsewhere, the composition of LAS sol used in this study was $Li_2O:Al_2O_3:SiO_2 = 0.5:1:4$. The rate of the hydrolysis–condensation reaction of $Al(OBu^s)_3$ was reduced by chemical modification of $Al(OBu^s)_3$ with ethylacetoacetate (β-dicarbonyl compound) which undergoes a rapid keto–enol tautomerism [3]. The procedure followed for the preparation of LAS sol for the dip-coating applications is outlined in Fig. 1.

Optimum reaction conditions of LAS sol formation for thin coating applications were deduced from rheological data. The parameters examined for this purpose were $H_2O$/total alkoxides molar ratio, pH, and gelation time. Throughout the text, the molar ratio $R$ is defined as (moles of $H_2O$)/(4 × total moles of alkoxides). Thus, $R = 1$ corresponds to 4 moles of $H_2O$ and 1 mole of total alkoxides in the reactant. Rheological flow characteristics of LAS sols were determined using a concentric cylinder viscometer (Model RV-100/CV-100, Haake, Germany). Steady rotational flow curves (i.e. shear stress versus shear rate) were generated by increasing the shear rate from zero to the maximum desired value, in 2 min, immediately followed by decreasing the shear rate back to zero in another 2 min.

The LAS gel-coated SiC fibres were prepared by passing the SiC yarn (NL 207, Nippon Carbon Co., Japan) through an LAS sol with a drawing speed of 6 $cm\ min^{-1}$ and drying the yarn fibres at 50 °C for 30 min, followed by a second-stage drying at 70 °C for 30 min. The process for making unitape composites is begun by winding the dried yarn on to a mandrel to form monolayer tapes and by cutting the resultant tapes into the appropriate length (50 mm) to fit the hot-pressing die. After organic burnout, the tapes were stacked in the die to obtain the desired thickness ($\sim$6 mm), and the assembly was hot-pressed at 800 °C (or well below 1000 °C) for 10 min under applied pressure of 10 MPa. Ceraming was accomplished by annealing the hot-pressed composites in air at 1100 °C for 30 min.

Microstructural observation of hot-pressed composites was done using a scanning electron microscope (S-570, Hitachi, Japan). Phase-formation characteristics and microchemical homogeneity were examined by XRD (Rigaku, DMAX-3B, Japan) and EDAX (Phillips, SEM 515, Netherlands). The fracture toughness, as expressed by the critical stress intensity factor, $K_{1c}$, of the SiC–LAS composite system was measured using the notched beam method. A 150 μm thick diamond saw blade was used to form the tip of the notch in the specimens. The notch depth to sample thickness ratio was 0.5 in all cases. The value of $K_{1c}$ was calculated from the equation formulated by Brown and Srawley [4].

## 3. Results and discussion

### 3.1. Rheological characteristics

Fig. 2 shows rheological flow curves for LAS sols prepared using various conditions of $H_2O$/total alkoxides molar ratio, and pH (about 250 h ageing time). The results show that the sol exhibits a transition in flow characteristics from Newtonian behaviour to shear thinning behaviour (i.e. the viscosity decreases with increasing shear rate) as the water content or pH in the reaction medium increases. This indicates that the hydrolysis–condensation–gelation is practically frozen at a lower water content ($R \sim 0.25$) and pH (below $\sim$1.5). Because a shear thinning (or pseudoplastic) character with relatively low viscosity values ($\sim$10 MPa s) is desirable for thin coating applications, we have examined the ageing behaviour

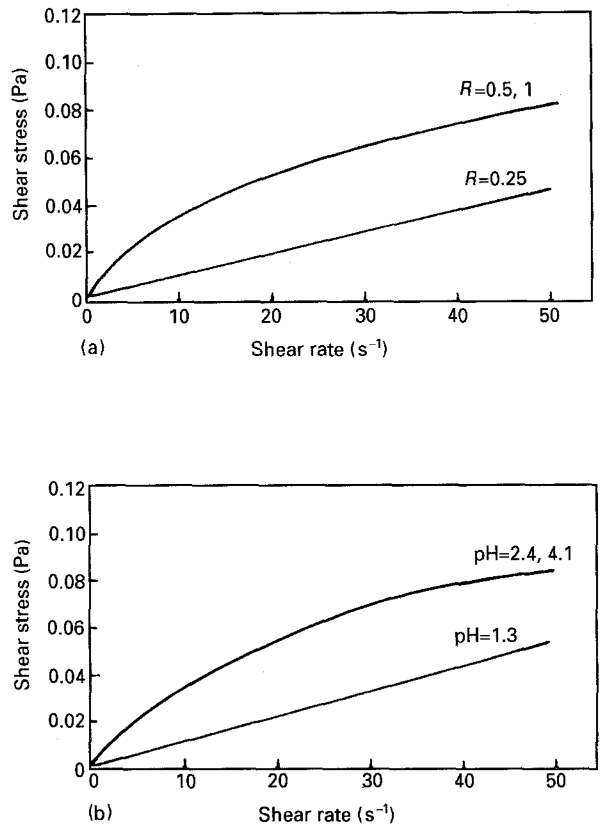


*Figure 2* Plots of shear stress versus shear rate (a) for various values of $R$, (b) for various values of pH.

