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Aluminium nitride coatings on silicon carbide fibres, prepared by pyrolysis of a polymeric precursor

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Metallic aluminium was anodically dissolved in an organic electrolyte. A viscous solution, containing a polyiminoalane precursor was obtained. Nicalon (SiC) fibres were thermally pretreated and then coated with this fluid. The coated fibres were dried and calcined at 900° C in anhydrous ammonia. Thermal pretreatment of the fibres in nitrogen at 1400° C and dip coating with solutions of relatively low aluminium concentrations resulted in dense, nearly uncracked aluminium nitride layers.

1. Introduction

Because of their potential toughness and high strength, reinforced ceramic matrix composites are considered favourable materials for structural applications. They can, in principle, be produced by the addition of fibres, whiskers or platelets. The most common material used as a reinforcement is silicon carbide. Addition of SiC whiskers to an aluminium matrix has been reported to improve significantly the mechanical properties [1] as well as reduce the high-temperature creep, in comparison to pure alumina ceramics [2]. SiC whiskers have also been incorporated into matrices such as mullite [3], cordierite [4], zirconia [5], magnesium aluminium spinell [5], $MoSi_2$ [6], Si_3N_4 [7], SiC [8], glass and glass ceramics [9]. Composites have, in general, been fabricated by uniaxial hot pressing. Their mechanical properties strongly depend on powder processing and hot-pressing conditions [1–8].

The possible toughening mechanisms in ceramic matrix composites are: crack deflection, fibre pullout, and wake toughening. These toughening mechanisms (e.g. fibre pullout) require a fibre with a transverse fracture toughness that is considerably higher than that of the fibre matrix interface. Only then can crack propagation occur along the interface preferentially prior to fibre failure, thus increasing the fracture toughness as a result of the additional frictional energy required when the fibre is pulled out. The fracture toughness, therefore, depends on the shear resistance of the fibre–matrix interface and is strongly influenced by the chemical and mechanical bonding.

Especially important is the chemical bonding. Therefore, surface modifications are suitable to control the interfacial zone, a demand which can, for example, be accomplished by ceramic coatings on whiskers, fibres or platelets. Boron nitride or carbon-rich surface layers have proved to be advantageous for the mechanical performance of composites by preventing too strong a chemical interaction between the matrix and the fibre [10, 11].

Another future material for reaction barrier coatings may be aluminium nitride. In the presence of silicon carbide it is thermodynamically stable up to temperatures in the region of 1900° C; at higher temperatures a solid solution is formed [12, 13]. Also, it is chemically stable in the presence of possible matrix materials like Al_2O_3, where only at temperatures above 1700° C are AlON-phases formed. Furthermore, when in contact with oxygen contaminations on SiC fibres, e.g. as an SiO_2 surface layer, AlN should form SiAlON phases of comparably high melting points, whereas, by contrast, oxygen-containing SiC fibres are attacked by Al_2O_3 to form compounds with low melting points, so that the fibre might be destroyed. Aluminium nitride can, therefore, be considered as a promising material, protecting the fibre from a chemical attack from the matrix material.

This paper introduces a way to obtain comparatively thick, fully dense coatings of aluminium nitride. Derived from the sol–gel process for the preparation of oxide ceramics, this method was only recently developed and is based on the pyrolytic decomposition of a ceramic precursor to produce aluminium nitride powder [14] which can be sintered pressurelessly without any additives [15]. This investigation was carried out with SiC fibres, but with some modifications it should be possible to apply the same technique to the formation of AlN layers on SiC whiskers, platelets or other ceramic substrates. The comparatively high diameter of fibres, however, facilitates the characterization of the coatings obtained.

2. Experimental procedure

2.1. Preparation of the polymeric precursor

Metallic aluminium is anodically dissolved in an electrolyte consisting of *n*-propylamine, acetonitrile and tetraalkylammoniumbromide. Cathodes and anodes are formed by sheets of metallic aluminium. The experimental details and the apparatus for the electrolysis have already been described elsewhere [13].

