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Optimization of chemical reactions between alumina/silica fibres and aluminium-magnesium alloys during composite processing

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An Al–Si–Cu–Mg alloy reinforced with alumina/silica fibres (Fiberfrax®, alumina/silica ratio = 45/55) has been extensively characterized in terms of microstructure, interfacial chemical reactions and mechanical properties. The composite was fabricated by squeeze casting. The above characteristics were measured as a function of (a) calcination temperature of the fibre preform before infiltration, and (b) subsequent composite heat treatment. The main reaction that occurs during the processing of aluminium alloy matrix composites is the reduction of silica in the binder and fibres by magnesium from the matrix. When calcined below 1000 °C, the fibres remain amorphous with a coating of porous silica binder. In this condition, the reinforcement reacts strongly with the matrix during heat treatment of the composite. In contrast, at high calcination temperatures (1200 °C), the fibres transform partially into mullite and the silica binder densifies; these fibres are somewhat less reactive with the matrix. In both cases, the matrix/reinforcement reactions are very strong during high-temperature heat treatment, leading to a complete reduction of silica in some cases. The degradation caused by chemical reactions adversely affects the mechanical properties of these composites. Therefore, in order to optimize the mechanical properties of this composite, the fibre preform first must be calcined at high temperature, then the composite heat treatment limited to low temperature.

1. Introduction

The aluminium-alloy/alumina composites constitute an important class of materials for low-cost, high-performance applications in the automotive industry. Reinforcement with short ceramic fibres improves mechanical strength, stiffness and wear resistance in comparison to monolithic aluminium alloys. Several types of Al/Al_2O_3 composites exist, which differ in one or more of the following aspects: matrix composition, fibre composition, fibre treatment, binder composition, processing technique and composite heat treatment. These variables govern the microstructure and control the chemical interactions between the matrix and the reinforcement during fabrication. The aluminium alloy matrix usually contains magnesium as an alloying element added to produce a fine distribution of intermetallic precipitates (such as Mg_2Si and Al_2CuMg), which promote precipitation strengthening. Unfortunately, magnesium reacts with silica in the binder and the fibre, and also with alumina. As a consequence of such reactions, the fibre stiffness is reduced and the matrix is depleted of magnesium. Loss of magnesium diminishes precipitation strengthening, and the mechanical properties of the composite are adversely affected. However, a limited amount of reaction between magnesium and the reinforcement can be beneficial because it enhances interfacial wetting. Clearly, there is a need to control the processing conditions in order to optimize the chemical interactions between the constituents of a composite.

Squeeze-cast Al/Al_2O_3 type composites have been extensively characterized in terms of microstructure, chemical reactions and mechanical properties. However, reports in the literature differ in matrix

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composition, fibre and binder materials, and processing conditions, making it difficult to compare the results of these studies. There are conflicting observations regarding the extent of chemical reactions and the nature of the products formed, especially during the squeeze-casting process. For example, Cappleman *et al.* [1], Clyne *et al.* [2], and Stephenson *et al.* [3] detected very little or no interaction between the aluminium-base matrix and alumina-type fibres. On the other hand, Petitcorps *et al.* [4], Munitz *et al.* [5], Liu *et al.* [6], Karlsen *et al.* [7] and Soni *et al.* [8] reported formation of MgO or Al_2MgO_4 as a result of matrix/fibre reactions during the casting process.

A distinct feature of the present study is the use of kaolin glass-based Fiberfrax® (registered trademark, the Carborundum Company) fibres that contain an amorphous mixture of 45% alumina and 55% silica. These fibres are a low-cost alternative to Saffil fibres for reinforcement of aluminium alloy matrices. In a previous study, it was demonstrated that reinforcement of aluminium alloys with Fiberfrax® fibres bestowed properties and in-service performance comparable to those of Saffil-reinforced alloys [9]. The goal of this study was to understand further the chemical phenomena occurring during fabrication and subsequent processing of the Fiberfrax®-reinforced aluminium alloys. Towards this goal, transmission electron microscopy (TEM), secondary ion mass spectrometry (SIMS), and Auger electron spectroscopy (AES) have been employed. The effect of calcination temperature on fibre preforms made of Fiberfrax® fibres has been evaluated. The effect of subsequent heat treatment on the composite microstructure, chemical reactions and mechanical properties is also discussed. A specific objective of this study was to establish optimal processing conditions for the manufacture of Fiberfrax®-reinforced aluminium alloy composites.