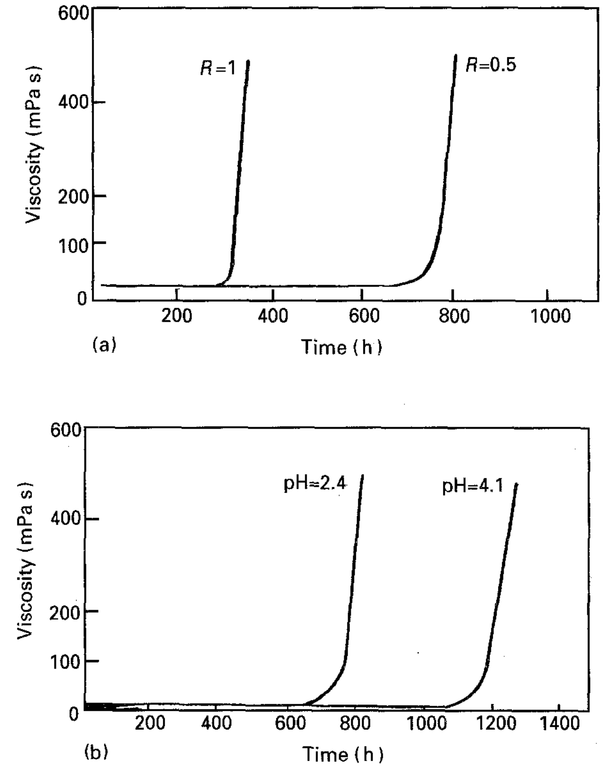


*Figure 3* Plots of viscosity versus ageing time for LAS sols prepared using various reaction conditions: (a) for pH = 2.5, (b) for $R$ = 0.5.

of LAS sol having shear thinning characteristics. As shown in Fig. 3, the viscosity of the shear thinning sol (at a shear rate of 5 s$^{-1}$) is essentially independent of reaction conditions ($R$, pH) below the gelation point.

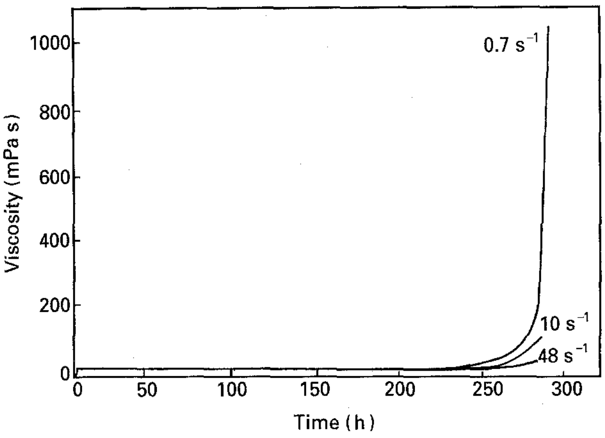


*Figure 4* Plots of viscosity (at indicated shear rate) versus ageing time for the sol having $R$ = 1 and pH = 2.5.

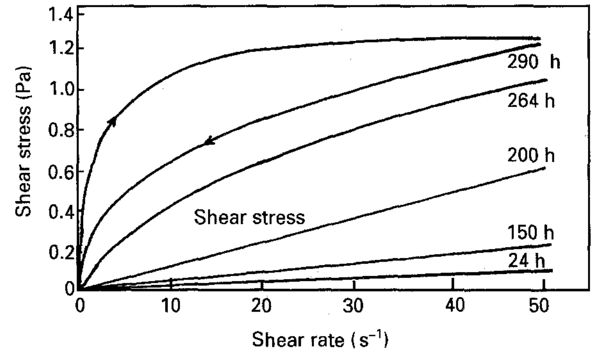


*Figure 5* Shear stress versus shear rate for the sol having $R$ = 1 and pH = 2.5 for various ageing times.

The hydrolysis–condensation of silicon alkoxide in the acid catalysed medium with a low water content usually produces polysiloxane species which are less branched and more chain-like [5, 6]. This linear chain induces an extremely slow gelation. As the water content increases, the hydrolysis–condensation reaction produces highly branched, polymeric polysiloxane clusters [6] via the nucleophilic substitution mechanism, $S_{N_2}$. This results in a rapid increase in the gelation rate and effective solids loading because the void space within a cluster agglomerate contains liquid that is unavailable for flow. Therefore, the results shown in Fig. 3a indicate that the above arguments (i.e. effect of water content on gelation time) also apply to the LAS sol derived from the hydrolysis–condensation route. An extremely slow gelation observed for the sol having pH $\geq$ 4.0 (Fig. 3b) presumably indicates that the sol particle obtained in this condition has a non-fractal character and is close to a discrete colloid particle rather than a branched lyophilic polymer.

A plot of viscosity versus ageing time for the sol (with $R = 1$ and pH 2.5) suitable for thin coating applications is shown in Fig. 4. Up to 250 h ageing time, the viscosity is essentially independent of shear rate. For longer ageing times, the viscosity becomes increasingly dependent on shear rate. Fig. 5 shows shear stress versus shear rate curves for the above sol at five ageing times. With continued ageing, condensation growth and agglomeration of polymeric clusters

