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Hi-Nicalon reinforced silicon nitride matrix composites

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The present paper reports on the fabrication and the mechanical properties of SiC (Hi-Nicalon) fibres reinforced Si_3N_4 matrix composites. The composite was fabricated by liquid infiltration of an aqueous Si_3N_4 slurry followed by hot-pressing. The effect of fibre coating layers was investigated with a 400 nm thick pyrolytic carbon. The fibre coating was found to have a significant effect on the frictional stress of the fibre-matrix interface and consequently on the fracture behaviour of the composite.

1. Introduction

The strengthening and toughening of silicon nitride by reinforcement with continuous fibres has received considerable attention in recent years. Si_3N_4 reinforced with carbon fibres can be fabricated by high temperature sintering (1800 °C) to produce a stable composite with good mechanical properties [1], but with the intrinsic problem of the oxidation of the fibre phase at temperatures above 450 °C.

Most of the reported studies have been performed with SiC fibres, obtained from a Japanese supplier who uses the trade name Nicalon (Nippon Carbon). However its intrinsic oxygen content of up to 12 wt % present as an amorphous $Si_xO_yC_z$ phase [2] results in self degradation above 1200 °C with a decrease in the strength and Young's modulus values [3].

Recently a new generation of Nicalon fibres called "Hi-Nicalon" [4] that contain a less than 0.5 wt % oxygen content and with improved thermal stability and creep resistance over the conventional Nicalon have been developed [5, 6].This improved oxygen stoichiometry is achieved by a new curing process for polycarbosilane using electron beam irradiation in an oxygen-free atmosphere. The degradation of the fibres during the high temperature processing of Si_3N_4 can now be solved by use of this new generation of SiC fibres that are derived from polymer precursors [7, 8].

This paper reports on the fabrication of a uniform and dense SiC(Hi-Nicalon)/Si_3N_4 composite by slurry infiltration and hot-pressing. The fibres are arranged unidirectionally and are coated with a pyrolytic carbon layer which modifies the fibre-matrix bond to optimize the mechanical properties of the composite. The mechanical behaviour of both coated and non-coated composites were evaluated by room temperature strength measurements and the frictional stress of the fibre-matrix interface was determined using indentation tests. Finally the microstructure of the interface was characterized by transmission electron microscopy (TEM).

2. Experimental procedure

The Hi-Nicalon fibres (see Table I) were pre-coated with a 400 nm thick pyrolytic carbon layer at ONERA (France) [9]. The carbon layer was deposited using a low pressure chemical vapour deposition process in which propylene was decomposed in an argon atmosphere at 1000 °C using conditions that produced graphitic planes that lay mostly parallel tothe fibres (turbostratic microstructure). The application of the carbon coating was observed not to change the tensile mechanical properties of the Hi-Nicalon fibre.

The green formation of the composite followed the procedure developed for carbon fibre reinforcement which is described elsewhere [10]. A deionized water based slurry consisting of a mixture of 65 wt % solids, of which 90 wt % was submicron dimension α-phase silicon nitride powder, plus 6.9 wt % Y_2O_3 and 3.1 wt % Al_2O_3 that were added as sintering aids (see Table II) was attrition milled with 2 mm diameter silicon nitride balls for 1.5 h in water to break up agglomerates and the pH was adjusted to 10.5 with tetramethylammoniumhydroxide (TMAH) solution. An ammonium polymethacrylate (Darvan C) was used to assist dispersion and the surfactant Aerosol OT, to enhance fibre wetting and the penetration of the slurry into the fibre preform.