2. Experimental procedure

The aluminium alloy F332 used as the alloy matrix has the following composition (wt %): 9.5 Si, 3 Cu, 1 Mg, balance Al. The impurities in this alloy are iron, nickel, manganese, zinc and titanium, and total ~ 0.5 wt %. This alloy was reinforced with Fiberfrax® fibres, which are composed of an amorphous mixture of alumina and silica in nearly equal proportions. The fibres were coated with a silica binder and fabricated into a preform shape containing 15–20% fibre by volume. The preform was calcined at either 850 or 1200 °C in order to transform the fibre structure and to consolidate the silica binder. The preform was subsequently infiltrated with molten aluminium alloy at 675–760 °C and solidified under a high pressure in a squeeze-casting press. The composite was then heat treated to modify the matrix microstructure. Two heat treatments were performed: (i) T5, a low-temperature ageing treatment, typically 11 h at 200 °C followed by air-cooling; and (ii) T6, a high-temperature solution treatment at 530 °C for 6 h followed by water-quenching. The processing conditions of the four samples used in this study are listed in Table I.

TABLE I. Processing specifications of the composite samples used in this study

Sample	Fibre preform calcination treatment	Composite heat treatment[a]
A	850 °C, 3h	T5
B	1200 °C, 3h	T5
C	850 °C, 3h	T6
D	1200 °C, 3h	T6

[a] T5, 200 °C/11 h, air-cooling; T6, 530 °C/6 h, water-quenching. Alloy matrix: Al–9.5Si–3Cu–1Mg (wt%). Fiberfrax® fibres: 45% alumina, 55% silica.

SIMS analysis was performed with a unique scanning ion microprobe developed at The University of Chicago [10, 11]. The design of this SIMS instrument and its application in the microanalysis of composites have been discussed in detail elsewhere [12, 13]. Bulk samples for SIMS analysis were polished using standard metallographic procedures and sputter-coated with gold to prevent charging. Transmission electron microscopy (TEM) analysis was performed with a Jeol 4000 or 1200EX instrument. Specimens for TEM analysis were prepared by thinning 3 mm diameter slices of the sample to ~100 μm and subsequently grinding with a dimpler to ~60 μm. The samples were further thinned to perforation in an argon-ion mill at 4 kV. Scanning Auger analysis was performed with a PHI 660 instrument equipped with an *in situ* fracture stage.

3. Results

3.1. Microstructural characterization with electron microscopy

Composite samples A and B were T5 heat treated but with different preform firing temperatures: A was calcined at 850 °C and B at 1200 °C. The objective of this comparison was to evaluate the effect of fibre crystallization on chemical reactions between the fibre and matrix during a T5 heat treatment.

Fig. 1 shows a bright-field transmission electron micrograph of sample A, in which the porous structure of SiO_2 binder between two fibres can be seen. The fine particles of silica sol, used to “glue” the preform structure before and during squeeze infiltration, do not coalesce during calcination at 850 °C. Electron diffraction indicated that both the fibres and the binder are completely amorphous in this sample.

Fig. 2a and b are high-resolution transmission electron micrographs of the sample B; Fig. 2b is a magnified view of the contact region in Fig. 2a. The silica particles in the binder fuse during the higher calcination of the preform and consolidate into a dense amorphous layer surrounding the fibres. The fibres contain small crystalline regions which are identified as mullite ($3Al_2O_3 \cdot 2SiO_2$ or $Al_6Si_2O_{13}$). In a separate study of calcined Fiberfrax® fibres by X-ray diffraction, it was found that crystallization of fibres starts above 900 °C and the fraction of mullite increases at higher temperatures. Fiberfrax® calcined at 1200 °C contains ~50% mullite by volume as determined by X-ray diffraction [14].

Figure 1 Bright-field TEM image of MMC sample A showing portions of two Fiberfrax® fibres joined by a porous web of silica sol particles from the silica binder used in the fibre preform. A section of the aluminium alloy matrix appears in the upper right corner. In this sample, the fibre preform was calcined at 850 °C prior to melt infiltration and the MMC was T5 treated.