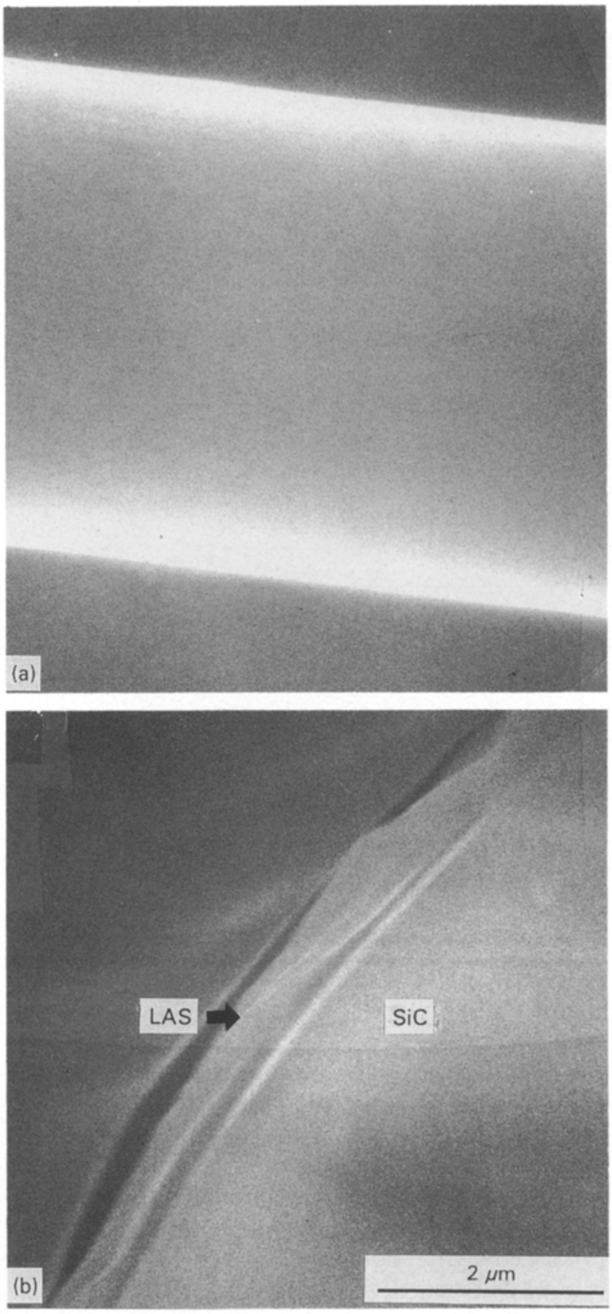


*Figure 6* Scanning electron micrographs of SiC fibre coated with a thin layer of LAS gel: (a) overview of coated fibre; (b) cross-section of fractured fibre.

results in the formation of a continuous, three-dimensional network. The elastic character of the network is characterized by the observation of yield stress at 290 h ageing. A breakdown of the network occurs after the yield stress is exceeded. Therefore, hysteresis is observed in the flow curve above a certain critical ageing time, and the sol becomes thixotropic. Because the best spinnability is usually obtained prior to the transition to thixotropic behaviour [7], optimum conditions of LAS sol coating can be summarized as $R = 1$, pH $= 2.5$, and ageing time $= \sim 250$ h.

## 3.2. Coating characteristics

Scanning electron micrographs of the SiC fibre coated with a uniform, thin layer (0.3–0.4 μm) of LAS gel are shown in Fig. 6. The coating was derived from the sol having the above-mentioned optimal conditions. A cross-sectional view of the fractured surface for a bundle of SiC fibres (yarn) is shown in Fig. 7. The LAS gel matrix between the fibres was prepared by a repeated coating (eight times) of the sol having $R = 1$ and pH 2.5. The solvent used in the thick coating process (Fig. 7) is a mixture of ethanol, methanol, and 2-propanol to remove rapidly the residual solvent from the gel matrix during the drying stage.

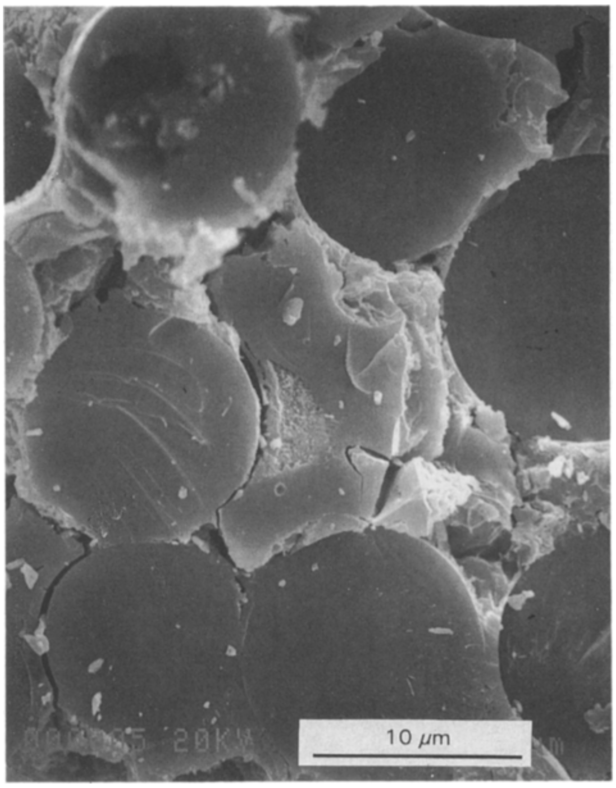
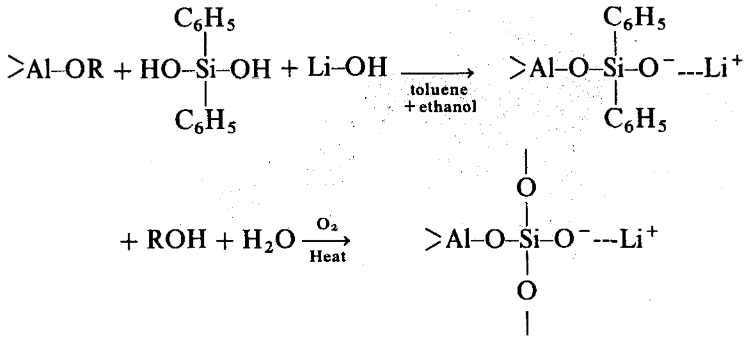


*Figure 7* Scanning electron micrograph of a bundle of SiC fibres filled with LAS gel derived from the hydrolysis–condensation route (before sintering).

The above-mentioned hydrolysis–condensation route practically has two limitations for an actual fabrication of SiC fibre-reinforced matrix composite. Firstly, as shown in Fig. 5, it takes approximately 250 h before the optimum conditions of the LAS sol coating can be obtained. Secondly, it is very difficult to maintain optimum values of viscosity ($< 50$ MPa s) at higher concentrations of LAS sol. The dip-coating procedure outlined in Fig. 1 is applicable only for a dilute LAS sol, and therefore it takes approximately ten repeated coatings at an ageing time of 250 h. At a higher concentration of LAS sol, the transition from pseudoplastic to thixotropic behaviour proceeds rather quickly, and thus it is practically difficult to complete the repeated coating cycle (dip coating and drying at 70 °C) while maintaining shear thinning characteristics (Fig. 5).

