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Carbon Fibre/Nickel Compatibility

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The effects of evaporated pure nickel coatings on the room-temperature fracture strength and microstructure of individual carbon fibres have been investigated. The fracture strength of a nickel-coated fibre was not affected by anneals in a 10^{-6} torr vacuum below 1000° C. However, after higher temperature anneals a reduction in strength was noted, the magnitude of which was time-dependent, but almost independent of the thickness of the coating. The reduction in strength was not related to fibre recrystallisation, but appeared to be controlled by the formation of a carbon-nickel interface, with an energy for adhesion of approximately 110 kcal mole^{-1}.

1. Introduction

The successful development of high-strength, high-modulus carbon fibres [1] has provided an opportunity for the design of carbon fibre/metal matrix composites with high-temperature mechanical properties superior to the metallic alloys currently available. Of the refractory metals available for use as the matrix material, nickel is perhaps the most suitable as it does not form a stable carbide. However, it has proved experimentally difficult to realise the theoretical values of fracture strength predicted for a carbon fibre/nickel composite, and dramatic reductions in fracture strength have resulted from comparatively low temperature annealing treatments. In recent publications, Jackson and Marjoram [2, 3] found a significant reduction in the fracture strength of a "micro-composite" of graphitised carbon fibres in nickel (containing approximately fifteen carbon fibres) after treatment at temperatures $> 800°$C, an effect which was attributed to recrystallisation of the carbon fibre. This paper reports an investigation of the effects of evaporated pure nickel coatings on the fracture strength of individual carbon fibres. Most significantly, the fracture strength of the individual nickel-coated carbon fibres was not affected by anneals in a 10^{-6} torr vacuum below 1000° C and the reduction in strength produced by treatments above this temperature was not related to fibre recrystallisation, but appeared to be controlled by the formation of a suitable carbon-nickel interface.

2. Experimental Procedure

The carbon fibres used in the investigation were Royal Aircraft Establishment Type I fibres graphitised at approximately 2500°C, and with diameters ranging from 7.2 to 8.0 μm. This type of fibre is polycrystalline, with graphite basal planes preferentially oriented along the fibre axis, but turbostratically displaced [4]. The fracture strength (the breaking load/original area) of individual carbon fibres at room temperature was determined. Each fibre was mounted with polystyrene on a thin cardboard holder, which gave an approximately 5 cm gauge length and deformed to fracture at a strain rate of 10^{-5} sec^{-1}. The diameter of each fibre was measured with a Watson Image-Shearing Eyepiece calibrated against known length standards. A minimum of thirty fibres were tested in any condition from which the average and standard deviation of the fracture strength were calculated.

The carbon fibres were tested in the "as-received" condition, after heat-treatments in the 800 to 1200° C temperature range under various atmospheres, after coating by vacuum evaporation with ~ 400 Å and ~ 0.7 μm layers of pure nickel, and after various combinations of these conditions.

The effects of the nickel coating on the structure of the carbon fibres were assessed by X-ray diffraction and electron microscopy. Particular attention was given in the X-ray examination to the possibility of carbon-fibre recrystallisation. About 1000 fibres were mounted in a 10 cm long holder and exposed to nickel-filtered CuKα X-radiation in a Philips powder camera. Surface replicas were prepared from the carbon fibres and examined in a JEOL-7 electron microscope. Some carbon fibres were also vibrated ultrasonically and the detached segments examined by transmission electron microscopy.

3. Results

3.1. Measurement of Fracture Strength

The average fracture strength measured at room temperature for the "as-received" carbon fibres was 280000 psi (1930 MN/m^2) with one standard deviation of 49000 psi (337 MN/m^2). It was found that annealing the "as-received" carbon fibres for 24 h at temperatures up to approximately 1100° C did not significantly affect the room-temperature fracture strength (i.e. the average value was within the standard deviation), provided that the anneal was performed with a 10^{-6} torr vacuum. These results are shown plotted in fig. 1. The atmosphere was critical: as a variable reduction in the fracture strength was obtained if the level of the vacuum was reduced to 10^{-5} — 10^{-4} torr, after anneals at temperatures as low as 600° C. Similarly, it was found difficult to obtain reproducible fracture strength results with an argon atmosphere. In all cases the fibres were heated slowly to the annealing temperature to allow the evolution of dissolved gas. After treatment at temperatures above 1100° C the fracture strength of the carbon fibres decreased appreciably, even in a 10^{-6} torr vacuum (e.g. 147000 psi (1020 MN/m^2) after 1200° C/24 h). For this reason the effect of nickel coating on the carbon fibres was mainly investigated for temperatures less than 1100° C.