The electron microscopy results of T5-treated composites can be summarized as follows: preforms fired at 850 °C have fibres containing an amorphous mixture of alumina/silica covered with a porous web of silica sol particles. Preform calcination at 1200 °C results in partial crystallization of the fibres into mullite and consolidation of the silica binder into a dense layer. The chemical interactions between matrix/reinforcement as determined by SIMS are discussed in the following section.

3.2. SIMS imaging microanalysis of chemical reactions

3.2.1. T5 heat treatment

Fig. 3a–c show Al^+, Si^+, and Mg^+ SIMS elemental distribution maps, all acquired from the same 40 μm × 40 μm area of specimen A. Pure silicon phase appears bright in the Si^+ map and, conversely, the darkest in the Al^+ map. The SiO_2 binder is devoid of aluminium and is dark in the Al^+ map but bright in the Si^+ map, as expected. The binder layer is bright in the Mg^+ map also; this correspondence between the silicon and magnesium distributions in the fibre regions indicates that magnesium from the matrix has diffused into the binder. Magnesium penetrates all the way to the binder/fibre boundary, being concentrated uniformly throughout the binder layer. The attack of magnesium is limited to the binder; no diffusion of magnesium is detected inside the fibres. Magnesium is also present in the matrix as fine precipitates probably as Mg_2Si and Al_2CuMg phases, below the resolution limit of the imaging-SIMS instrument. Copper does not participate in the reaction.

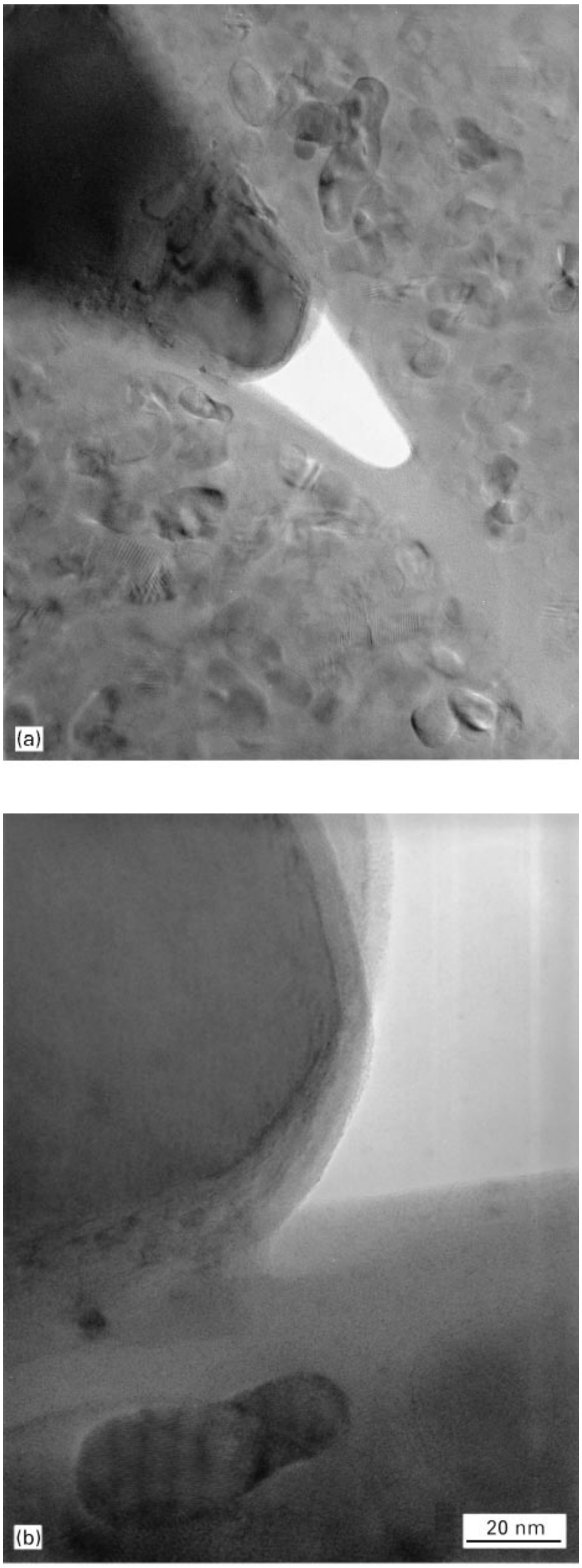
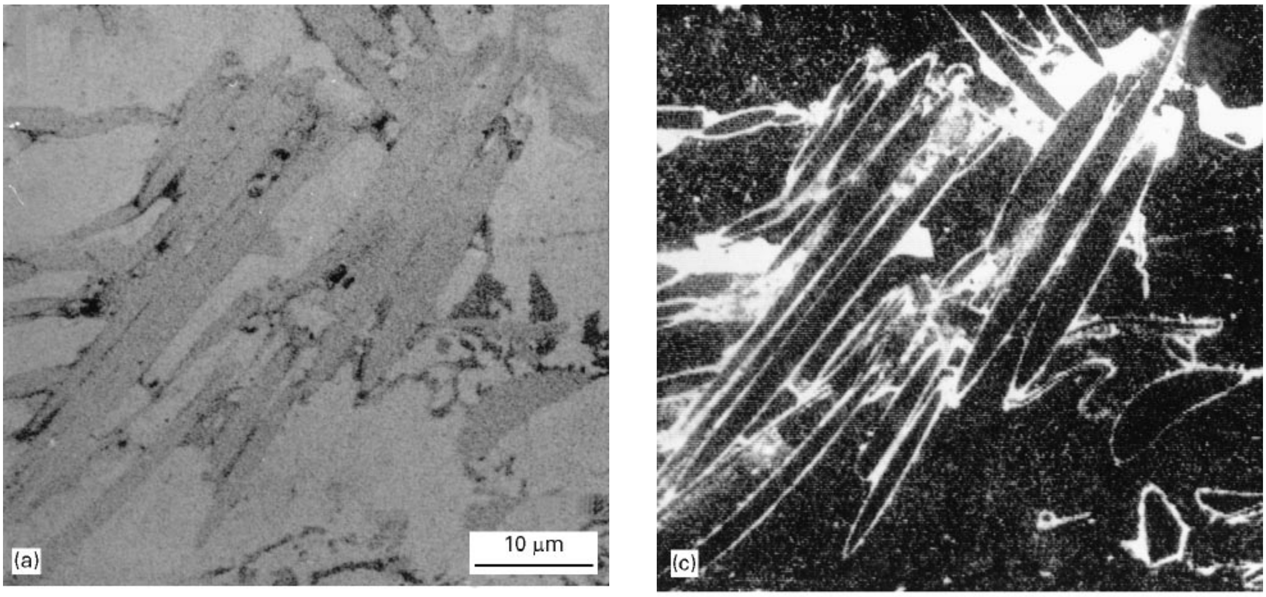