To shorten the coating time (including gelation time) and to avoid the problems associated with the formation of a three-dimensional network in the hydrolysis–condensation of relevant metal alkoxides, we have employed an alternative condensation route in a non-aqueous solvent using diphenylsilanediol. The relevant condensation reaction can be represented as



$$>\mathrm{Al{-}OR} + \mathrm{HO{-}}\overset{\mathrm{C_6H_5}}{\underset{\mathrm{C_6H_5}}{\mathrm{Si}}}\mathrm{{-}OH} + \mathrm{Li{-}OH} \xrightarrow[\text{toluene + ethanol}]{} >\mathrm{Al{-}O{-}}\overset{\mathrm{C_6H_5}}{\underset{\mathrm{C_6H_5}}{\mathrm{Si}}}\mathrm{{-}O^{-}{-}{-}{-}Li^{+}}$$

$$+ \mathrm{ROH} + \mathrm{H_2O} \xrightarrow[\text{Heat}]{\mathrm{O_2}} >\mathrm{Al{-}O{-}}\overset{\overset{|}{\mathrm{O}}}{\underset{\underset{|}{\mathrm{O}}}{\mathrm{Si}}}\mathrm{{-}O^{-}{-}{-}{-}Li^{+}}$$

where R designates alkyl groups. Owing to the two phenyl groups attached to the silicon atom, the condensation of $Al(OR)_3$ with diphenylsilanediol is expected to proceed smoothly without an extensive formation of a three-dimensional network even at high concentrations of reactants. Thus, the condensation route provides a fast, convenient method of sol coating with a relatively low viscosity even for a concentrated sol. It takes only 30 min for five repeated coating cycles. The condensation of $Al(OR)_3$ with diphenylsilanediol was successfully used for the fabrication of a crack-free sol–gel thin film [8].

As shown in the micrographs (Fig. 8), the non-aqueous condensation reaction offers a more efficient coating route. The condensation route yields a 1 μm coating thickness for each coating cycle (Fig. 8), as compared with 0.3–0.4 μm coating thickness in the hydrolysis–condensation route (Fig 6). A cross-sectional view presented in Fig. 9 indicates that, in the non-aqueous condensation route, SiC yarn fibres can be effectively filled with LAS gel by five repeated sol coatings.

### 3.3. SiC fibre-reinforced composites

Fig. 10 shows fracture surfaces of LAS–SiC composites hot pressed at 800 °C for 10 min and subsequently heat treated at 1100 °C for 30 min for crystallization. Fig. 10a corresponds to the composite fabricated by the hydrolysis–condensation route, whereas Fig. 10b shows the composite prepared by the condensation route using diphenylsilanediol and aluminium butoxide. As shown in the micrographs, the composite fabricated by the hydrolysis–condensation route shows more uniform microstructure, and SiC fibres are uniformly filled with LAS matrix.

The XRD pattern (Fig. 11a) of the hot-pressed matrix (without SiC fibres) indicates that, except for an incipient crystallization of hexagonal $LiAl(SiO_3)_2$ phase [9], the LAS matrix ($Li_2O:Al_2O_3:SiO_2 = 0.5:1:4$) is essentially in the glassy state after hot pressing at 800 °C for 10 min. On the other hand, the LAS gel having β-spondumene composition (i.e. $Li_2O:Al_2O_3:SiO_2 = 1:1:4$) crystallized to hexagonal $LiAl(SiO_3)_2$ phase with a small amount of β-spondumene after hot pressing at 800 °C for 10 min. It was observed that lowering the lithium content in the LAS gel by a factor of 1/2 raises the crystallization temperature by ~300 °C, i.e. 600 °C for 1:1:4 composition versus 900 °C for 0.5:1:4 composition [10]. Therefore, to minimize the fibre damage during hot pressing, the LAS gel having 0.5:1:4 composition was used in the fabrication of SiC fibre-reinforced composites. The results of Fig. 11b indicate that the LAS matrix

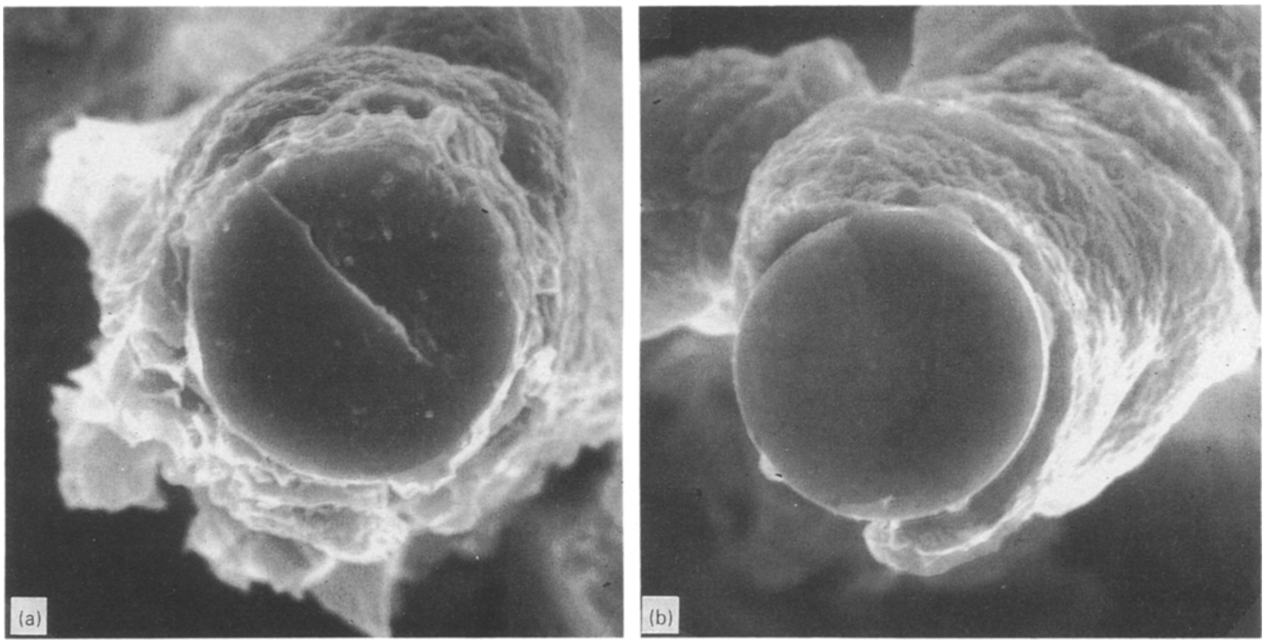


*Figure 8* (a, b) Scanning electron micrographs of SiC fibre repeatedly coated with LAS gel prepared by the non-aqueous condensation route using diphenylsilanediol and aluminium butoxide.

