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Optimization of the interfaces in Nicalon-fibre-reinforced-AlPO-matrix composite materials

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The optimization of fibre/matrix interfaces in Nicalon-fibre-reinforced aluminium-phosphate-matrix composite materials is addressed. First, the structure and chemical composition of the fibre/matrix interfaces were characterized for the as-fabricated composite materials and for the same materials after high-temperature exposures simulating the conditions of their intended application. Transmission electron microscopy (TEM) showed considerable Si diffusion from the fibres into the matrix accompanied by the formation of an interfacial diffusion/reaction zone in the process of heat treatment at 816 °C and higher temperatures. A BN-fibre coating did not prevent Si diffusion. Next, the interfacial bond strength was measured for the uncoated and some of the coated interfaces. The measurements showed a much lower bond strength in the carbon and carbon/BN coated interfaces than in the uncoated and BN-coated interfaces. Finite-element modelling was used to evaluate the interfacial bond strength which would result in the highest strength of the composite material. This optimal bond strength was found to be characterized by a critical energy-release rate close to 50 $J m^{-2}$. Further increase in the interfacial bond strength above 50 $J m^{-2}$ resulted in brittle failure of the composite materials. Finally, the potential fibre coatings which were stable and not reactive with the fibres and the matrix at elevated temperatures were identified for the projected service temperatures of 816 and 1093 °C.

1. Introduction

A promising approach for achieving structural materials which combine high-temperature strength characteristics of ceramics with the toughness and damage-tolerance characteristics of metals is the development of ceramic-fibre-reinforced ceramic-matrix composites. These materials are of particular interest for applications involving gas turbines, supersonic vehicles and energy-conversion systems. In these applications, an increase in the maximum service temperatures of the components allows an increase in combustion temperatures resulting in higher efficiency and reduced fuel consumption. The fuel consumption can be further decreased by a reduction in the weight of components, afforded by the low density of ceramic materials.

Reliable high strength and toughness cannot be obtained by the selection of appropriate fibres and the matrix alone; careful design of fibre/matrix interfaces is also required. On the one hand, load transfer from the fibres to the matrix depends on the interfacial bond strength, and as a result, higher bulk strength of composite materials require higher interfacial bond strength. On the other hand, the major toughening mechanisms in composite materials are fibre pull-out and crack deflection; i.e. higher toughness can be achieved with lower interfacial bond strengths. Due to the contradiction between these two requirements, a compromise has to be found. The compromise is an optimal bond strength which depends on the particular application of a composite material.

In this work, we addressed the design of optimal fibre/matrix interfaces in Nicalon-fibre-reinforced-aluminium-phosphate-matrix composite materials. These materials were recently developed by Alcoa [1]. They are chemically bonded and present the advantages of low processing temperatures (< 385 °C) that do not damage the fibres, while being amenable to forming into complex shapes.

Initially, the structure and chemistry of interfaces were studied in the as-processed state and after heat treatments representing temperature conditions for the potential applications of these materials. Next, a combination of experimental interfacial-bond-strength measurements with modelling calculations was used to evaluate the optimal interfacial bond strength for this composite system. And finally, the problem of selecting fibre coatings capable of providing the necessary interfacial bond strength was addressed.

2. Experimental procedure

2.1. Materials

The ceramic–matrix composite materials studied in this work were prepared by infiltration of Nicalon-fibre cloth with a slurry containing a mixture of mono-aluminium phosphate with α-alumina (50 wt %) or, alternatively, a mixture of phosphoric acid with alumina. The main components of the Nicalon fibres are: Si (54%), C (30%) and O (12%). Composite panels were produced using the process described in [1].

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BN-fibre coatings, 200 nm thick, and duplex coatings consisting of a pyrolytic carbon layer, 100 nm thick, and a BN layer, 100 nm thick, were deposited by chemical vapour deposition (CVD).

Heat treatments of the coated and uncoated materials were conducted at the temperature of their intended applications, 816 °C for 48 h, and a higher temperature of 1540 °C for 10 h.

Screening tests for compatibility of the coating materials with the fibres and the matrix were conducted by preparing mixtures of the powdered coating materials with the materials they will contact during processing and service. To imitate processing conditions, they were tested in contact with the slurry and with the crushed fibres, separately. The mixtures were initially heat treated at 385 °C for 1 h, which simulated the thermal conditions of processing. To simulate elevated-temperature service conditions, additional heat treatments were conducted at 816 and 1093 °C.

2.2. Characterization techniques

Interfaces in the composite materials were characterized by transmission electron microscopy (TEM). To prepare TEM samples, a composite-material sample was vacuum impregnated with epoxy resin in order to limit contamination of the examined material with nickel or copper and other elements of the plating bath during the electroplating process that followed. The epoxy-impregnated sample was sputtered with gold to provide a coating 10–20 nm thick. It was subsequently electroplated with nickel or copper to produce a coating about 1.5 mm thick. Then the sample was cut with a diamond saw and mechanically polished. Finally, it was dimpled and cold-stage ion milled, to produce thin areas for TEM examination.

The reactivity of the coating materials with the fibres and the matrix was tested by X-ray diffraction (XRD) and solid-state magic-angle nuclear magnetic resonance (NMR) techniques. The interfacial bond strength was measured by a microbond method described later.

3. Results and discussion

3.1. Characterization of the Nicalon/AlPO interfaces after high-temperature exposures

3.1.1. Uncoated interfaces

The main difficulties in chemical and crystallographic characterization of interfaces lie in their small thicknesses, which range from a few tenths of nanometres to a few micrometres, and in the difficulty of access to these regions by analyser probes.

The technique that gave the most useful information about structure of interfacial areas in composite materials was TEM. The main problem, however, was sample preparation because of the brittleness of the material and the difference in the properties of the fibres and the matrix. The details of the sample-preparation technique used in this work are given above.

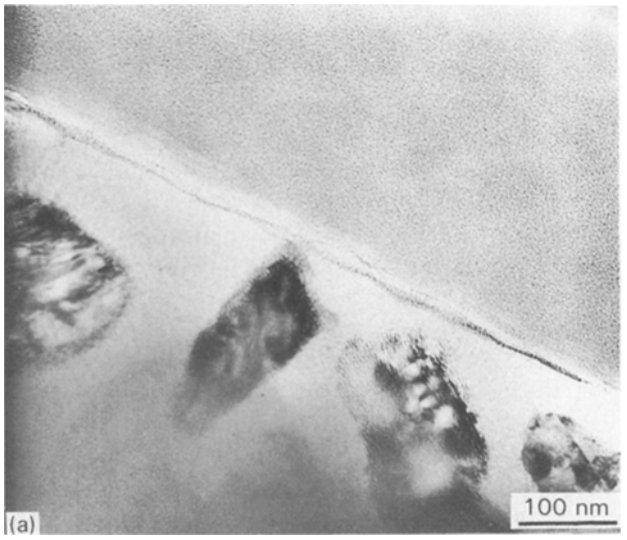
TEM studies showed a significant diffusion of silicon from the fibres into the matrix in the process of heat treatment at 816 °C and at higher temperatures. This can be seen by comparing the microstructure of as-processed Nicalon/AlPO composite material, which is presented in Fig. 1a, with the microstructure of the same material heat treated at 816 °C for 48 h, presented in Fig. 2a. The as-processed uncoated material in Fig. 1a shows no diffusion or interfacial reaction zone. The fibres and the matrix with the filler particles have the expected compositions, as can be seen in the energy dispersive X-ray (EDX) spectra in Fig. 1b. In contrast, a TEM micrograph of the same material, heat treated at 816 °C, in Fig. 2a, shows an interfacial zone with a structure different from the rest of the matrix. The EDX spectra in Fig. 2b show a considerable amount of Si in this zone, in addition to the matrix components, Al and P. The elements with atomic numbers less than 11 including O, C, N and B, are not represented on these spectra. These data indicate that diffusion of Si from the fibres into the matrix took place during heat treatment.

