

# Effect of pre-treatment and annealing temperature on the strength of SiC-Ni monofilament composites

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Monofilament composites were prepared by plating nickel on Nicalon, a commercial SiC fibre obtained from a precursor of polycarbosilane. The surface condition of the fibre was controlled by pre-treatments prior to the nickel plating. The tensile strength of the monofilament composite decreased with increasing annealing temperature, especially above 973 K, where reaction between the fibre and nickel begins. The extent of degradation of the composite caused by the reaction was different for different pre-treatment and annealing temperatures. The degradation was explained by the Griffith theory. The calculated strength of annealed composites agreed fairly well with the measured values. SEM observations showed that the strength is closely related to the morphology of the reaction products.

## 1. Introduction

A new process to produce continuous SiC fibres from a precursor of polycarbosilane has recently been developed [1, 2]. The fibre has obvious economical advantages with its high strength and oxidation resistance. The characteristics are attractive as reinforcement in heat resisting alloys. In artificial composites, however, the interface reaction between reinforcement and matrix often leads to breakdowns and the high-temperature compatibility of the composite must be studied. The reaction between the fibre and nickel [3, 4] is suspected to have an undesirable effect on the mechanical properties of the composite. This study investigates the effects of fibre surface conditioning and annealing temperature on the interface reaction and tensile behaviour of monofilament composites.

## 2. Experimental details

The reinforcement used was a commercial SiC fibre, Nicalon, with an average tensile strength

of 2550 MPa and an average diameter of 14  $\mu\text{m}$ . The fibre diameters were found to scatter in the range from 5  $\mu\text{m}$  to more than 30  $\mu\text{m}$ . Before nickel was coated on the fibres, they were subjected to one of the following pre-treatments: (a) Heated in air at 873 K for  $1.8 \times 10^3$  sec to remove organic coatings on the fibre surface and then immersed in a boiling alkaline solution (NaOH 20%,  $\text{K}_3\text{Fe}(\text{CN})_6$  20%,  $\text{H}_2\text{O}$  60%) for  $0.3 \times 10^3$  sec; (b) heated at 1273 K for  $3.6 \times 10^3$  sec in air. The tensile strength of fibres after treatment (a) was 2750 MPa and after (b) it was 1950 MPa (both values are averages of about 100 measurements). For conductivity a thin layer of nickel was vacuum-evaporated on the fibres before they were electroplated with nickel [4]. The thickness of the nickel layer was regulated to about 3  $\mu\text{m}$ , and this thickness results in a fibre volume fraction,  $V_f$ , of 0.5 for a 14  $\mu\text{m}$  diameter fibre. Below, monofilament composites will be referred to as A composites for those with pre-treatment (a) and B composites for those with

pre-treatment (b). All were annealed in vacuum for  $3.6 \times 10^3$  sec at temperatures between 673 K and 1273 K. Some of the composites were immersed in a boiling acid solution (HCl 10%,  $\text{NH}_3$  30%,  $\text{H}_2\text{O}$  60%) to dissolve the nickel layer and to expose the fibres. The tensile strengths of the annealed composites and the exposed fibres were tested at room temperature. The gauge length was 20 mm, and the diameter of each specimen was measured with an optical microscope to obtain the tensile strength. The fibres and composites were further studied under a scanning electron microscope (SEM).

### 3. Experimental results

#### 3.1. Tensile test of monofilament composites

The tensile strength of a thin fibre generally depends on the diameter, and the fibre investigated here follows this relation [5]. The tensile test was carried out on composites of fibres of 10 to  $20 \mu\text{m}$  diameter, which provide a  $V_f$  of about 0.4 to 0.6. As shown in Fig. 1 the tensile strength of both A and B composites decreased gradually with annealing temperature up to 873 K; the A composites were stronger than the B composites at lower temperatures but the strength of the A composite decreased dramatically above 973 K.