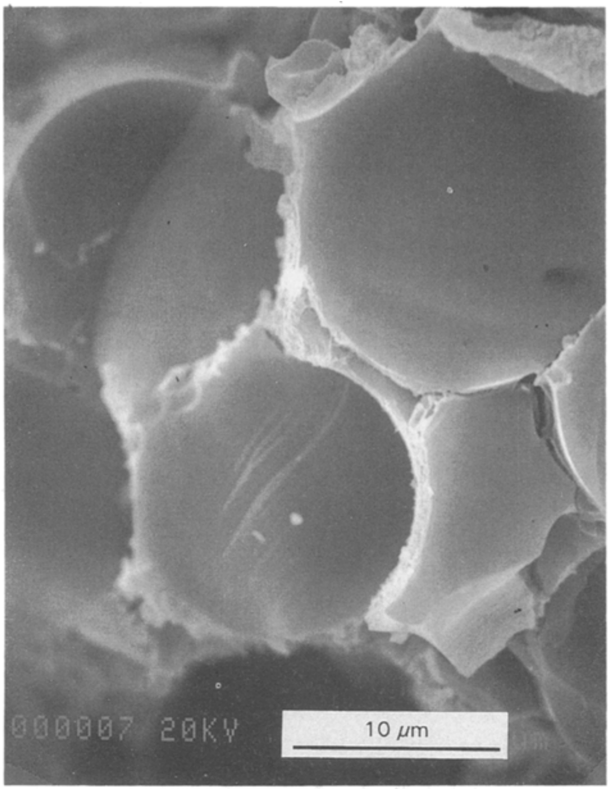


*Figure 9* Scanning electron micrograph of a bundle of SiC fibres filled with LAS gel derived from the non-aqueous condensation route (before sintering).

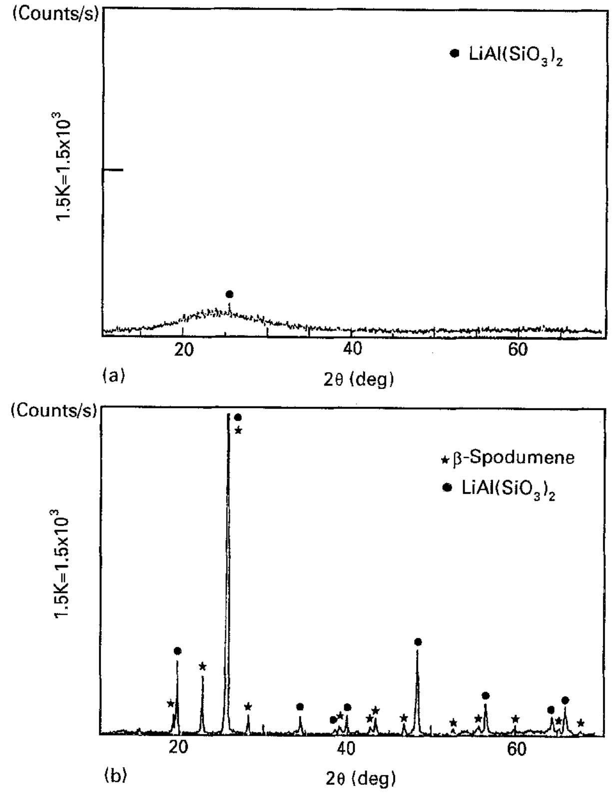


*Figure 11* XRD patterns of gel-derived LAS matrix having 0.5:1:4 composition: (a) after hot pressing at 800 °C for 10 min; (b) after hot pressing at 800 °C for 10 min and subsequent crystallization at 1100 °C for 30 min.