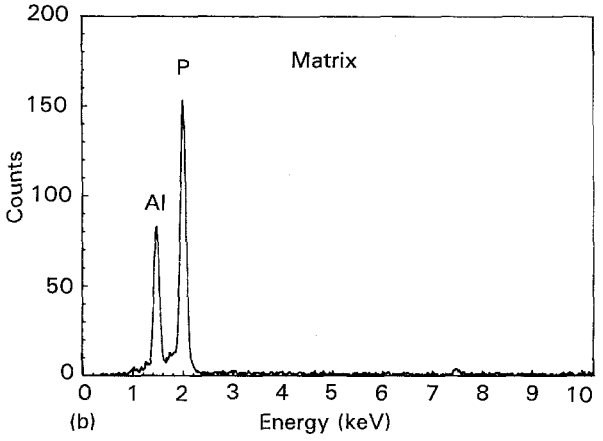
Silicon diffusion most likely took place in conjunction with the reaction of SiO_2 with the matrix. Nicalon-fibre surfaces contain SiO_2 which can react with H_3PO_4, one of the matrix components, to form $SiO_2 \cdot P_2O_5$ and $2SiO_2 \cdot P_2O_5$ at temperatures as low as 300 °C [2]. These reactions are detrimental to the performance of the composite material, because they cause fibre degradation, increase interfacial bonding due to diffusion, and form compounds with comparatively low melting temperatures (1000 °C for $SiO_2 \cdot P_2O_5$ and 1200 °C for $2SiO_2 \cdot P_2O_5$).

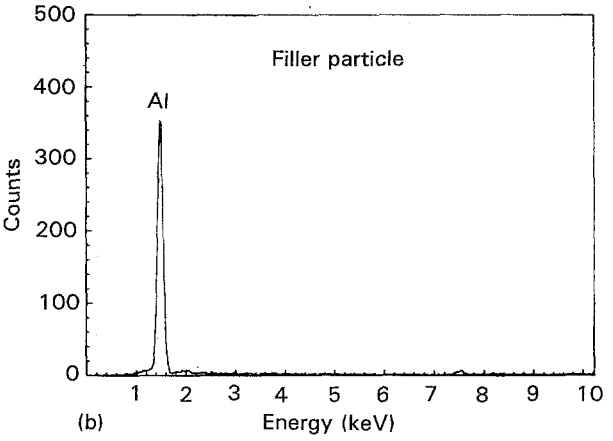
As far as crystallographic structures are concerned, almost all the phases involved were found to be amorphous, with the exception of the filler alumina particles, as shown by the selected-area electron-diffraction patterns in Fig. 2c. Comparing the diffraction patterns in Fig. 2c, the spacing and intensities of the diffuse rings in the electron-diffraction patterns for the interfacial zone are different from those for the matrix and the fibres. This indicates that a different amorphous phase is formed at the interface.

Heat treatment at a much higher temperature, 1540 °C, for 10 h resulted in long-distance silicon diffusion and matrix depletion of phosphorus. These effects can be observed in the spectrum of the matrix in Fig. 3c, which shows a large amount of silicon and no phosphorus. Even the filler particles were found to contain considerable amounts of silicon. Thermodynamic analysis [3] showed that at 1540 °C volatile, phosphorus-containing phases could form and leave the system.

As a result of interfacial reaction, the fibre surfaces had a wavy appearance as demonstrated in Figure 3a. In Fig. 3a, the dark zone on the left is a fibre, the slightly lighter area next to the fibre with a wavy appearance is an interfacial zone and the large area further to the right, which includes alumina particles P, is the matrix. Electron diffraction of the dark-zone adjacent to the wavy boundary showed SiC is the main component, indicating that this is likely to be a part of the fibre eroded by the interfacial reaction. A higher-magnification image of the fibre–matrix interface is given in Fig. 3b; the lower region is the wavy interfacial zone shown in Fig. 3a and the top is







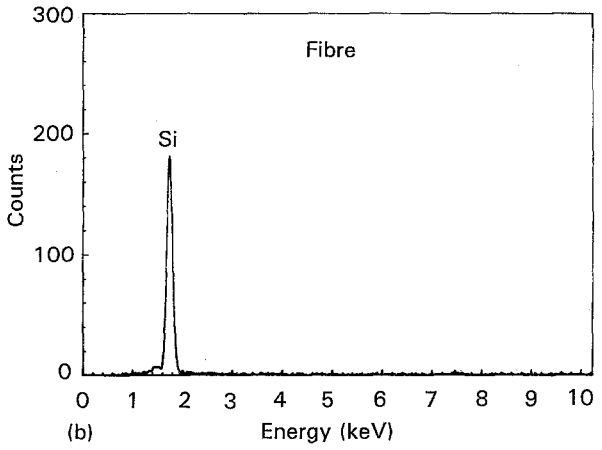


Figure 1 (a) TEM bright-field image of the SiC/AlPO composite material. (b) EDX spectra of the SiC/AlPO composite material.

