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Fracture of aluminium-coated carbon fibres

S. J. BAKER*, W. BONFIELD
Department of Materials, Queen Mary College, London, UK

A degradation in the ultimate tensile strength (UTS) of aluminium-coated carbon fibres was associated with the formation of a reaction layer of aluminium carbide during annealing treatments $\geqslant 475^\circ$ C for high tensile fibres (HT) and $\geqslant 550^\circ$ C for high modulus fibres (HM). It was established that for a given annealing treatment, the UTS depended on the square root of the original coating thickness and proposed that fracture was controlled by cracks in the aluminium carbide, with a specific surface energy (γ) and intrinsic crack length (c_0) of 2.33 J m^{-2} and ~ 30 nm for HT fibres, and of 0.64 to 0.77 J m^{-2} and ~ 20 nm for HM fibres.

1. Introduction

For a carbon fibre reinforced aluminium composite, it has been established [1] that the components react at temperatures above 400° C to form aluminium carbide and that the reaction rate increases with temperature [2]. The aluminium carbide forms as platelets, which coalesce to form a continuous sheath [2, 3]. While a reduction in the ultimate tensile strength (UTS) of graphitized carbon fibres was attributed to fibre surface damage produced by the aluminium carbide coating, the nature of the surface damage was not established. In this paper, it is demonstrated that the UTS of individual aluminium-coated carbon fibres after high temperature anneals depends on the thickness of the original aluminium coating, which in turn controls the length of cracks formed in the reacted aluminium carbide.

2. Experimental procedure

Three types of carbon fibre, Courtaulds HM-S, HM-U and HT-S (HM – high modulus, HT – high tensile strength, S – a proprietary surface treatment, U – no surface treatment) were coated with aluminium (of 99.999% purity) by vapour deposition in a vacuum of $< 10^{-5}$ Torr. Some fibres were individually mounted on cardboard testing cards, each card having a 5 cm gauge length, and deformed to fracture at a strain rate of 10^{-5} sec^{-1} in an Instron testing machine. The Young's modulus (E) and ultimate tensile strength (UTS) for each fibre were calculated from the observed fracture load, fracture strain and original cross-sectional area. Other fibres, coated with 180 nm of aluminium, were annealed for 24 to 100 h at various temperatures up to 650° C, while a series of fibres coated with aluminium thicknesses between 46 and 540 nm were annealed for 100 h at 600° C, all in a vacuum $< 10^{-5}$ Torr. The annealed fibres were subsequently tensile-tested at room temperature and examined in a JEOL-JEM 7 electron microscope, a Cambridge S4 "Stereoscan" and by X-ray diffraction, both before and after removal of the aluminium coating with 10% sodium hydroxide.

3. Results

3.1. Effect of annealing temperature on aluminium-coated carbon fibres

The room temperature ultimate tensile strength (UTS) and Young's modulus (E) of as-coated carbon fibres (i.e. prior to annealing) are shown compared with those of uncoated fibres in Table I, for HM-S and HT-S fibres. It can be seen that coating did not significantly affect these properties (with perhaps some enhancement of the UTS). The values of E and UTS of uncoated carbon fibres were also not altered by anneals in vacuum at 650° C for 100 h (and 850° C for 100 h) as

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*Now at Development Division, Pye Unicam Ltd., Cambridge, UK.

TABLE I The effect of aluminium coating on E and UTS of HT-S and HM-S carbon fibres

Fibre	Al coating thickness (nm)	UTS (GN m^{-2})	E (GN m^{-2})
HT-S	–	2.11 ± 0.74	216 ± 19
HT-S	46	2.89 ± 0.60	243 ± 28
HT-S	180	2.08 ± 0.38	196 ± 12
HT-S	540	2.14 ± 0.39	213 ± 17
HM-S	–	1.34 ± 0.43	290 ± 17
HM-S	46	1.65 ± 0.43	278 ± 37
HM-S	180	1.70 ± 0.33	279 ± 21
HM-S	540	1.80 ± 0.50	290 ± 18

TABLE II The effect of annealing on E and UTS of uncoated HT-S and HM-S carbon fibres

