JOURNAL OF MATERIALS SCIENCE 28 (1993) 760–768

Control of interfaces in Al–C fibre composites

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The interface of Al–C fibre composite was modified by coating a silver layer on the surface of carbon fibres prior to making composites, in an attempt to improve the wettability between molten aluminium and carbon fibres during infiltration. An electroless plating technique was adopted and perfected to provide a homogeneous silver coating on the carbon fibre surface. Al–C fibre composites were prepared using a liquid infiltration technique in a vacuum. It was found that silver coating promoted the wetting between aluminium and carbon fibres, particularly with polyacrylonitrile-base carbon fibres. However, due to rapid dissolution of silver in molten aluminium, it was believed that the improved infiltration was not due to the wetting behaviour between molten aluminium and silver. The cleaning of the fibre surface and the preservation of the cleaned carbon surface with silver coating was considered to be the prime reason for the improved wettability. Interfacial reactions between aluminium and carbon fibres were observed. Amorphous carbon was found to react more with aluminium than graphitic carbon. This is believed to be because of the inertness of the graphitic basal planes.

1. Introduction

Carbon–aluminium composites have been an area of considerable interest over the last two decades primarily for their high specific strength, high-temperature applications and excellent thermal and electrical conductivity. They have many applications in aircraft, missiles, rocket propulsion systems, spacecraft and electrical machinery [1].

The major problems associated with the processing of Al–C composites by the liquid infiltration technique are that aluminium wets carbon only at temperatures around 1000 °C [2] and that the wetting causes degradation of the fibres, due to the reaction between carbon and aluminium forming aluminium carbide at the interface, which reduces the strength of the composite [3, 4]. One of the common ways to offset the above problem is to coat the fibres using techniques like electroplating, electroless plating and chemical vapour deposition. The primary purpose of the coating is to form a diffusion barrier against fibre–matrix reaction and to promote wetting.

Carbon fibres are generally coated with metallic or ceramic layers. Silver coating on carbon fibres has been seen to enhance the wetting characteristics of aluminium [5] and prevent contamination of fibre surface during processing. The formation of aluminium carbide, which degrades the fibre, during the fabrication process, is however one of the major concerns of such a process. It is the purpose of this paper to study the effect of silver coating on the formation of reaction products at the metal–fibre interface during the fabrication of Al–C composites.

2. Experimental procedure

2.1. Coating of fibres

Three types of fibre with varying degrees of graphitization, including polyacrylonitrile (PAN) base carbon fibres, chemical vapour deposition (CVD) annealed graphite fibres and pitch-base graphite fibres having an average diameter of 10 μm, were employed in this study. The fibres were coated with a layer of silver using a technique similar to that discussed by Cheng *et al.* [6]. This coating technique involves coating the fibres with copper and silver in sequence. Copper was coated on the fibres by employing an electroless deposition technique as given below:

(i) Removal of epoxy coating by immersion in acetone for 15 min.

(ii) Etching of the fibres by immersion in 68% HNO_3 for 15 min.

(iii) Sensitization in an aqueous solution of 10 $kg\,m^{-3}$ $SnCl_2$ and $4 \times 10^{-2}\,m^3\,m^{-3}$ of 38% HCl for 20 min.

(iv) Catalysis in an aqueous solution of 0.25 $kg\,m^{-3}$ $PdCl_2$ and $2.5 \times 10^{-3}\,m^3\,m^{-3}$ of 38% HCl for 5 min.

(v) Deposition of copper for 10 min in a solution consisting of 10 $kg\,m^{-3}$ $CuSO_4$, 25 $kg\,m^{-3}$ $KNaC_4H_4O_6 \cdot 4H_2O$ (sodium potassium tartarate), 15 $kg\,m^{-3}$ NaOH and $5 \times 10^{-3}\,m^3\,m^{-3}$ of HCHO (formaldehyde). This solution was prepared every time plating was to be done and formaldehyde was introduced just before the plating to prevent deposition of copper on to the container.

Silver was deposited on the copper-coated fibres by soaking for 15 min in aqueous solutions consisting of

(a) 57.69 $kg\,m^{-3}$ $AgNO_3$, 38.46 $kg\,m^{-3}$ NaOH, 0.833 $m^3\,m^{-3}$ NH_4OH and

(b) 40 $kg\,m^{-3}$ $C_6H_{12}O_6$ (glucose), 4 $kg\,m^{-3}$ $H_2C_4H_4O_6$ (tartaric acid) 0.1 $m^3\,m^{-3}$ C_2H_5OH (ethanol).

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The fibres were rinsed with distilled water after each treatment. Modifications, discussed elsewhere [7], were made to the process described by Cheng *et al.* [6] by setting the exact amount of formaldehyde and NH_4OH used and optimizing the sequence of the process. The silver-coated fibres were then treated with potassium hexafluoro zirconate, a flux used in light-metal foundries.

2.2. Liquid metal infiltration

The coated fibres were stacked in the lower half of a graphite crucible (Fig. 1) and infiltrated with 6063 aluminium in a vacuum of 1.3×10^{-7} MPa at various temperatures and times. The experimental set-up is shown in Fig. 2. In all cases, argon was used to backfill the reaction tube after 45 min to reduce the reaction. After the experiment, the crucible was cooled naturally in the furnace to room temperature.

The only known attempt to make Al–C composites by applying a silver coating on the fibres is the work done by Sara [5]. However, in that case the silver coating, deposited by electroplating, was not homogeneous and so complete infiltration was not obtained.

2.3. Examinations and testing

SEM and energy-dispersive X-ray (EDX) analysis were used to examine the matrix–fibre interface in the composite. The thickness of the silver layer deposited was monitored by SEM. The degree of graphitization in the fibres was determined by X-ray diffraction techniques. The tensile strengths of composites were measured by testing both round and rectangular samples using an Instron tensile testing machine.

3. Results

Composites of 6063 aluminium with reinforcements of CVD carbon fibres, pitch-base carbon fibres and PAN-base carbon fibres were made. The composite interfaces observed are presented below. For each type of reinforcement, both with and without silver coating on fibres, composites were prepared.

3.1. Interface in Al–CVD carbon fibre composite

3.1.1. With silver coating

SEM examination of the interface revealed good wetting of the fibres by molten aluminium (Figs 3 and 4). The interface was a chemical bond consisting of reaction products. EDX analysis of the interface showed the presence of aluminium and zirconium. Silver, however, was not observed at the interface. In fact, it was estimated that the silver coating would have been dissolved completely in less than a few minutes. The presence of zirconium at the interface could be from the reaction of the flux (K_2ZrF_6) with aluminium forming Al_3Zr as suggested by Rocher *et al.* [8]. Results from EDX analysis of NaOH-etched composites appeared similar to those before etching and did not reveal any silver. Composites were fabricated at various temperatures and times. The reaction zone in the case of high temperatures and short time were almost identical to that for low temperatures and long time. Composites fabricated at 1020 °C for 60 min and at 1100 °C for 30 min are shown in Fig. 4.