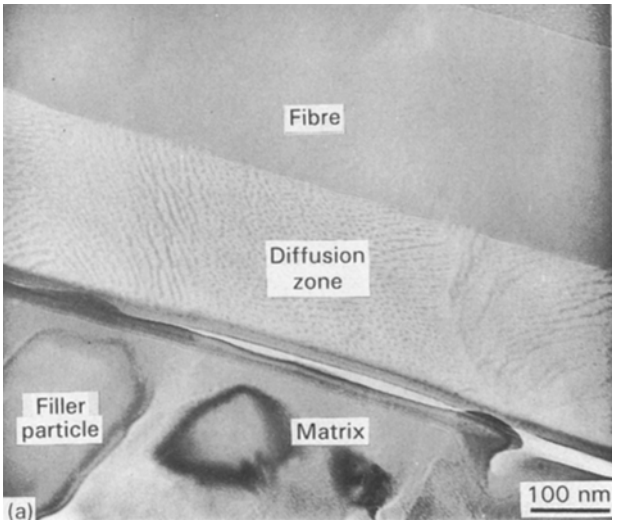


Figure 2(a) continued

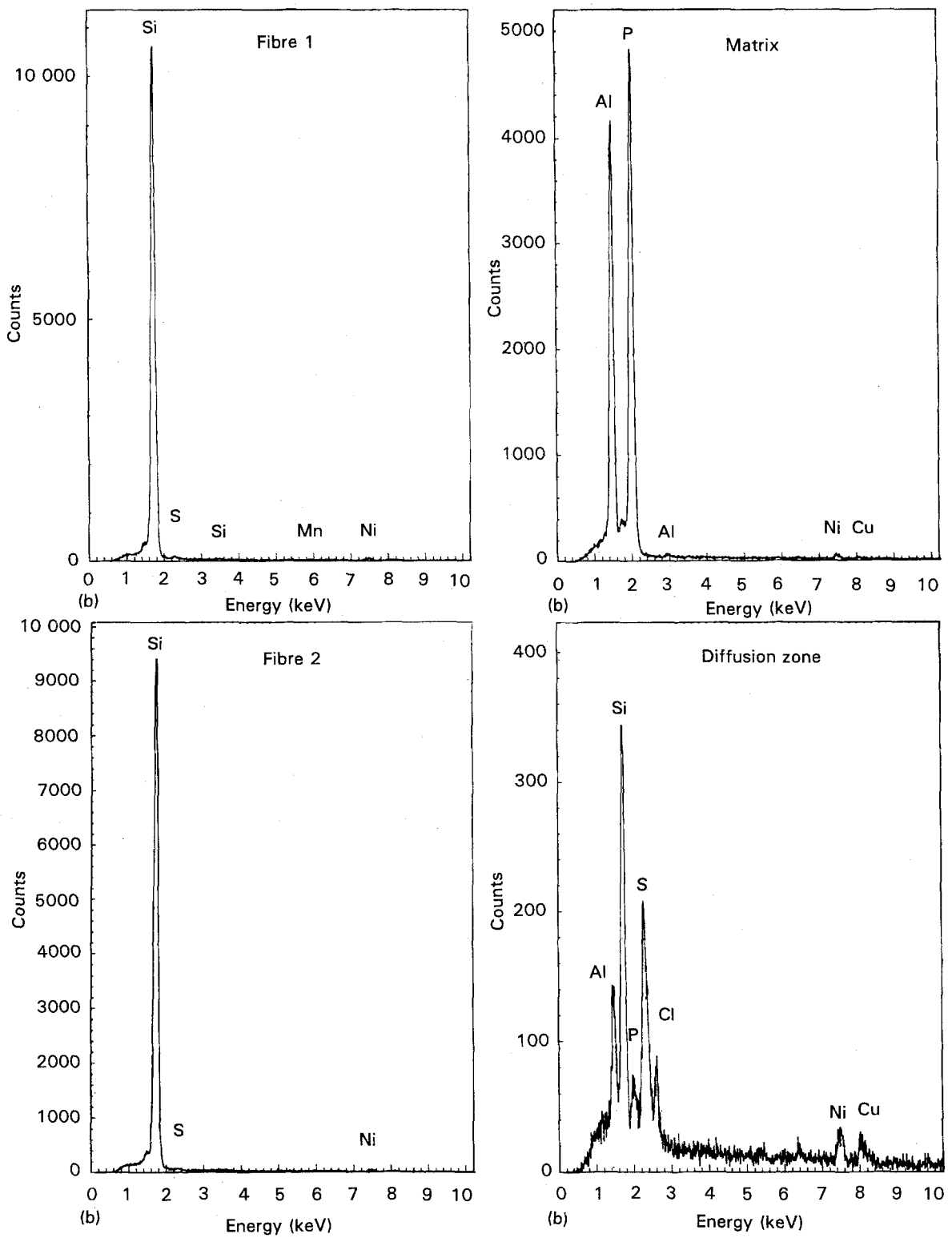


Figure 2(b) continued

the matrix. This gradient character of the interface indicates considerable interfacial diffusion.

In addition, the process of heat treatment at 1540 °C led to an increase in fibre crystallinity. This is demonstrated by comparison of the fibre electron-diffraction pattern after the high-temperature treatments at 816 and at 1540 °C (Fig. 3d). The fibres heat treated at 1540 °C show sharper electron-diffraction rings, which correspond to a higher degree of crystallinity than the fibres heat treated at a lower temperature.

3.1.2. *Interfaces in composite materials with BN-coated fibres*

BN was selected as a fibre-coating material because of the literature on the improvement in the mechanical properties of composite materials containing BN-coated fibres [4]. Our TEM/EDX examination, however, showed that the BN-fibre coating did not prevent silicon diffusing from the fibres into the matrix during heat treatment at 816 °C for 48 h. Moreover, the BN coating was found to separate from the fibres in many