The pressure filtration technique of Jamet *et al.* [11] has been adapted for the present work. Hi-Nicalon fibre pre-forms (1D) were fabricated by fibre winding and individually infiltrated with the ceramic slurry in

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TABLE I Typical properties of Hi-Nicalon fibres [4]

Fibre diameter (μm)	14
Tensile strength (GPa)	2.8
Tensile modulus (GPa)	270
Elongation (%)	1.0
Density ($kg\,m^{-3}$)	2740
Chemical composition (wt %)	
Si	63.7
C	35.8
O	0.5

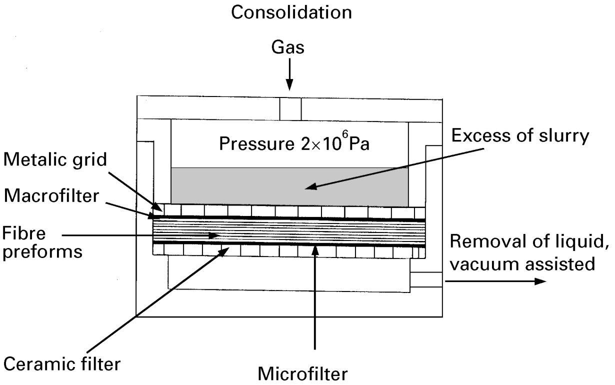

Figure 1 Slurry infiltration process.

a bath (Fig. 1). Infiltrated mats were stacked alternately and compacted by gas pressure (2 MPa). Green bodies containing 30 vol % fibres were dried in a dessicator, heat treated at 400 °C in air to remove the organic additives and hot-pressed at 1600 °C under a 27 MPa pressure.

Room-temperature mechanical properties were measured by four-point bending, with an outer/inner span ratio of 30 : 10 and a crosshead speed of 0.1 mm min^{-1} using $45 \times 4 \times 3\ mm^3$ sized sample. The fibre/matrix frictional stress was measured using a diamond Vickers microhardness indenter technique as developed by Marshall [12]. The morphology of the fracture surfaces was examined by Scanning electron microscopy (SEM) and the microstructure of the interface was examined by transmission electron microscopy.

3. Results and discussion

3.1. Consolidation and hot-pressing

The hot-pressing conditions are a compromise between minimizing fibre degradation and achieving full densification. The sintering aids (Y_2O_3 and Al_2O_3) used in the present work allowed a sintering temperature as low as 1600 °C with a duration of 1 h. In addition pressure was applied to close the porosity as soon as the grain boundary phase began to soften (1200 °C), but late enough to avoid damaging the fibre. This early application of the pressure inhibits gas evolution thus inhibiting any possible reaction of Si_3N_4 and secondary grain boundary phase with the pyrolytic carbon interphase. The resulting structure reveals a fully dense composite with no matrix cracks and a uniform distribution of the coated Hi-Nicalon fibres (Fig. 2). X-ray diffraction analysis shows that the composite consists of α-Si_3N_4 and β-Si_3N_4 from the matrix and β-SiC from the Hi-Nicalon fibres.

3.2. Fracture behaviour and interfacial characterization

The flexural strength of the Hi-Nicalon reinforced Si_3N_4 was investigated at room temperature. Typical stress–displacement curves for the composites are shown in Fig. 3. The composite fabricated with uncoated fibres exhibited a poor performance with a sudden load drop immediately after the maximum load (260 MPa). The fracture surface was smooth with no sign of pull-out (Fig. 4). This brittle behaviour can be attributed to a very strong bond between the fibres and the matrix which does not allow debonding and crack deflection at the interface.