#### 3.2. Tensile strength of exposed fibres

Fig. 2 shows the effect of annealing temperature on the tensile strength of fibres exposed from annealed monofilament composites. The strength

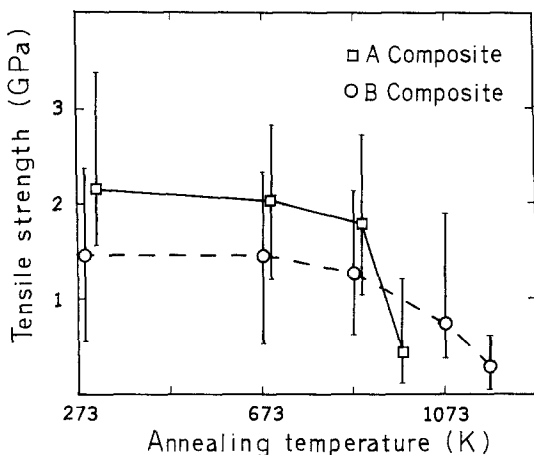


Figure 1 Relationship between annealing temperature and composite tensile strength at room temperature.

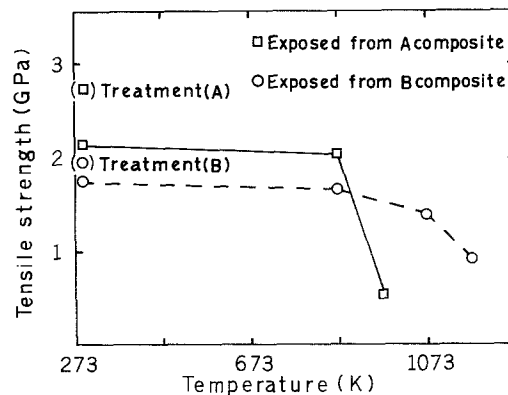


Figure 2 Relationship between composite annealing temperature and exposed fibre strength.

of the exposed fibres remained almost unchanged at temperatures lower than 873 K whereas it decreased considerably above 973 K. It can be concluded from Figs. 1 and 2 that a softening of the plated nickel by the annealing is responsible for the gradual decrease in composite strength in the lower temperature range, while the remarkable decrease at higher temperatures is mainly due to degradation of the fibre. Fig. 2 also shows the strength of fibres after pre-treatment (a) and (b), and they are stronger than the exposed fibres. This difference may be a result of an increase of flaws on the fibre surface during handling.

#### 3.3. Metallographic observations

It has been reported that the reaction between nickel and SiC fibre made from polycarbosilane is closely related to the surface condition of the fibre [3, 4]. Fig. 3 shows examples of reaction on cross-sections of monofilament composites after annealing. Lamellae are seen at the fibre-nickel interface in the A composite annealed at 973 K (Fig. 3a). From XMA and X-ray diffraction studies it has been reported that this lamellar structure is related to the formation of  $\gamma$ -phase ( $\text{Ni}_5\text{Si}_2$ ) [6]. At higher temperatures, for example 1073 K, the whole area of the cross-section was covered with lamellae (Fig. 3b). When B composite was annealed at 1173 K, a relatively bright granular region was formed in the fibre (Fig. 3c). This granular structure is related to the formation of  $\gamma$ -phase ( $\text{Ni}_2\text{Si}$ ) [6]. The granular structure covers the whole cross-section at 1273 K (Fig. 3d). Composites having structures as Figs. 3b and d were completely degraded and these structures appear