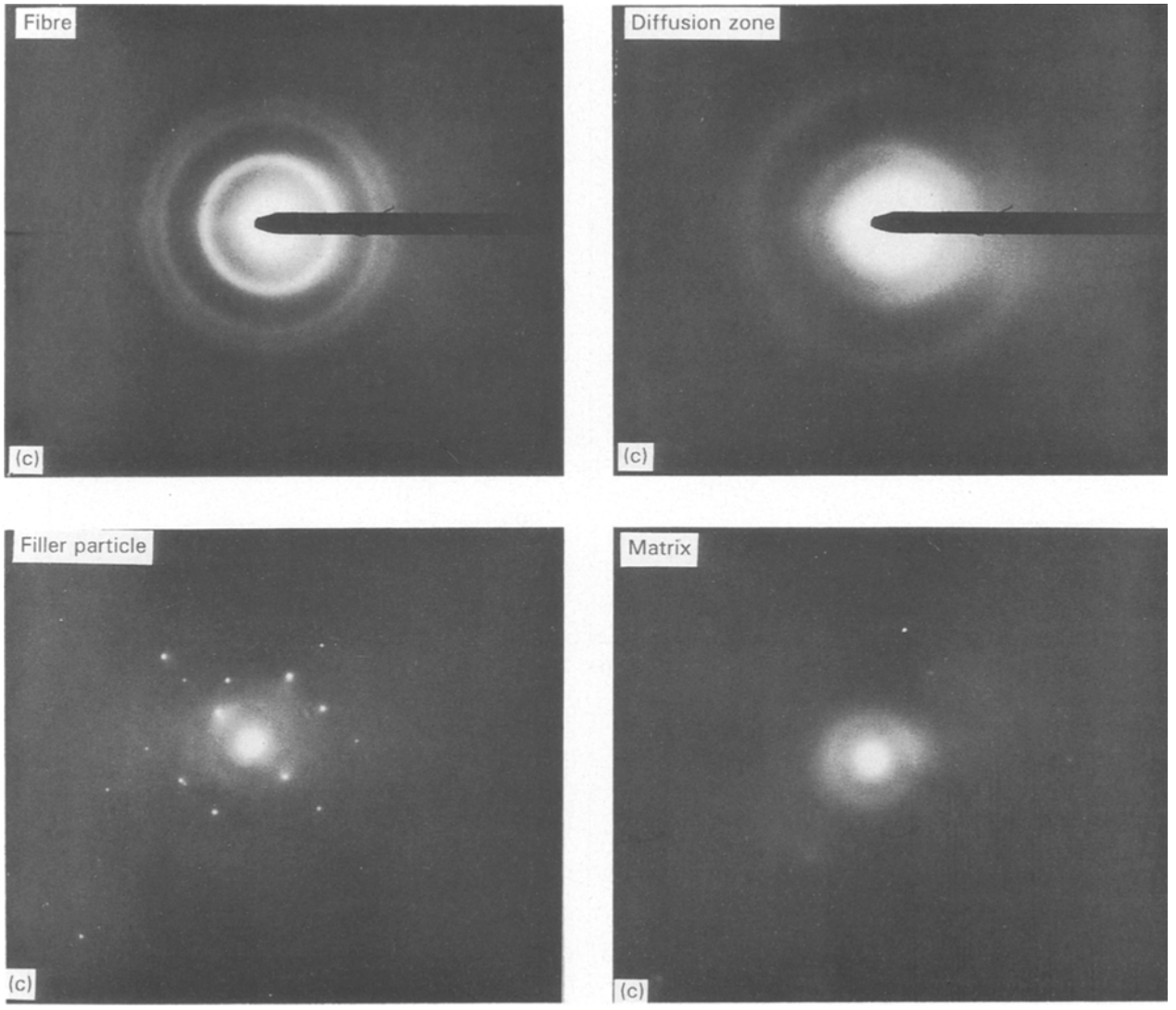


Figure 2 (*a*) TEM bright-field image of the SiC/AlPO composite material heat treated at 816 °C for 48 h. (b) EDX spectra of the SiC/AlPO composite material after heat treatment at 816 °C for 48 h. (c) selected-area electron-diffraction patterns of the SiC/AlPO composite material heat treated at 816 °C for 48 h.

places, with the space between them filled with material containing a large amount of silicon in addition to the matrix elements, phosphorus and aluminium. These features can be seen in Fig. 4a, where the coating has separated from the fibre by the intermediate phase containing phosphorus, aluminium and silicon, as indicated by the EDX spectra in Fig. 4b. The matrix outside the coated fibre also contains a considerable amount of silicon, as shown in Fig. 4b.

The separation of the BN coatings from the fibres could be caused by the pressure of SiO and CO gases, which are formed in the process of internal oxidation of the free carbon coming in contact with the silicon dioxide inside the fibres [5].

An NMR study of the BN-coating behaviour reported in [6] showed that even at the low processing temperatures characteristic for this composite, BN reacts with the AlPO matrix or matrix precursor to form boron phosphate. Formation of boron-containing glasses was observed after heat treatment at 1093 °C for 24 h. Boron oxide and boron-containing glasses have low melting temperatures (460 °C for B_2O_3). The presence of molten phases would accelerate diffusion processes, leading to degradation of the composite. As a result, BN-fibre coating is detrimental to the high-temperature performance of Nicalon/AlPO composite materials.

3.2. Mechanical properties of interfaces

To measure the interfacial bond strength, we modified and applied a microbond technique which was initially introduced to test the interfacial bonding in polymer-matrix composites [7]. The geometry of this test is shown in Fig. 5. The single reinforcing fibres, in this case, Nicalon fibres, were taped across a frame and fine droplets of slurry were deposited on them. The fibres with the slurry were placed in an oven and cured according to a routine procedure, producing small beads of the matrix attached to the fibres. Then the bond strength between the fibres and the matrix beads was tested in an Instron testing machine with a microvice as shown in Fig. 5. When the fibre was pulled up, the plates of the vice caused debonding of the matrix bead.

A typical load–displacement curve is shown in Fig. 6. Initially, elastic deformation of a fibre was recorded, in the linear part of the curve. Next, the

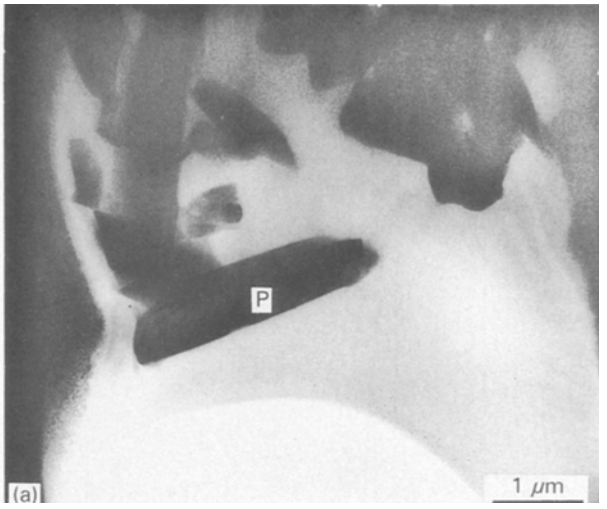
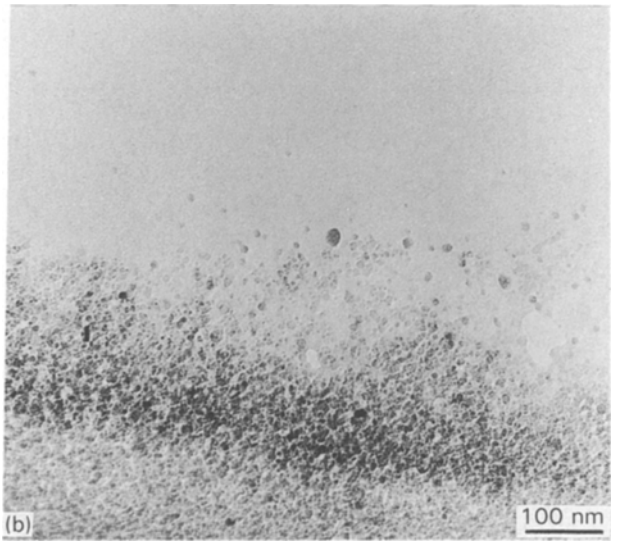


Figure 3(a–b) continued



point of abrupt decrease indicated the load at debonding, and further, as the matrix was sliding down the fibre, the frictional force was recorded.

The microbond test was used to measure the interfacial bond strength at the fibre/matrix interfaces in Nicalon/AlPO materials with uncoated fibres and with fibres coated with BN, pyrolytic carbon, and a duplex, carbon/BN coating, 200 nm thick.

The experimental data for the duplex-coated fibres are presented in Fig. 7. They show a high variation in the load of debonding for the same embedded fibre length. The scatter could be caused by the chemical and physical inhomogeneities on the fibre surfaces and in the matrix, which are of comparable size to the bead size. The inhomogeneities may be pores and filler-particle agglomerates in the matrix, or variations in surface functionality or surface energy of the fibres. The testing procedure could involve additional sources of variations: bending of the fibres or variations in the position of the contact points of the vice on the bead surface.