Fibre	Annealing temperature (° C)	Annealing time (h)	UTS (GN m^{-2})	E (GN m^{-2})
HT-S	No anneal		2.11 ± 0.74	216 ± 19
HT-S	475	100	2.11 ± 0.45	199 ± 36
HT-S	650	100	2.15 ± 0.51	200 ± 19
HT-S	850	24	2.03 ± 0.37	204 ± 13
HM-S	No anneal		1.34 ± 0.43	290 ± 17
HM-S	550	100	1.67 ± 0.43	289 ± 23
HM-S	650	100	1.37 ± 0.56	288 ± 20
HM-S	850	24	1.86 ± 0.32	284 ± 22

shown in Table II. However, HT-S fibres coated with 180 nm of aluminium exhibited a reduced room temperature ultimate tensile strength after anneals at temperatures ⩾ 475° C (Fig. 1). The extent of the degradation in UTS increased with an increase in annealing temperature up to 650° C and a minimum UTS value of approximately 30% of the original strength value was produced. Aluminium-coated HM-S and HM-U fibres showed similar behaviour, with a reduction in UTS after anneals at ⩾ 550° C (Fig. 1) and a minimum UTS value at 45% of the original strength.

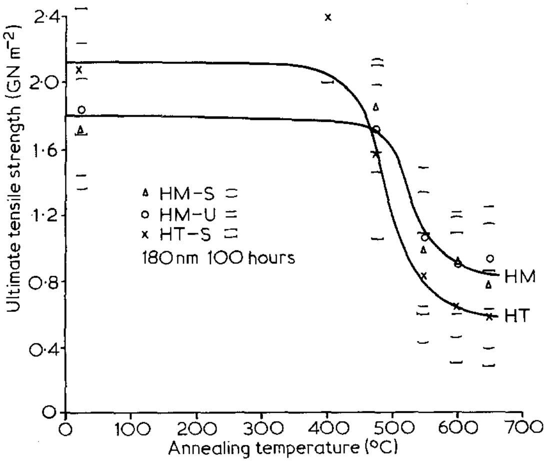


Figure 1 Effect of prior annealing temperature, (in vacuum for 100 h) on the room temperature ultimate tensile strength of aluminum-coated (180 nm) carbon fibres.

In contrast, the Young's moduli of the three types of fibres were not significantly changed after these annealing treatments.

3.2. Effect of aluminium coating thickness

The room temperature ultimate tensile strength of the three fibre types after similar anneals (600° C for 100 h) decreased with an increase in the original aluminium coating thickness from 46 to 540 nm. The values of UTS (σ) are plotted in Fig. 2 as a function of the square root of Young's modulus (E) divided by coating thickness (c), a procedure which reveals an approximately linear dependence, as

$$\sigma = A(E/c)^{\frac{1}{2}} \pm B \qquad (1)$$

where A, B are constants for each of the fibre types.

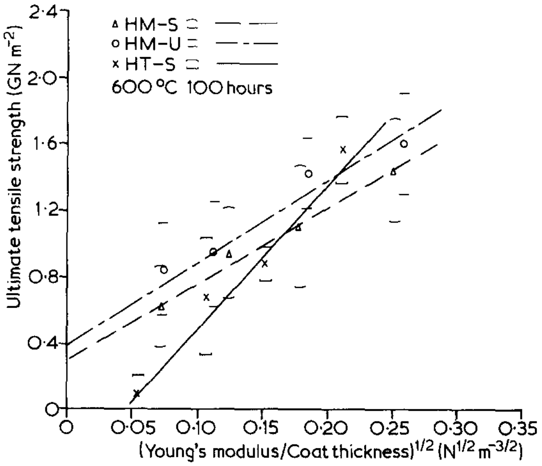


Figure 2 Effect of initial aluminium coating thickness on the room temperature ultimate tensile strength of carbon fibres, after an anneal at 600° C for 100 h in vacuum (which forms an aluminium carbide reaction layer).