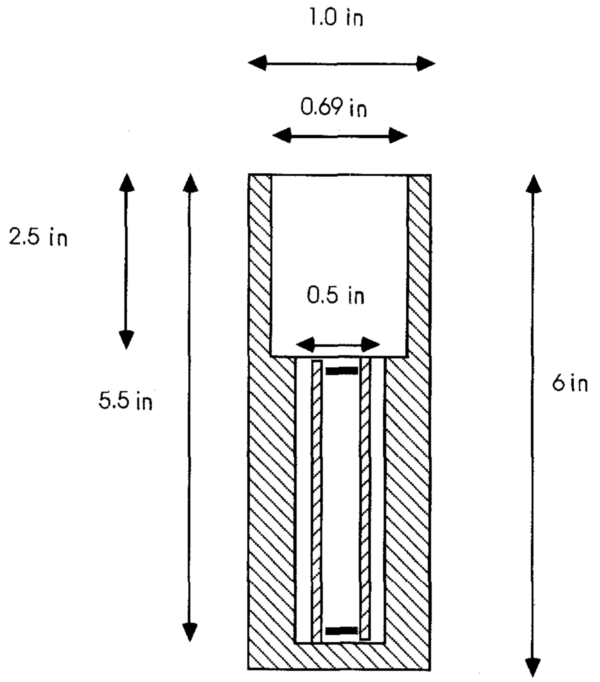

Figure 1 Sketch of graphite crucible used. 1″ (1 in.) = 25.4 mm.

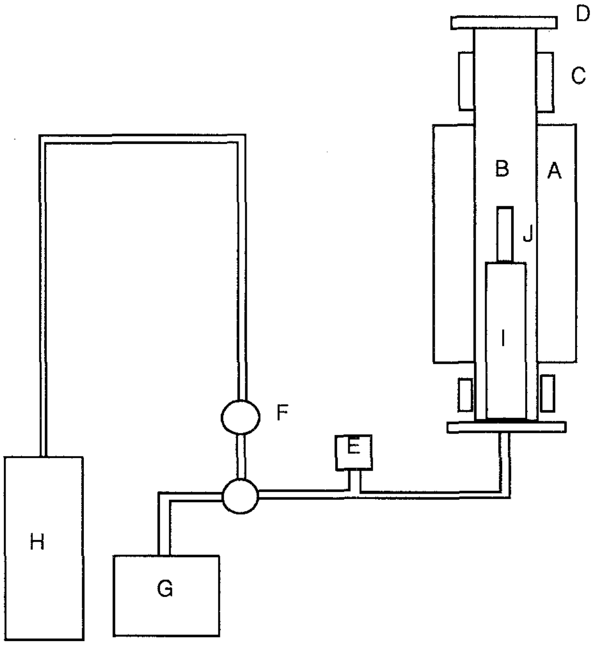

Figure 2 Schematic representation of the experimental set-up: (A) furnace, (B) reaction tube, (C) cooling system, (D) end cap, (E) thermocouple gauge, (F) valve, (G) pump, (H) argon cylinder, (I) platform and (J) crucible.

3.1.2. Without silver coating

The wetting characteristics without silver coating were similar to those with silver coating only as far as distribution and EDX analysis were concerned. The

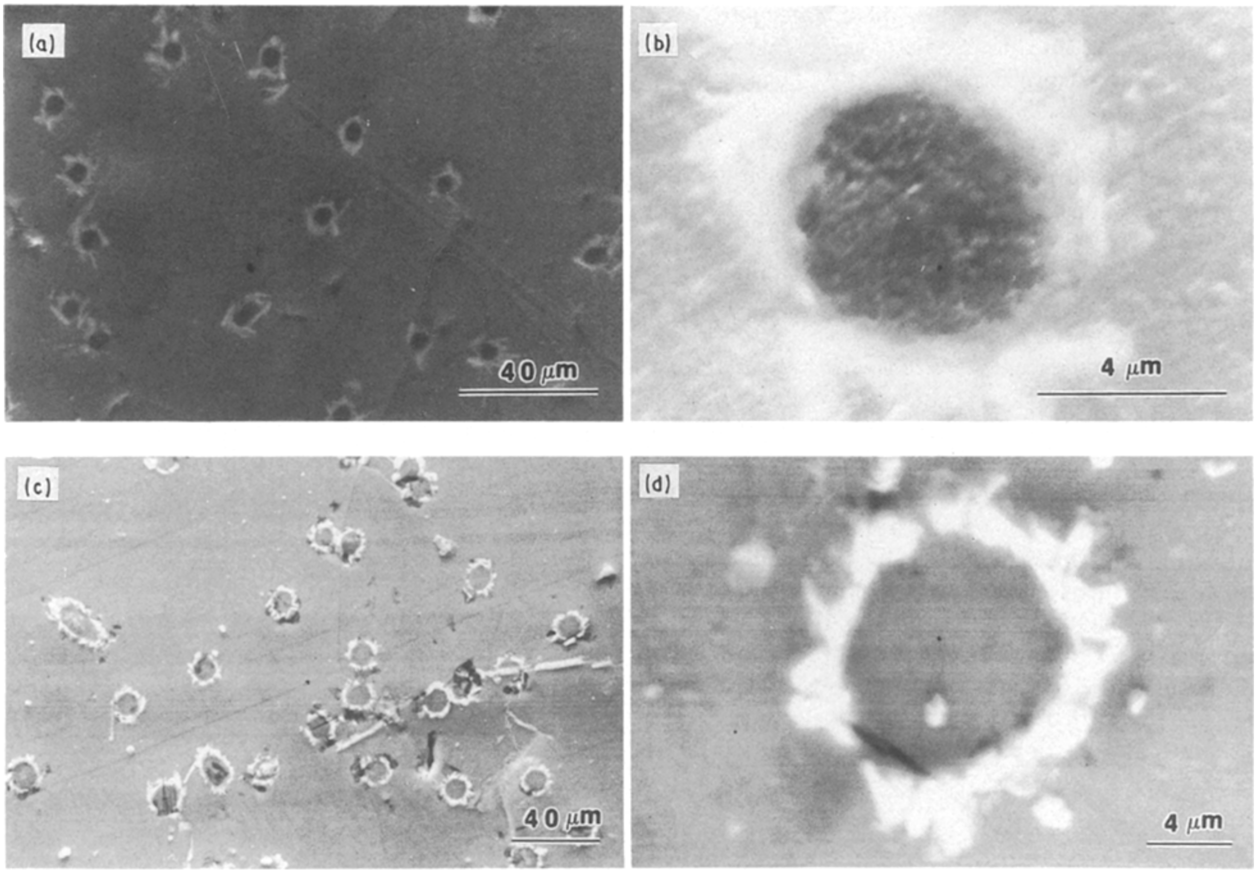

Figure 3 Aluminium–CVD fibre composite fabricated at 1000 °C for 120 min: (a, b) with silver coating, (c, d) without silver coating.