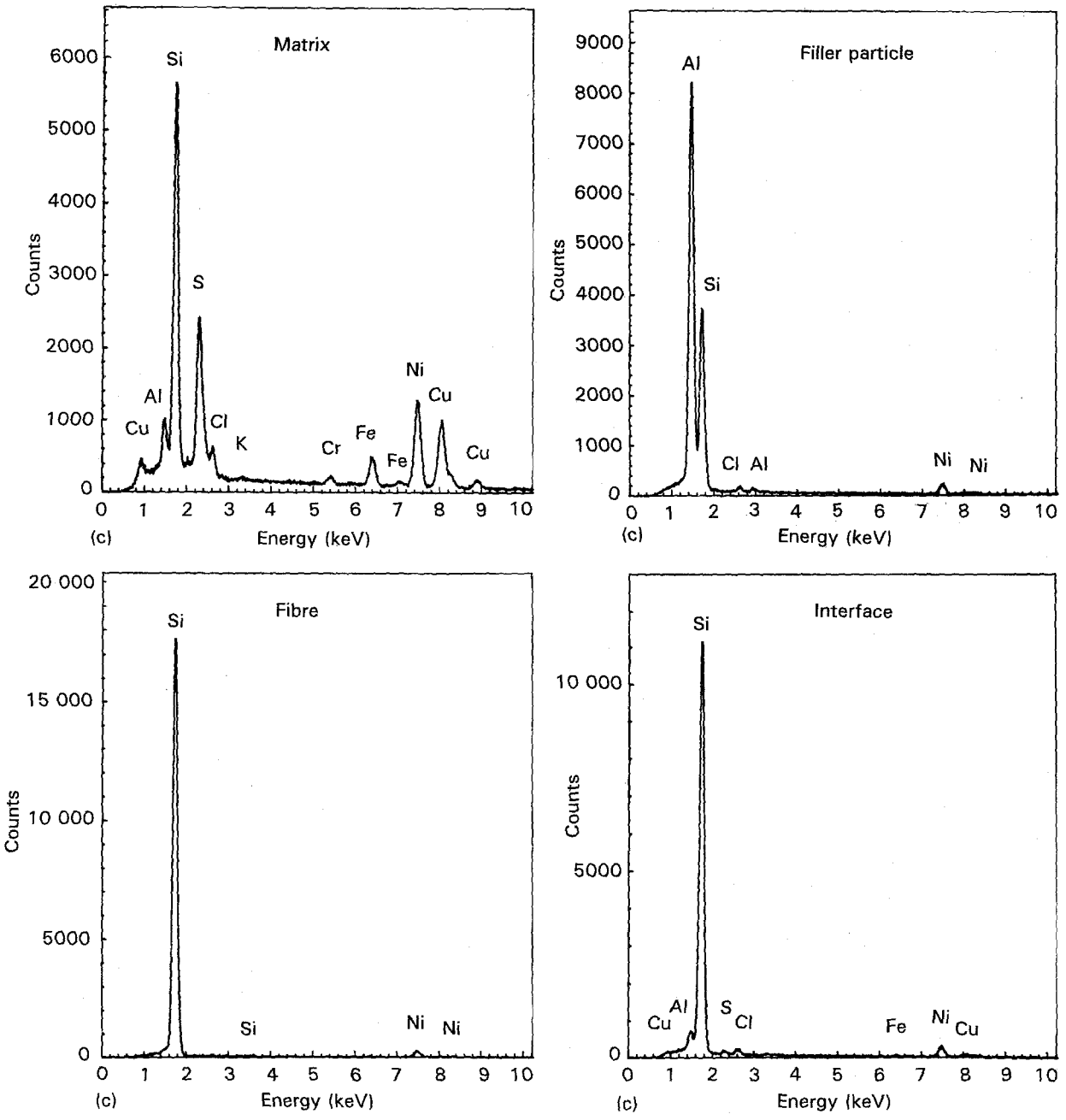
To obtain interfacial properties from the microbond-test results, numerical calculations were conducted for the test geometry shown in Fig. 5. A typical result of these calculations is presented in Fig. 8. Three failure modes were considered in the analysis. These are interfacial shear failure, unstable interfacial crack propagation, and fibre failure, characterized by interface shear strength τ_c, critical energy release rate G_c and fibre strength σ_f, respectively, as shown in Fig. 8. Comparing these numerical results, with the experimental data presented in Fig. 7 shows that the failure of the duplex and carbon-coated fibres was controlled by unstable interfacial crack propagation. The values of the critical driving energy, G_c, for these coated fibre composites are listed in Table I. For the uncoated and BN-coated Nicalon fibres, the dominant mode of failure was fibre failure. Although the exact values of the interfacial properties for the uncoated and BN-coated composites could not be obtained from the microbond test, these results indicate that the critical driving energy at the fibre/matrix interface for these composites was larger than 60 J m^{-2}.

When composites exhibit a relatively weak fibre/matrix interface, such as in the case of the duplex and carbon-coated Nicalon fibres, the tensile strength, σ_t, of unidirectional fibre-reinforced composites can be obtained as a function of the critical driving energy G_c [8]:

$$\sigma_t = 2v_f \left\{ \left[\frac{v_f E_f}{(1 - v_f) E_m} + 1 \right] \frac{E_f G_c}{a} \right\}^{1/2} \quad (1)$$

where v_f is the fibre volume fraction and E_f and E_m are the Young's moduli for the fibre and matrix, respectively.

The relationship between the tensile strength and the critical driving energy, based on Equation 1, is shown in Fig. 9, up to the point C, which indicates the fibre failure ($\sigma_t = v_f \sigma_f$). Experimental results for the tension test of the Nicalon/AlPO composite materials with various fibre coatings are listed in Table II and plotted in Fig. 9. Note that the bulk AlPO-matrix composite materials reinforced with the uncoated or with the BN-coated Nicalon fibres demonstrated a brittle fracture with very little fibre pull-out, whereas the composite materials containing carbon-coated or duplex-coated fibres showed much larger fibre pull-out, which indicated the higher toughness of these materials.