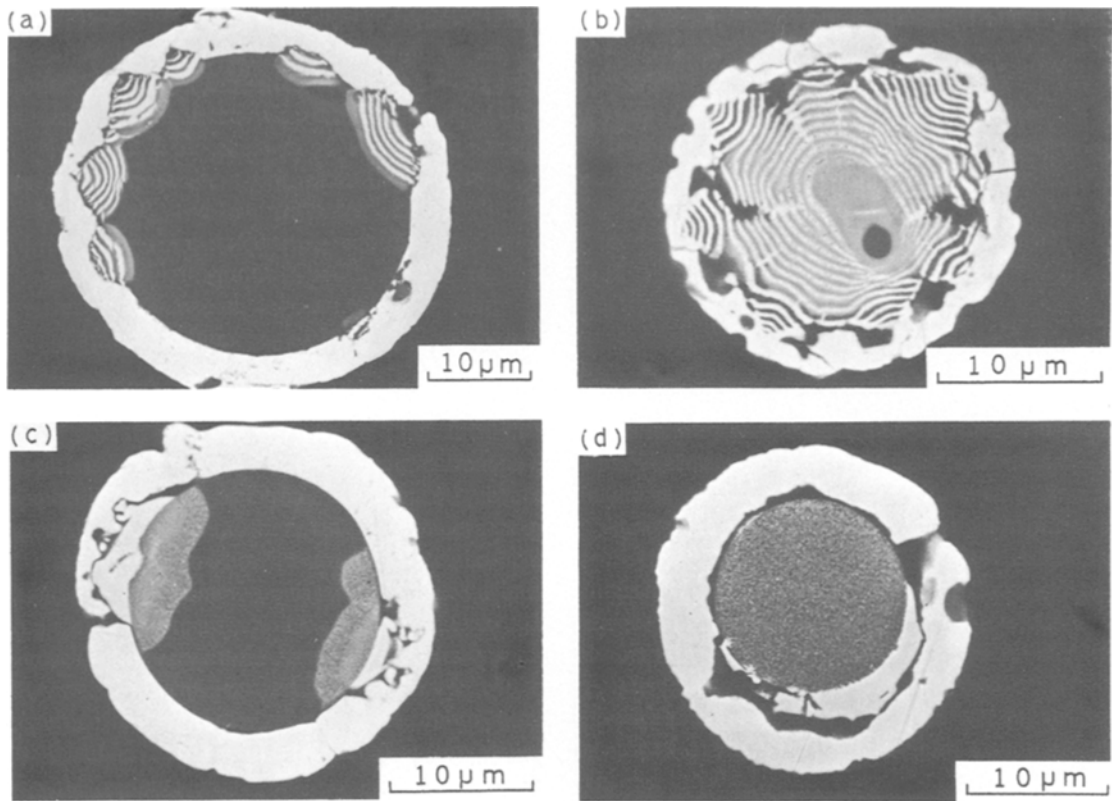


Figure 3 Cross-sections of A composites annealed at (a) 973 K, (b) 1073 K, and of B composites annealed at (c) 1173 K and (d) 1273 K.

on the cross-sections at temperatures where the remarkable decrease in strength occurred.

In Fig. 4 several examples of fractured surfaces are shown. The reaction products indicated by arrows were visible in specimens annealed at higher temperatures. It should be noted that the fractured surface of reacted fibres is very flat and perpendicular to the length direction.

### 3.4. Comparisons with the rule of mixture

In the lower temperature range (up to 873 K), there was little change in fibre strength and the strength of monofilament composites decreased gradually due to the softening of the plated nickel. In this region the strength follows the rule of mixture given by Kelly and Tyson [7]:

$$\sigma_c = \sigma_f V_f + \sigma_m^* (1 - V_f) \quad (1)$$

where  $\sigma_c$  is the tensile strength of the composite,  $\sigma_f$  the fibre strength,  $\sigma_m^*$  the flow stress of nickel matrix at which the stress in a fibre reaches  $\sigma_f$ , and  $V_f$  is the volume fraction of the fibre. The value of  $\sigma_c$ , calculated from Equation 1 by using  $\sigma_f$  for the exposed fibre (Fig. 2), was lower than

the measured strength shown in Fig. 1. This can probably be ascribed to the lower strength of the exposed fibre. On the other hand,  $\sigma_c$ , calculated using the value of 2750 MPa for an A composite and 1950 MPa for a B composite, almost corresponded to the measured values.

In the higher temperature range (above 973 K), the composite strength decreased by the reaction between nickel and fibre as was found in a previous report [4], and the A composite lost more strength. From investigations of cross-sections of A and B composites annealed at 973 and 1173 K, it is clear that the fraction of reacted composite was relatively small while the strength was only as 20 to 25% of the initial composite. For B composites, which were annealed at 1073 K, no trace of reaction was found on the cross-section, but the strength of exposed fibres decreased greatly as shown in Fig. 2.