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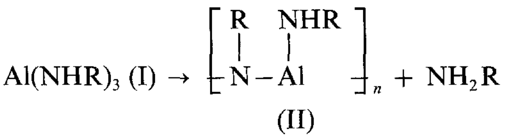
The assumed chemical reactions at the electrodes can be described by

$$\begin{array}{lrcl} \text{anodic reaction} & Al & \rightarrow & Al^{3+} + 3e^- \\ \text{cathodic reaction} & 3NH_2R + 3e^- & \rightarrow & 3NHR^- + 3/2\,H_2 \\ \hline & Al + 3NH_2R & \rightarrow & Al(NHR)_3 + 3/2\,H_2 \qquad (1) \end{array}$$

The aminoalane compound, $Al(NHR)_3$ (I), is assumed to be formed as an intermediate which polycondensates to a highly polymeric polyiminoalane compound (II)



$$Al(NHR)_3\ (I) \rightarrow \left[\begin{array}{cc} R & NHR \\ | & | \\ -N- & Al- \end{array}\right]_n + NH_2R \qquad (2)$$

(II)

Further polycondensation should lead to the three-dimensional polycondensed polyiminoalane compound (III)

$$\underset{(II)}{} \rightarrow \underset{(III)}{Al(NR)_{1.5}} + NH_2R \qquad (3)$$

In the course of the electrolysis, a more and more viscous solution and finally a fluid of sol-like consistency is obtained. The duration of the electrolysis determines the amount of dissolved aluminium and the viscosity. It has already been shown [12, 13] that compound (III) can be dried and transferred to aluminium nitride by calcination in an atmosphere of anhydrous ammonia or dried nitrogen. The ceramic yield related to the dried precursor is 42 wt %.

$$\underset{(III)}{Al(NR)_{1.5}} \rightarrow \underset{(IV)}{AlN} + 1/2\,NR_3 \qquad (4)$$

The electrolysis was carried out in a volume of 500 ml electrolyte, a current of 20 to 22 A and a voltage between 5 and 5.7 V. The polarity was switched every 15 min to achieve a homogeneous dissolution of all electrodes.

2.2. Pretreatment and coating procedure of the SiC fibres

For all experiments, commercially available SiC fibres (Nicalon fibres, Nippon Carbon Co. Ltd, Tokyo) with a diameter of 15 μm were used. For the purpose of better handling they were cut to a length of approximately 3 mm. A part of this investigation was performed with fibres that had been pretreated by heating them up to 1100° C in anhydrous ammonia for 5 h or to 1400° C in dried, purified nitrogen for 1 h.

The fibres were coated with the fluid containing the precursor (sol) immediately after the heat treatment. For this purpose, the fibres were dispersed in anhydrous propylamine prior to the addition of the sol, and subsequently the mixture was dried by a gradual raising of the temperature under vacuum. In another series of experiments the fibres were placed into a grid and dipped into a glass vessel containing the sol under an atmosphere of dried argon. After some seconds the sol was removed from the vessel. Drying of the coated fibres was performed by evaporating the solvent and excess amine in a gas stream of argon.

The fibres coated with the polymeric precursor were subsequently calcined at 900° C for 1 h in a silica tube under anhydrous ammonia with heating rate 2.5° C min^{-1}.

3. Results and discussion

Table I summarizes analytical data of the oxygen and nitrogen content of Nicalon fibres as-received and after heat treatment in nitrogen and ammonia, respectively. Thermal treatment in anhydrous ammonia at 1100° C was found hardly to affect the oxygen content at all, whereas calcination in nitrogen atmosphere at 1400° C results in a significant decrease from initially 12.9 to 9.0 wt %. The low nitrogen content of untreated fibres (0.2 wt %) increases during calcination in ammonia (1.1 wt %) and nitrogen (1.5 wt %). It should be remarked that the high oxygen content of the Nicalon fibres, which is due to their fabrication process, was considerably reduced by the heat treatment in a nitrogen atmosphere at 1400° C.

Fig. 1 shows a scanning electron micrograph of an as-received fibre with a remarkably smooth and uniform surface. An effect of the various heat treatments on the appearance could not be detected by the scanning electron microscopy.