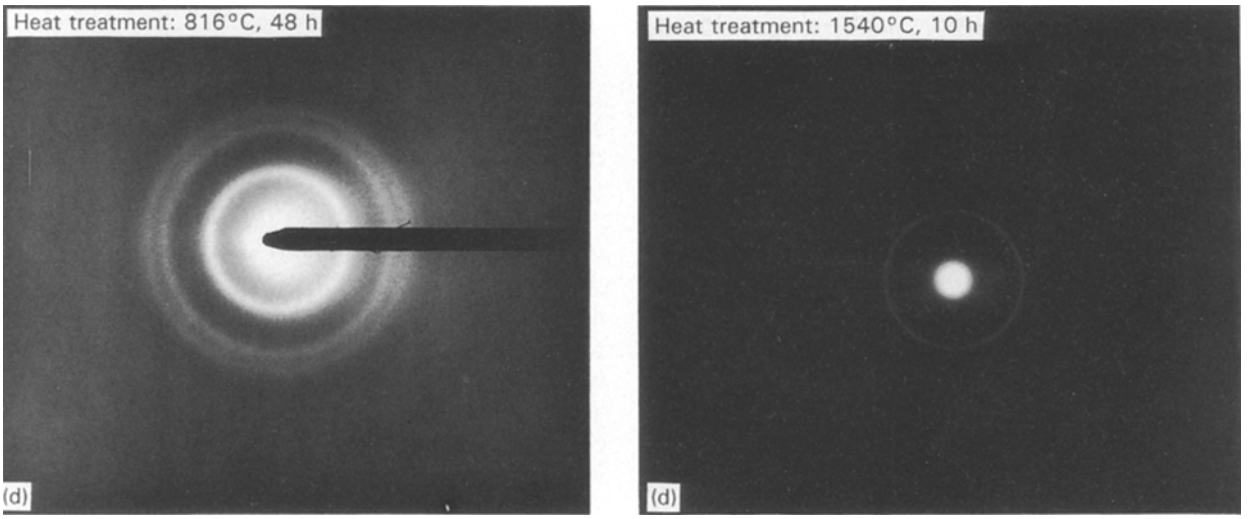


Figure 3 (a) TEM bright-field image of the SiC/AlPO composite material heat treated at 1540 °C for 10 h. (b) TEM bright-field image of the boundary between the interfacial zone and the matrix in the SiC/AlPO composite material heat treated at 1540 °C for 10 h. (c) EDX spectra of the SiC/AlPO composite material heat treated at 1540 °C for 10 h. (d) Selected area electron diffraction patterns of the fibres in the SiC/AlPO composite material when heat treated at 816 °C for 48 h and heat treated at 1540 °C for 10 h.

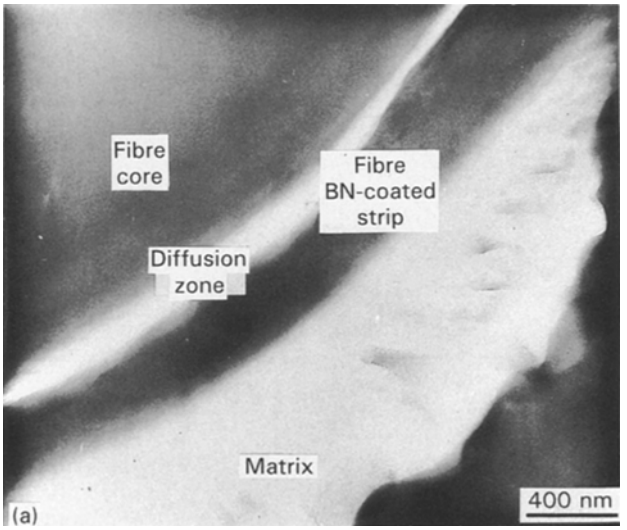
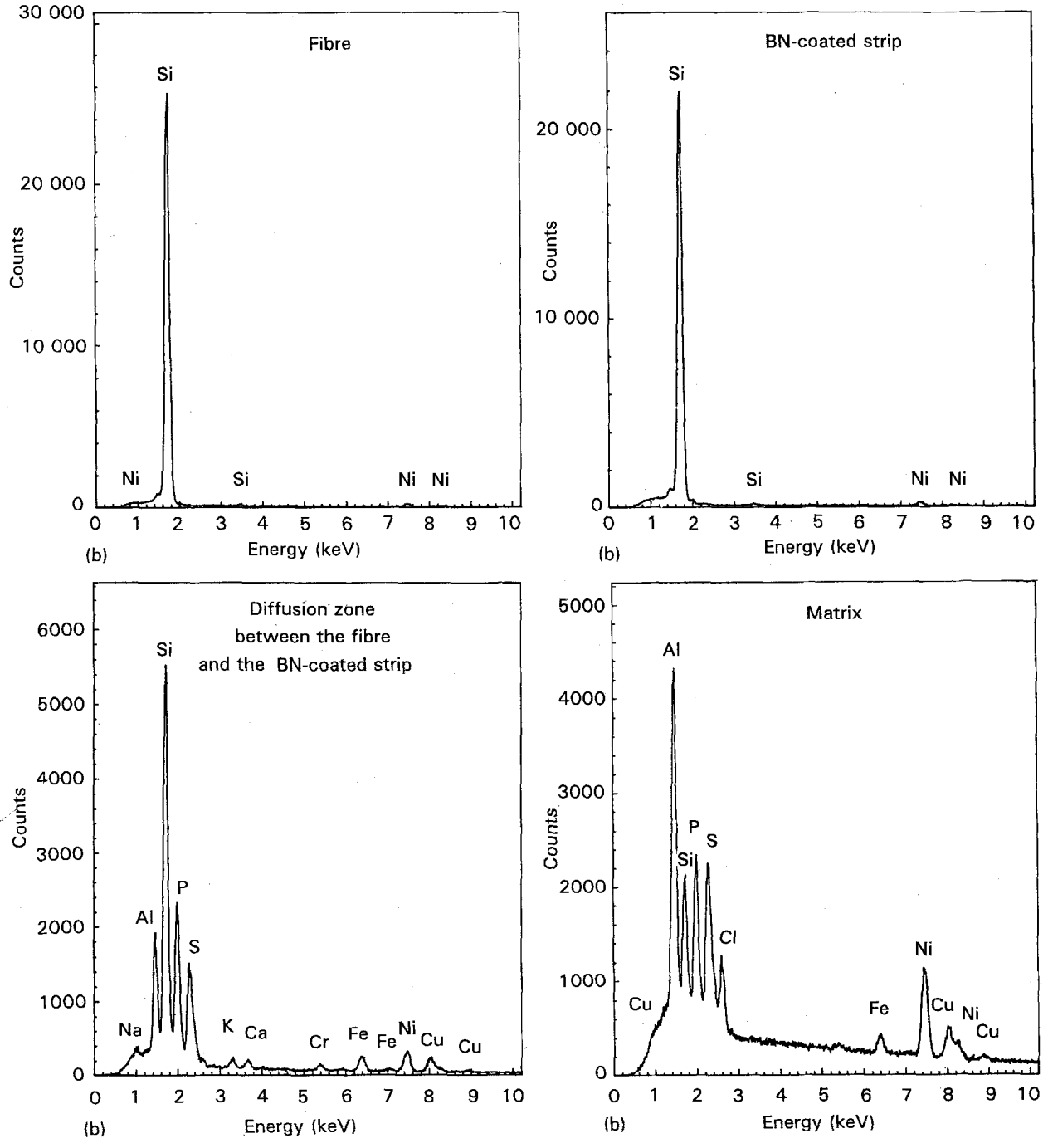


Figure 4 (*a*) TEM bright-field images of the SiC/AlPO composite material with the BN-coated fibres heat treated at 816 °C for 48 h. (b) EXD spectra of the SiC/AlPO composite material with the BN-coated fibres after heat treatment at 816 °C for 48 h.



