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Fibre coatings for the fabrication of graphite-reinforced magnesium composites

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A new fabrication technique for graphite-fibre-reinforced magnesium is presented. An air-stable silicon dioxide coating is deposited on the fibre surfaces from an organometallic precursor solution. The fibres are passed through this solution, followed by hydrolysis or pyrolysis of the organometallic compound to form silicon dioxide on the fibre surfaces. The silicon dioxide coating facilitates wetting and bonding when the fibres are immersed in molten magnesium. A modification of this coating technique was developed for coating fibres with amorphous carbon, which was found to improve the adhesion between the graphite fibres and the silicon dioxide coating. Composites containing either T300, P55, or P100 graphite fibres in pure magnesium, magnesium–1 wt% silicon, and magnesium alloy AZ91 have been fabricated. Preliminary mechanical property data are presented.

1. Introduction

Graphite-fibre-reinforced magnesium is emerging as a valuable new structural material. It combines high specific strength and stiffness with a near-zero coefficient of thermal expansion, high electrical and thermal conductivity, and is non-outgassing. The primary difficulty with fabricating this material is that molten magnesium does not wet or bond to graphite fibres. Because molten magnesium does not wet or bond to graphite fibres, it is impossible to achieve load transfer from the matrix to the fibres. To overcome this problem the fibres must be coated with a material that is wet by molten magnesium, and which also protects the fibres against chemical degradation during processing and use.

The currently used process relies on the chemical vapour deposition (CVD) of a thin layer of titanium and boron on to the fibres to achieve wetting [1]. However, there is an inherent problem associated with this process. The titanium–boron coating is rapidly oxidized when exposed to air, and molten magnesium does not wet the oxidized coating. Consequently, the coated fibres cannot be exposed to air before immersion in molten magnesium. This severely limits the material shapes that can be fabricated by using this process. To date, only fibre-reinforced magnesium wire has successfully been made. This wire must then undergo costly secondary fabrication to produce useful structural shapes such as plates or tubes. In fact, the final shapes have been limited to plates and tubes due to the rigidity of the wires.

We have solved this fabrication problem for graphite-fibre-reinforced magnesium with the development of an air-stable coating of silicon dioxide, which is easily wet by magnesium. The coatings are deposited on the fibre surfaces using silicon-based organometallic compounds. Fibres are simply passed through a solution of the organometallic, which is then chemically converted by either hydrolysis or pyrolysis to form the silicon dioxide coating. The flexible, coated fibres may then be wound or laid up and held in place with a removable binder for selective reinforcement. They are then incorporated into the magnesium by casting near-net-shape structures [2]. Not only can complex structural shapes be made by this method, but the fibre volume fraction can be controlled to a much greater degree than is possible using the earlier CVD technique. The fibre volume fraction is critical in determining the thermal expansion, strength and stiffness of the composite.

2. Fibre coatings

2.1. Technique

We have deposited thin, uniform oxide coatings on graphite fibres by using alkoxides, a class of organometallic compounds in which metal atoms are bonded to hydrocarbon groups by bridging oxygen atoms [3]. These compounds are currently being widely investigated as precursors for ceramics and glasses [4, 5]. They hydrolyse when exposed to water or water vapour to form hydroxides or hydrated oxides, which can then be converted to oxides by heating to relatively low temperatures. Alternatively, alkoxides can be pyrolysed at similarly low temperatures to yield oxides directly. Elements for which alkoxides are commercially available include aluminium, boron, lithium, magnesium, niobium, potassium, silicon, sodium, tantalum, titanium, vanadium and zirconium. These compounds can be dissolved in various organic solvents (toluene, for example), and solutions which hydrolyse to produce various mixed oxides can easily be made.

The chlorides of boron, silicon and titanium are also easily hydrolysed by water or water vapour. These compounds are generally more reactive than alkoxides and are also soluble in toluene. Therefore, a

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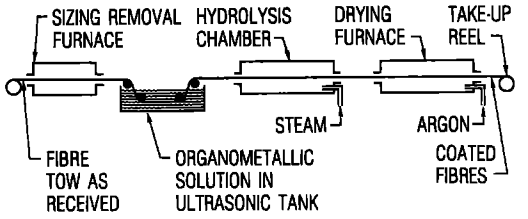

Figure 1 Schematic diagram of the solution-coating process used to coat fibres with various oxides.

mixture of chlorides and alkoxides can be used to control the reactivity of the toluene solution.

