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The interface in carbon–magnesium composites: fibre and matrix effects

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Two types of carbon fibres were incorporated into magnesium alloy matrices by squeeze casting. Mechanical testing showed that surface treatment of the fibres led to a marked increase in the interfacial shear strength and a corresponding decrease in the longitudinal tensile strength. A small amount of fine Al_4C_3 forms at the fibre matrix interface in simple binary Mg–Al matrices. $Mg_{17}Al_{12}$ and Mg_2Si form at the interface in the Mg–Al–Si matrix: precipitation is greatly enhanced by residual stresses at the interface and many fibres are surrounded by a brittle layer leading to inferior mechanical properties.

1. Introduction

Carbon–magnesium metal matrix composites (MMCs) are of great technological interest for use in space structures because of their high specific strength and stiffness and because of the possibility of tailoring them to have a zero coefficient of expansion. Fabrication of these composites is frequently via a liquid metal process, such as squeeze casting, and there has been much concern over detrimental chemical reactions at the fibre/matrix interface. Attempts have been made to minimize these reactions by depositing a protective coating, such as TiB_2, on the fibre surface prior to infiltration [1].

Recent work has shown that the mechanical properties achieved are often strongly influenced by the matrix composition, interface microstructure, surface pre-treatments and choice of fibre [2, 3]. The present report summarizes results obtained in investigations of two different carbon–magnesium MMC systems in which the effects of experimental variables are shown to be not consistent from one system to the other. The complex interrelationship between fibre surface treatment and matrix alloying effects is clearly demonstrated.

2. Experimental procedure

The unidirectionally reinforced samples used in this study were prepared by squeeze casting by Honda R.&D. Co. Ltd, Wako-shi, Japan, and the fibre volume fraction was nominally 30 vol % in all cases. Two groups of samples were examined and the bulk of the observations will concern the X550/AS41 (or c.p. Mg) system. The AS41 alloy is Mg–4Al–1Si–0.3Mn. The other samples are from the T300/Mg–Al (or c.p. Mg) system. Some tensile data for the T300/Mg system have been previously published elsewhere [4] but they are included here with new interfacial shear test data to allow some interesting comparisons to be drawn.

In their normal condition the X550 fibres have an epoxy-based sizing and a surface treatment to facilitate their use in FRP but here they were also obtained without sizing. The fibres were surface treated by anodic oxidation. Preforms were made using a resin which was then substantially burnt off before infiltration with the liquid metal. The manufacturing process itself, therefore, presents several occasions for the fibre surface to undergo modification. The X550 fibres have a Young's modulus of 235 GPa and a tensile strength of 4500 MPa.

T300 fibres have a Young's modulus of 232 GPa and a tensile strength of 3300 MPa. They were used in an unsized condition, designated T300-99, and an unsized but surface-treated condition, designated T300-90. The nomenclature of the composite systems studied and their tensile strengths are given in Table I: the Young's moduli did not vary significantly within each composite system and remained within ~ 10% of the rule of mixtures values. Cylindrical tensile samples with a diameter of 5 mm and a gauge length of 10 mm were fitted with strain gauges and tested in tension at a strain rate of $2 \times 10^{-2}\,sec^{-1}$. At least three samples were tested in each condition. The broken samples were subjected to fractographic examination and specimens were also prepared for optical and transmission electron microscopy as described previously [4]. The interfacial shear strength of some of the samples was measured by a method described in detail elsewhere [6, 7].