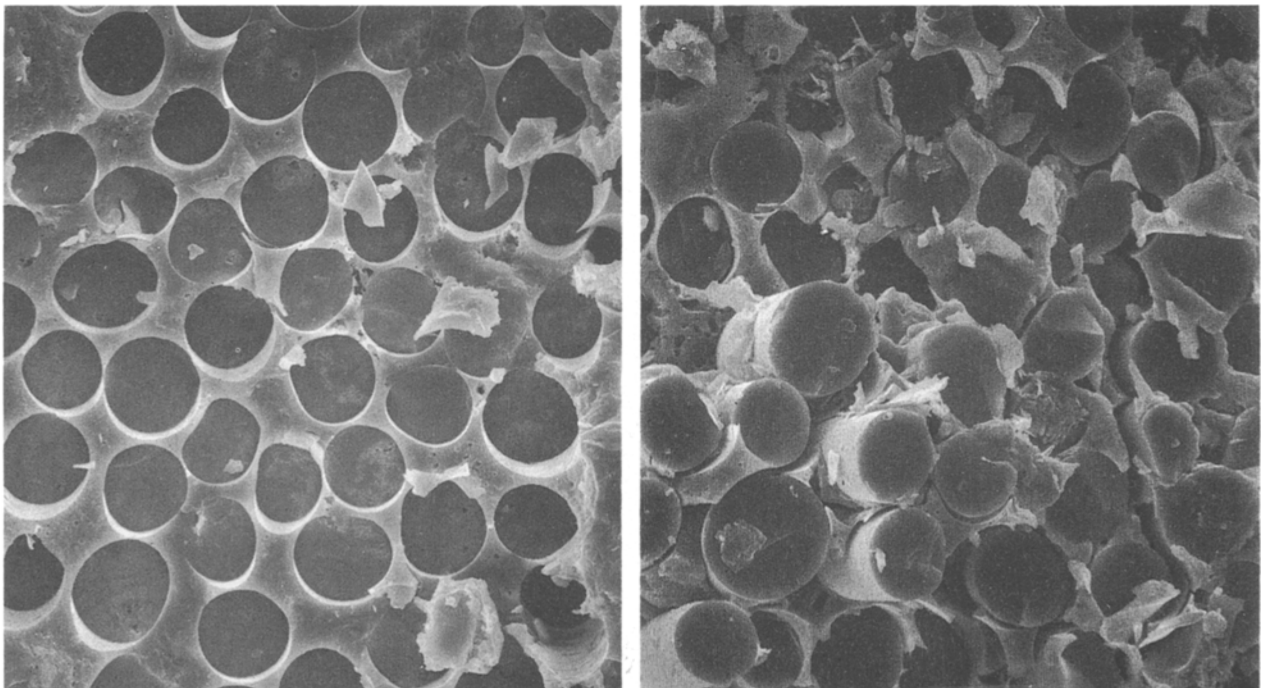


*Figure 10* Scanning electron micrographs of SiC fibre-reinforced LAS matrix composites hot pressed at 800 °C and 10 MPa for 10 min and subsequently heat treated at 1100 °C for 30 min: (a) prepared by the hydrolysis–condensation route: (b) prepared by the non-aqueous condensation route.

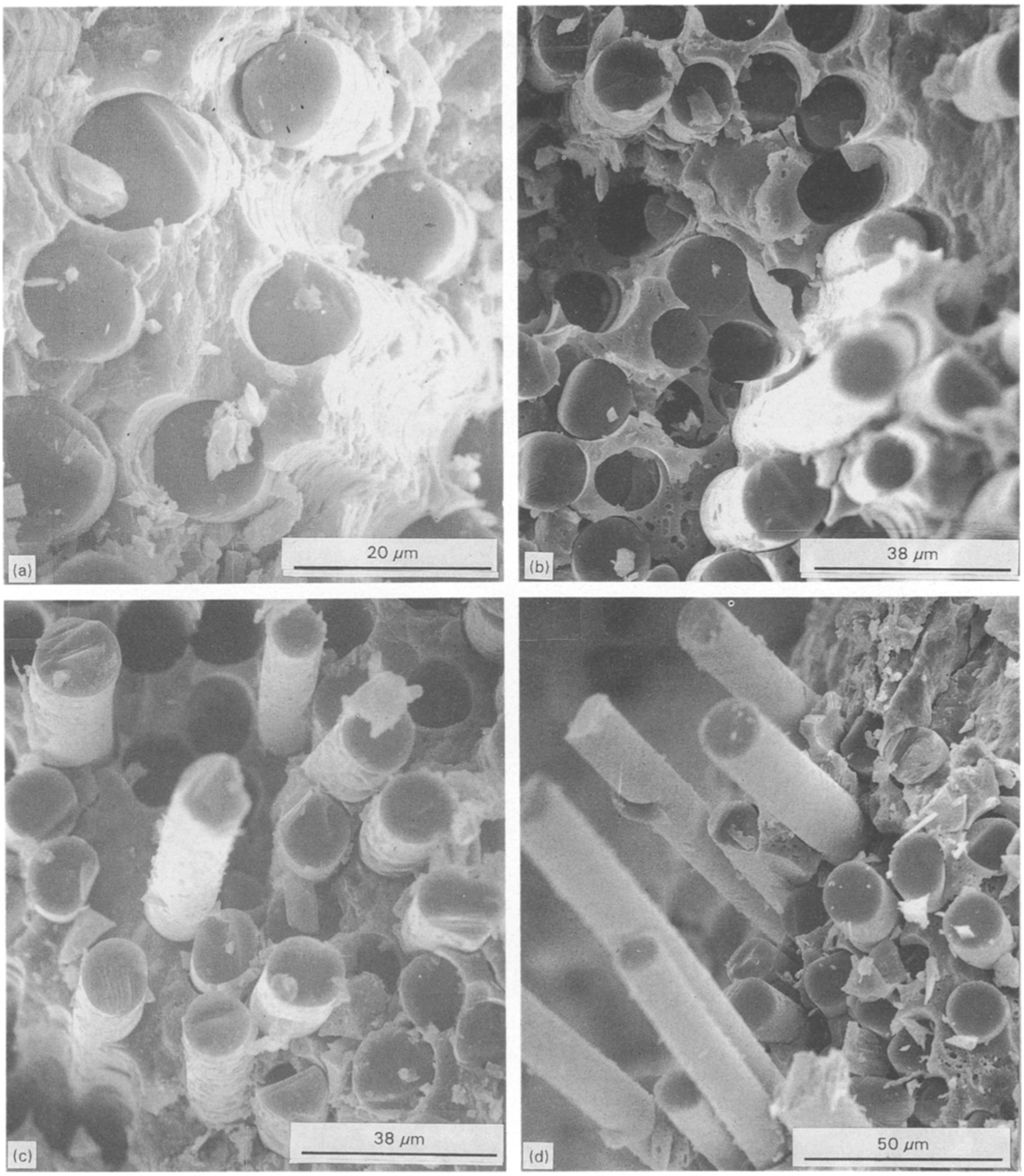


*Figure 12* Fracture surfaces of SiC fibre/LAS matrix composites hot pressed at 800 °C and 10 MPa for 10 min and subsequently heat treated at 1100 °C for 30 min: (a, b) fracture surfaces of undoped composite; (c, d) fracture surfaces of 5 wt% $Nb_2O_5$-doped composite, showing debonding and fibre pullout.

completely transforms to the crystalline state (tetragonal β-spondumene + hexagonal $LiAl(SiO_3)_2$ phase) after heat treatment at 1100 °C for 30 min.