A continuous process that takes advantage of the chemical behaviour was developed for coating fibres with various oxides (Fig. 1). It is a solution coating process in which the fibres are passed through a furnace in which the sizing on the fibres, applied by the manufacturer to aid in handling, is vaporized and removed. This is followed by immersion in an ultrasonic bath containing the organometallic solution. Ultrasonic vibration ensures that the solution penetrates into the fibre bundle and that each of the many thousand filaments is equally coated. The uniformity and thickness of the resultant coating is controlled by the concentration and reactivity of the solution as well as the time and temperature of immersion. The alkoxide-coated fibres are then passed through a chamber containing flowing steam in which the alkoxides are hydrolysed, followed by an argon-atmosphere drying furnace in which the hydrated oxide is converted to an oxide. Any residual solvent or water is vaporized, and any unhydrolysed alkoxide is pyrolysed in this last step.

2.2. Experimental details

We have found that a silicon dioxide coating on carbon fibres facilitates wetting by molten magnesium [6]. Three carbon fibres were investigated: T300, P55, and P100 (all from Union Carbide Corp.) The SiO_2 coatings were applied using the solution-coating process previously described. The fibres were passed through a furnace containing argon at 475° C to remove their sizing, followed by immersion in an ultrasonically vibrated toluene solution containing 5 vol % tetraethyoxy silane, $Si(OC_2H_5)_4$ (also called tetraethyl orthosilicate) and 5 vol % silicon tetrachloride, $SiCl_4$ (both from Alfa Products, Danvers, Massachusetts). The $SiCl_4$ increases the reactivity of the solution which is kept at 25 to 30° C. The silicon compounds are hydrolysed by passing the coated fibres through a chamber containing flowing steam. They then travel through a furnace at 550° C containing flowing argon, which serves to transform the hydrated oxide to a SiO_2 coating on each fibre surface. The fibres move at a rate of 2 to 10 ft min^{-1} (60 to 300 cm min^{-1}) which results in a residence time of 5 to 30 sec for each step. The most efficacious coatings were obtained by repeating the process and applying the coating twice.

2.3. Characterization of coated fibres

Coated fibres were examined with scanning electron microscopy (SEM) equipped with energy-dispersive X-ray analysis (EDX), transmission electron microscopy (TEM), scanning Auger microscopy (SAM), X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), and X-ray diffraction (XRD). SEM (Fig. 2a) shows that each fibre is uniformly and continuously coated and that there is no bridging or joining of the fibres due to the coatings. The coated fibres remain pliable, and the coatings adhere to the fibres even after flexing. No differences in tensile strengths were found between coated fibres and as-received fibres, indicating that the coating process does not degrade the strength of the fibres.

EDX (Fig. 2b) shows that every fibre in the bundle is coated and that even the bare-looking areas are coated. No residual chlorine is found in the SiO_2 coatings by EDX, SAM or XPS. SAM depth profiles (Fig. 3) indicate that the thickness of the coatings varies from 70 to 150 nm with an average value of approximately 100 nm. The argon-ion sputter rate for the depth profiling was calibrated with tantalum oxide standards. The thickness values are verified by TEM (Fig. 4). In Fig. 4 the edge of the as-coated fibre is illuminated with electrons from behind. The grey area adjacent to the black fibre is the coating. Both electron and X-ray diffraction indicate that the coatings are amorphous.

The SAM elemental depth profiles (Fig. 3) show that the oxide coatings contain some carbon. Elemental concentrations were estimated using handbook sensitivities [7]. The carbon originates in the carbon fibre, not the organometallic compound or solvent, since similarly applied coatings on FP alumina fibres