3. Results

3.1. X550 composites

The tensile strength of these composites was strongly dependent upon the matrix composition and to a lesser extent upon the surface condition. Compared with commercially pure magnesium, the presence of aluminium and silicon in the matrix reduced the

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TABLE I

Matrix/fibre	Sample number	Sized/surface treated	Tensile strength (MPa)	Interfacial shear strength (MPa)
AS41/X550	1	yes/yes	360	-
c.p. Mg/X550	2	yes/yes	680	-
AS41/X550	3	no/yes	298	-
c.p. Mg/T300-90	4	no/yes	325	133 ± 5
c.p. Mg/T300-99	5	no/no	522	40 ± 4
Mg-4Al/T300-90	6	no/yes	328	140 ± 4
Mg-4Al/T300-99	7	no/no	645	20 ± 5

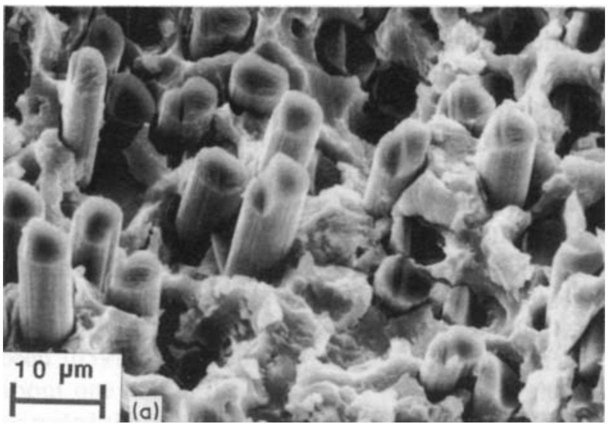
composite strength by ~ 50%; compare samples 1 and 2. Also, the presence of a sizing led to a slight increase in strength when compared with composites made with unsized fibres; compare 1 and 3.

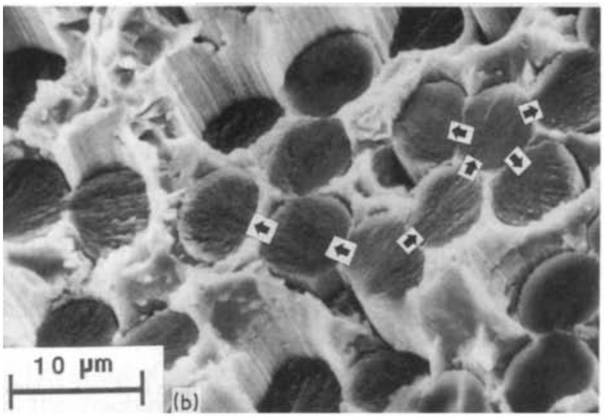
The fracture surfaces of samples 1 showed very little pull-out and extensive regions of brittle failure in the matrix, Fig. 1a. Samples 3 showed even less pull-out and it was clear that fracture had proceeded from fibre to fibre, as shown by the arrows in Fig. 1b, in a fracture mode which is usually called catastrophic. The fracture surfaces of the c.p. Mg matrix composite showed significantly more pull-out, Fig. 1c, and fracture had occurred by a fracture mode resembling that referred to as cumulative.

Optical microscopy of the AS41 matrix composites revealed a grain size of ~ 150 μm which showed vestiges of the cast structure. Extensive areas of $Mg_{17}Al_{12}$ were observed as well as occasional islands of Mg_2Si in chinese script form. The c.p. Mg matrix composite was essentially single phase with a similar grain size and occasional second-phase particles resulting from the presence of a low level of impurity elements.

Transmission electron microscopy was used to investigate whether the fibre/matrix interfacial structure was affected by the sizing and/or surface treatments. Apart from the normal twins and dislocations, the matrix and interface of c.p. Mg composites were featureless except for the presence of a few particles with compositions approximating to FeMn and which nucleated in the surface ridges of the fibres as shown in Fig. 2. High resolution electron microscopy (HREM) did not reveal any interfacial layer or reaction product in freshly prepared samples although an interfacial layer of magnesium oxide began to form within a few hours in specimens exposed to the atmosphere.