The average room temperature fracture strength measured for the carbon fibres coated with ~ 400 Å of evaporated nickel was 277000 psi (1910 MN/m^2), which was similar to that of the "as-received" uncoated fibres. The mechanical contribution of a coating of this thickness to the strength was assumed to be negligible and the fracture strength was calculated on the basis of the carbon fibre area alone.

The room temperature fracture strength of the nickel-coated carbon fibres was not reduced by anneals up to 1000° C for 24 h, but as shown in fig. 1, a possible reduction was measured after 1080° C/24 h with a definite reduction after 1100° C/24 h. The fracture strength also appeared to be time-dependent as after 1000° C/48 h there was a small reduction in strength with a correspondingly larger reduction after 1100° C/48 h (see fig. 1).

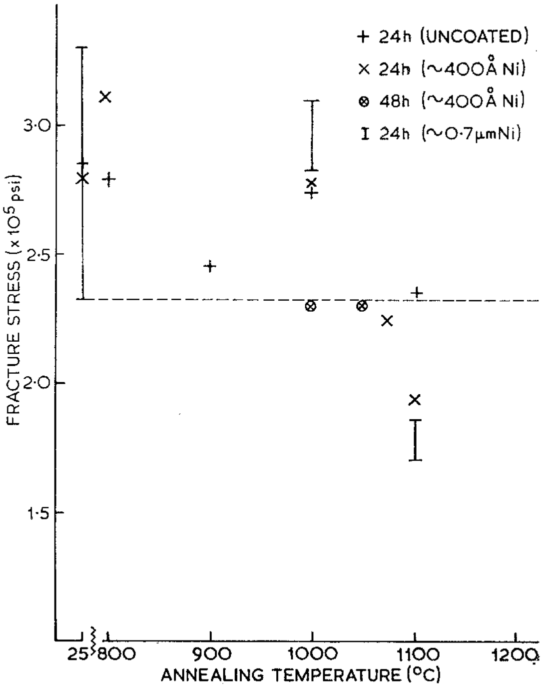


Figure 1 The effect of annealing on the fracture strength of uncoated and nickel-coated carbon fibres.

Some measurements were also made on carbon fibres coated with a substantially thicker layer of nickel (approximately 0.7 μm). The fracture strength of these carbon fibres (σ_c) was calculated in two ways; first, neglecting the contribution of the nickel, i.e. on the basis of the carbon fibre diameter alone and, second, assuming the nickel coating does contribute to the fracture strength and using the composite rule of mixtures. For example, after a treatment at 1000° C/24 h, we obtained by the two methods:

(Method 1)

$$\sigma_c = 314\,000 \text{ psi } 2160 \text{MN/m}^2 \quad (1)$$

$$\sigma_{c+\text{Ni}} = \sigma_c V_c + \sigma_{\text{Ni}} V_{\text{Ni}} \quad (2)$$

$$\sigma_{\text{Ni}}/\sigma_c = E_{\text{Ni}} V_{\text{Ni}} / Ec Vc \quad (3)$$

where E is Young's modulus and V the volume fraction.

By substitution in (2) and (3) we obtain:

(Method 2)

$$\sigma_c = 287000 \text{ psi } (1970 \text{ MN/m}^2)$$

Hence it is reasonable to consider these two value as the limits after the 1000° C/24 h treatment. This factor is important in assessing the reduction in strength produced by an 1100°C/24 h anneal. In this case limits of 170000 to 185000 (1170 to 1270 MN/m^2) psi were obtained, which as shown in fig. 1 are very near to the fracture strength measured on carbon fibres with a "thin" nickel coating after a similar anneal (193000 psi) (1330 MN/m^2.