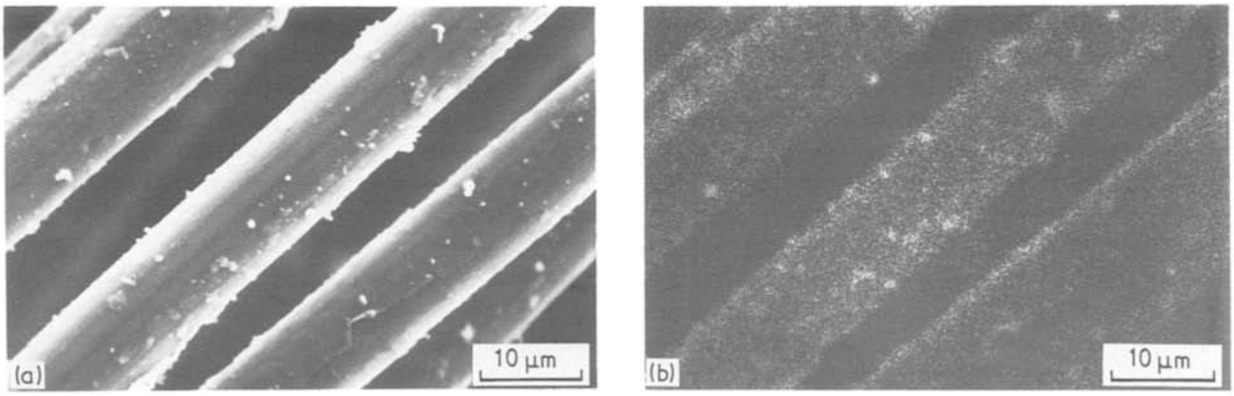

Figure 2 (a) Scanning electron photomicrograph of silicon dioxide-coated P55 fibres. (b) An energy-dispersive X-ray silicon map of the same area. The light areas correspond to X-rays emitted by silicon.

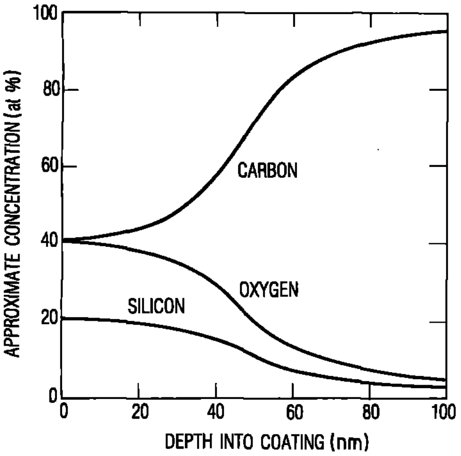

Figure 3 Scanning Auger microprobe elemental depth profiles of a carbon fibre coated with silicon dioxide.

(DuPont Corp.) contain no carbon. XPS was employed to determine the chemical nature of this carbon as well as to determine the nature of the bonding between the coating and the fibre. The XPS spectra (Fig. 5) show that the silicon in the coating is present only as SiO_2, not SiC [8]. The carbon spectrum (Fig. 5b) shows a main peak corresponding to graphitic carbon, with a shoulder indicating some carbon–oxygen bonding. However, after argon-ion sputtering for 15 min (Fig. 5d), only the graphitic carbon peak remains. The binding energy of the silicon 2p peak is unchanged after sputtering (Fig. 5c). This indicates that the coating is SiO_2, with some graphitic carbon from the fibre dispersed in it.

3. Composite fabrication

3.1. T300 and P55 fibres in magnesium

Silicon-dioxide coated T300 or P55 graphite fibres are wet, and the fibre bundles are uniformly infiltrated when immersed in molten magnesium at 670 to 700° C for 10 to 30 sec. Fig. 6 shows an optical photomicrograph of a polished cross-section of P55 fibres in a pure magnesium matrix. Wetting is achieved by a reaction between the molten magnesium and the silicon dioxide coating to form magnesium oxide and

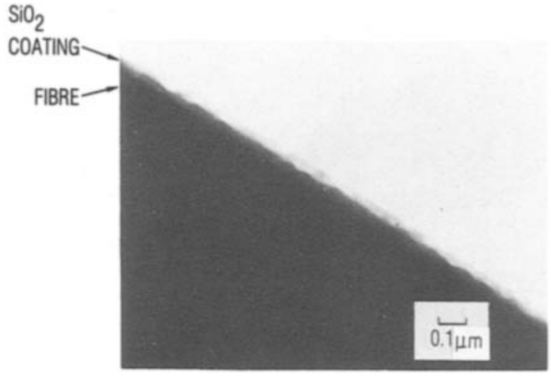

Figure 4 Transmission electron photomicrograph of a T300 fibre coated with silicon dioxide.

magnesium silicate:

$$2Mg + SiO_2 \rightarrow 2MgO + Si$$

$$\Delta G^0_{670^\circ C} = -76\,\text{kcal}\ (-318\,\text{kJ})\ [9]$$

$$2Mg + 2SiO_2 \rightarrow Mg_2SiO_4 + Si$$

$$\Delta G^0_{670^\circ C} = -104\,\text{kcal}\ (-435\,\text{kJ})\ [9]$$

$$2Mg + 3SiO_2 \rightarrow Mg_2SiO_3 + Si$$

$$\Delta G^0_{670^\circ C} = -122\,\text{kcal}\ (-511\,\text{kJ})\ [9]$$

Both SAM and SIMS confirm the presence of magnesium, silicon and oxygen at the interface between fibre and matrix (Fig. 7). This mixed-oxide phase forms a graded junction and assures good bonding between the magnesium and the fibres.