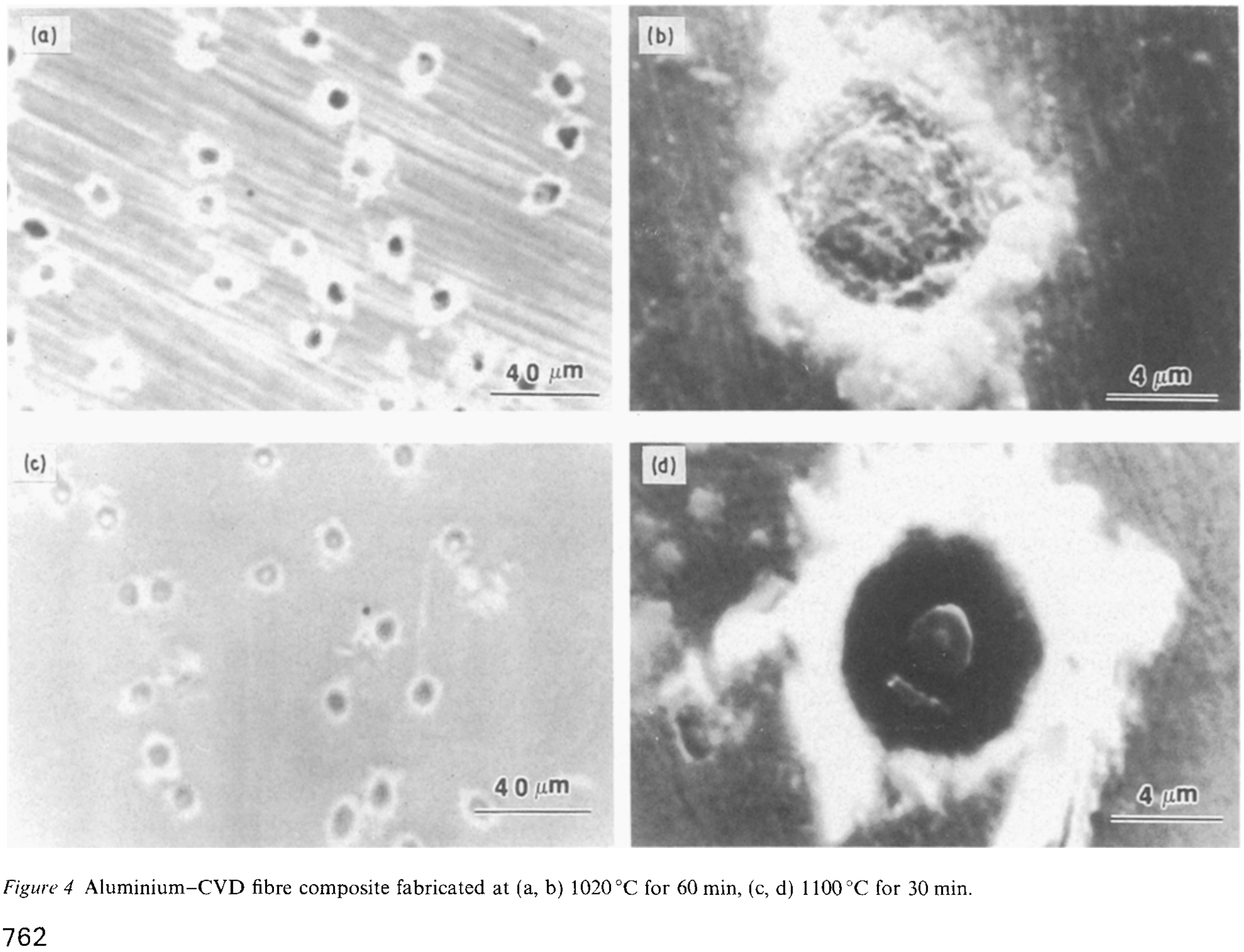

Figure 4 Aluminium–CVD fibre composite fabricated at (a, b) 1020 °C for 60 min, (c, d) 1100 °C for 30 min.

reaction products at the interface, as in the previous case, analysed by EDX, showed the presence of aluminium and zirconium. However, the reaction zone was slightly reduced when a silver coating was applied (Fig. 3). The average thickness of the reaction zone was observed to be about 1.5 μm when carbon fibres were coated with silver and about 2.0 μm without coating under the processing condition of 1000 °C and 120 min. The reaction zone without silver coating was discontinuous when observed at high magnification.

3.2. Interface in Al–pitch-base carbon fibre composite

3.2.1. With silver coating

Cross-sections of the fabricated composites (Fig. 5) show a good distribution of the fibres. Micrographs at higher magnification show a thin reaction zone which appears to be discontinuous. The reaction zone is not uniform and appears to be faceted at some areas on the fibre surface.

3.2.2. Without silver coating

As with CVD fibres, composites could also be produced using pitch-base fibres without the silver coating. The reaction products are not uniform in all directions perpendicular to the fibre axis. The thickness of the reaction zone is nearly the same as that of CVD fibre composites under similar conditions of fabrication. It is about 1.5 μm with silver coating and about 2.0 μm without silver coating.

3.3 Interface in Al–PAN-base carbon fibre composite

3.3.1. With silver coating

Composites fabricated at temperatures of 980 to 1020 °C and a processing time of 60 to 120 min are shown in Fig. 6. It can be seen that the layer of reaction zone of Al_4C_3 at lower temperatures and holding time is discontinuous. However, at higher temperatures and time the reaction zone appears to be continuous. This is probably because aluminium carbide forms as platelets on the fibre surface. These platelets grow with time and temperature until they impinge upon each other, giving the layer an appearance of continuity, as suggested by Khan [4]. Also the reaction zone is thinner at lower temperatures and time. The effect of argon backfilling to reduce the reaction is quite apparent from Fig. 7. The composites produced without argon backfilling had fibres excessively reacted, whereas with argon backfilling the reaction products were much thinner. Eustathopoulos *et al.* [2] had seen that the contact angles of Al on carbon were 77 and 110° at 1000 °C under a vacuum of 10^{-6} torr and in argon, respectively. The lower contact angle in a vacuum than that in argon could account for the greater extent of the reaction in a vacuum.

3.3.2. Without silver coating

Aluminium-matrix composites with PAN-base carbon fibre reinforcement could not be fabricated without the silver coating because the wettability of aluminium on PAN-base fibres was poor. It appears that