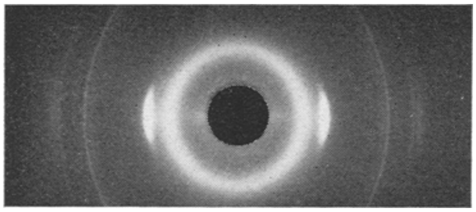


Figure 2 X-ray diffraction pattern from an aligned bundle of as-received carbon fibres.

3.2. X-ray Diffraction

A characteristic X-ray powder pattern taken from an aligned bundle of about 1000 as-received carbon fibres is shown in fig. 2. The important reflection is the arc from the (002) basal planes (a faint arc from the (004) planes can also be seen) which results from the preferred orientation of these planes along the carbon fibre axis. The angular spread of the arc (approximately 10%) is due to small deviations about the fibre axis and any misorientation of the individual fibres in the specimen holder. X-ray powder patterns were also taken after all the anneals of the uncoated and nickel coated carbon fibres, but no significant change in the as-received fibre pattern shown in fig. 2 was noted. In particular the (002) arc was maintained, indicating the existence of preferred orientation and the corresponding absence of recrystallisation.

3.3. Electron Microscopy

The structure of the carbon fibres was investigated on a finer scale by vibrating some fibres ultrasonically and examining the detached surface fragments using transmission electron microscopy. A typical fragment from an as-received fibre which is shown in fig. 3, reveals the (002) plane alignment and the turbostratic arrangement previously reported [4]. Fragments were also obtained from the annealed nickel-coated carbon fibres. However, although the amount of material which became detached after treatment > 1050°C increased considerably there was no change in the structure (or the diffraction patterns) of the individual fragments, as shown in fig. 4 (after 1080°C/24 h) and fig. 5 (after 1170°C/24h). Therefore, these results are in agreement with the X-ray findings that there is no recrystallisation of the carbon fibres for the conditions investigated.

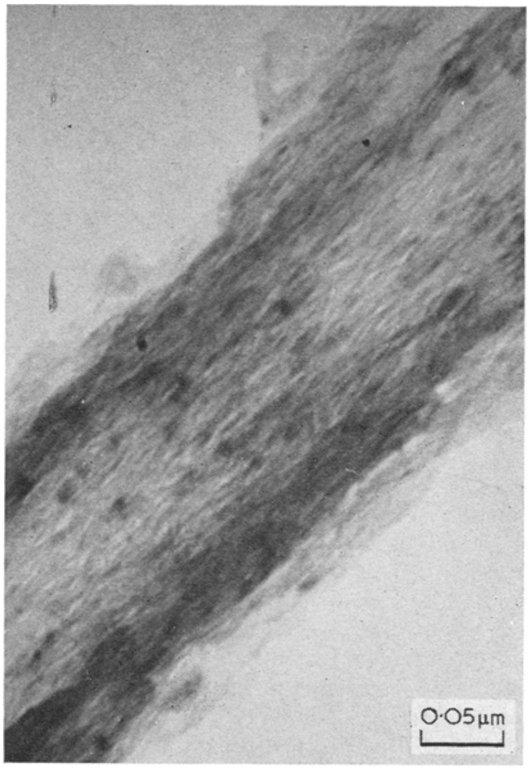


Figure 3 Electron micrograph of a detached fragment of an as-received carbon fibre.

Surface replicas prepared from nickel-coated (approximately 400 Å) carbon fibres were also examined in the electron microscope. It was found that after anneals above 800°C the nickel coating broke up into a series of spheroidal particles. As a result the replica technique was utilised to determine the time required to form an effective bond between the carbon fibre and the nickel spheroids. A series of replicas were prepared for various times at a given temperature. The time for adhesion was then established by the transition from almost complete detachement of the nickel spheroids by the replication process to almost no nickel spheroids being present in the replica. This process is illustrated in figs. 6a, b, and c, which show replicas taken after 15 min, 30 min, and 1 h at 1100°C respectively. It can be seen that there are many detached nickel sphe-