By contrast, the AS41 matrices and the corresponding interfaces were highly complex. The matrix showed a large volume fraction of second-phase particles which were identified by electron diffraction and energy dispersive spectroscopic (EDS) analysis principally as $Mg_{17}Al_{12}$. These were present in three morphologies, lamellar particles within the magnesium matrix, coarse particles formed by a eutectic reaction and very fine lath-shaped precipitates, all of which are seen in Fig. 3a. Fig. 3b is a typical electron diffraction (CBED) pattern from one of the lamellar





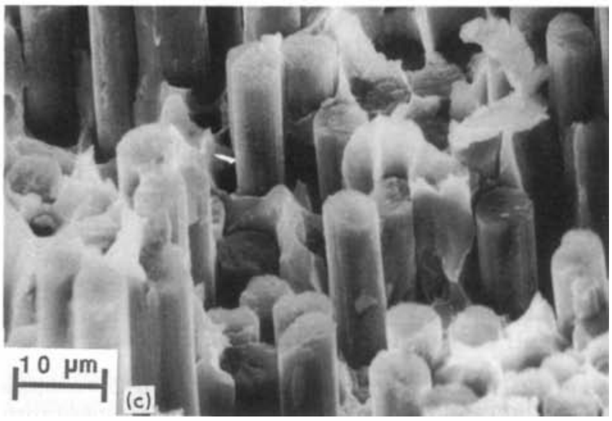


Figure 1 (a) AS41/X550 fracture surface showing relatively little pull-out and little matrix ductility. (b) AS41/X550 showing so-called "catastrophic" fracture arising from the rapid passage of a crack from one fibre to the next as shown by the arrows. Cracking is prevented where the matrix layer is relatively thick. (c) C.p. Mg/X550 showing relatively more pull-out and considerable matrix ductility.

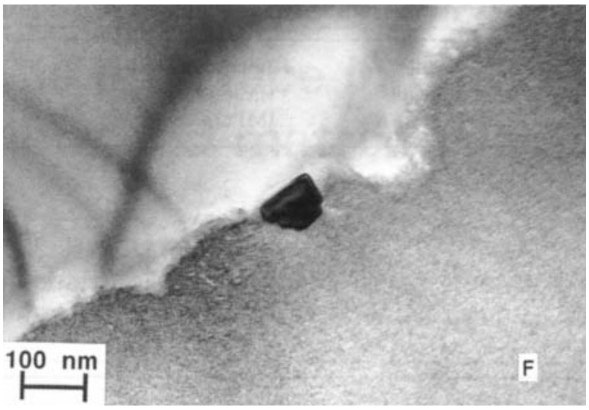


Figure 2 FeMn particle at the otherwise featureless interface of a c.p. Mg/X550 composite. F, fibre.

particles showing the cubic symmetry of the $Mg_{17}Al_{12}$ crystals.

The fine lath-shaped particles were observed in two main configurations, homogeneously precipitated throughout certain matrix grains and inhomogeneously precipitated close to fibre/matrix interfaces. The latter mode of precipitation is shown in Fig. 4a and in greater detail in Fig. 4b where it can be seen that they lie on the $(0001)_{Mg}$ plane. These fine precipitates surrounded some, but not all, of the fibres in a thin layer about 1 μm thick. The matrix structures for specimens 1 and 3 were, as might be expected, unaffected by fibre treatments.

The fibre/matrix interface structures were similarly complex and contained a variety of second-phase particles, some of which can already be seen in Fig. 4b. First were equiaxed particles, 0.1 to 0.3 μm in size, which were identified generally as either FeMn, similar to the particles already illustrated in the c.p. Mg matrix, or $Mg_{17}Al_{12}$.

Next were found very thin, often crooked, needle-like precipitates which grew outwards from the interface into the matrix. These were present in large numbers and are shown in Fig. 5a in a section taken perpendicular to the fibre/matrix interface from a composite in which the fibres had a surface treatment but no sizing. Fig. 5b shows a section almost parallel to, and containing, the fibre/matrix interface. The slender, crooked needles are clearly seen, therefore, to have originated at the fibre/matrix interface but no preferred orientation is discernible. The needles were too small for quantitative EDS analysis but it is shown below that the aluminium content was significantly higher within the needles than in the matrix generally.

No interfacial microstructure differences were found between samples 1 and 3, i.e. with or without sizing.