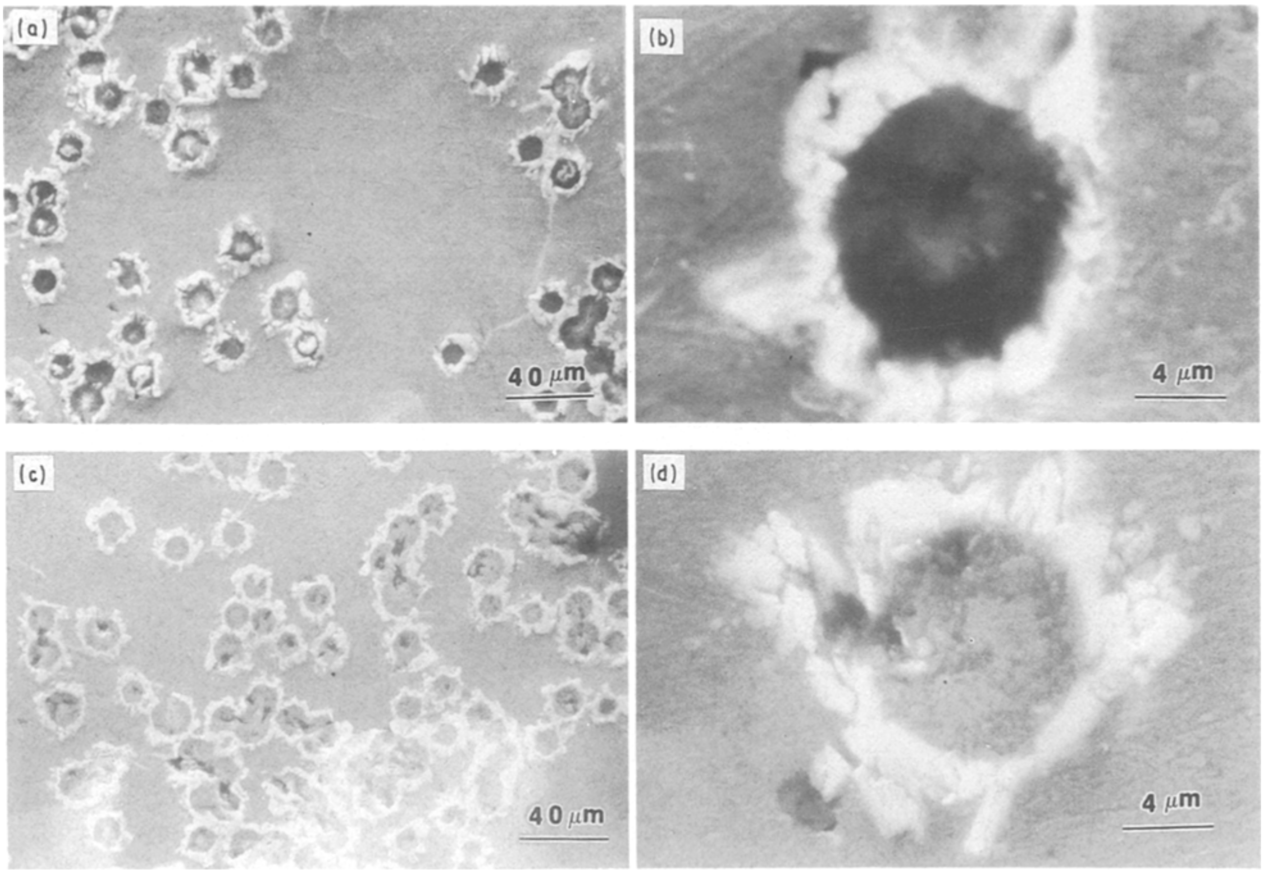

Figure 5 Pitch-base fibre–aluminium composite fabricated at 1000 °C for 120 min: (a, b) with silver coating, (c, d) without silver coating.

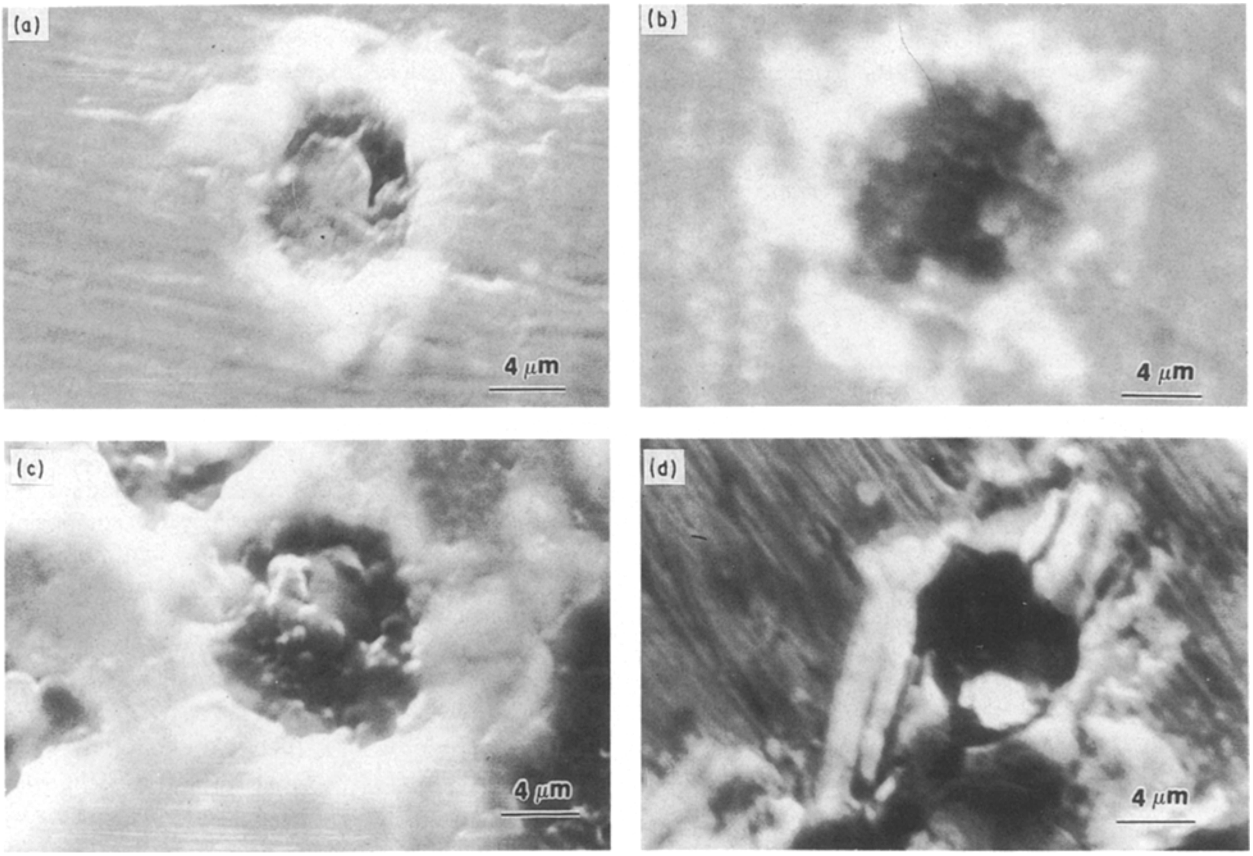

Figure 6 Aluminium–PAN-base fibre composite fabricated at (a) 1000 °C for 120 min. (b) 1000 °C for 60 min, (c) 1020 °C for 90 min, (d) 980 °C for 90 min.