3.2. P100 fibres in magnesium

Higher-modulus fibres such as P100 can also be coated with oxides using the solution-coating process previously described. Scanning Auger microscopy indicates similar coating thickness and uniformity as for T300 or P55 fibres. However, when silicon dioxide coated P100 fibres are immersed in molten magnesium, very little magnesium adheres to the fibres. SAM reveals that immersion in liquid magnesium causes the SiO_2 coating to separate from the fibres, indicating that the oxide coating does not adhere to P100 fibres as well as to T300 or P55 fibres.

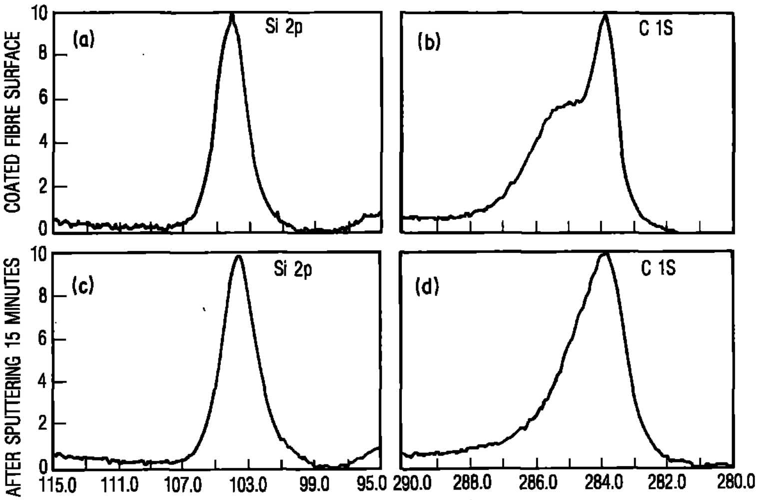

Figure 5 (a) X-ray photoelectron spectra of a carbon fibre coated with silicon dioxide; Si 2p peak from the coated fibre surface. (b) X-ray photoelectron spectra of a carbon fibre coated with silicon dioxide; C 1s peak from the coated fibre surface. (c) X-ray photoelectron spectra of a carbon fibre coated with silicon dioxide; Si 2p peak after argon-ion sputtering for 15 min. (d) X-ray photoelectron spectra of a carbon fibre coated with silicon dioxide; C 1s peak after argon-ion sputtering for 15 min.

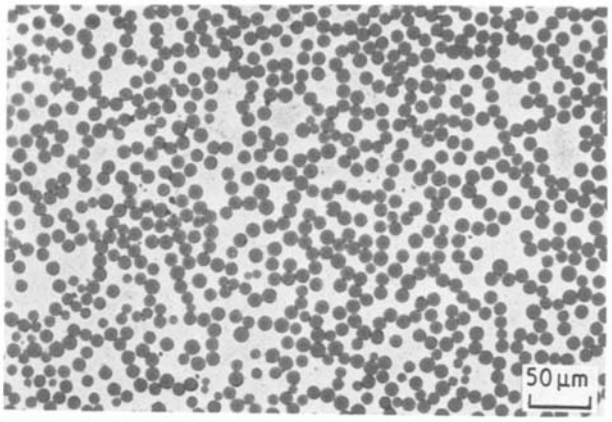

Figure 6 Optical photomicrograph of polished cross-section of P55 fibres in a pure magnesium matrix.

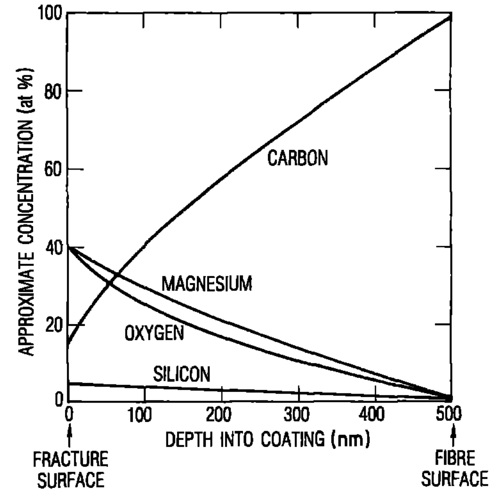

Figure 7 Scanning Auger microprobe elemental depth profiles of the coating adhering to a fibre after fracture.