Figure 2 (a) Bright-field TEM image of MMC sample B showing portions of two partially crystallized Fiberfrax® fibres (upper right and lower left), the amorphous silica binder, and aluminium alloy matrix (upper left). The central area is shown at higher magnification in (b). The central white area is a void formed during specimen preparation. (b) Bright-field TEM image of sample B at higher magnification showing a mullite crystallite in the Fiberfrax® fibre (bottom), the amorphous binder and aluminium alloy matrix (upper left).



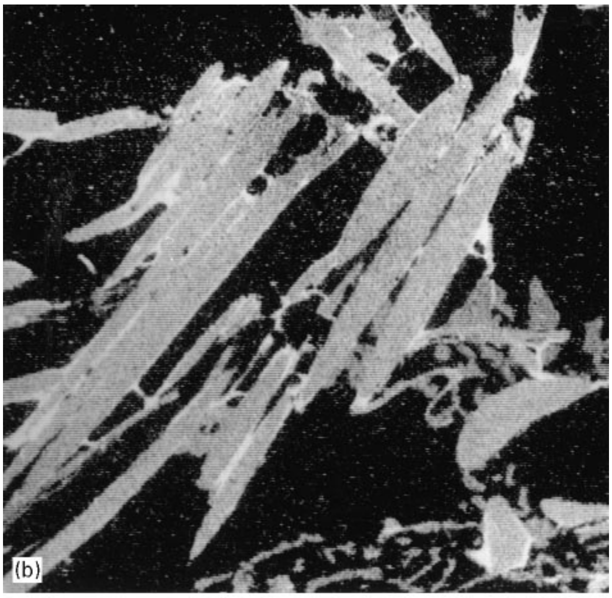


Figure 3 SIMS maps of sample A that was introduced in Fig. 1, acquired with a high-resolution scanning ion microprobe. All SIMS maps in this article were constructed from 512 × 512 raster scans, and each was accumulated in times of less than 524 s. Images are displayed in a logarithmic grey scale, in order to enhance brightness in and aid interpretation of low-intensity areas. SIMS distribution maps: (a) Al^+, (b) Si^+, and (c) Mg^+. The fibres dominate in the silicon map and appear surrounded by a bright rim of silica binder. Magnesium from the matrix migrates to the binder region.