3.3. Structural observations

A typical X-ray diffraction pattern from uncoated HM-U and HM-S carbon fibres is shown in Fig. 3a, in which seven of the nine lines observed were positively indexed. X-ray diffraction patterns from uncoated HT-S fibres were fainter and only the carbon (0 0 2) arcs and (1 0 0) lines were clearly resolved. For fibres coated with ⩾ 180 nm of aluminium, the presence of aluminium carbide lines was established, by X-ray diffraction, after anneals for 100 h at either ⩾ 475° C (HT-S fibres) or ⩾ 550° C (HM-U, HM-S fibres), as shown for com-

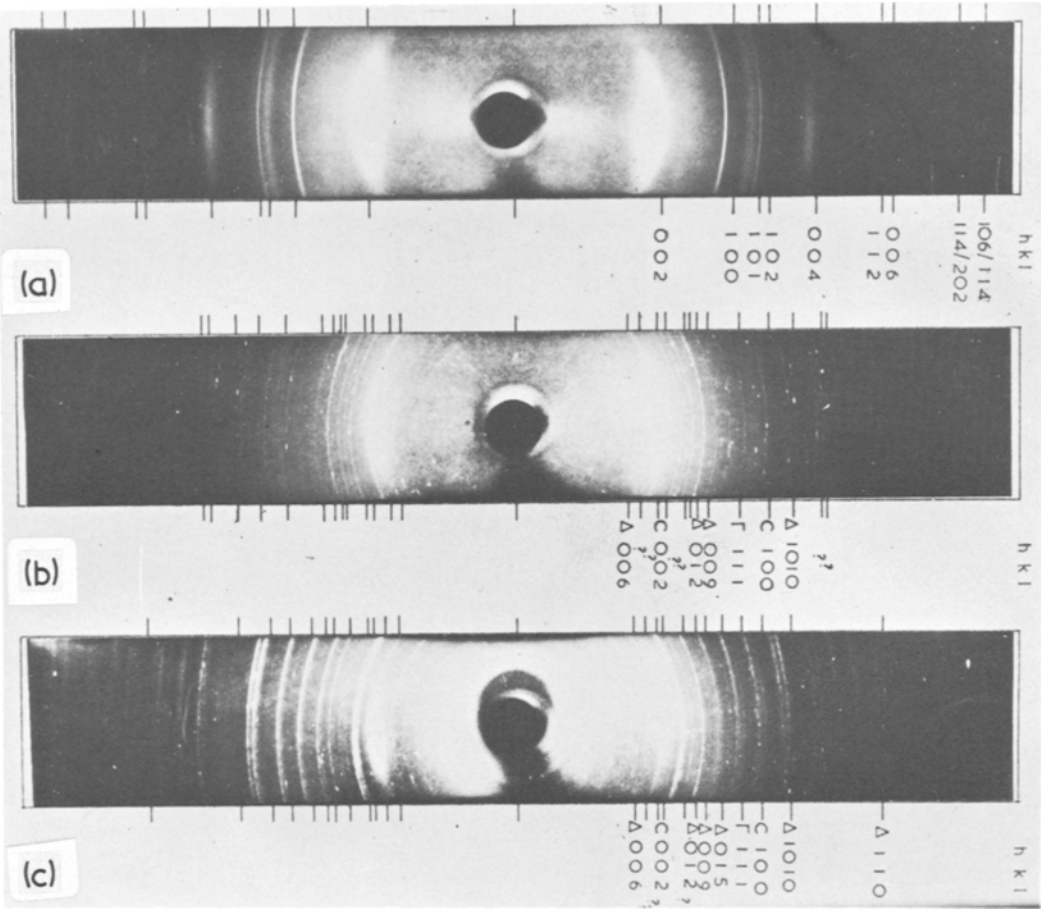


Figure 3 X-ray diffraction patterns (90 fibres, CuKα, 50 kV, 20 mA, 24 h) from: (a) Uncoated HM-U fibres. (b) HT-S fibres, coated with 180 nm of Al, annealed at 475° C for 100 h. (c) HM-U fibres, coated with 180 nm of Al, annealed at 550° C for 100 h. Symbols: C – carbon, Δ – Al_4C_3, I – Al, ? – unknown. Lines not indexed correspond to more than one reflection.

parison in Figs. 3b and c. The X-ray technique was not sufficiently sensitive to identify aluminium or aluminium carbide lines from fibres with coating thicknesses $\leqslant 90$ nm, but for these specimens, as well as for all the other coating thicknesses investigated, the presence of aluminium carbide after suitable anneals was confirmed by electron diffraction, as shown in Fig. 4.