## 4. Discussion

### 4.1. Effect of reaction zone thickness on the fibre strength

When reaction between nickel and fibre occurs,

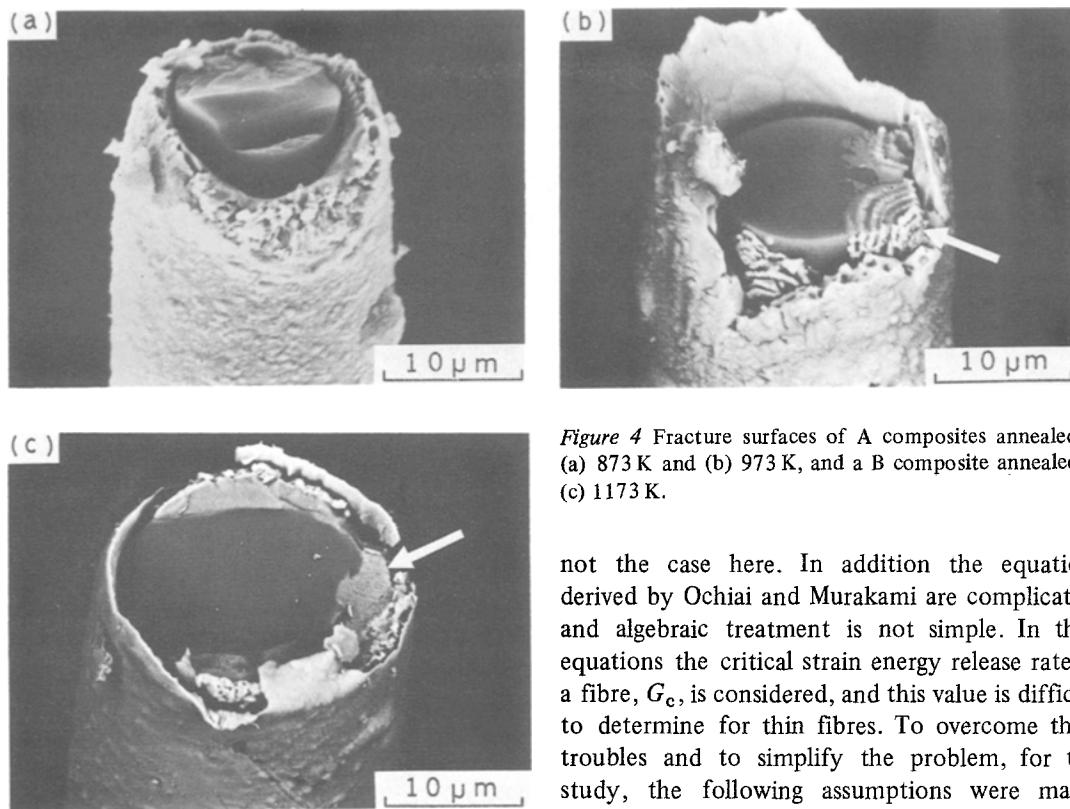


Figure 4 Fracture surfaces of A composites annealed at (a) 873 K and (b) 973 K, and a B composite annealed at (c) 1173 K.

reaction products are formed at the interface, weakening the monofilament composites. One explanation of the weakening of composites considers the decrease in effective volume fraction of the fibres. This does not always seem to hold, however, and there have been studies showing this not to be the case [8–11].

Metcalfe and Clein [9] and Baker and Bonfield [11] suggested that when the thickness of the reaction product zone,  $c$ , increases, the strength of the fibre decreases in proportion to  $1/c^{1/2}$ . Ochiai and Murakami [12] derived more elaborated equations using fracture mechanics. According to Ochiai and Murakami the strength of an elastic fibre depends on  $c$  when it is uniformly surrounded with a brittle zone, and the fibre and the brittle zone are tightly bound to each other. When  $c$  exceeds a critical value,  $c_I$ , the strength decreases in proportion to  $1/c^{1/2}$  and when  $c$  increases further to exceed another critical value,  $c_{II}$ , the strength is determined by the strength of the reaction product zone. There exist, however, some difficulties in applying the theory to the present case. First it was assumed that the fibre is uniformly enclosed by the reaction zone, which is

not the case here. In addition the equations derived by Ochiai and Murakami are complicated, and algebraic treatment is not simple. In their equations the critical strain energy release rate of a fibre,  $G_c$ , is considered, and this value is difficult to determine for thin fibres. To overcome these troubles and to simplify the problem, for this study, the following assumptions were made: (a) the reaction products are brittle and the bond between fibre and reaction products is strong; (b) factors related to the morphology of the reaction products are negligible; (c) the fibre is elastic.