As shown in Fig. 12, debonding and fibre pullout are more pronounced in the niobium-doped composites. This can be attributed to the formation of amorphous carbon/NbC microcrystal layer at the SiC fibre/LAS matrix interface [11, 12]. The fracture toughness, $K_{1c}$, also increases from ~11 MPa m$^{1/2}$ for the undoped composite to ~16 MPa m$^{1/2}$ for the 5 wt% $Nb_2O_5$-doped composite. This observation suggests that the debonding/fibre pullout contributes significantly to the toughening of SiC fibre-reinforced LAS matrix composites.

It has been observed that the crystallization of LAS matrix (after hot pressing at 800 °C) above 1200 °C usually deteriorates the microstructures of composites. Interfacial reactions between SiC fibre and LAS matrix are not significant in the undoped composite, but the fibres are eroded internally, as marked

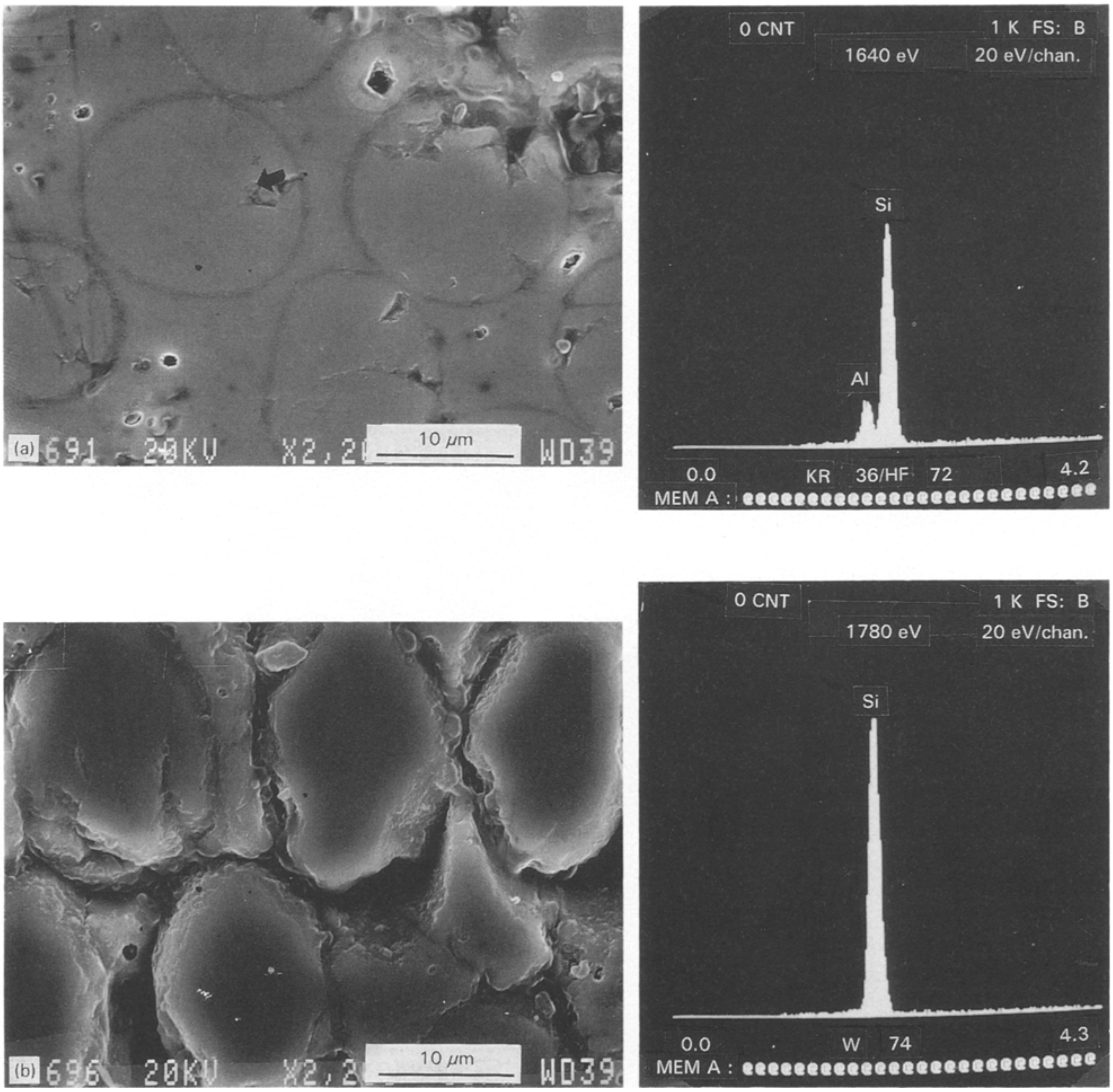


*Figure 13* Scanning electron micrographs and EDAX spectra of SiC fibre/LAS matrix composites hot pressed at 800 °C for 10 min and subsequently annealed at 1300 °C for 30 min: (a) polished surface of undoped composite, showing SiC fibre eroded internally; (b) polished surface of 5 wt% $Nb_2O_5$-doped composite.

with the arrow in Fig. 13a. Microchemical examination of the internally eroded region indicates that the aluminium atoms in the matrix diffuse into the fibre at 1300 °C, as shown in the EDAX spectrum of Fig. 13a. According to the studies done by Bender *et al.* [13] and Luthra [14], the aluminium atoms in the matrix diffuse inward and react with carbon atoms in the SiC fibre, forming $Al_4C_3$ [14]. On the other hand, interfacial reactions and subsequent erosion occur extensively in the $Nb_2O_5$-doped composite, but the SiC fibres are not eroded internally, as shown in the EDAX spectrum of Fig. 13b. The observed suppression of internal erosion in the presence of $Nb_2O_5$ can be attributed to the formation of NbC microcrystal layer at the interfacial region, which practically acts as a diffusion barrier for aluminium atoms.