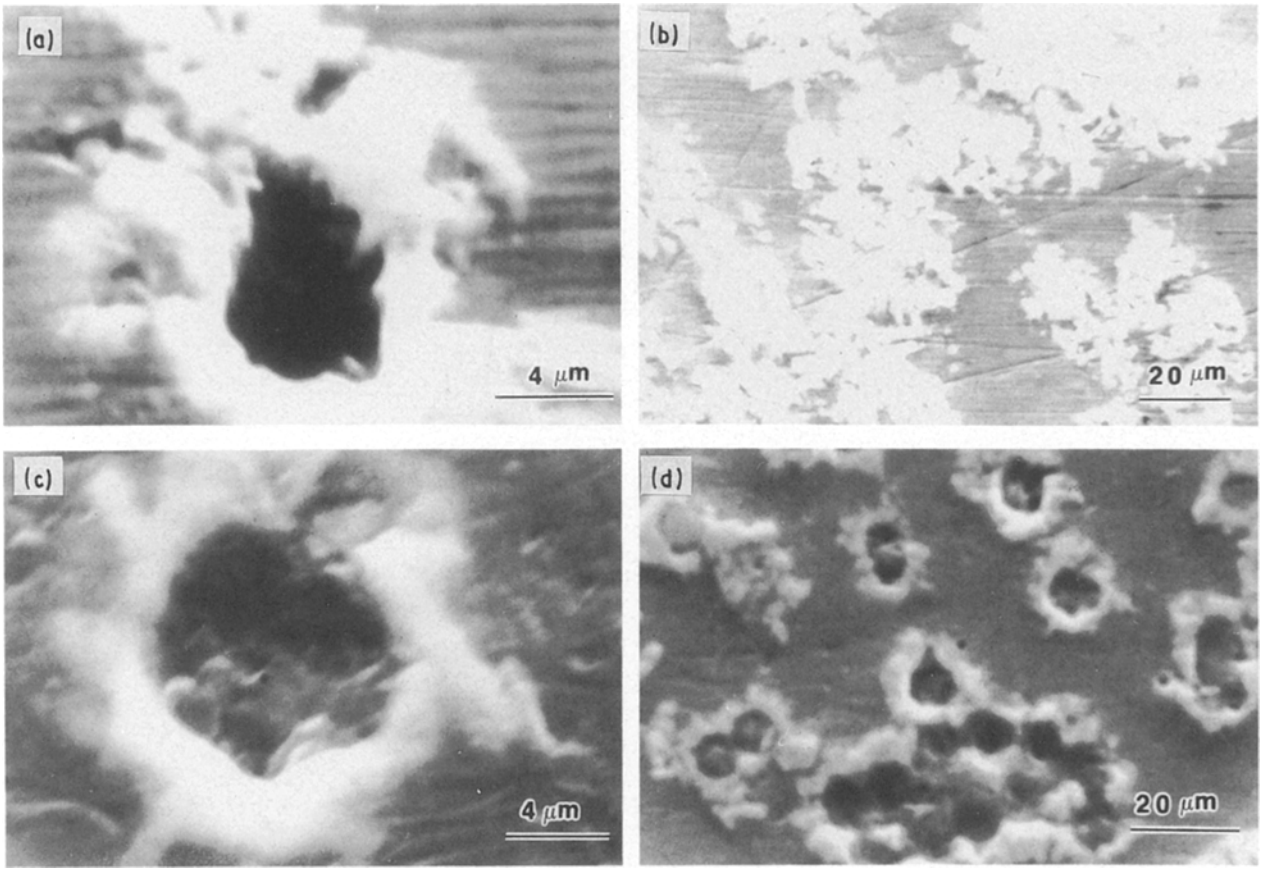

Figure 7 Aluminium–PAN-base fibre composite fabricated at 1000 °C for 120 min: (a, b) without argon backfilling, (c, d) with argon backfilling after 45 min.

with only amorphous carbon in PAN fibres, the wetting of molten aluminium on fibres was poor.

4. Discussion

4.1. Effect of silver coating on interfacial reaction

Silver coating plays a significant role in the fabrication of both carbon and graphite fibre composites. In the case of carbon fibres, the coating was necessary for infiltration and in the case of graphite fibres, the coating decreased the interfacial reaction slightly.

Although at the operating temperature of 1000 °C both silver and aluminium exist in the liquid form, the penetration of aluminium into the lower half of the crucible may start near 900 °C. Thus, as the liquid aluminium front proceeds through the silver-coated fibre bundle, silver will be quickly dissolved into bulk aluminium. Assuming that the diffusion coefficient of silver in liquid aluminium is of the order of 10^{-5} $cm^2 s^{-1}$, the dissolution of 1 μm of silver coating takes only a very short time. Also, silver was not observed at the interface during EDX analysis after fabrication of the composite, thus suggesting that aluminium could have completely dissolved the silver. In fact, using a rapid heating furnace, we have found that a silver foil of 0.125 mm thickness was dissolved in molten aluminium at 800 °C within 90 s. In other words, the silver coating could not have acted as a diffusion barrier. The primary function of the coating might have been to clean and protect the fibre from contamination during processing.

Since the silver is initially on the fibre, at the beginning of infiltration the solution immediately next to the fibre will be rich in silver. The whole solution will ultimately get homogenized because the processing time is relatively long. A process which goes on simultaneously is the formation of aluminium carbide from the reaction of aluminium and carbon. Two separate mechanisms are likely to have occurred: (i) diffusion of aluminium from the aluminium-rich solution to the carbide–metal interface through the silver-rich area, and (ii) diffusion of carbon across the Al_4C_3 barrier to the carbide–metal interface. The diffusion of aluminium can also occur through the carbide layer to carbon to form aluminium carbide. Khan [4] suggested that since carbon has a lower atomic mass, the diffusion of carbon would be faster through the reaction zone. The diffusion of aluminium which is in the liquid form through liquid alloy is relatively faster than that of carbon, which has to diffuse through solid Al_4C_3. Thus the rate-controlling step has to be the diffusion of carbon through the carbide layer.

In the case of PAN-base carbon fibres, the necessity of silver coating for aluminium infiltration could be due to the enhancement of the wetting characteristics of otherwise non-wetting carbon fibre. The presence of silver, however, was not necessary for graphite fibres which have better wetting characteristics than carbon fibres. The way silver helps to reduce aluminium carbide formation in pitch and CVD carbon fibres is not obvious. The decrease in reaction zone thickness is from about 2.0 μm without coating to about 1.5 μm with coating. One of the possible explanations can be that transfer of aluminium through the silver-rich zone may not be as easy as it appears.

4.2. Effect of degree of graphitization on interfacial reaction

The reactions observed in the case of PAN base carbon fibres are more extensive than in the case of either CVD or pitch-base carbon fibres. The size of the reaction zone for 1000 °C and 120 min holding is about 3 μm in the case of PAN and about 1.5 μm in the case of both CVD and pitch. The degree of graphitization of the fibres, calculated on a relative scale with pure graphite and determined, by X-ray diffraction (Figs 8 to 11), gave 96% for CVD fibres, 66% for pitch-base fibres and 0% for PAN-base fibres. The basal planes in graphite fibres are relatively unreactive as compared to the basal edges, so the nucleation of Al_4C_3 should occur on the basal edges. Once a layer of Al_4C_3 is formed on basal plane edges, further reaction can occur either by the reaction of the inactive basal planes or by the diffusion of carbon through the Al_4C_3 layer on the basal edges. Thus the formation of aluminium carbide, primarily caused by carbon diffusion [4], will be greater in the case of amorphous carbon than graphite. Kohara and Muto [9] suggested that pitch-base fibres are less degraded by molten aluminium than PAN-base fibres. Kitamura [10] indicated that high-modulus PAN-base fibres were less degraded than high-strength PAN-base fibres. This study shows that the degradation of the PAN-base fibres, which are not graphitic, is greater than that of CVD and pitch-base graphitic fibres.