Assumption (a) is substantiated in that no opening was observed between the fibre and reaction products and they never separated even at fracture (Figs. 3 and 4). The fracture strain of the fibre is about 0.015 and this is thought to be higher than that of the reaction products, and it allows considering the reaction zone brittle. It is hard to account for the morphological factors in assumption (b), but when the thickness of the zone is thin compared with the fibre diameter, as in the case of the early stage of the reaction, they may be ignored. Assumption (c) appears reasonable for these fibres and furthermore, the fibres show practically no plasticity.

From assumption (a), the initial condition reduces to the fracture of the brittle zone, and from assumption (b) difficulties arising from geometrical features are greatly simplified. As a result, the fibre can be treated as one where a wide plate has an edge crack of length  $c$ , as shown in Fig. 5. From assumption (c) Griffith's equation for brittle fracture is applicable. Then, the fracture

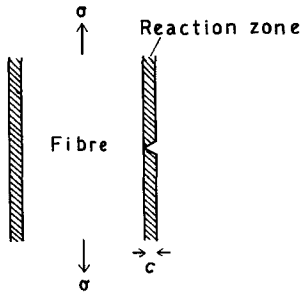


Figure 5 Edge crack model.

stress of the fibre,  $\sigma$ , having a surface crack of length  $c$  is given by [13]

$$\sigma = (2E_f\gamma/\pi c)^{1/2}, \quad (2)$$

where  $E_f$  is Young's modulus and  $\gamma$  the surface energy of the fibre before the reaction occurs. If  $E_f$  and  $\gamma$  are inherent constants of the material,  $\sigma$  depends only on  $c$  and the nominal fracture stress of the fibre,  $\sigma_f(c)$ , is expressed by

$$\sigma_f(c) = A/c^{1/2}, \quad (3)$$

where  $A = (2E_f\gamma/\pi)^{1/2}$ .  $\sigma_f$  increases with decreasing  $c$ . Since the value of  $\sigma_f(c)$  does not exceed the original fibre strength,  $\sigma_f$ , the maximum value of  $\sigma_f^{\max}(c)$  is

$$\sigma_f^{\max}(c) = \sigma_f. \quad (4)$$

Thus, there exists a critical value of  $c$  which is given by

$$A/c_I^{1/2} = \sigma_f \quad (5)$$

and

$$c_I = 2E_f\gamma/\pi\sigma_f^2. \quad (6)$$

Since the initial condition of the problem is the fracture of the brittle zone, the nominal fibre strength cannot be lower than the stress at which the brittle zone fractures. When the thickness of the zone is far thinner than the diameter of fibre, the stress in the fibre at fracture of the zone is expressed by

$$\sigma_f(c) = \epsilon_b E_f \quad (7)$$

where  $\epsilon_b$  is the fracture strain of the brittle zone. The other critical value of  $c$  is then given by

$$A/c_{II}^{1/2} = \epsilon_b E_f \quad (8)$$

and

$$c_{II} = 2\gamma/\pi\epsilon_b^2 E_f. \quad (9)$$

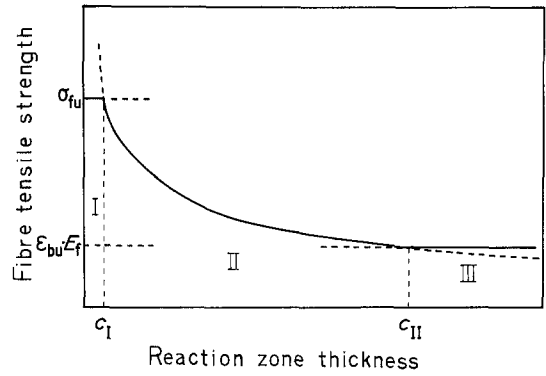


Figure 6 Relationship between fibre strength and reaction zone thickness.