Similar behaviour was also observed in the SiC whisker-reinforced LAS matrix composites fabricated by the hydrolysis–condensation route. The undoped whisker-reinforced composite heat treated at 1200 °C for 30 min (after hot pressing at 800 °C) did not show any evidence for interfacial reactions or an internal erosion consequent upon the internal diffusion of aluminium atoms (Fig. 14a). As the temperature increased to 1300 °C, the SiC whiskers degraded extensively. Microchemical examination also indicates that the region B in Fig. 14b is aluminium-rich, indicating the formation of $Al_4C_3$ above 1200 °C. Therefore, an optimization of the heating schedule (especially for crystallization) is important for a successful fabrication of SiC fibre or whisker-reinforced glass-ceramic composite.

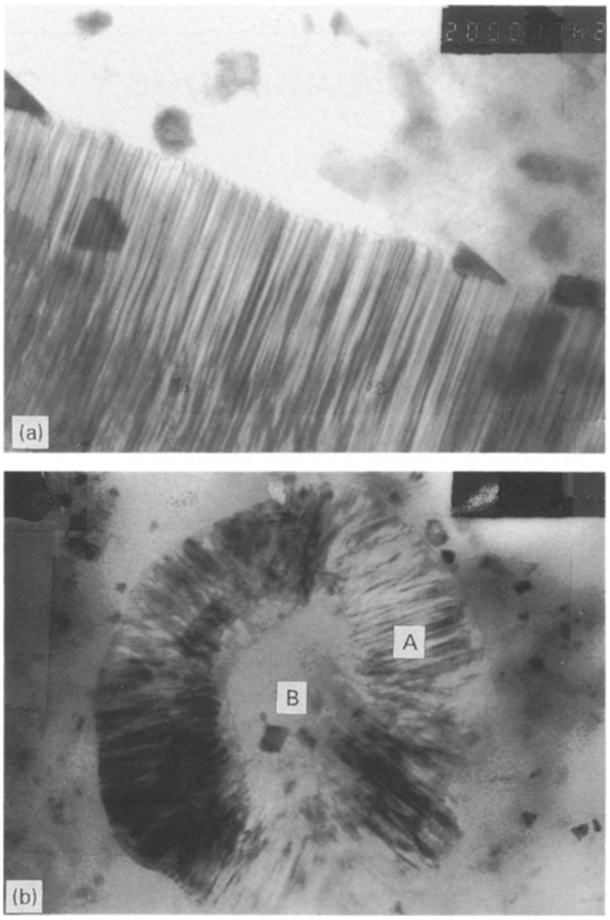


*Figure 14* Transmission electron micrographs of the interfacial region of SiC whisker/LAS matrix composite hot pressed at 800 °C for 10 min and annealed at 1200 °C for 30 min (a), annealed at 1300 °C for 30 min (b). Region A corresponds to the intact SiC whisker near the interface.

## 4. Conclusions

SiC fibre-reinforced LAS matrix composites were fabricated by (i) the hydrolysis–condensation reaction of relevant metal alkoxides, and (ii) the non-aqueous condensation route using diphenylsilanediol and aluminium butoxide. The following conclusions were drawn.

1. Optimum reaction conditions of LAS sol formation for thin-coating applications in the hydrolysis–condensation route were derived from rheological measurements, and these can be summarized as: $H_2O$/total alkoxides molar ratio $= 4$ ($R = 1$), pH $= 2.5$ and an ageing time of 250 h.

2. The non-aqueous condensation route provides a fast, convenient method of sol coating with a relatively low viscosity even for a concentrated sol.

3. The debonding/fibre pullout seems to contribute significantly to the toughening of SiC fibre-reinforced LAS matrix composites, and it was more pronounced in the niobium-doped composites.

4. The crystallization of LAS matrix (after hot pressing at 800 °C) above 1200 °C deteriorated the microstructure of composites. The observed internal erosion of SiC fibre was associated with the diffusion of aluminium atoms into the fibre and the subsequent reaction with carbon atoms, forming aluminium carbide.

## References

1. J. J. BRENNAN and K. M. PREWO, *J. Mater. Sci.* **17** (1982) 2371.
2. K. M. PREWO, J. J. BRENNAN and G. K. LAYDEN, *Am. Ceram. Soc. Bull.* **65** (1986) 305.
3. A. STREITWIESER Jr and C. H. HEATHCOCK, "Introduction to Organic Chemistry", 2nd Edn (Macmillan, New York, 1981) p. 369.
4. W. F. BROWN Jr and J. E. SRAWLEY, "Plane Strain Crack Toughness Testing of High-Strength Metallic Materials", ASTMSTP 410 (American Society for Testing and Materials, Philadelphia, PA, 1966) pp. 13–15.
5. S. SAKKA and K. KAMIYA, *J. Non-Cryst. Solids* **48** (1982) 31.
6. C. J. BRINKER, K. D. KEEFER, D. W. SCHAEFER and C. S. ASHBY, *ibid.* **48** (1982) 47.
7. M. D. SACKS and R. SHEU, in "Science of Ceramic Chemical Processing", edited by L. L. Hench and D. R. Ulrich (Wiley, New York, 1986) p. 100.
8. H. SCHMIDT, G. RINN, R. NAß and D. SPORN, Materials Research Society Symposia Proceedings, Vol. 121, edited by C. J. Brinker, D. E. Clark and D. R. Ulrich (Materials Research Society, Pittsburgh, PA, 1988) p. 743.
9. JCPDS, Powder Diffraction Files (1981) Set. 31-706.
10. H. M. JANG, K. S. KIM and C. J. JUNG, *J. Mater. Res.* **7** (1992) 2273.
11. R. CHAIM and A. H. HEUER, *Adv. Ceram. Mater.* **2** (1987) 154.
12. E. BISCOFF, M. RÜHLE, O. SBAIZERO and A. G. EVANS, *J. Am. Ceram. Soc.* **72** (1989) 741.
13. B. A. BENDER, D. LEWIS, W. S. COBLENZ and R. W. RICE, *Ceram. Eng. Sci. Proc.* **5** (1984) 513.
14. K. L. LUTHRA, *J. Am. Ceram. Soc.* **71** (1988) 1114.

*Received 9 September 1993*
*and accepted 9 June 1994*