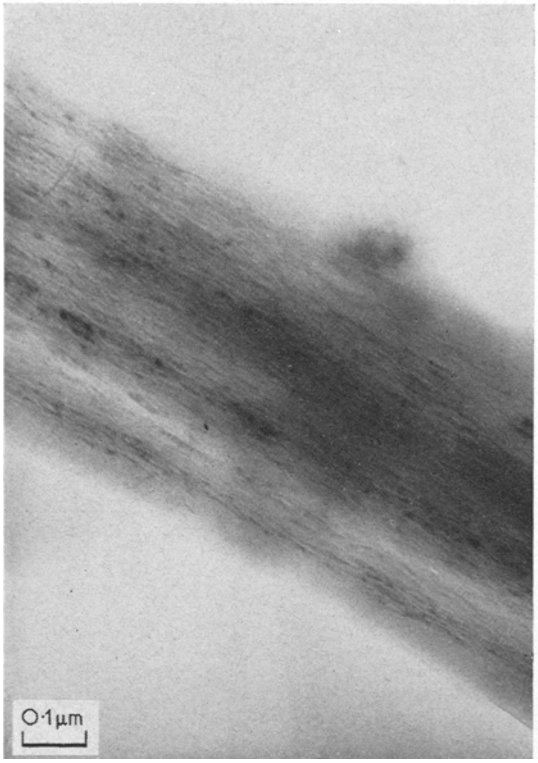


Figure 4 Electron micrograph of a nickel-coated carbon fibre, annealed at 1080° C/24 h.

roids in figs. 6a and b, while only a few are present in fig. 6c. In this manner times for adhesion of ~ 1, ~ 2, ~ 5 and ~ 24 h were established respectively for temperatures of 1100, 1080, 1050 and 1000° C.

Replicas prepared from nickel-coated fibres after adhesion had been developed, revealed that the nickel spheroids tended to spread along the surface and create a continuous nickel coating. This effect is shown in fig. 6d (1100° C/16 h) and fig. 6e (1100° C/24 h) which should be compared with figs. 6a, b, and c.

4. Discussion

The room temperature fracture strength of the uncoated carbon fibres was not affected by annealing treatments below 1100° C, if a 10^{-6} torr vacuum was maintained. However, with a $10^{-5} - 10^{-4}$ torr vacuum, or sometimes under an argon atmosphere, a variable reduction in the fracture strength was measured after anneals at temperatures as low as 600° C. Under all these conditions, liberation of dissolved or adsorbed gas from the carbon fibres occurred during the "warm-up" to the annealing temperature. Thus the reduction in strength in "low" vacuum (or argon) probably resulted from an oxygen concentration in the furnace atmosphere which was sufficient for reaction with the carbon to form carbon monoxide. These results emphasise that, in an investigation of the effects of nickel coating on the fracture strength of carbon fibres it is essential to maintain a 10^{-6} torr vacuum in order to avoid the complication of fibre-atmosphere reactions.

It was found that a 400 Å-thick nickel coating on the carbon fibre had no effect (i.e. the mean value was within one standard deviation of the as-received condition) on the fracture strength after anneals up to 1000° C for 24 h, but a small reduction was obtained after treatments at 1080° C for 24 h, with a further reduction after treatment at 1100° C for 24 h. (After higher temperature anneals (1130 to 1200° C), the fracture strength decreased markedly, but in this range some breakdown also resulted from the