3.2. T300 composites

Taking the strength of the T300-99/c.p. Mg composites, sample 5, as the baseline, it is seen from Table I that alloying with a few per cent of aluminium led to a significant strengthening effect. The tensile strengths of both these composites were, however, very adversely affected by the use of a surface treatment and dropped to almost identical values. The interfacial shear strength of the T300 composites was found to increase dramatically as a result of the surface treatment, irrespective of the matrix used.

Optical microscopy showed the grain sizes to be ~ 200 μm and the alloy matrix showed pronounced coring and occasional interdendritic islands of $Mg_{17}Al_{12}$.

The T300-90 samples all failed in a flat, catastrophic fracture mode irrespective of the matrix composition. T300-99 samples showed very extensive fibre pull-out on a generally rough fracture surface, considerably more pronounced than the cumulative fracture mode described above for sample 2, and the extent of fibre pull-out increased with aluminium content.

Transmission electron microscopy was then used to examine the interfaces beginning with the c.p. Mg matrices. These showed absolutely featureless interfaces, irrespective of whether the fibres were surface treated or not. The composites with alloy matrices showed large numbers of the fine, crooked needles at the interface. While the needles were too small for accurate EDS analysis, it was found that the aluminium content was significantly enriched in their immediate vicinity, as shown by Fig. 6a and b. The needles resemble in all respects those found in the AS41/X550

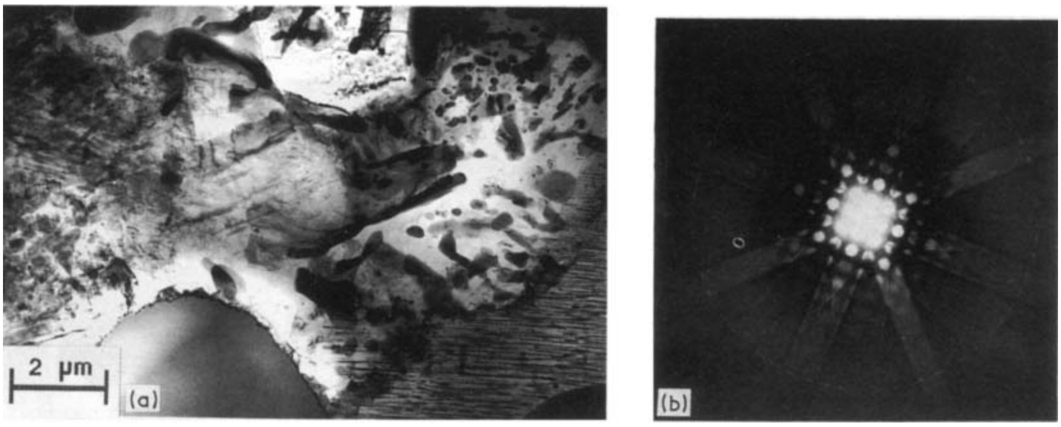


Figure 3 (a) General matrix microstructure of AS41/X550 composite showing $Mg_{17}Al_{12}$ of various morphologies. A fibre is shown at lower left. (b) CBED pattern from $Mg_{17}Al_{12}$ showing the four-fold symmetry.