The difference in adhesion is due to differences in both the surface morphology and chemical reactivity of the fibres. Fig. 8 shows SEM of the surfaces of T300 and P100 fibres. The surfaces of higher-modulus fibres such as P100 are smooth. Most of the graphite crystallites in the fibre have their basal planes aligned parallel to the fibre direction. Few plane edges are exposed. Lower-modulus fibres such as T300 have rougher and more porous fibre surfaces. Also, more plane edges are exposed. Since the edges of the graphite plane are chemically much more reactive than the plane faces, lower-modulus fibres are more reactive than higher-modulus ones. These differences lead to the difference in adhesion between the silicon dioxide coating and fibres of various moduli.

We succeeded in improving the adhesion between higher-modulus fibres and the silicon dioxide coatings by precoating the fibres with amorphous carbon. This allowed the production of magnesium reinforced with P100 fibres [10]. The amorphous carbon coating causes the higher-modulus fibre surfaces to resemble those of lower-modulus fibres, to which the oxide coating adheres very well. A schematic diagram of the coating process is shown in Fig. 9. The carbon coating is applied to the P100 fibres by passing them through a toluene solution of petroleum pitch (Ashland A240, Ashland Petroleum, Kentucky, USA) of 10 to 40 g l^{-1}, at 30 to 50° C. The solvent is vaporized, and the pitch is pyrolysed to carbon in a series of increasing temperature furnaces containing a counter-flow of argon. The optimum maximum temperature is 550° C. The carbon-coated P100 fibres are then coated with silicon dioxide twice using the solution-coating process previously described. When they are then immersed in molten magnesium, good wetting and infiltration result.

TEM of the amorphous carbon coating (Fig. 10) shows that the coating is about 20 nm thick. In Fig. 10 the coated fibre has been mounted in epoxy and thinned before analysis. Unfortunately, elemental surface analytical techniques cannot be used to distinguish between the coating and the fibre because the fibre coating is applied to a graphite substrate.

3.3. Mechanical properties

We have successfully fabricated graphite–magnesium composites containing either T300, P55 or P100 fibres in either pure magnesium, Mg–1 wt % Si, or magnesium alloy AZ91 (Mg–9% Al–1% Zn). Wires of each of these fibres in each of these matrices typically show room-temperature strengths that are 80 to 95% of the rule-of-mixtures values. These are comparable to the strengths measured in our laboratory of material made by the titanium–boron CVD process. A scanning electron micrograph of a tensile fracture surface of a P55/Mg wire is shown in Fig. 11. There is little

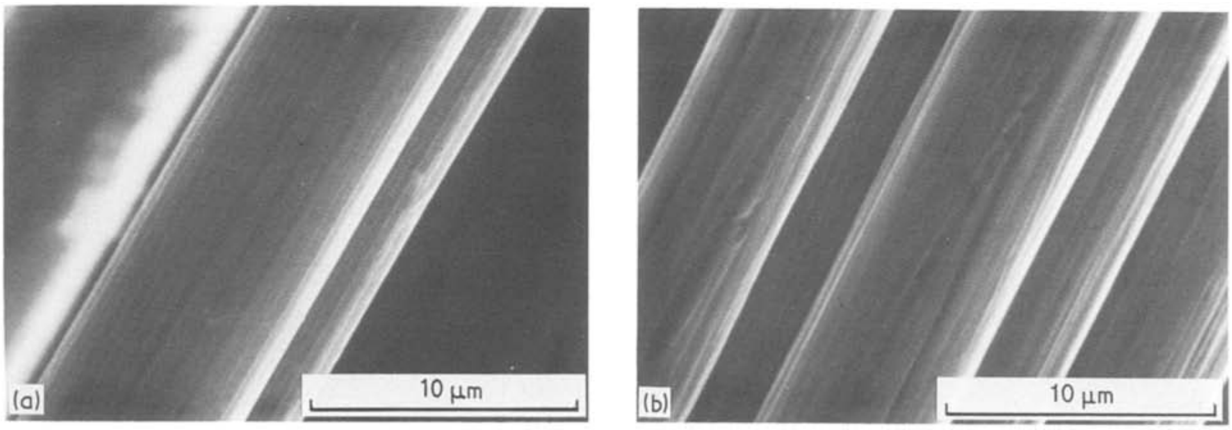

Figure 8 (a) Scanning electron photomicrograph of T300 fibres. (b) Scanning electron photomicrograph of P100 fibres.