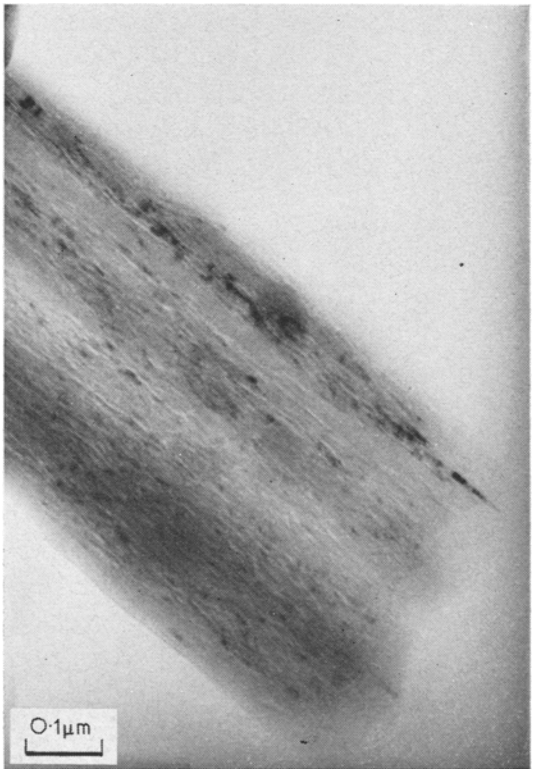
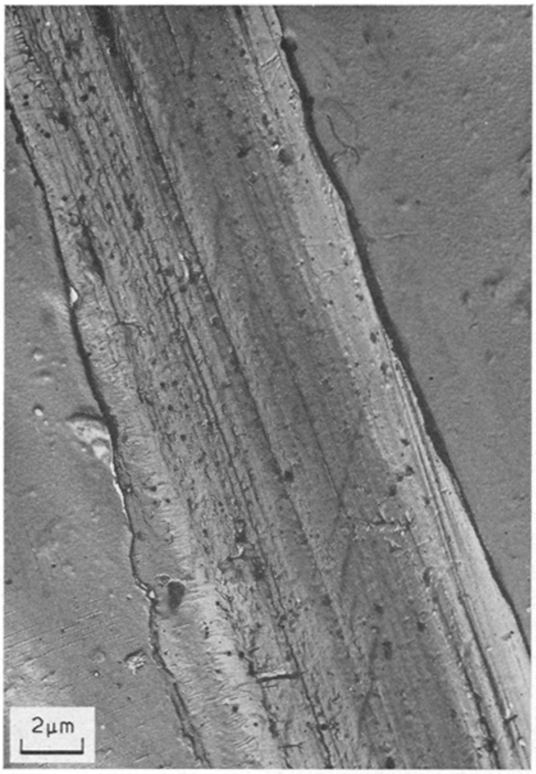
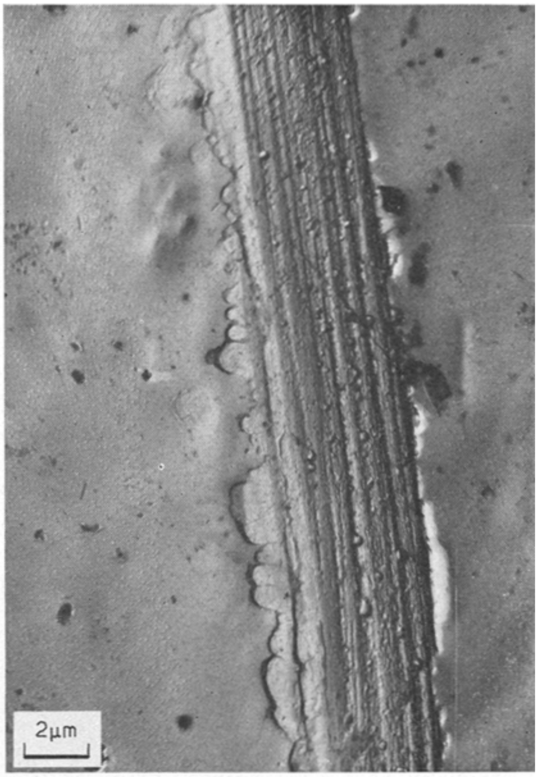


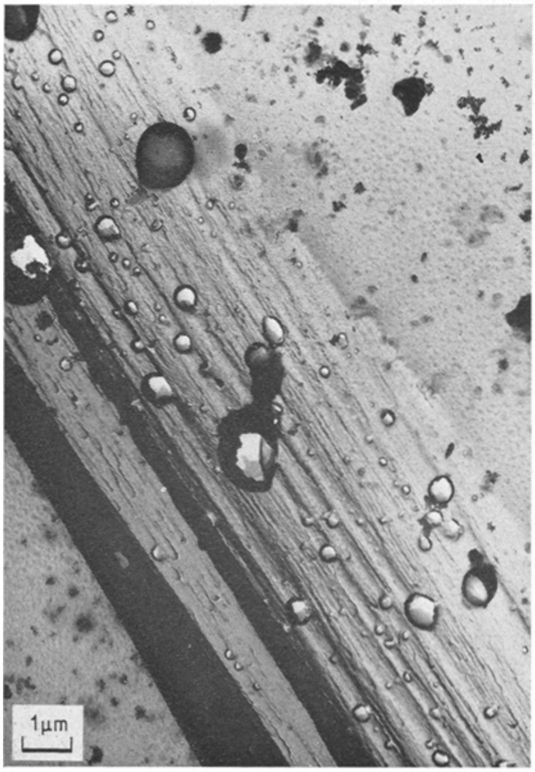
Figure 5 Electron micrograph of nickel-coated carbon fibre, annealed at 1170° C/24 h.