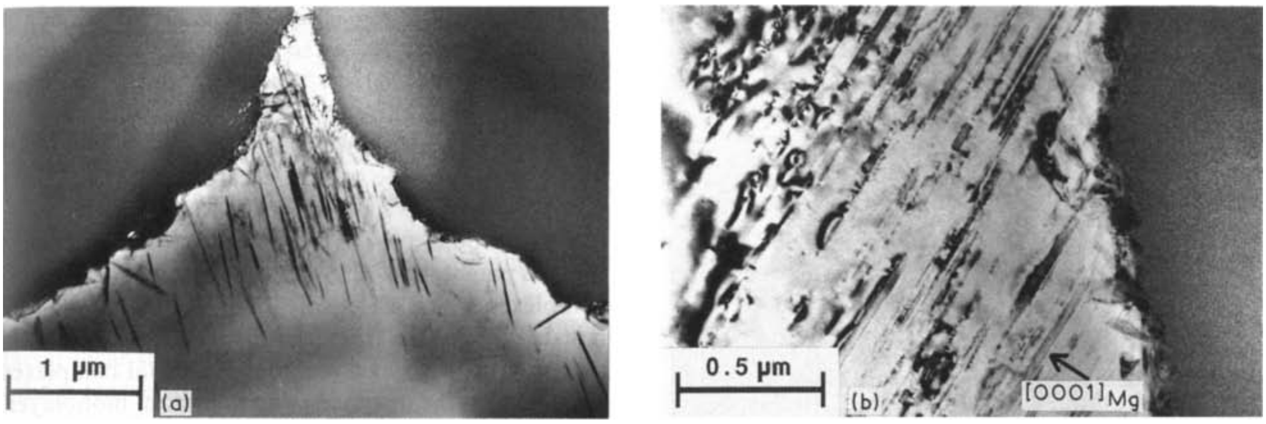


Figure 4 (a) Lath-shaped precipitates of $Mg_{17}Al_{12}$ at the fibre/matrix interface of AS41/X550 composite. (b) Higher magnification view showing the similarly oriented precipitates.

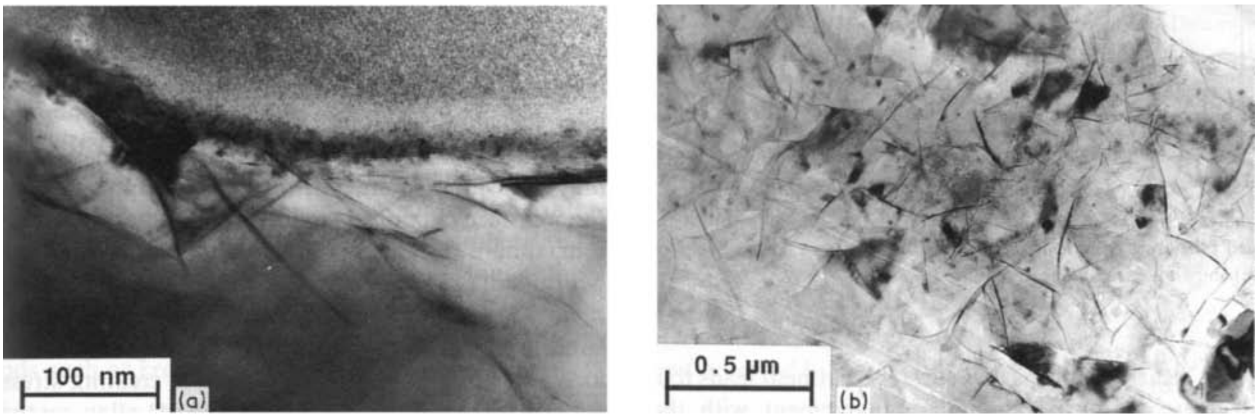


Figure 5 (a) Slender, crooked carbide precipitates at the fibre/matrix interface in AS41/X550 composites. (b) Section parallel to and containing the fibre/matrix interface showing the large number of carbides present.

composites. In addition, there were many small, ~ 100 to 200 nm, particles of $Mg_{17}Al_{12}$.

4. Discussion

The results show that the mechanical properties are strongly dependent upon the matrix alloy and the precise fibre surface condition. Based upon the usual rule of mixtures estimates, the tensile strength of the X550/c.p. Mg composites should have been 1450 MPa and that of the T300/c.p. Mg composites should have been 1059 MPa. The measured values are in each case about one half of the theoretical values but it should be noted that the X550/c.p. Mg specimens used fibres which were both sized and surface treated while the T300-99/c.p. Mg specimens used fibres which were neither sized nor surface treated.

It is, therefore, tempting to conclude initially that sizing or surface treatment has little influence upon the mechanical properties. However, this is not borne out by comparison of the data for samples 4 and 6 with data for samples 5 and 7 which clearly show that the surface treatment has reduced the tensile strength by more than 200 MPa. The influence of surface treatment is obvious but the influence of the sizing is not yet clear.