The coating surface morphology after annealing was similar to that of the fibre surface for thicknesses $\leqslant 180$ nm, while the thicker coatings exhibited a more irregular appearance, as shown in Fig. 5. However, for all thicknesses, the fibre surface *under* the coating appeared similar to its original condition (Fig. 5e).

4. Discussion

The degradation in the room temperature UTS of the aluminium-coated (180 nm) HM-S (and HM-U) and HT-S carbon fibres, after anneals $\geqslant 550°$ C or $\geqslant 475°$ C, respectively, contrasts with no similar effect on the UTS produced by: (1) annealing uncoated fibres, and (2) coating fibres, without a subsequent annealing procedure.

The accompanying structural observations indicate that these annealing treatments produced aluminium carbide, presumably by the reaction:

$$3C + 4Al \rightarrow Al_4C_3$$

As a result the surface coating was converted either to a mixture of aluminium and aluminium carbide (at 475 to 550° C) or to aluminium carbide alone (at 600 to 650° C, when the reaction appeared to proceed to completion). Hence it is concluded that the reduction in UTS of the carbon fibres was associated with the presence of aluminium carbide in the surface coating. It is suggested that fracture propagated from cracks in the reacted surface

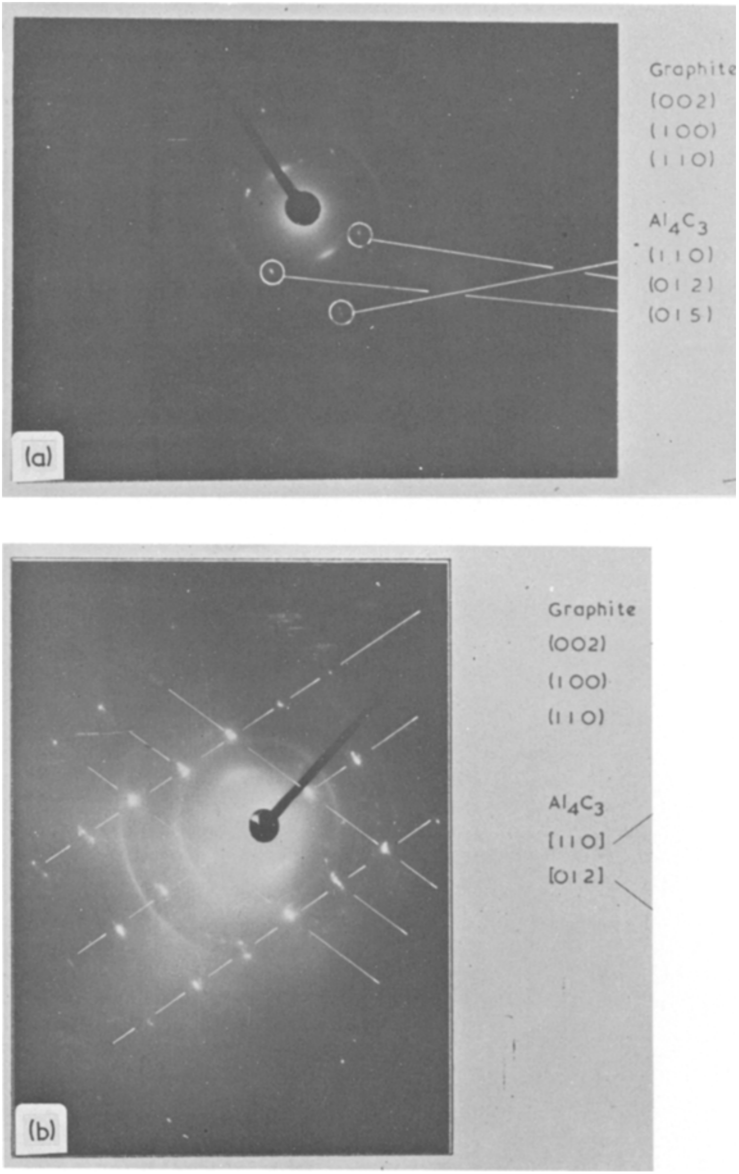


Figure 4 Electron diffraction pattern from surface fragments of: (a) HM-S fibre, coated with 46 nm of Al, annealed at 600° C for 24 h. (b) HM-U fibre, coated with 180 nm of Al, annealed at 650° C for 24 h with carbon (graphite) diffraction rings and Al_4C_3 diffraction spots.

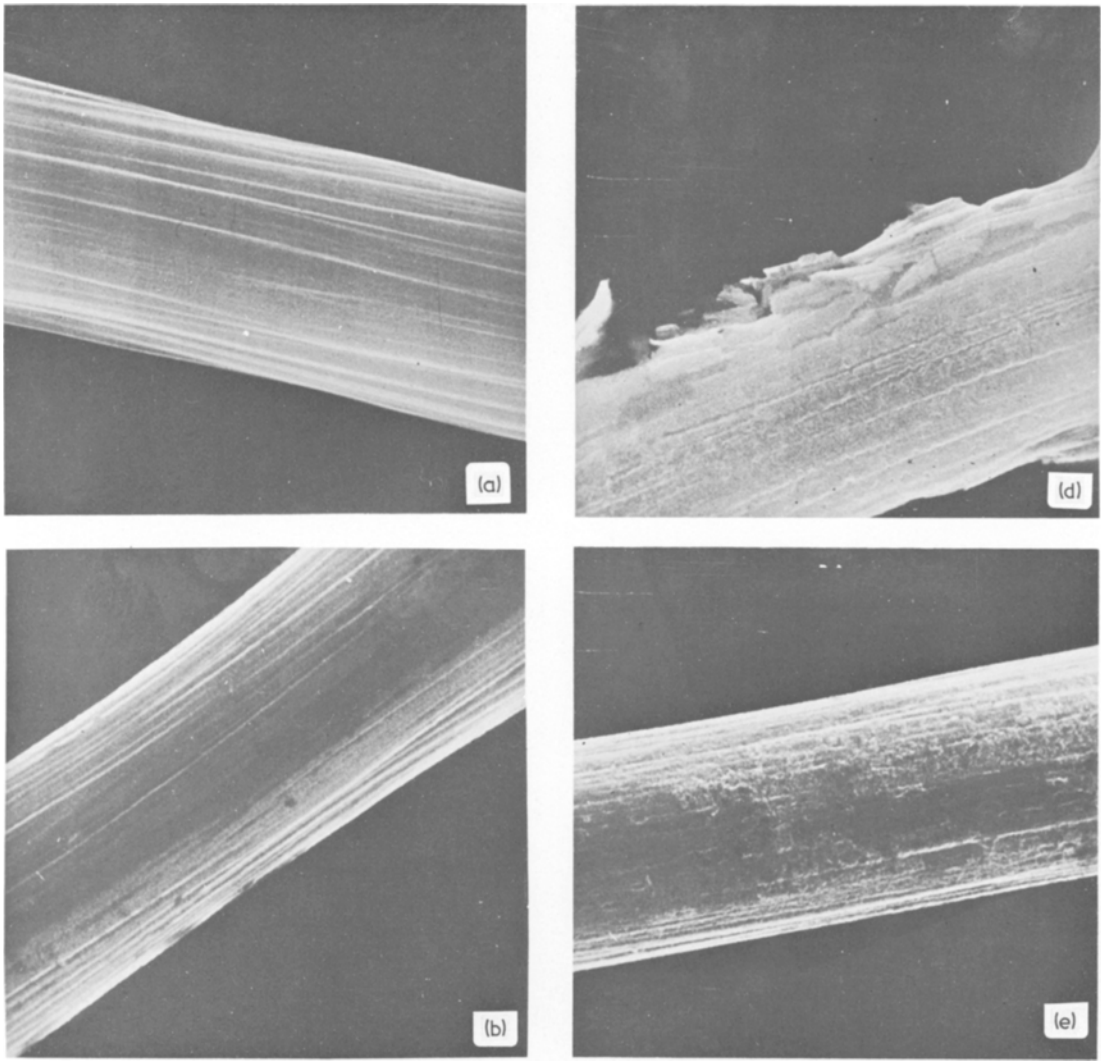
coating, the presence of which is demonstrated in Figs. 5c and d. With a complete aluminium carbide surface coating, the maximum possible crack length normal to the fibre axis is equal to the thickness of the aluminium carbide, which in turn is related to the thickness of the original aluminium coating. This model is consistent with the observation that the UTS, after annealing for a given temperature and time, decreased as the thickness of the aluminium coating was increased.