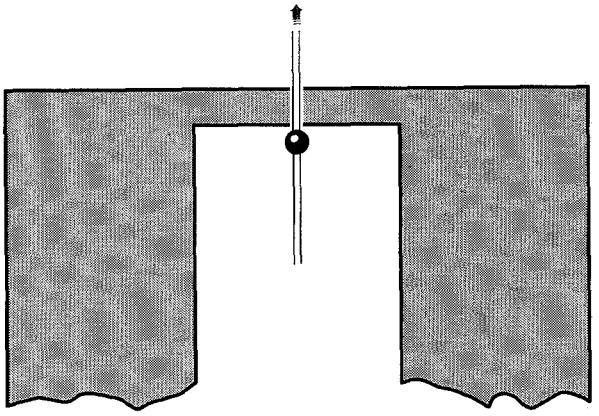


Figure 5 Microbond test for the determination of the shear strength at the fibre/matrix interface.

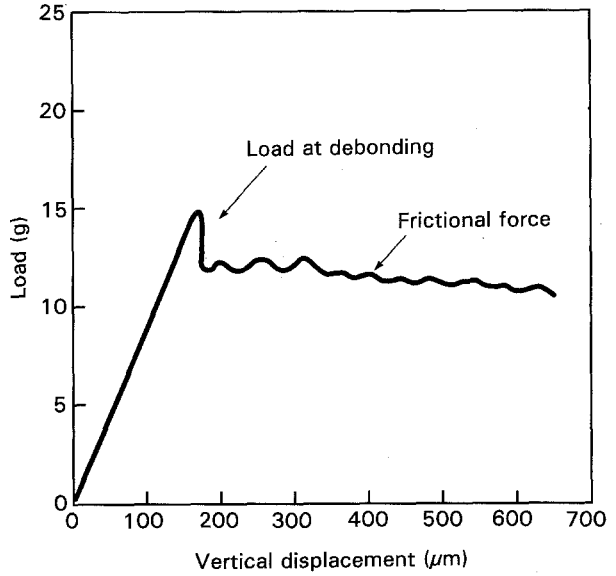


Figure 6 Load versus displacement plot in the microbond test.

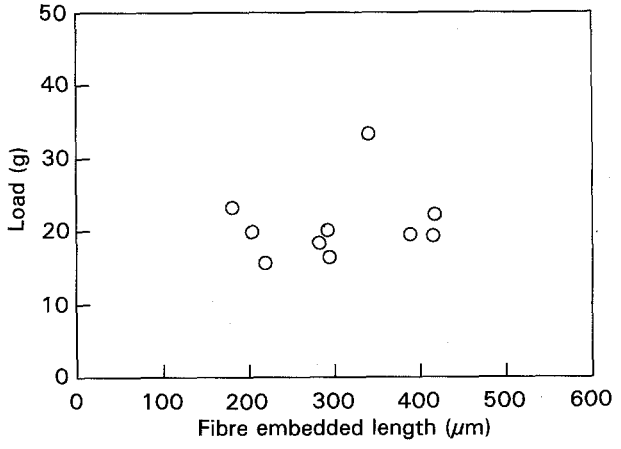


Figure 7 Experimental data on the load at failure versus embedded length obtained by the microbond test for the duplex-coated Nicalon/AlPO interfaces.

The results presented in Fig. 9 show that when the critical driving energy is smaller than 50 J m^{-2} (point C), an increase in critical driving energy favourably affects the tensile strength of the bulk composite material. On the other hand, when the critical driving energy is larger than 50 J m^{-2}, the tensile strength will decrease significantly and abruptly due to brittle

TABLE I Microbond test results

Coating	Critical driving energy, G_c (J m^{-2})
Duplex (boron nitride + carbon)	11.7
Carbon	14.8
Boron nitride	> 60
None	> 60

TABLE II Lamina tensile-strength-test results

Coating	σ_t(ksi)	Failure Mode
Duplex (boron nitride + carbon)	33.8	Fibre pull-out
Carbon	38.9	Fibre pull-out
Boron nitride	12.2	Brittle fracture
None	11.8	Brittle fracture

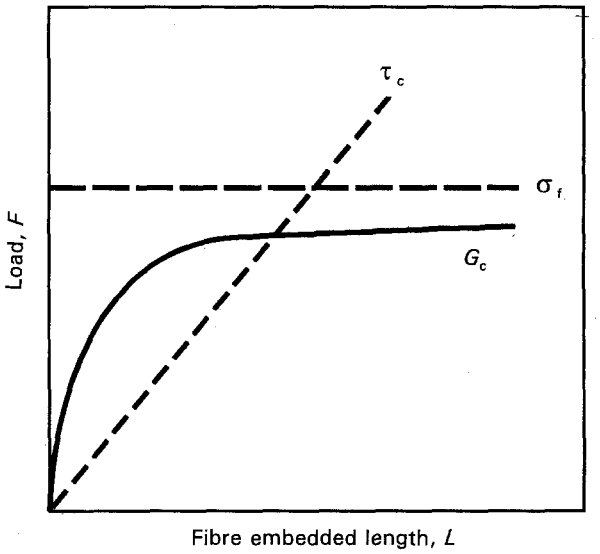


Figure 8 Failure load, F, versus embedded fibre length. L, for 3 modes of failure in the microbond test: τ_c, interfacial shear strength; G_c, critical energy-release rate for the interfacial crack; and σ_f, fibre tensile strength.

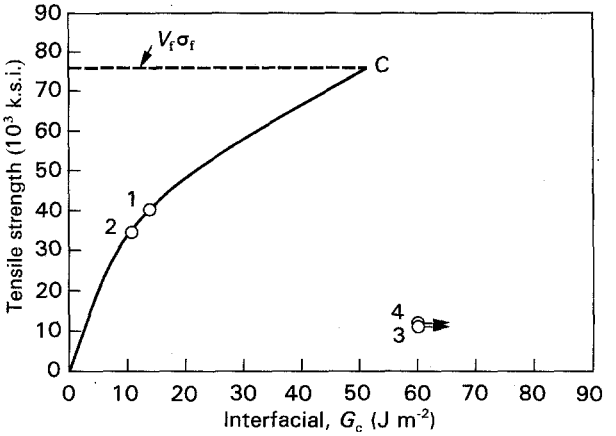


Figure 9 Relationship between the tensile strength of the Nicalon/AlPO composite material and the interfacial critical energy-release rate, G_c: (—) fibre pull-out, and (○) experimental data. σ_f, fibre tensile strength, V_f volume concentration of fibres. Experimental data points for the SiC/A1PO composite material: (1) pyrolytic carbon coated, (2) duplex coated, (3) uncoated, and (4) BN coated.

failure. This is illustrated by our experimental results for the composite materials with various fibre coatings. The materials with uncoated and BN-coated fibres had a critical driving energy (points 3 and 4 in Fig. 9) higher than $50\,J\,m^{-2}$, which led to a brittle failure and a lower tensile strength of the bulk materials. At the same time, the materials with carbon-coated and duplex-coated fibres had a critical driving energy (points 1 and 2) lower than $50\,J\,m^{-2}$ and exhibited higher tensile strength.