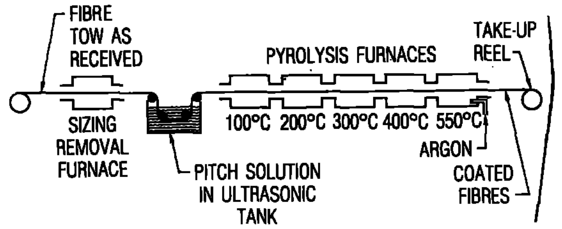

Figure 9 Schematic diagram of the process used to coat fibres with amorphous carbon.

fibre pull-out, indicating relatively good bonding between the fibres and the matrix. Limited data on plates of P55 in magnesium and Mg–1% Si indicates a minimum transverse tensile strength of 2 to 3 ksi (14 to 21 MPa). This contrasts with a maximum of 1 to 2 ksi (7 to 14 MPa) found in material made by the CVD process. SAM of samples fractured *in situ* under high vacuum shows the presence of magnesium, silicon and oxygen on both the fibre and the matrix side of the fracture. This indicates that the fracture occurs through the interfacial oxide layer.

4. Conclusions

A technique for the fabrication of graphite-fibre-reinforced magnesium composites has been demonstrated. It relies on the deposition of a thin air-stable coating of silicon dioxide on to the fibre surfaces from an organometallic precursor solution, to facilitate wetting when the coated fibres are immersed in molten magnesium. This coating was specifically developed for graphite fibres, but has also been successfully used to fabricate magnesium composites reinforced with FP alumina or Nicalon silicon carbide fibres (Nippon Carbon Co.). A modification of the coating technique can be used to coat fibres with amorphous carbon, which improves the adhesion between higher-modulus fibres and the silicon dioxide coatings. The amorphous carbon coating is expected to find wider use as fibres with even higher moduli and, therefore, even less reactive surfaces are developed. Finally, we expect that coatings from organometallic precursor solutions will also prove effective in controlling the fibre–matrix bond strength in ceramic matrix composites.

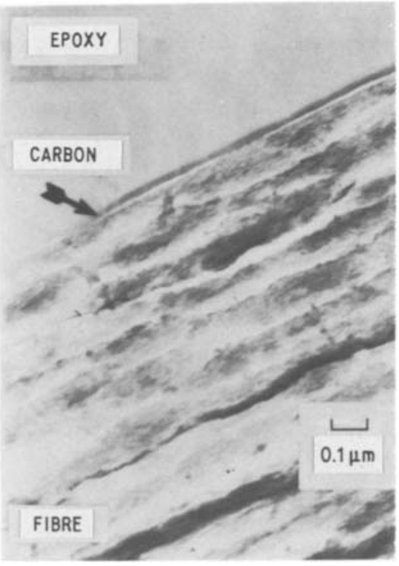

Figure 10 Transmission electron photomicrograph of a carbon fibre coated with amorphous carbon (mounted in epoxy).

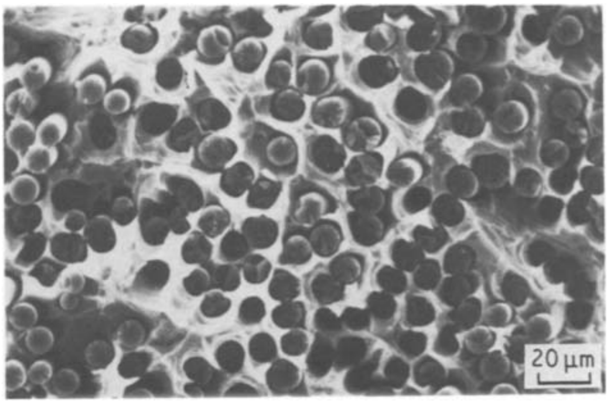

Figure 11 Scanning electron photomicrograph of the tensile fracture surface of a P55/pure magnesium composite plate.

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