The effect of surface treatment is also clearly visible in the fracture surfaces which show that the flat, cumulative fracture mode operates in all cases, irrespective of fibre type, alloy content or sizing. Close inspection of the fractographs shows that fracture proceeds from one fibre to the adjoining fibre, for example, as shown by the arrows in Fig. 1a. Note that this type of fracture requires that the fibres be essentially touching or only separated by a very thin layer of matrix.

This behaviour is predicted by the work of Shoshorov *et al.* [8] who related the longitudinal tensile strength of unidirectionally reinforced composites to the interfacial shear strength and the fraction of fibres that fail in a non-cumulative mode, θ, by an equation of the form

$$\sigma = \sigma_{max}\theta^{(1/1+\beta)}(1 - \theta) \qquad (1)$$

where β is the Weibull distribution parameter and σ_{max} is the stress in the fibres at the instant of fracture. The interfacial shear strength, τ_i, is related to θ by an equation of the form

$$\tau_i = \tau_m\theta \qquad (2)$$

where τ_m is the matrix shear strength and represents the maximum obtainable value of the interfacial shear strength. The tensile strength is thus predicted to rise to a maximum value and then decrease as the interfacial shear strength increases past some critical value. Comparison of samples 4 and 6 with 5 and 7, respect-

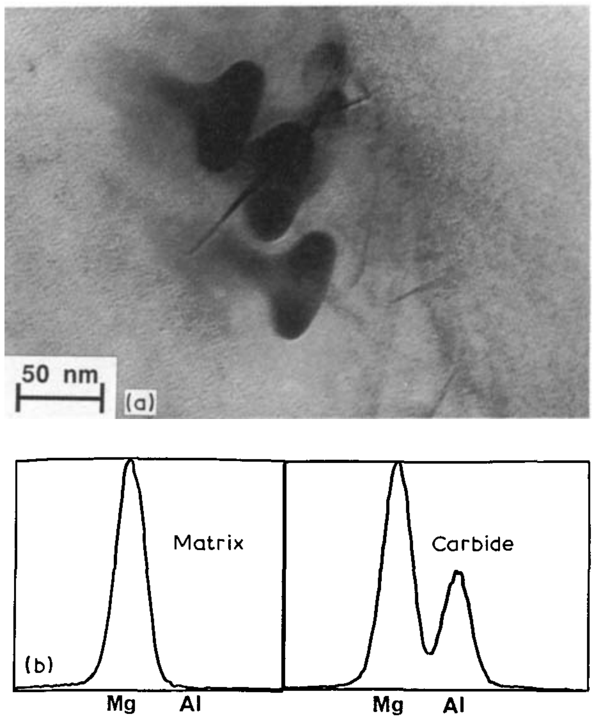


Figure 6 (a) Areas within the matrix and straddling a carbide, analysed by EDS and showing the contamination spots. (b) Enlarged portion of spectra from the matrix and needle, respectively, of (a) showing enrichment in aluminium.

ively, clearly confirms that surface treatment leads to a decrease in tensile strength in agreement with the model of Shoshorov *et al.* [8]. The present X550 data neither confirm nor contradict this trend because there are no interfacial shear strength data available for c.p. Mg/X550 without surface treatment. However, other experimental work in this laboratory with a large variety of systems has shown that surface treatments always increase the interfacial shear strength and decrease the longitudinal tensile strength of both carbon–magnesium and carbon–aluminium composites [6, 7, 9]. Clearly, the critical value of interfacial shear strength above which the tensile strength decreases is very low indeed.

Although the effect of surface treatment on interfacial shear strength and, hence, on mechanical properties has been satisfactorily modelled, and confirmed by these experiments, it is still unclear how the increase in interfacial shear strength is brought about. In the case of carbon–aluminium MMCs it has been shown that surface treatment can lead to an increase in the amount of Al_4C_3 formed at the interface during infiltration. However, the present TEM observations show no reaction whatsoever in samples 4 or 5 and this appears to rule out interfacial reaction as a factor in increasing the interfacial shear strength unless the reaction products are of sub-nanometre dimensions.