If we assume that: (1) the thickness of aluminium carbide is equal to that of the original aluminium coating (c), and (2) Griffiths equation for brittle fracture is applicable, following [4], then an estimate of the fracture parameters is given by:

$$\sigma = (2\gamma/\pi)(E/c)^{\frac{1}{2}} \tag{2}$$

where γ is the specific surface energy for fracture (i.e. surface energy per unit area).

From Equations 1 and 2, values of 0.64, 0.77 and 2.33 J m^{-2} are obtained for γ of HM-S, HM-U and HT-S carbon fibres, respectively. These values compare with derived specific surface energies of 0.14 J m^{-2} for graphite basal planes, 4.8 J m^{-2} for graphite prismatic planes [5] and a range from 14 to 55 J m^{-2} for high tensile strength carbon fibres [4]. An estimate of the intrinsic crack length (c_0) associated with fracture of the *uncoated* carbon



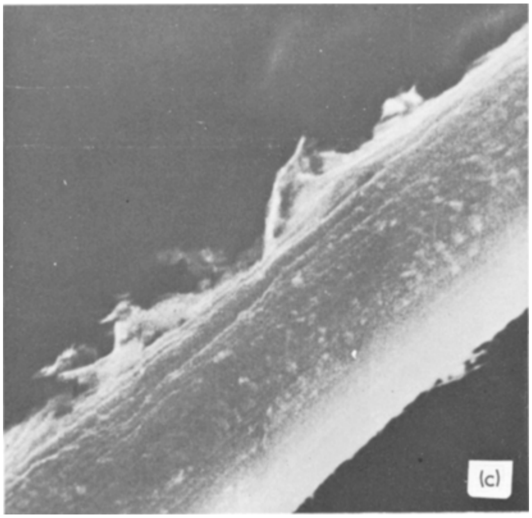


Figure 5 SEM comparison of (a) Uncoated HT-S fibre (annealed at 850° C for 24 h). (b) HT-S fibre, coated with 46 nm of Al annealed at 650° C for 100 h. (c) HT-S fibre, coated with 180 nm of Al, annealed at 600° C for 100 h. (d) HM-S fibre, coated with 540 nm of Al, annealed at 600° C for 100 h. (e) HT-S fibre, coated with 180 nm of Al annealed at 600° C for 100 h, *after* removal of the surface coating with 10% NaOH (fibre diameter ~ 8 μm).

fibres may be obtained by extrapolating the slopes in Fig. 1 to the corresponding values of σ. This procedure gives intrinsic crack lengths of ~20 nm (HM-U, HM-S fibres) and ~30 nm (HT-S fibres).

5. Conclusions

(1) The room temperature UTS of aluminium-coated carbon fibres is reduced by annealing treatments, in vacuum, $\geqslant 475°$ C for high tensile fibres (HT) and $\geqslant 550°$ C for high modulus fibres (HM).

(2) For a given annealing treatment $\geqslant 475^\circ$ C (HT fibres) or $\geqslant 550^\circ$ C (HM fibres), the UTS depends on $c^{-1/2}$, where c is the original coating thickness.

(3) Estimates of the specific surface energy for fracture (γ) and intrinsic crack length (c_0) are, respectively 2.33 J m^{-2} and ~ 30 nm for HT fibres and 0.64 to 0.77 J m^{-2} and ~ 20 nm for HM fibres.

Acknowledgements

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