Figs 2 to 4 all refer to fibres which had been dispersed in propylamine, coated by the polymeric precursor (electrolysis time 150 min, aluminium content 33.6 g l^{-1}) and subsequently dried and calcined in anhydrous ammonia. An example of a thermally untreated fibre is given in Fig. 2. The coating is very inhomogeneous with only some distinct areas of the fibre being covered by an uneven and fragmented ceramic layer. Fibre pretreatment in anhydrous ammonia did not result in a satisfactory coating either (see Fig. 3). Wide areas of the fibre surface were not coated at all, but in some small regions, supposedly dense fragments of the ceramic layer can be observed still adhering to the fibre. Evidently, the coating has scaled off during processing, as implies the upper part of the micrograph where a partially loosened fragment can be seen. The appearance of the fibres treated in nitrogen at 1400° C prior to coating is remarkably different, as Fig. 4 reveals. Large parts of the surface are covered with an evidently dense, but fractured

TABLE I Oxygen and nitrogen content of Nicalon fibres before and after thermal pretreatment

	Oxygen content (wt %)	Nitrogen content (wt %)
Without pretreatment	12.9	0.2
Pretreatment in ammonia at 1100° C	12.8	1.1
Pretreatment in nitrogen at 1400° C	9.0	1.5

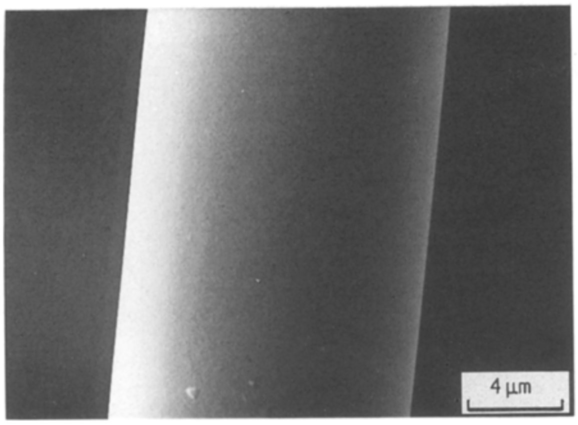


Figure 1 Scanning electron micrograph of a Nicalon SiC fibre as commercially available.

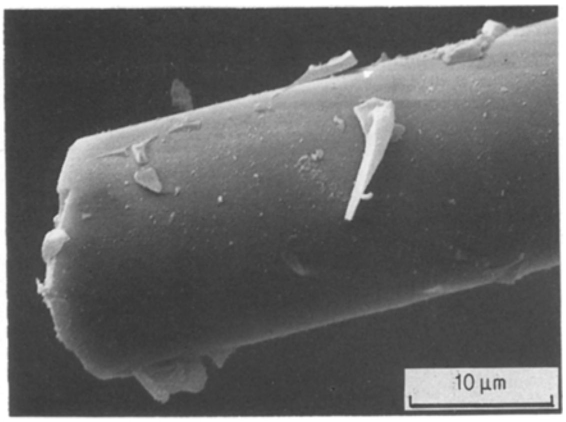


Figure 3 Scanning electron micrograph of a Nicalon SiC fibre, thermally pretreated at 1100° C in anhydrous ammonia, coated with the polymeric precursor (electrolysis time 150 min) and then calcined in anhydrous ammonia.

layer characterized by radial cracks and a quite non-uniform thickness. The left part of Fig. 4 shows a rather thick layer (about 1.2 μm) with wide spacings between the cracked edges. On the right side of the micrograph, however, the coating is comparatively thin (about 0.5 μm) and the crack width is remarkably reduced. These cracks are assumed to form during drying and calcination of the polymer coating. Although, in the upper part of Fig. 4, the coating is partially scaled off, it can be concluded that the thermal pretreatment of the nicalon fibres in dried nitrogen at 1400° C is more efficient and leads to a stronger adhesion during drying and calcining. This effect may be due to the decrease in oxygen content at the fibre surface. A comparison between the left and the right side of Fig. 4 suggests that the reduction of the layer thickness should allow drying and calcining without crack formation.