(6a)



(6b)



(6c)

(6d)

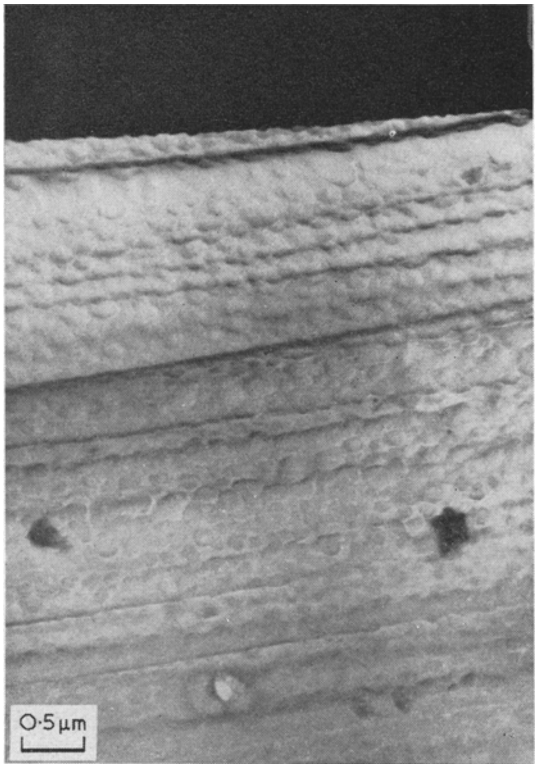


Figure 6 Surface replicas for nickel-coated carbon fibres annealed at 1100°C for (a) 15 min (b) 30 min (c) 1 h (d) 16 h (e) 24 h.

carbon-atmosphere reaction.) As the fracture strengths of the coated fibres are smaller than those measured for the uncoated fibres after equivalent treatments in the 1000 to 1100°C range, it is concluded that the reduction in strength is produced by the nickel coating. It is reasonable to conclude that the reduction in strength is a consequence of the dissolution of carbon atoms in the nickel coating, as carbon has an appreciable solubility in nickel in the 1000 to 1100°C temperature range [5] (~ 1.2 to 2.0 at. %).

However, calculation of the rate for the diffusion of carbon into nickel suggests shorter times (t) for saturation than those measured experimentally for a reduction in strength. For example assuming a slab configuration, we have

$$t = l^2/D \quad (l = \text{coating thickness})$$

at 1000°C, as $D \sim 10^{-8}$ cm^2/sec

$$l = 4 \times 10^{-6}\ \text{cm} \quad (D = \text{diffusion coefficient})$$

$$\text{and } t \ll 1\ \text{sec}$$

whereas for a reduction in fracture strength, we have

$$t > 24\ \text{h}$$

This suggests that the rate-controlling process is not the diffusion of carbon into nickel, but is the establishment of a suitable carbon-nickel interface. Such a concept appears to be confirmed by the replica measurements of the times (t) required for carbon-nickel adhesion which varied from > 24 h at 1000°C to ~ 1 h at 1100°C. An estimate of the activation energy (Q) for the adhesion process may be derived from the rate equation.

$$\log \frac{1}{t} = \log K - \frac{Q}{RT} \tag{4}$$

where K represents a pre-exponential constant, R the gas constant and T absolute temperature. The data are shown plotted in fig. 7 and give an approximate activation energy of 110 kcal. mole^{-1}. This value may be compared with bond energies of 83 and 147 kcal. mole^{-1} quoted respectively for single and double carbon-carbon bonds. Hence it is possible that the rate-controlling process is the breaking of a carbon-carbon