Another possibility is that surface treatment increases surface rugosity and this leads to improved mechanical interlocking. Careful comparison of transverse sections of surface treated and untreated fibres, such as shown in Fig. 2, showed no such macroscopic effect. If this is a contributing factor it must, again, be a sub-nanometre scale phenomenon.

If the above two factors are assumed to be of negligible importance, as seems likely, the remaining possibility is that surface treatment renders the fibre surface more receptive to metal–carbon bonding. Previous studies have shown that surface treatment leads to an increase in the oxygen/carbon ratio at the fibre surface due to the formation of carboxyl and similar reactive groups [10–12]. It is, therefore, concluded that, in magnesium MMCs, these groups form metal complexes which effectively bond the fibre and the matrix without the formation of a macroscopic reaction product such as a carbide. The metal complexes must form at the interface as an interfacial monolayer.

An apparently paradoxical situation arises when the effect of alloying elements is examined. It is seen that the addition of 4% Al to the c.p. Mg matrix leads to an increase in strength for T300-99 samples whereas the addition of 4% Al plus 1% Si leads to a severe decrease in the strength of the X550 composites. The reasons for the different effects of alloy additions can be understood by reference to fractography and the microstructural analyses.

The Mg–4Al alloy is essentially single phase with only occasional interdendritic areas of $Mg_{17}Al_{12}$ and the interface contained small carbides in a layer with a maximum thickness of layer < 0.1 μm. Ochiai and Murukami [13] have calculated that brittle layers less than 170 nm thick would not cause critical stress concentrations in carbon fibres. This layer is, therefore, too small to be of significance in creating stress concentrations at the interface. The AS41 alloy, on the other hand, contained extensive areas of various intermetallic compounds which frequently surrounded individual fibres and provided bridges from one to the next. These bridges of brittle compound present convenient locations for the generation of critical length cracks which lead to reduced tensile strength. Furthermore, precipitation around the fibres as shown in Fig. 4 yields an embrittled region > 1 μm thick which is also effective in reducing the crack-arresting properties of the matrix between fibres.

Finally, it has been shown that there is no detectable reaction between carbon fibres and a pure magnesium matrix but the addition of aluminium leads to the formation of fine aluminium-containing precipitates which are, presumably, a type of aluminium carbide. The carbides in this case, though, are thin and crooked whereas aluminium carbides in aluminium matrices generally appear as straight, stubby needles.

As mentioned above, and also shown by examination of the fracture surfaces, the matrix is seen to be of importance in providing crack arrest between fibres. When little or no matrix is present between fibres and when the fibres do not debond, catastrophic crack propagation occurs at relatively low stresses: this is the case with surface-treated fibres in T300-90/c.p. Mg composites. Conversely, when the interfacial shear strength is lower and debonding and fibre pull-out occur more easily, tensile strength is not adversely affected. The clear conclusion is that fibre placement, and the assurance of the presence of a layer of matrix around each fibre, is of great importance in achieving optimum properties. Present squeeze-casting processes tend to push the fibres into contact with one another and future development must be directed to obtaining more uniform fibre placement.

5. Conclusions

From the present mechanical testing and detailed metallographic observations on a variety of carbon–magnesium composites the following conclusions may be drawn.

1. Surface treatment, while improving the interfacial shear strength, can drastically reduce the longitudinal tensile strength.

2. Attractive mechanical properties are achievable by squeeze casting without expensive fibre coating treatments.

3. Alloy additions to the pure magnesium matrix can improve the tensile strength provided that continuous crack paths through brittle phases are avoided.

4. Fibre placement and the presence of a layer of matrix around each fibre are important in realizing optimum properties.

5. Precipitation events are strongly influenced by the residual stresses present at fibre/matrix interfaces.

6. While surface treatment can improve the interfacial shear strength (and transverse properties), it appears to be uniformly deleterious to longitudinal strength. This implies that attempts to develop good transverse strength should be directed at other methods such as cross-plying or hybrid composites.

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