The values of  $c_I$  and  $c_{II}$  are calculated from Equations 6 and 9 by substituting  $E_f$ ,  $\gamma$ ,  $\sigma_f$ , and  $\epsilon_b$ .  $\gamma$  which had been measured for SiC cannot directly be assigned for the present fibre. An estimation of  $\gamma$  for the fibre here was made by [14]:

$$\gamma = Ea/4\pi^2, \quad (10)$$

where  $a$  is the lattice spacing. The use of Equation 10 can be justified as the fractures of the reacted fibres are almost all of a cleavage type (Figs. 4b and c). When the lattice spacing of  $\beta$ -SiC is taken as  $a$  and  $\epsilon_b$  is taken to be 0.004, which is the average fracture strain of cleavage fractured specimens,  $c_I$  and  $c_{II}$  become 31 and 440 nm. These values are adequately small when compared with the diameter of the fibre.

The relationship between fibre strength and zone thickness is shown in Fig. 6. A similar feature has been obtained by Metcalfe and Clein [9] and Ochiai and Murakami [12].  $\sigma_f(c)$  for  $c \geq c_{II}$  is approximated by Equation 7. When  $c$  is large and the relative amount of reaction zone cannot be neglected, the strength of the fibre is given by

$$\sigma_f(c) = \sigma_f^* V_f' + \sigma_b(1 - V_f'), \quad (11)$$

where  $\sigma_b$  is the strength of the brittle reaction zone,  $\sigma_f^*$  is the stress in the effective fibre (i.e. the fibre which has not still reacted) when fracture of the reaction zone takes place, and  $V_f'$  is the volume fraction of the effective fibre. When  $V_f'$  reaches 1, Equation 11 coincides with Equation 7 because  $\sigma_f^*$  is  $\epsilon_b E_f$ . Since it is clear from Figs. 3 and 4 that the maximum thickness of the zone is larger than  $c_{II}$ , the strength of the fibre is in region III in Fig. 6. Their values are obtained from Equation 11 and are close to  $\epsilon_b E_f$ , roughly esti-

TABLE I Tensile strength of the reacted composites

Sample	Annealing temperature (K)	$\sigma_m^* \dagger$ (MPa)	$\sigma_{c(cal)} \ddagger$ (MPa)	$\sigma_{c(meas)}$ (MPa)
A composite	973	140	410	450
B composite	1173	50	365	290

$\dagger$  These values were obtained from electroplated and annealed Ni.

$\ddagger$   $V_f$  was assumed to be 0.5.

mated to be 680 MPa. This value agrees well with the strength of the fibre exposed from the A composite annealed at 973 K, it differs considerably from the fibre exposed from the B composite annealed at 1173 K. Substituting the values into Equation 1, the strengths of the reacted monofilament composites were calculated and are shown as  $\sigma_{c(cal)}$  in Table I and they agree well with the measured strength. The slight difference is thought to be due to: (1)  $\epsilon_b$  not being directly determined and it would be different from each reaction product; (2) the relative amounts of reaction products being ignored and Equation 11 rather than Equation 7 should have been used; (3) the measured values in Table I being obtained by averaging more than 30 measurements whereas the calculation was conducted from only a few points as shown in Fig. 4.

#### 4.2. Effect of the morphology of the reaction zone

From the metallographic observations of the cross-sections of composites it can be said that the fraction of reacted fibre is much smaller than could be expected from the large decrease in strength. Fig. 7 represents the surface of an exposed fibre. Protrusions consisting of concentric circles are seen in Fig. 7b; these correspond to the lamellar structure in Fig. 3b. It is clear that the reaction does not take place uniformly on the fibre surface. If just one point on the surface is degraded by the reaction, the strength at this point becomes the strength of the fibre, but in practice such points are only rarely seen on cross-sections. The lower strength may have resulted from a higher number of fibres subjected to reaction than could be expected from the observation.