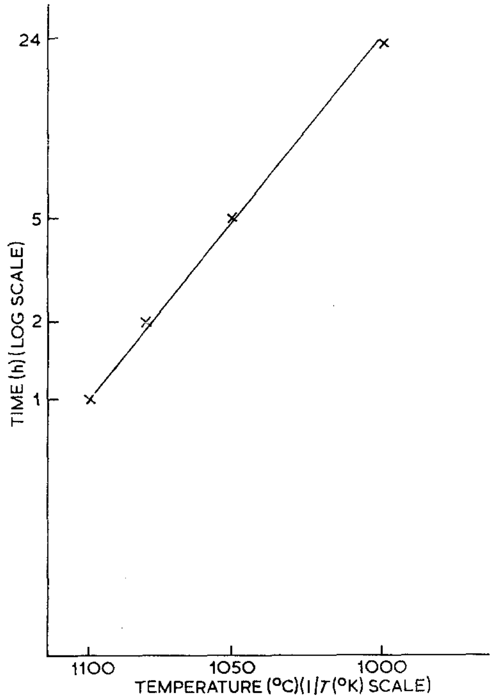


Figure 7 The effect of temperature (T) on the time (t) for C-Ni adhesion.

bond, which is required before diffusion of carbon into the nickel can occur.

During the time period prior to adhesion, the initially homogeneous nickel coating broke up into a series of spheroids. This effect, which is promoted by the attendant reduction in surface energy, has also been observed with thin coatings on sapphire whiskers [6]. As a result, when adhesion is established and carbon diffusion into the nickel begins, there is partial nickel coverage of the fibre surface and hence only local depletion of carbon. This situation changes with time as the nickel spheroids spread over the surface, presumably due to a surface tension reduction, and eventually a continuous coating is formed which then permits diffusion of carbon into nickel from all points on the fibre.

Spheroidisation and recombination of nickel coatings will only occur in relatively thin coatings. Hence it is important to establish whether a thicker nickel coating, which remains continuous at all times, has a similar effect on the fracture strength. In fact the values of fracture strength measured for carbon fibres with a 0.7 μm nickel coating (after treatments at 1000 and 1100° C for 24 h) were reasonably similar to those of the carbon fibres with the 400 Å coating. The particular annealing treatment chosen allowed two comparisons to be made. Firstly, after 1000° C for 24 h, the 400 Å coating was spheroidised, while the 0.7 μm coating was continuous and, secondly, after 1100°C for 24 h, both coatings were continuous. Hence the similarity of the experimental measurements suggests that the carbon fibre fracture strength is independent of both the area of contact and the thickness of the nickel coating.

This conclusion suggests that it is reasonable to compare the present results on nickel-coated carbon fibres with Jackson and Marjoram's [2, 3] findings on graphitised carbon fibre-nickel microcomposites. There are two major differences between the results. The first difference is the carbon fibre recrystallisation noted in the microcomposites, but not observed in the nickel-coated carbon fibres. Recrystallisation was attributed to the diffusion, dissolution and precipitation of nickel within the carbon fibre, but its complete absence in the present experiments with evaporated nickel suggests that the process may be promoted by the impurities intrinsic to electroplated nickel. The second difference is the larger reduction in strength, measured in the microcomposites for any given temperature/time treatment. At first sight, it would appear that this results simply from recrystallisation. However, there is an area of overlap between the results as after a 1000° C/24 h treatment a reduction in strength was measured in the microcomposite, but there was no corresponding increase in crystallite size [3]. Therefore it is possible that in the absence of recrystallisation, a similar mechanism could apply in both the nickel-coated carbon fibres and microcomposites. The larger reduction in strength in the microcomposites could then be attributed to the presence of C-"impurity atom" bonds (e.g. C-S, bond energy 62 kcal. mole^{-1}) which facilitate the establishment of a carbon-nickel interface.

5. Conclusions

(1) The room temperature fracture strength of uncoated Type I carbon fibres is not affected by anneals up to 1100°C for 24 h in a 10^{-6} torr vacuum.

(2) An evaporated coating of pure nickel produces a significant reduction in the room temperature fracture strength after a treatment at 1080°C for 24 h. The reduction in strength becomes greater with an increase in temperature, or time at a given temperature but is almost independent of the thickness of the coating (to $\sim$ 0.7 μm).

(3) The reduction in strength is not related to recrystallisation of the fibre, but associated with the dissolution of carbon in the nickel coating. The rate-controlling step in this process appears to be the establishment of a carbon-nickel interface, with an activation energy for adhesion of $\sim$ 110 kcal. mole^{-1}.

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