For that purpose the electrolysis (see Section 2.1) was interrupted after 90 min (aluminium content 20.2 $\mathrm{g\,l^{-1}}$) and 120 min (aluminium content 26.8 $\mathrm{g\,l^{-1}}$) and these less concentrated solutions were used for dip-coating experiments. At an electrolysis time of 120 min, the fibres were hardly wetted by the highly viscous solution, and subsequently a ceramic layer could not be observed after calcination. Energy dispersive X-ray (EDX) analysis did not yield any evidence of aluminium being present either. By contrast, a rather thin layer was obtained when the sol was produced by interrupting the electrolysis after only 90 min (see Fig. 5). Over a wide range, a continuous undamaged coating had developed exhibiting quite a smooth and uniform surface that can hardly be distinguished from the uncoated fibre with the aid of scanning electron micrographs. Only in some small selected areas had cracking occurred (here shown in Fig. 5 upper part), thus allowing an estimation of the layer thickness which was about 0.5 μm.

Figure 6 shows an EDX analysis of the coated (curve a) and uncoated parts of the fibres (curve b). Only silicon can be detected at the uncoated parts, while measurements directly on the coating reveal peaks related to silicon as well as to aluminium. The additional peaks in both curves are due to gold sputtering. It is assumed that the penetration depth of the incident beam exceeds the thickness of the coating of 0.5 μm, so that the appearance of a silicon peak due to the fibre material cannot be avoided.

Curve b in Fig. 7 shows the X-ray diffraction (XRD) pattern of fibres coated after dispersion in propylamine. The observed XRD data exactly match literature data of hexagonal aluminium nitride

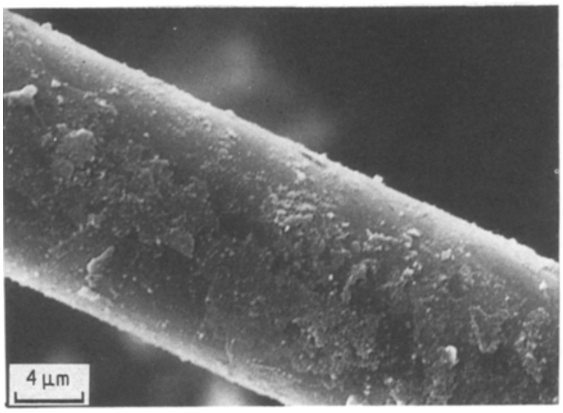


Figure 2 Scanning electron micrograph of a Nicalon SiC fibre, coated with the polymeric precursor (electrolysis time 150 min) without thermal pretreatment and then calcined in anhydrous ammonia.

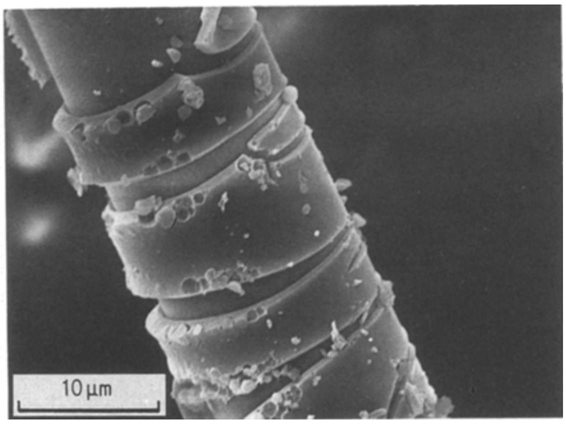


Figure 4 Scanning electron micrograph of a Nicalon SiC fibre, thermally pretreated at 1400° C in dried nitrogen, coated with the polymeric precursor (electrolysis time 150 min) and then calcined in anhydrous ammonia.

