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Compatibility of chromium carbide coated graphite fibres with metallic matrices

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Chromium carbide coating on graphite fibres was obtained by diffusing chromium through a coating of copper on a graphite fibre. Coated fibres, then, were infiltrated with liquid copper, aluminium and nickel alloys in a vacuum furnace. Chromium carbide proved to be reasonably wetted by those alloys, although the wettability is affected by the alloying elements.

1. Introduction

Graphite fibre reinforced metal matrix composites are very attractive because of their expected high specific properties and good retention of their properties up to very high temperatures. However, there are many problems to be solved in order to utilize the superior properties of the fibres. These problems originate from the incompatibility between the fibres and matrix metals, poor wettability of the fibres by inert liquid metals and limited oxidation protection afforded by matrix metals to the fibres.

Titanium–boron coating [1], of fibres developed in the early 1970's for better compatibility with metallic matrices, was used essentially for aluminium alloy matrices. The coating improved wettability by these alloys and prevented aluminium from reacting with carbon during the very short contact time of solidification of metal. Aluminium matrix is convenient to use because thermodynamically it can provide oxidation protection to the fibres up to its melting temperature. Although the applicability of the coating for other metals, such as copper, zinc, lead and magnesium was successfully demonstrated [2], in copper matrix composites, thermodynamically the matrix metal cannot provide sufficient oxidation protection to graphite fibres above as low a temperature as 80° C [3]. With nickel matrix, the coating does not seem to provide full protection either.

Carbide coating on graphite fibre appears to be the most suitable material to overcome the above problems. The theoretical analysis by Huggins [4] indicates that it can offer good oxidation protection. The wetting behaviors of carbides with various metals are fairly well investigated [5, 6]. Above all chromium carbide was found to be relatively stable even with nickel and iron [7].

Chromium coating can be done using various techniques. Recently a chemical reaction process was developed by the authors [8]. The process consists of copper–chromium duplex coating on graphite fibres and subsequent heat treatment. During heat treatment chromium diffuses through the copper layer and forms chromium carbide on the carbon fibres. This method was found, to a certain extent, to weaken the graphite fibres. This was attributed to the direct removal of carbon from their surfaces, to the in-grown Griffith cracks in the carbide layer and possible formation of new cracks in the layer during testing [9]. However, the strength and the elastic modulus of carbide coated fibres were still sufficiently high to produce a useful reinforcement in metallic matrices.

2. Materials and experimental procedure

The graphitized carbon fibres used in this study are commercially available fibres marketed under the trade name of Fortafil-6T and were purchased from Great Lakes Carbon Corp. The fibres were coated with chromium carbide by the method described above [8]. For a matrix metal the following alloys were used: an aluminium alloy (5356) (5.0 wt% Mg–0.13 wt% Ti–0.12 wt%

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Mn–0.12 wt% Cr–Balance Al), several copper alloys, such as Cu–1 wt% Cr, Cu–8 wt% Sn, Naval Brass (39.4 wt% Zn–0.7 wt% Sn–Balance Cu), Government A Bronze (6.0 wt% Sn–2.2 wt% Pb–1.0 wt% Ni–Balance Cu), and aluminium–silicon bronze (7.0 wt% Al–2.0 wt% Si–Balance Cu) and a nickel alloy (Hastelloy D) (10 wt% Si–3 wt% Cu–Balance Ni).

Infiltration experiments were carried out in a vacuum equipped with an electric resistance furnace. Carbide coated fibres, about 12 mm long, were put into an alumina tubing, and a piece of alloy was placed on the top of them; then the tubing was inserted into a stainless steel crucible. The crucible was hung at the end of the stainless steel tubing, which can be manipulated from the outside of the chamber without disturbing the vacuum. The temperature of the furnace and the temperature inside the crucible were measured using an alumel–chromel thermocouple and recorded on a strip chart recorder throughout the infiltrating operation. When the vacuum reached $< 10^{-5}$ torr, the furnace was switched on and maintained at predetermined temperatures; the crucible was then lowered into the furnace. After a suitable period of time, the crucible was withdrawn from the furnace and cooled in a flow of argon.