Transmission electron microscopy observation of the interface of the composite manufactured with non-coated fibres (Fig. 5) shows no indication of any chemical reaction between the fibres and the matrix. Pockets of an amorphous secondary phase (probably YSiAlON) and β-Si_3N_4 grains are both in contact with the fibre along the interface. Fig. 6 (a and b) are bright and dark-field images of the fibre. A value of 15 nm has been obtained for the average SiC grain size with, a few grains as large as 30–40 nm also being observed. Selected-area diffraction (SAD) (Fig. 6c) shows a discontinuous ring pattern which is characteristic of a very fine-grained polycrystalline aggregate of β-SiC corresponding to the standard SiC 8F (JCPDS 29-1129). The main rings were assigned to $\{1\,1\,1\}$, $\{2\,0\,0\}$, $\{2\,2\,0\}$ and $\{3\,1\,1\}$ reflections, corresponding respectively to 0.249, 0.218, 0.154 0.131 nm *d*-spacings. These observations are compatible with the observed mechanical properties. There is no indication of an *in-situ* formation of a weak interface as observed in conventional Nicalon fibre reinforced glass-ceramic matrices where the excess carbon and oxygen contained in the fibre form a thin (20–50 nm) carbon rich fibre/matrix interfacial layer during fabrication [13]. The very low amount of oxygen (0.5 wt %) in the

TABLE II Powder characteristics

Powder	Producer	Brunower–Emmett–Teller specific surface area ($m^2\,g^{-1}$)	Mean particle size d_{50} (μm)
Si_3N_4 (SN-E10)	UBE	10–14	0.55
Y_2O_3 (grade C)	H. C. Starck	10–16	< 1
Al_2O_3 (RA207LS)	Alcan Chemicals	7	0.5

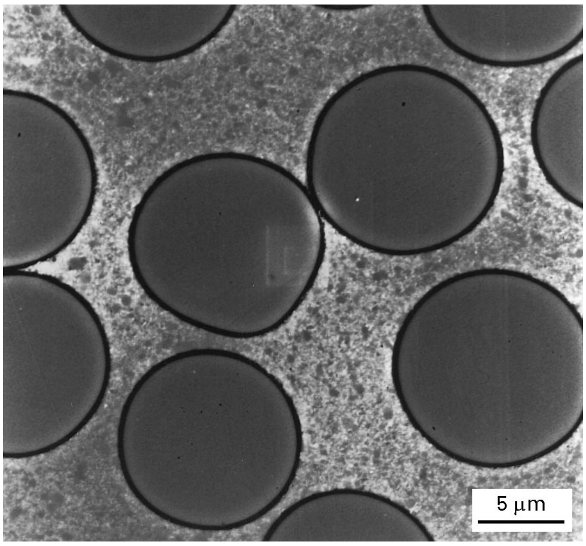

Figure 2 Microstructure of the pyrolytic carbon coated Hi-Nicalon fibre reinforced Si_3N_4 composite.

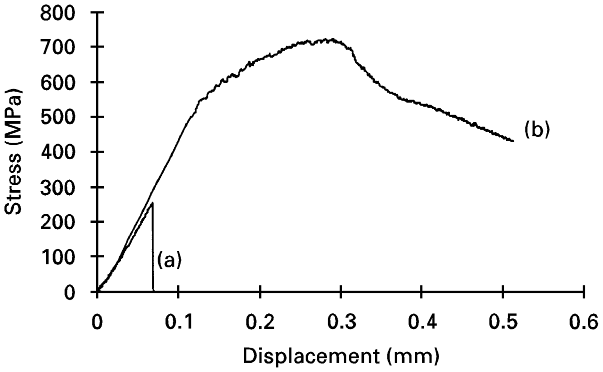

Figure 3 Flexure load–displacement curves of (a) non-coated and (b) 400 nm thick pyrolytic carbon coated Hi-Nicalon fibre reinforced Si_3N_4.