4.3. Effect of interfacial reaction on tensile strength

In a fibre-reinforced composite the volume fraction of the fibre reinforcement, f, has to be greater than the minimum amount of fibres for reinforcement ($f_{\min}$) to warrant the making of composites. Values of $f_{\min}$ for materials in this study were calculated by using the formula [11]

$$f_{\min} = \frac{\sigma_{\mathrm{mu}} - \sigma'_{\mathrm{m}}}{\sigma_{\mathrm{fu}} + \sigma_{\mathrm{mu}} - \sigma'_{\mathrm{m}}}$$

where σ_{mu} and σ_{fu} are the ultimate tensile strength (UTS) values for the metal and the fibre, respectively; σ'_{m} is the flow stress in the matrix at a strain equal to the fibre breaking stress.

The value of σ'_{m} was nearly equal to the UTS of aluminium. The value of $f_{\min}$ calculated from the above formula was very low. Thus, reinforcement of the aluminium matrix occurred with very little amount of carbon or graphite fibre reinforcement. This value of $f_{\min}$ was much lower than the amount of fibre used (about 7 vol % maximum).

Table I shows tensile test results for Al–C with CVD and pitch-base fibres. A substantial increase in tensile strength was observed in both CVD and pitch-base fibre-reinforced aluminium composites. The maximum value of tensile strength observed for CVD is

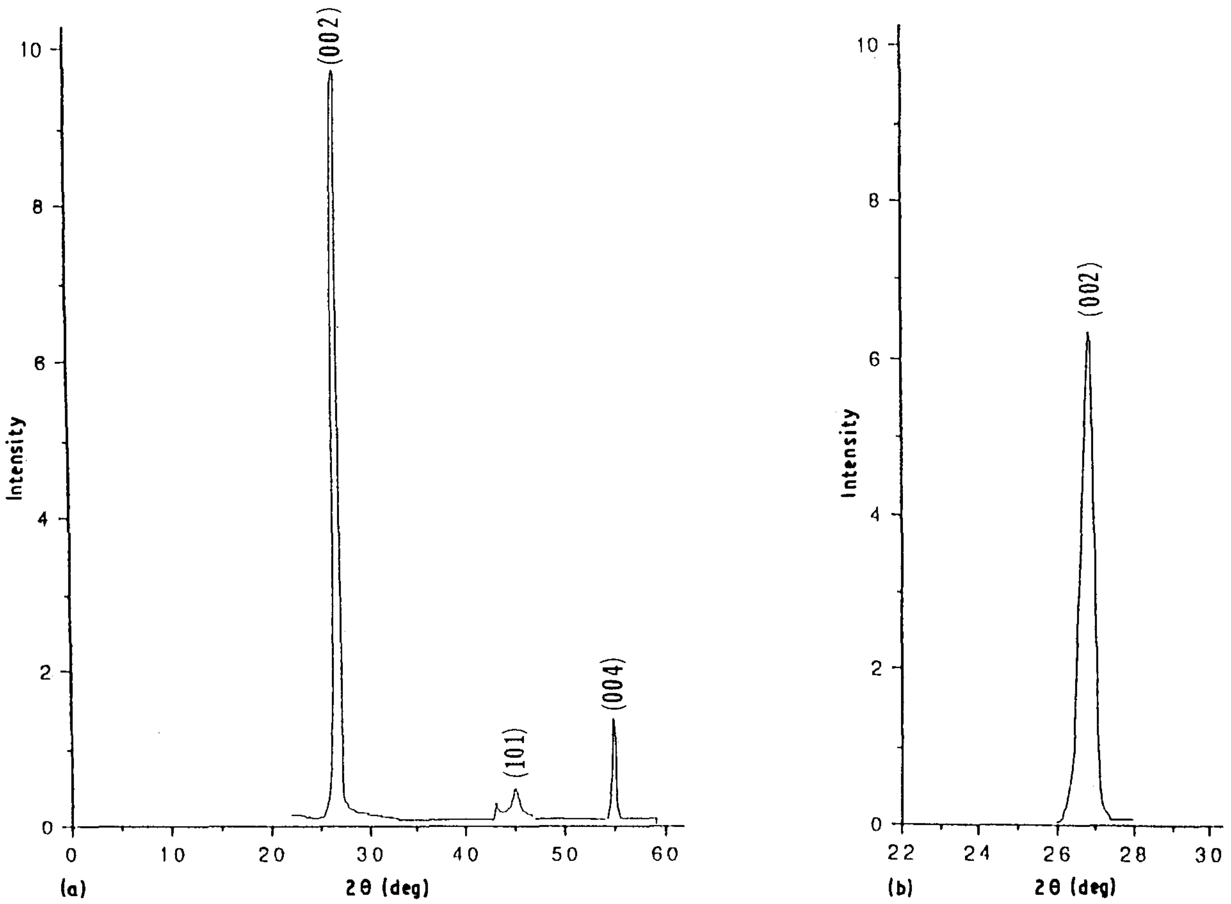

Figure 8 X-ray diffractograph of pure graphite (Cu-K_α, $\lambda = 0.154178$ nm): (a) scanned at 1° $\min^{-1}$ (range $= 3 \times 10^3$, time constant $= 0.3$); (b) scanned at 0.25° $\min^{-1}$ (range $= 10^4$, time constant $= 0.1$).