Infiltrated fibres were mounted in lucite and the microstructure was observed using an optical microscope.

3. Results

Chromium carbide coated fibres infiltrated with 5356 aluminium alloy at just above its liquid temperature for 3 min are shown in Fig. 1a and b. The infiltration was reasonable with some porosity in the centre of the bundle of fibres. No serious reaction at the interface between the fibres and the matrix was observed. In order to examine the interfacial reactions more closely, a much thicker carbide coating was produced on the fibres and infiltration was carried out under similar conditions as above. The result is shown in Fig. 1c. As may be seen, the fibre is fully protected by the coating.

As a representation example of copper alloy matrices, carbide coated fibres infiltrated with copper–chromium alloy at ~ 1230° C for 5 min are shown in Fig. 2a and b. The fibres are properly wetted by the matrix metal and show good compatibility with the matrix. Fig. 2c shows the interfacial conditions observed in a Cu–8 wt% Sn alloy matrix. The experiments with other copper alloy matrices showed that the interfacial conditions were very similar.

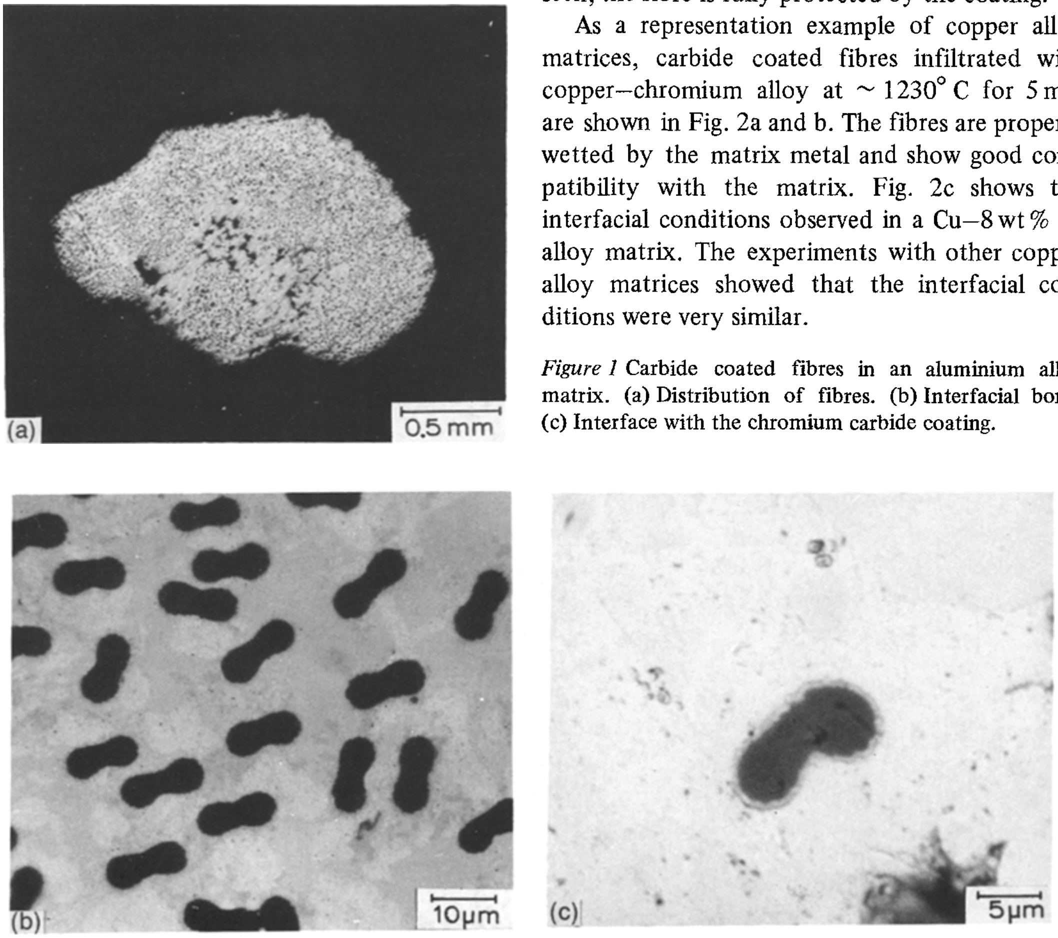
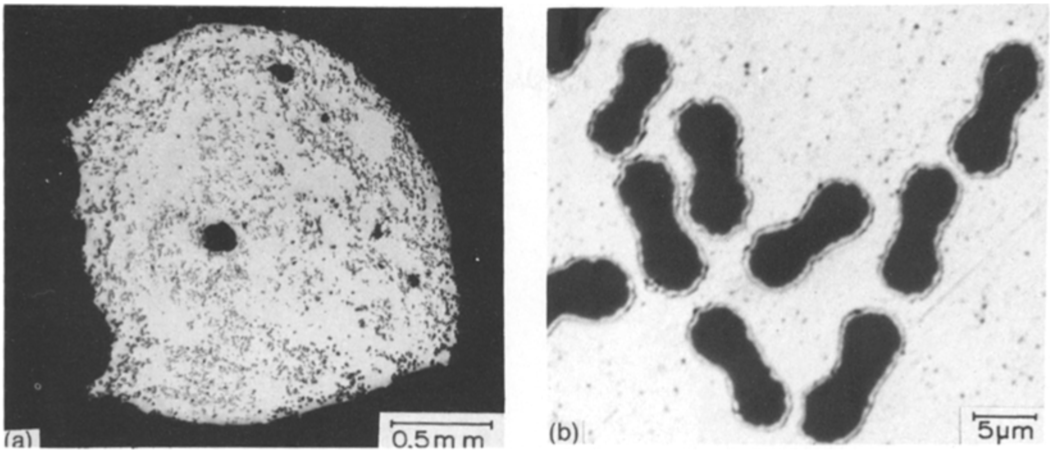