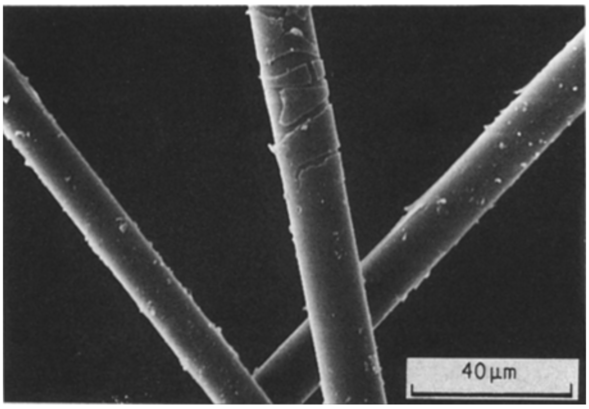


Figure 5 Scanning electron micrograph of a Nicalon SiC fibre, thermally pretreated at 1400° C in dried nitrogen, dip-coated with the polymeric precursor (electrolysis time 90 min) and then calcined in anhydrous ammonia.

(ASTM XRD card 25-1133) and are obviously not influenced or superimposed by XRD lines related to the substrate material (see Fig. 7). Additional peaks, due to the formation of AlON, SiAlON, oxycarbide or carbonitride phases could not be detected, but it cannot be excluded that additional phases might be present, especially at the fibre–coating interface. The peaks are considerably broadened and of low intensity, characteristic for microcrystallinity. With the aid of the Scherrer equation a mean crystallite size can be calculated to be in the range of about 30 nm

$$t = \frac{0.89\lambda}{B\cos\theta} \qquad (5)$$

where t is the mean crystallite size, λ the wavelength of the radiation ($\mathrm{Cu}K_\alpha = 0.154\,\mathrm{nm}$), B the line broadening, characterized by half-width and θ the Bragg angle. The mean crystallite size is in the same range as for aluminium nitride powder produced by the same method and calcined at the same temperature.

4. Conclusions

The investigations performed show that polyiminoalane solutions, prepared by anodic dissolution of metallic aluminium in an organic medium, are suited to realize the formation of aluminium nitride coatings on ceramic substrates at a temperature as low as 900° C.

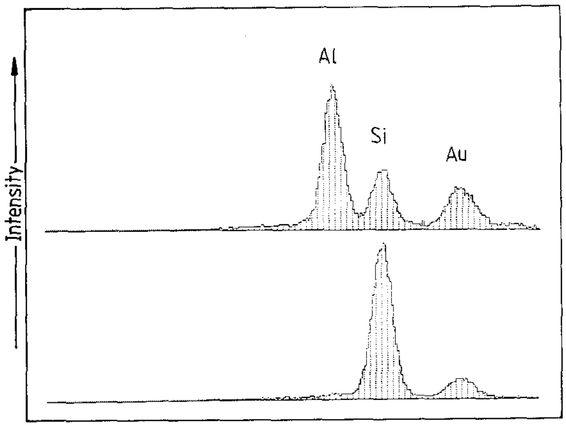


Figure 6 EDX analysis of the fibre coating (curve a) and uncoated parts of the fibre (curve b).

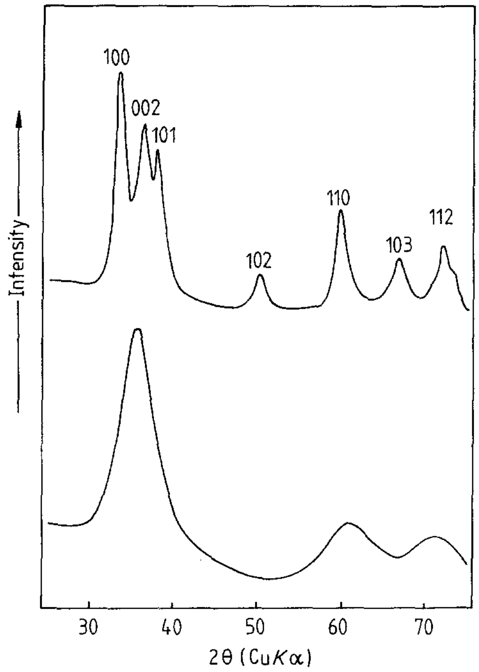


Figure 7 XRD patterns of the coated fibres (curve a) and Nicalon fibres as-received (curve b).

Thermal pretreatment of the fibres at 1400° C in nitrogen and dip coating with solutions of relatively low aluminium concentrations resulted in dense, nearly uncracked aluminium nitride layers.

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