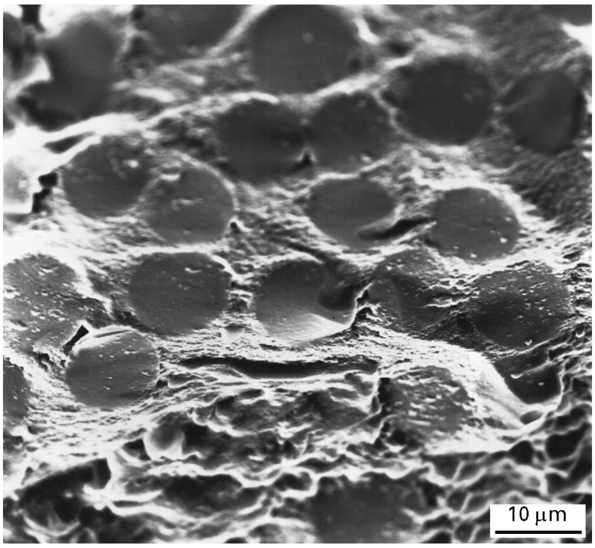

Figure 4 SEM micrograph showing fracture surface of non-coated Hi-Nicalon fibre reinforced Si_3N_4 composite.

Hi-Nicalon fibres limits this phenomena which implies that a coating should be applied onto the fibre surface before the composite is produced.

The appplication of a 400 nm pyrolytic carbon coating dramatically changes the flexural behaviour of

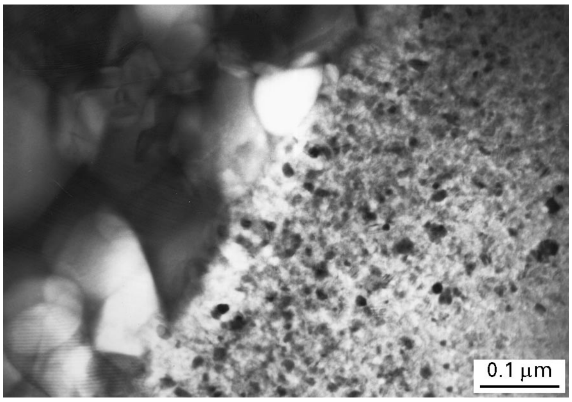

Figure 5 Bright field TEM micrograph of the fibre-matrix interface for non-coated Hi-Nicalon fibre reinforced Si_3N_4.