Figure 1 Carbide coated fibres in an aluminium alloy matrix. (a) Distribution of fibres. (b) Interfacial bond. (c) Interface with the chromium carbide coating.



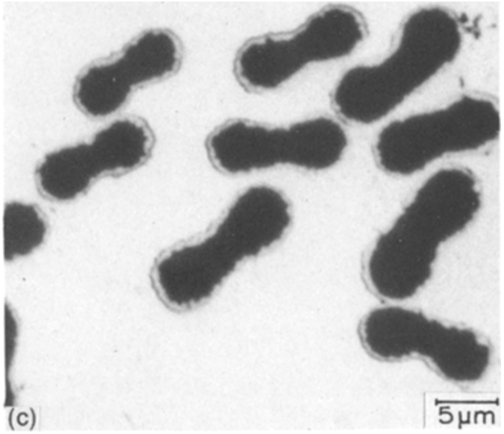


Figure 2 Carbide coated fibres in a copper alloy matrix. (a) Distribution of fibres. (b) Interfacial conditions in a Cu–Cr alloy. (c) Interfacial conditions in a Cu–Sn alloy.

Fig. 3a and b illustrate the Hastelloy D with carbide coated fibres. Infiltration was carried out at ~ 1160° C for ~ 2.7 min and resulted in a composite with acceptable interfacial conditions.

4. Discussion

4.1. Aluminium alloy matrix

Thermodynamically, chromium carbides have slightly larger negative free energies of formation than aluminium carbide [10]; therefore chromium carbides are (expected) to be stable. However, chromium carbides exposed to liquid aluminium for longer periods of time become unstable. As shown in Fig. 4, longer contact time with liquid aluminium caused reaction at the interface. Under these circumstances, the decomposition of chromium carbides and possible formation of aluminium carbide can be suspected because the difference in free energy of the two carbide systems is small.