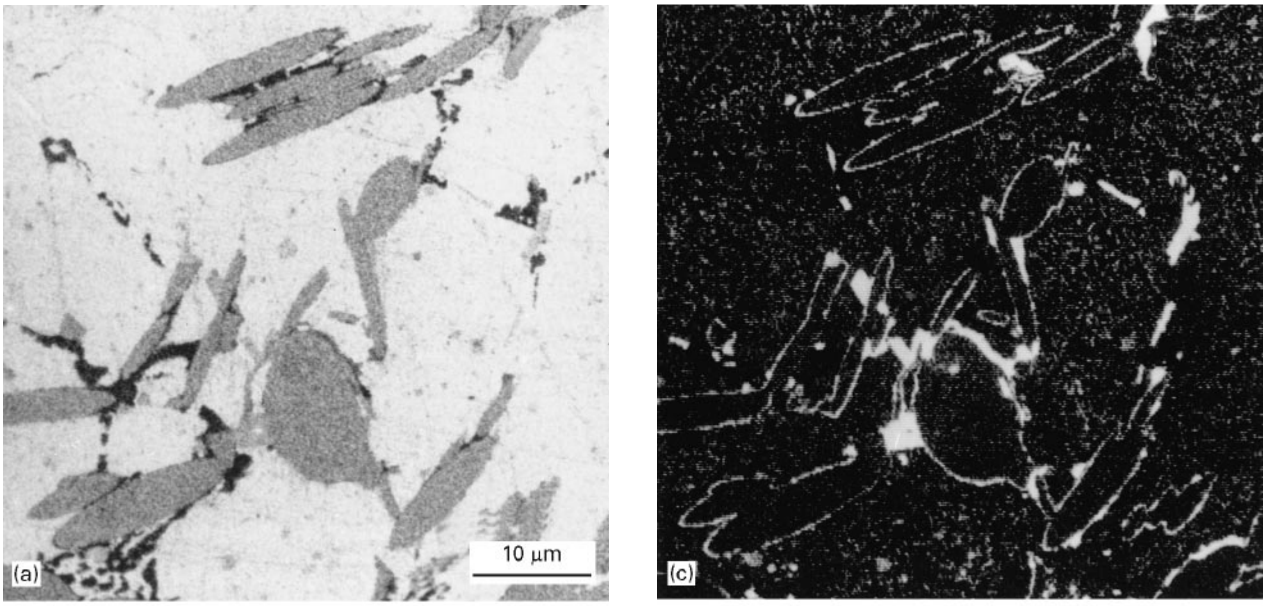
Fig. 4a–c show Al^+, Si^+, and Mg^+ SIMS maps of sample B. These maps are quite similar to those for sample A shown in Fig. 3. However, there are a few differences between the silicon and magnesium maps of the two samples. The silica binder cannot be distinguished in the silicon image (Fig. 4b) probably because firing at 1200 °C resulted in thinning of the binder. It is also likely that the Si^+ signals from the binder and the fibre are nearly the same intensity, a consequence of the high-temperature calcination of the fibre preform. These maps indicate that the penetration of magnesium and aluminium stops at the outer surface of the binder layer (i.e. at the binder/matrix interface). Therefore, reactions between the fibre and the matrix do not occur because of the presence of the dense, continuous layer of the silica binder. The consolidated binder layer here acts as an effective barrier to penetration of magnesium and aluminium, in contrast to the porous layer that is present after fibre calcination at lower temperature. Although some magnesium has reacted with the binder, the amount of magnesium remaining in the matrix was found to be ~30% higher than that seen in Fig. 3c. In other words, the Fiberfrax® fibre preform calcined at higher temperature is less reactive with respect to magnesium during the T5 treatment than one calcined at a lower temperature.