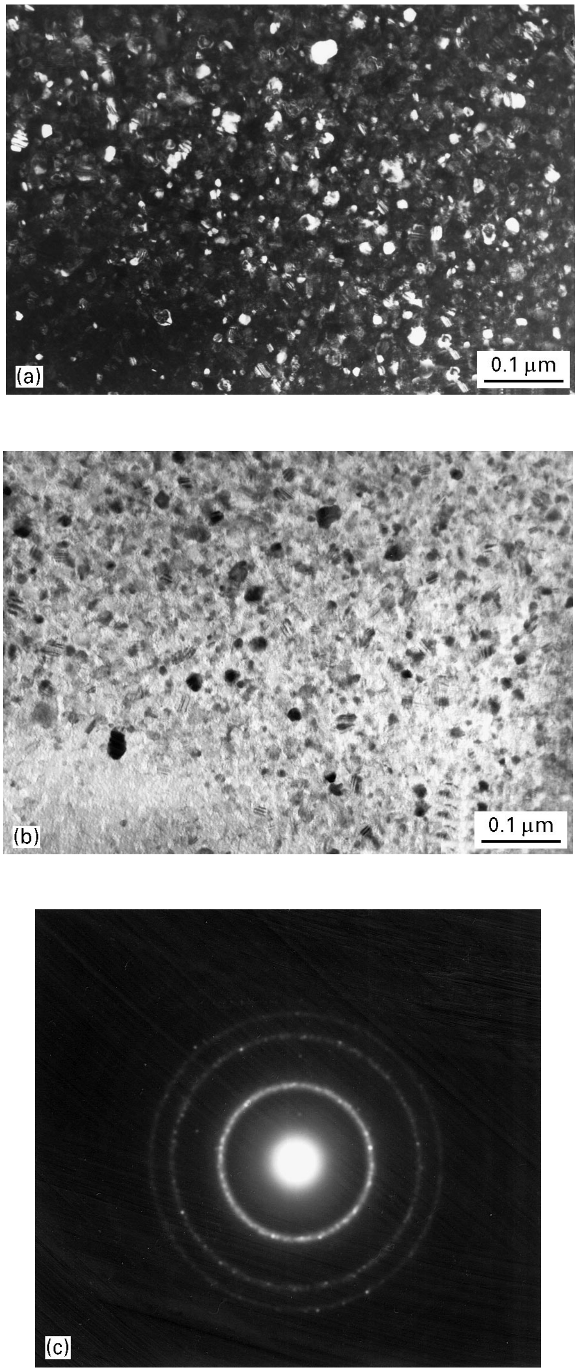

Figure 6 (a) dark and (b) bright field images of the Hi-Nicalon fibres with (c) selected area diffraction characterization of SiC.

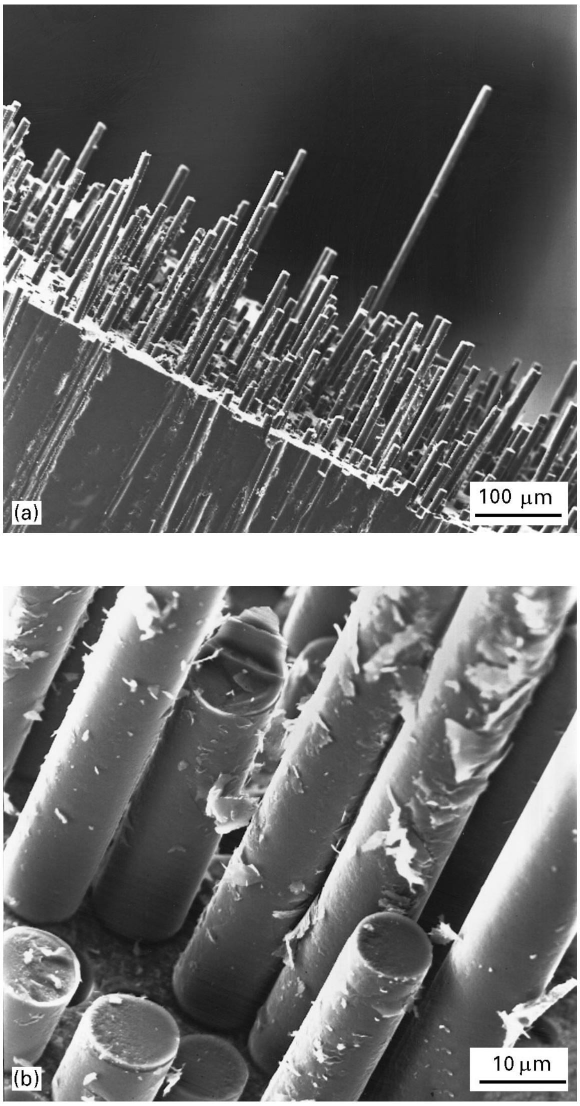

Figure 7 (a) and (b) SEM micrographs showing fracture surface of the pyrolitic carbon coated Hi-Nicalon fibre reinforced Si_3N_4 composite.

the composite (Fig. 3). The load–displacement curve was characterized by an initial linear elastic region up to about 500 MPa. The load continued to rise non-linearly to a maximum (750MPa) followed by continuous load decrease. The composite showed fibre pull-out, and the fracture path along the interface appears to be between the carbon pyrolytic coating and the matrix. (Fig. 7 (a and b)). Clearly the mechanical properties of the composite are influenced by an appropriate interphase between the fibre and the matrix which modifies the debonding energy and provides enhancement of the crack propagation along the interface.