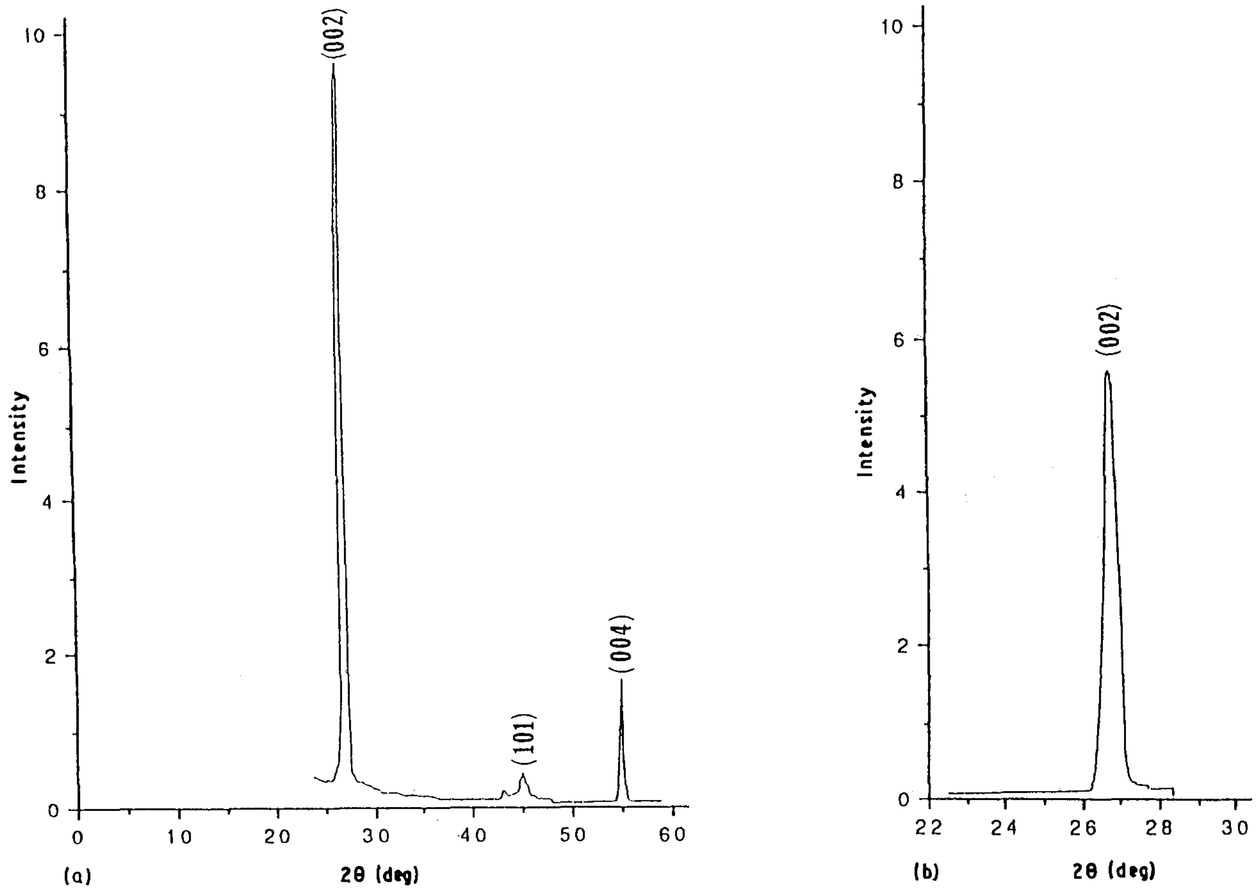

Figure 9 X-ray diffractograph of CVD graphite fibres (Cu-K_α, $\lambda = 0.154178$ nm: (a) scanned at 1° $\min^{-1}$ (range $= 3 \times 10^3$, time constant $= 0.3$); (b) scanned at 0.25° $\min^{-1}$ (range $= 10^4$, time constant $= 0.1$).

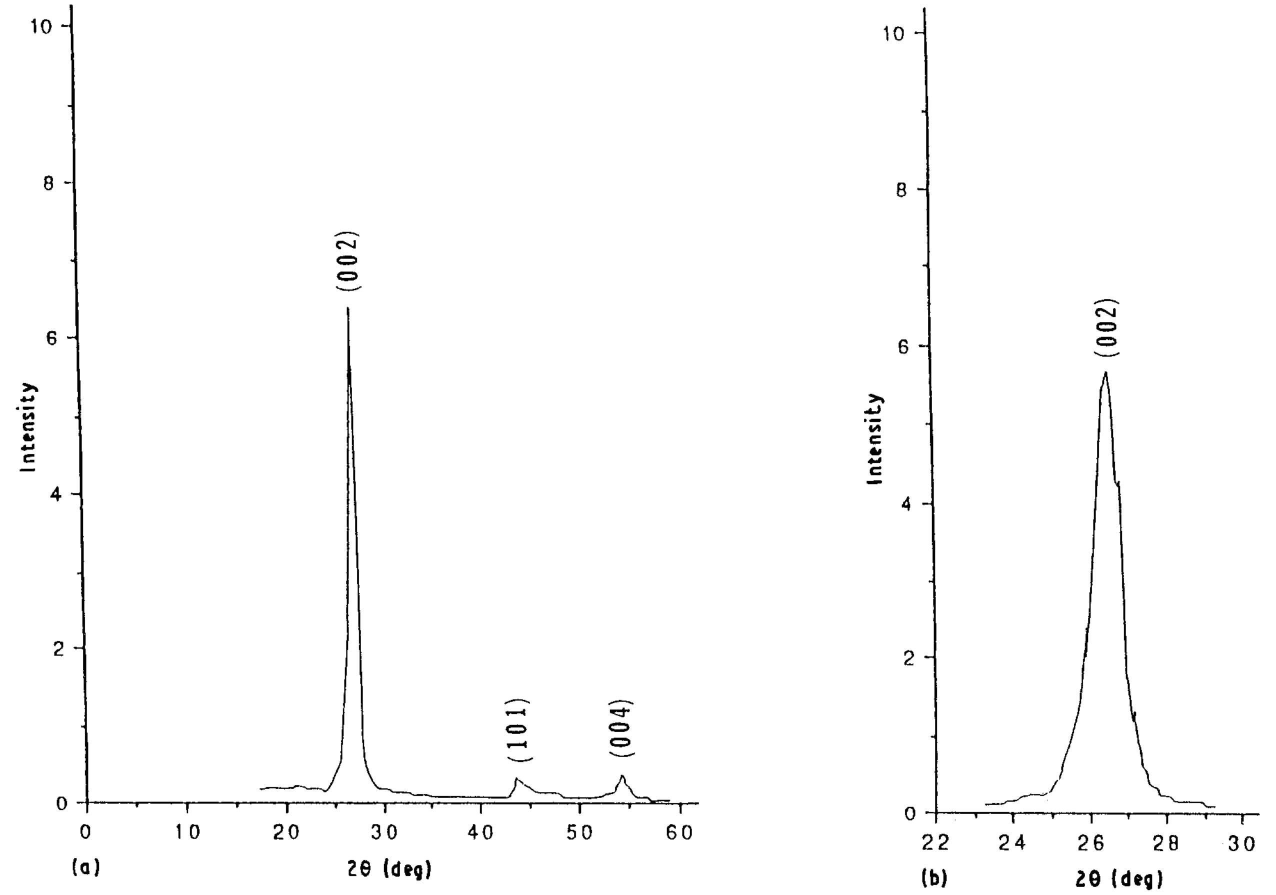

Figure 10 X-ray diffractograph of pitch-base graphite fibres (Cu-K_{α}, $\lambda = 0.154178$ nm: (a) scanned at 1° min^{-1} (range $= 3 \times 10^3$, time constant $= 0.3$); (b) scanned at 0.25° min^{-1} (range $= 3 \times 10^3$, time constant $= 0.3$).

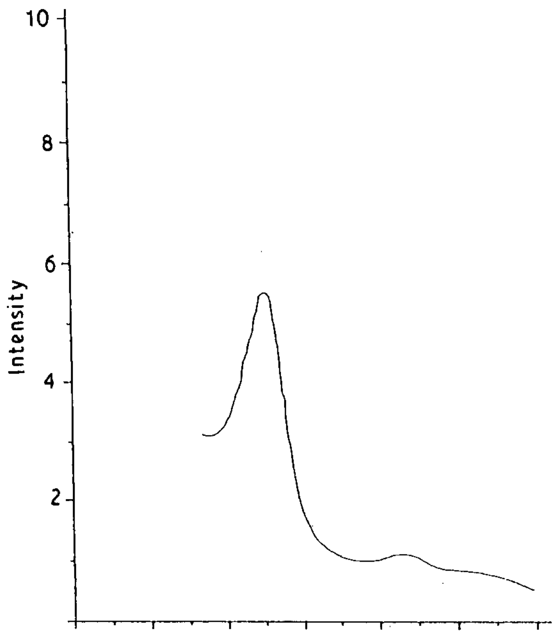

Figure 11 X-ray diffractograph of PAN-base carbon fibres (Cu-K_{α}, $\lambda = 0.154178$ nm); range $= 3 \times 10^3$, time constant $= 0.3$.