The data in Fig. 9 also indicate that there is room for further improvement in the interfacial properties of this Nicalon/AlPO composite system even at room temperature. Although the carbon and duplex coatings considerably improve interfacial properties and are stable at room temperature, the critical driving energy at the carbon and duplex-coated interface is considerably lower than the optimal value, $50\,J\,m^{-2}$. A fibre coating having a critical driving energy which is higher than the energies corresponding to points 1 and 2 in Fig. 9, but lower than the value $50\,J\,m^{-2}$, would increase the strength of the composite materials.

3.3. Selection of alternative coatings

It follows from the above that fibre coatings can improve the mechanical properties of composite materials if they provide chemical and mechanical decoupling between the fibres and the matrix. Several criteria characterize effective fibre coatings. First, the coating materials have to be stable in the temperature range of the intended applications; that is, they should not melt, decompose or oxidize. To provide chemical decoupling, the coatings must not react with the fibres and the matrix; they must serve as diffusion barriers between them. To provide mechanical decoupling in order to improve fracture toughness through increasing fibre pull-out, the coating materials should not be chemically bonded to the matrix.

As the experiments with the pyrolytic-carbon-coated fibres have shown, some decrease in the frictional component of the interfacial bonding is also needed in order to avoid a brittle failure of the composite materials. Therefore, materials known as high-temperature lubricants were evaluated as prospective coatings.

Initially, we listed the materials which exhibit a high-temperature stability and are not reactive with phosphoric acid. The listing contained interstitial and diamond-like carbides, amphoteric oxides and reportedly less chemically reactive nitrides and borides.

Compatibility of the candidate coating materials with the matrix and the fibres was then evaluated thermodynamically by free-energy calculations of possible reactions with the fibre and matrix ingredients [9]. However, such calculations have a limited value because the oxidation rate depends on kinetic factors. To identify the kinetically oxidation-resistant coating materials which are not reactive with the matrix and the fibres, we ran a series of experimental compatibility tests. The tests were conducted with all the materials which were identified as thermodynamically compatible with the fibres and the matrix. In addition, we experimentally tested materials which were reported in the literature to have good lubricating properties and/or to be chemically inert, even when they were found not to be thermodynamically compatible with the fibres (ZrN, ZrC, TiO_2) or the matrix (AlN, CaF_2, BaF_2, LiF). The final listing of the experimentally tested materials was as follows:

HfC, NbC, TaC, WC, Mo_2C, TiC, VC, SiC, Cr_3C_2, ZrC;
HfO_2, Nb_2O_5, ZrO_2, TiO_2;
TiN, Si_3N_4, ZrN, AlN;
ZrB_2, TiB_2, WB_2;
MoS_2, WS_2, CaF_2, BaF_2, LiF; and
Ce, Mo, W, Pt.

Metals were added to the listing due to their ability to dissipate the energy of a propagating crack by yielding, which can improve the fracture toughness of composite materials. We selected comparatively inert metals which were reported to have a low reactivity with phosphoric acid. The coating/fibre and coating/matrix mixtures were initially subjected to a heat treatment at 385 °C which imitated heat exposure during the processing of composite materials. The samples were examined to establish the presence of reaction products. Examination was conducted with XRD and NMR techniques. NMR was very useful due to a large number of amorphous phases in the system which could not be identified by XRD. It is highly sensitive to a change in the chemical states of the components and can indicate the early stages of chemical reactions.

Most of the tested coating materials, with the exception of BaF_2, ZrB_2, TiB_2 and WB_2, did not demonstrate large-scale reactivity at the processing temperature of 385 °C. These materials were tested further by heat treatments at the projected service temperatures of 816 °C and 1093 °C for 1 h followed by XRD and NMR examinations. At this stage, most of the tested materials (except oxides) oxidized or reacted with the matrix. Some of the oxidized materials subsequently also reacted with the matrix.

The only group of materials found to be compatible with the aluminium-phosphate matrix and with the Nicalon and Nextel fibres was TiO_2, SiC, and Si_3N_4. In addition, two oxides, Cr_2O_3 and ZrO_2, were found not to be reactive up to 816 °C, but ZrO_2 reacted with the matrix at 1093 °C. This narrows the selection down to TiO_2, SiC and Si_3N_4. In order to improve composite toughness by increasing fibre pull-out, these coatings have to be combined with coatings having lubricating properties. This combination may be a duplex coating with an internal layer being a lubricant, for example, carbon, and an external layer – one of the high-temperature coatings identified above.

4. Conclusions

The structure /chemistry of uncoated and BN-coated Nicalon/AlPO composite materials was as follows

1. Diffusion of Si from the fibres into the matrix took place in the composite materials subjected to

heat treatment at 816 °C for 48 h. It resulted in the formation of Si-rich reaction/diffusion zones around the fibres.

2. Heat treatment at 1540 °C for 10 h resulted in a large-scale Si diffusion from the fibres throughout the matrix, a depletion of phosphorus from the matrix and an increase in the crystallinity of the β-SiC component of the fibres.

3. The BN-fibre coating did not prevent Si diffusion at 816 °C. The coating delaminated from the fibres in many locations, probably due to the pressure of SiO and CO formed in the fibres in the process of internal oxidation.

The bond-strength measurements of uncoated composite materials and those coated with BN, C and C + BN showed the following.

4. Microbond test measurements of interfacial bond strength complemented by modelling calculations of the critical energy-release rate, G_c, indicated much lower bond strengths ($G_c = 12$–$15\ J\,m^{-2}$) in the carbon- and duplex-coated interfaces than in the uncoated and BN-coated interfaces ($G_c > 50\ J\,m^{-2}$).

Finite-element modelling of strength as a function of interfacial bond strength showed the following.

5. The optimal bond strength in unidirectional Nicalon/AlPO composite material is characterized by a critical energy-release rate close to $G_c = 50\ J\,m^{-2}$.

6. Below $G_c = 50\ J\,m^{-2}$ an increase in the interfacial bond strength improves the tensile strength of the composite material.

7. A further increase in the interfacial bond strength above $G_c = 50\ J\,m^{-2}$ results in brittle failure of the material.

8. The critical energy-release rate in carbon- and duplex-coated composites was found to be below the critical value, which correlates with the significant pull-out and higher tensile strength of these materials.

9. The critical energy-release rate in uncoated and BN-coated composite materials was found to be higher than the critical value, leading to a brittle failure and lower values of the bulk tensile strength.

Identification of potential coating materials:

10. Carbon and duplex coatings showing acceptable interfacial bond strength are easily oxidized in air at elevated temperatures. Therefore, an alternative fibre coating has to be developed.

The alternate coating should be stable at elevated temperatures, not reactive with the fibres and the matrix, provide chemical decoupling between them and have lubricating properties in order to improve toughness through fibre pull-out. Duplex coatings are the most likely candidates.

11. At the projected service temperatures, 816 °C and 1093 °C, SiC, Si_3N_4 and TiO_2 demonstrated oxidation resistance and compatibility with the matrix and the fibres. The other tested coating materials oxidized and/or reacted with the matrix or the fibres at these temperatures.

12. Cr_2O_3 and ZrO_2 showed no reactivity with the matrix and the fibres up to 816 °C.

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