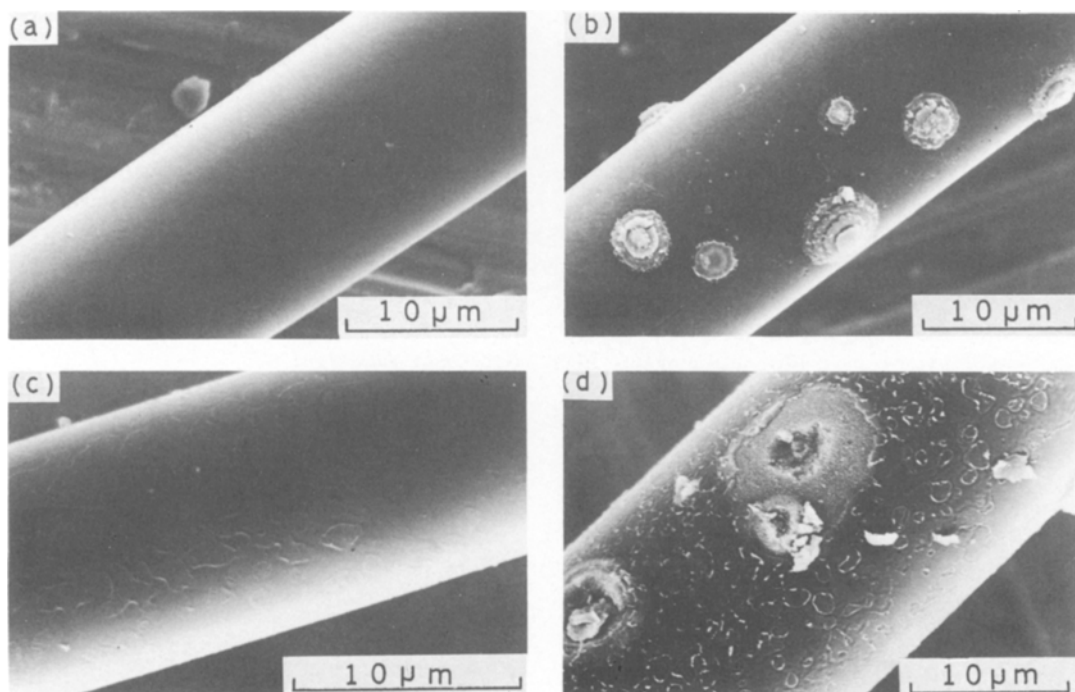


Figure 7 Surfaces of fibres extracted from A composites (a) before annealing, and (b) annealed at 973 K, and from B composites annealed at (c) 1073 K, and (d) 1173 K.

In Fig. 3c a phase is visible between the granular phase and nickel and it is suspected from Fig. 7d that this phase is dissolved in the acid with nickel when exposing the fibre. The tensile properties of this exposed fibre are thought to be different from those of the fibre in the composite. This could explain the difference between the  $\epsilon_b E_f$  estimated from the fracture strain of the composite and the measured strength of exposed fibres from B composites annealed at 1173 K.

In Fig. 7c no reaction product but a network structure is seen on the surface of a fibre exposed from a B composite which was annealed at 1073 K. The network is more remarkable for the specimen annealed at higher temperatures (Fig. 7d). The surface roughening due to the development of the network corresponds to the decrease in strength of the B composite when annealed at 1073 K.

## 5. Conclusions

Continuous SiC fibres obtained from a precursor of polycarbosilane were subjected to two kinds of pre-treatment to adjust the surface condition. Monofilament composites were prepared by plating the fibres with nickel and the composites were annealed in vacuum at temperatures between 673 and 1173 K. The pre-treatment and annealing changes in tensile strength of the composites, and the fibres exposed from the composite, were studied. The results may be summarized as follows:

1 The tensile strength decreased rapidly when the composite is annealed at temperatures above that where reaction between fibre and nickel occurs. The extent of composite degradation by the reaction differed with the pre-treatment and annealing temperature. The degradation behaviour agreed with that reported in our previous study on compatibility between fibre and nickel at high temperatures;

2 The Griffith theory for crack propagation was used to explain the degradation caused by the reaction;

3 SEM observations showed that the average values of the tensile strength of composites are related to the morphology of the reaction products.

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