3.2.2. T6 heat treatment

Samples C and D were T6 heat treated which involved heating at 527 °C for 6 h followed by water quenching. T6 is a solution heat treatment usually administered to cast alloys in order to homogenize the alloy composition. Samples C and D were studied to evaluate the effect of fibre calcining temperature on fibre/matrix reactions that occur during T6 heat treatment.

Fig. 5a–c show Al^+, Si^+, and Mg^+ maps of the composite sample C. The darkest regions in the Al^+ map are elemental silicon precipitates, which are bright in the Si^+ image (Fig. 5b). The fibres are surrounded by a dark rim in the Al^+ map, at the location of the original SiO_2 binder. Remarkably, the binder is no longer present and there is no silicon remaining in the fibres. The silica from both the fibre and binder has reacted with magnesium and aluminium from the alloy. During this process, the fibres are converted into Al_2O_3. Magnesium is mainly present, probably as MgO, in locations previously occupied by the SiO_2 binder. Magnesium is nearly absent in the alloy matrix and has also diffused at low concentration into the fibre. The silicon from the fibres is converted to elemental silicon and diffuses to large silicon precipitates in the Al–Si–Cu alloy matrix.

Fig. 6a–c are correlative Al^+, Si^+ and Mg^+ SIMS maps of sample D. The extent of the fibre/matrix reaction is much less than that in the previous sample



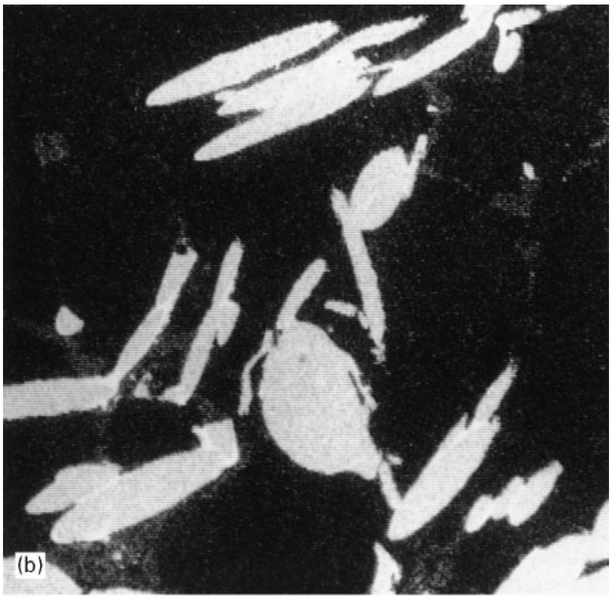


Figure 4 Correlative SIMS maps of composite B described in Fig. 2: (a) Al^+, (b) Si^+, and (c) Mg^+. Magnesium reacts with silica binder although to a smaller extent than that observed in Fig. 3c. Magnesium is still present in the matrix.

(shown in Fig. 5). The Si^+ map (Fig. 6b) clearly shows that most of the SiO_2 is still present in the fibres. Large silicon particles formed by reduction of silica border the fibres. However, the reduction of SiO_2 by magnesium and aluminium is very non-uniform: the attack occurs at certain locations on the fibre surface and its extent varies from fibre to fibre. A thin MgO layer uniformly surrounds the fibres. Magnesium has migrated into the fibres, and the distributions of magnesium and silicon are complementary inside the fibres. The magnesium-rich areas in the fibre also contain aluminium and are probably Al_2MgO_4 spinel phase. Another significant difference from sample C is that some magnesium is still present in the matrix, whereas magnesium was completely depleted from the alloy in the case of fibres calcined at 850 °C (cf. Figs 5c and 6c).

The SIMS micrographs in Figs 5 and 6 demonstrate that the fibres are severely attacked during T6 treatment, although the extent of this attack is noticeably less for fibres calcined at higher temperature. This attack not only degrades the binder and the fibre, but also depletes out magnesium from the matrix.