Attempts to use Al–Si alloy at its eutectic composition were made because of its low melting

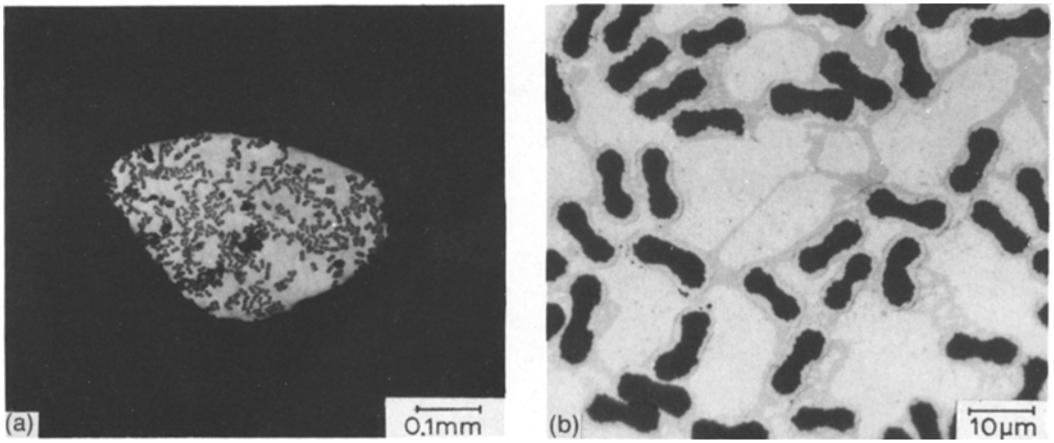


Figure 3 Carbide coated fibres in a nickel alloy matrix. (a) Distribution of fibres. (b) Interfacial conditions.

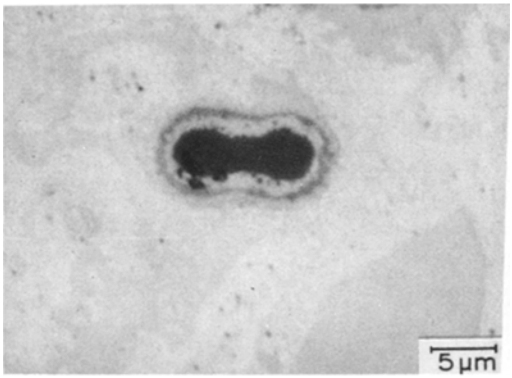


Figure 4 Carbide coated fibre in an aluminium matrix showing chemical reaction between the coating and the matrix.

temperature. However, it was found that superheating the alloy to 660° C did not infiltrate the fibres. This could have been caused by the higher surface tension of the Al–Si alloy. The addition of magnesium to aluminium can reduce the surface tension of aluminium considerably [11], therefore Al–Mg alloys may be more suitable for the manufacture of this kind of composite.

4.2. Copper alloy matrices

As reported by Mortimer and Nicholas [6], chromium carbides can be wetted by copper and its alloys, and their results were confirmed in this experiment. However, the wettability of copper alloys seems to vary depending on the composition of the alloys. The experiments indicated qualitatively that addition of tin does not appear to have noticeable effects, but aluminium and zinc appear to reduce wettability.

Graphite fibre reinforced Cu–Sn alloy composites fabricated with chromium carbide coated fibres may have better wear resistance than reported by Eliezer *et al.* [12] for composites with titanium–boron coated fibres, because of the presence of hard carbides.

4.3. Hastelloy D

The high reactivity and high melting temperature of pure nickel led to the selection of Hastelloy D as a matrix metal. The alloy has a liquidus temperature at 1120° C and the addition of silicon and copper are expected to reduce the reactivity. Although prolonged contact with the liquid alloy was found to destroy chromium carbide coatings, the selection of suitable infiltration conditions may result in successful infiltration.

5. Conclusions

Chromium carbide coating on graphite fibres for metal matrices were successfully demonstrated. However, in order to achieve this, suitable infiltration conditions should be selected. In particular prolonged contact times with reactive metals should be avoided.

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