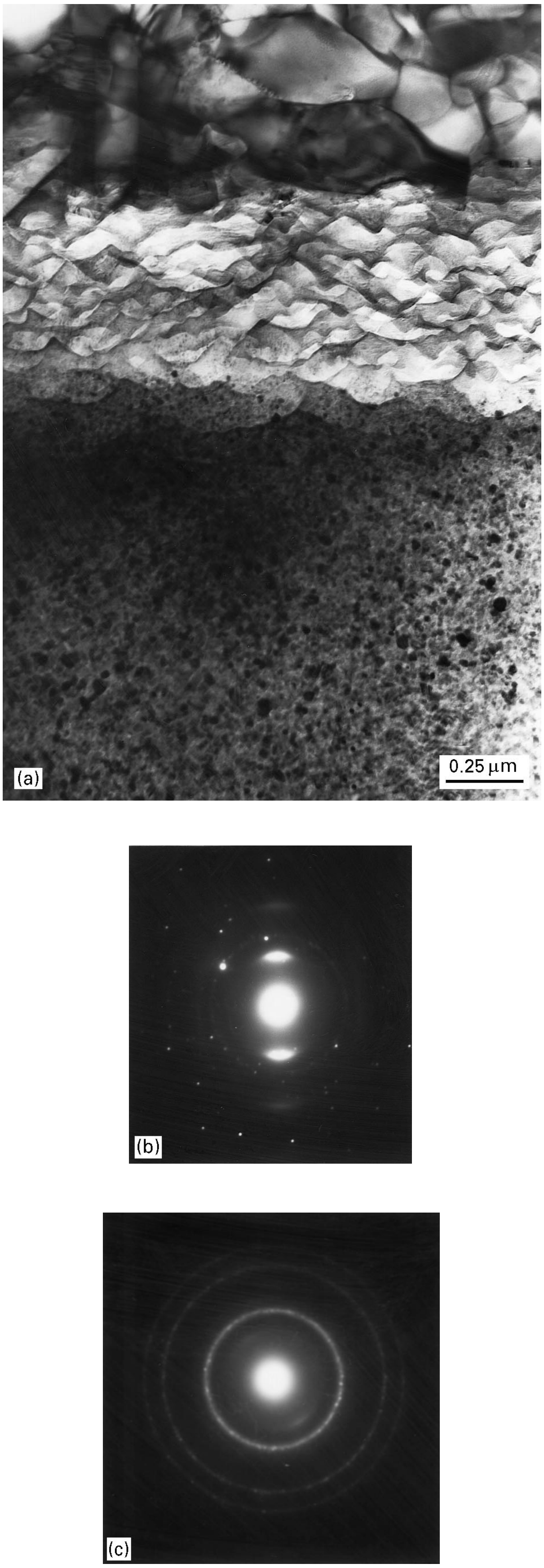

Figure 8 (a) TEM image (BF) of the Hi-Nicalon fibre/$C_{pyr.}$/Si_3N_4 interface (b) with selected area diffraction of $C_{pyr.}$ and (c) SiC.

Fig. 8a is a TEM picture of the pyrolitic carbon coated fibre reinforced Si_3N_4 interface. Both sides of the coating are strongly attached to the matrix and the Hi-Nicalon fibre. There is also no indication of chemical reactions between the three phases. Similarly to the composites reinforced with non-coated fibres the matrix consists of β-Si_3N_4 grains with a glassy second phase. The SiC fibres have the same characteristics in that they are polycrystalline with small β-SiC grains (Fig. 8b) of 15 nm average size. The nature of the coating is such that the $\{0\,0\,1\}$ layers of the carbon are parallel to the surface of the fibres (Fig. 8c). A deviation of ± 20° around this preferred orientation can be observed.

3.3. Matrix–fibre frictional stress

The indentation technique used to measure τ_f (interface frictional stress) employed a diamond Vickers microhardness indenter, as developed by Marshall [12] (see Fig. 9). The indenter is loaded onto the centre of the fibre in a polished section normal to the fibre axis. The force, F, applied to the fibre causes sliding along the matrix/fibre interface and depresses the surface of the fibre a distance u below the matrix surface. A simple model can be used to determine τ_f using the following formula:

$$\tau_f = \frac{a^4 H^2}{\pi^2 R^3 E_f (b - a) \cot \psi} \qquad (1)$$

where H is the hardness of the fibre, 2Ψ the angle between opposite edges of the indenter R the radius of the fibre, E_f the young modulus of the fibre, a the size of the print on the fibre and b the size of the print on the matrix. A typical example of an indented fibre is shown in Fig. 10. The value obtained for the interface frictional shear stress was 25 ± 4 MPa. This is higher than most values reported in the literature but close to a SiC (Nicalon, NL 202) reinforced cordierite [14]. Such values are often associated with residual compressive thermal stresses at the interface that develop during the manufacturing process and also to differences in the thermal expansion coefficients of the matrix and the fibres. However, in the case of Hi-Nicalon reinforced Si_3N_4 the fibre-matrix interface is in tension, but since the carbon coating is able to deform and thus accommodating the clamping stress of the matrix the degree of bonding will be strong enough to allow the load transfer from the matrix to reinforcing fibres when the matrix fail.

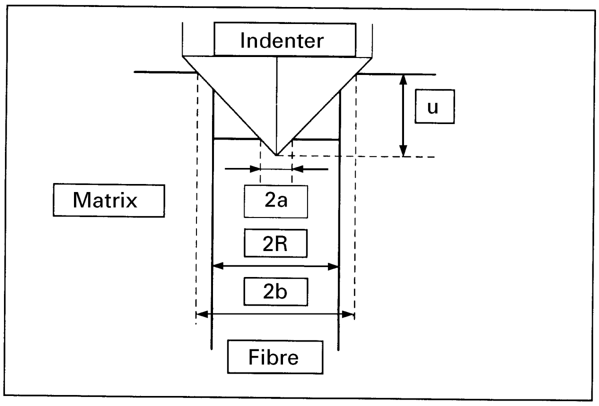

Figure 9 Indentation technique as developed by Marshall [11].

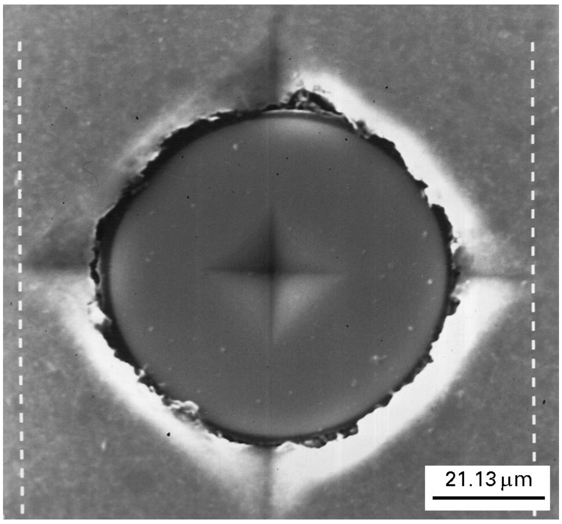

Figure 10 Indented fibre in the Pyrolytic carbon coated Hi-Nicalon fibre/Si_3N_4 composite.

4. Conclusions

A technique for the fabrication of Hi-Nicalon fibre reinforced Si_3N_4 composites by slurry infiltration followed by hot-pressing has been optimized to produce fully infiltrated composites. Sintering at 1600 °C for 1 h produced a dense composite containing a uniform fibre distribution of 30 vol %. With non-coated fibres an extremely strong bond at the fibre matrix interface results in a low ultimate strength (260 MPa) and brittle behaviour of the composite. A 400 nm thick pyrolytic carbon layer applied on the fibres prior to fabrication significantly modified the mechanical properties of the composite that consisted of an initial linear elastic region up to 500 MPa and an ultimate strength of 730 MPa with gradual composite failure. The characterization of the interface showed no indication of chemical reactions between the carbon/fibre and fibre/matrix interfaces. The interface frictional stress measured using the indentation method on composites with coated fibres was 25 MPa allowing efficient load transfer from the matrix to the fibres thus leading to toughening by crack deflection.

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