109 MPa. The rule of mixtures (ROM) strength for 5 vol % reinforcement is 168 MPa (UTS of CVD fibres = 2.07 GPa). The observed percentage of the ROM value (% ROM) is 65%. The tensile strength without silver coating was found to be less (79 MPa) which is about 47% of the ROM value. This clearly shows that silver coating helps to increase the strength of the composite. In the case of pitch-base fibres, tensile strength values observed were 130 MPa with silver coating and 124 MPa without silver. The ROM strength for 7 vol % fibre is 210 MPa (UTS of pitch-base fibres = 2.07 GPa). The % ROM value for silver-coated fibre composite is 62% and for that without coating is about 59%.

Fig. 12 shows the tensile strength of aluminium–PAN-base fibre composite as a function of processing parameters. It was observed that the maximum value of the tensile strength was obtained at a processing temperature of 1000 °C and at a holding time of 120 min. The tensile strength of the 6063 Al used was 68 MPa. Using the ROM, the theoretical strength calculated was 135 MPa for 2.5 vol % C fibers with a UTS of 2.75 GPa. The observed strength (78 MPa) was about 58% of the ROM strength. In order to check whether the increase in strength was due to transfer of load to the fibres and not due to any hardening mechanism in the matrix, tensile tests were done for a second time on the same sample by modifying the shape of the sample to permit two pulls. The tensile strength value in the second pull was about 33% lower than the original value. The fact that the second pull showed a 33% reduction in strength suggests that the matrix has not been hardened and that the strengthening of the aluminium-matrix composite observed in the first pull was indeed due to the fibre reinforcement.

The reason for low % ROM values of strength (maximum 65%) could be due to interfacial reactions

TABLE I Tensile test data for fibre-reinforced composites

Material	Fibre	Coating	Processing temperature (°C)	Processing time (min)	UTS (MPa)
Al-6063	–	–	1000	120	68
C–Al	CVD	Silver	1000	120	109
C–Al	CVD	None	1000	120	79
C–Al	CVD	Silver	1020	120	71
C–Al	Pitch	Silver	1000	120	130
C–Al	Pitch	None	1000	120	124

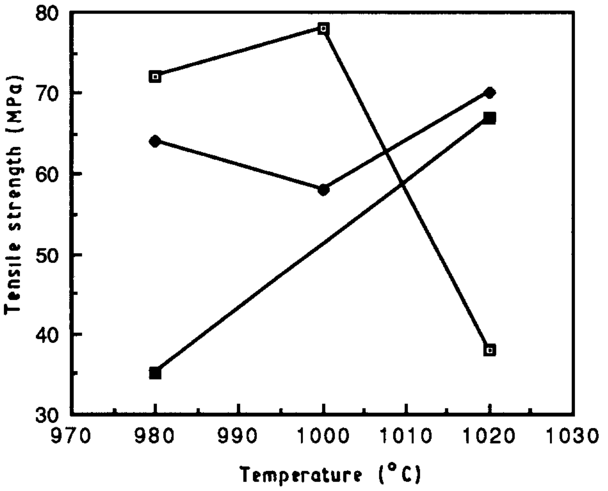

Figure 12 Variation in tensile strength of PAN-base carbon fibre–aluminium composite with processing parameters: (■) 60 min, (◆), 90 min, (⊡) 120 min.

which result in degradation and loss of strength of the fibre. Also the sharp edges of Al_4C_3 could act as potential sites for crack initiation. Percentage ROM values were always higher when the fibres were coated with silver. This could be due to lower interfacial reactions between the fibre and the matrix in the presence of silver.

The appearance of an optimum processing parameter in Fig. 12 can be explained by the fact that higher temperatures of processing and a longer holding time cause excessive reaction to occur, resulting in a decrease in strength. On the other hand, at lower temperatures and time, incomplete penetration was observed which again resulted in lower strength.

5. Conclusions

Silver coating on carbon and graphite fibres helps the infiltration of fibre bundles by molten aluminium. This could be due to the formation of an eutectic between silver and aluminium, and to the silver coating preventing contamination of fibres during processing. The coating was found to be necessary for infiltration of PAN-base carbon fibres and was seen to reduce the reaction in CVD and pitch-base graphite fibres. The decrease in the reaction zone in the case of graphite fibres, could be due to a diffusion barrier formed by the aluminium–silver system. The need for silver in the case of PAN fibres indicated that the wettability of aluminium on graphite is better than that on carbon.

The reaction zone, primarily consisting of platelets of aluminium carbide, was observed to be larger in carbon fibres than in graphite fibres. Inert basal planes, which lie parallel to the fibre axis in graphite fibres, were thought to be responsible for this behaviour. The reaction zone in all Al–C composites appeared to be continuous at low magnification but at higher magnification, discontinuity was observed. This indicated that Al_4C_3 formed as platelets, upon growth, impinged upon each other giving the reaction zone a look of continuity. Tensile tests indicated that the strength of the composite decreased with increasing processing temperature, possibly due to the greater amount of reaction. The lowest value of percentage rule of mixtures (%ROM) strength was seen in PAN–base fibre composites. The greater extent of reaction in PAN-base fibres, as compared to CVD and pitch-base fibres, was thought to be responsible for its low strength. The low %ROM values of strength could be due to interfacial reactions which result in degradation of the fibres and the creation of sites for crack initiation.

Acknowledgements

The authors wish to acknowledge the financial support from the Thomas Edison Program, Ohio Department of Development and NASA Space Engineering Research Center.

References

1. J. E. SCHOUTENS and K. TEMPO, in "Introduction to Metal Matrix Composite Materials" (DOD Metal Matrix Composite Information Analysis Center, Santa Barbara 1982) pp. 3–20.
2. N. EUSTATHOPOULOS, J.C. JOUD, P. DESRE and J. M. HICTER, *J. Mater. Sci.* **9** (1974) 1233.
3. M. F. AMATEAU, *J. Compos. Mater.* **10** (1976) 279.
4. I.H. KHAN, *Metall. Trans.* **7A** (1976) 1281.
5. R. V. SARA, in "Integrated Research on Carbon Composite Materials, " AFML TR-66-310 (Wright Patterson AFB, Dayton, Ohio, 1966) p. 193.
6. H. M. CHENG, B. L. ZHOU, Z. G. ZHENG, Z. M. WANG and C. X. SHI, *Plating Surfa. Finishing* **77** (5) (1990) 130.
7. S. G. WARRIER and R. Y. LIN, submitted to *J. Mater. Sci.*
8. J. P. ROCHER, J. M. QUENISSET and R. NASLAIN, *J. Mater. Sci. Lett.* **4** (1985) 1527.
9. S. KOHARA and N. MUTO, in Proceedings of 5th International Conference on Composite Materials, San Diego, 1985, edited by W.C. Harrigan, J. Strife and A.K. Dhingra (Metallurgical Society, Pennsylvania, 1985) p. 631.
10. A. KITAMURA, in Proceedings of 28th Conference on Space Science and Technology, Tokyo, 1984, p. 34.
11. G. E. DIETER, "Mechanical Metallurgy", 3rd Edn, (McGraw-Hill, New York, 1986) p. 223.

Received 18 November 1991
and accepted 2 June 1992