3.3. Scanning auger analysis of fibre chemistry

Scanning Auger microscopy was performed on a composite that is similar to sample C but contains 20 vol% of fibres instead of 15%. It was assumed that the chemical interactions will be similar in these composite materials. Fig. 7a is the secondary electron micrograph of a polished cross section of this composite specimen, showing the alloy matrix (1) and a portion of a fibre containing reacted (2) and unreacted (3) zones. Auger spectra (Fig. 7b, c) acquired from the reacted and unreacted portions of the fibre show that the former contains magnesium but is depleted of silicon. The unreacted central core still contains silicon but no magnesium. These observations are in agreement with the Mg^+ and Si^+ SIMS maps (cf. Figs 7b, c and 5). The Auger spectra also contain information about the chemical state of the elements. A comparison of the aluminium Auger peaks from the alloy matrix, the reaction and unreacted zone of the fibre is presented in Fig. 7d. The matrix contains aluminium in the elemental form (Al^0) at 1392 eV, whereas the unreacted region consists of aluminium oxide (Al^{3+}) at 1382 eV, as expected. However, the aluminium signal from the reaction zone in the fibre showed characteristics of both the elemental aluminium and aluminium oxide peaks. In order to ensure that the presence of metallic aluminium was not the result of smearing of the matrix during polishing of the specimen, another Auger analysis was performed. A similar sample was fractured under high vacuum inside the Auger microscope and was transferred directly into the analysis chamber without exposure to air. Auger spectra acquired from the reaction zone and the unreacted core were similar to those from the polished sample, thus confirming the presence of metallic aluminium in the reaction zone.

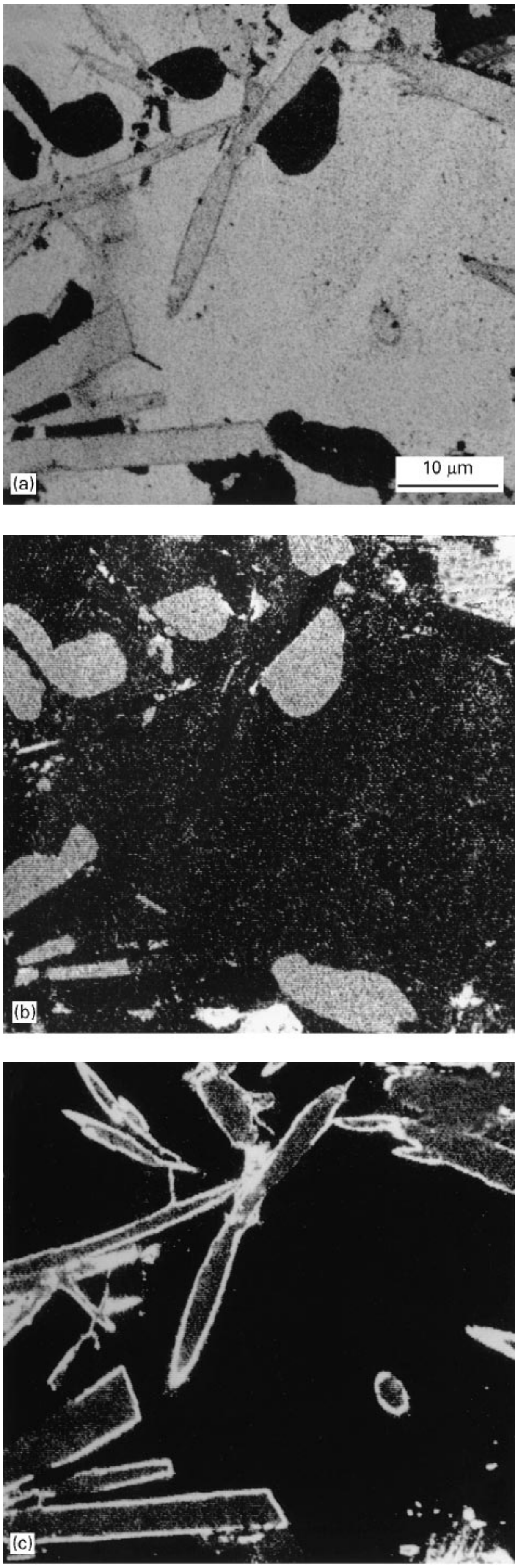


Figure 5 Correlative SIMS maps of composite sample C cast with fibres calcined at 850 °C and then T6 treated: (a) Al^+, (b) Si^+, and (c) Mg^+. There is no silica left in the fibre and binder as a result of chemical reactions between the fibre and the matrix. Elemental silicon is precipitated in the matrix.

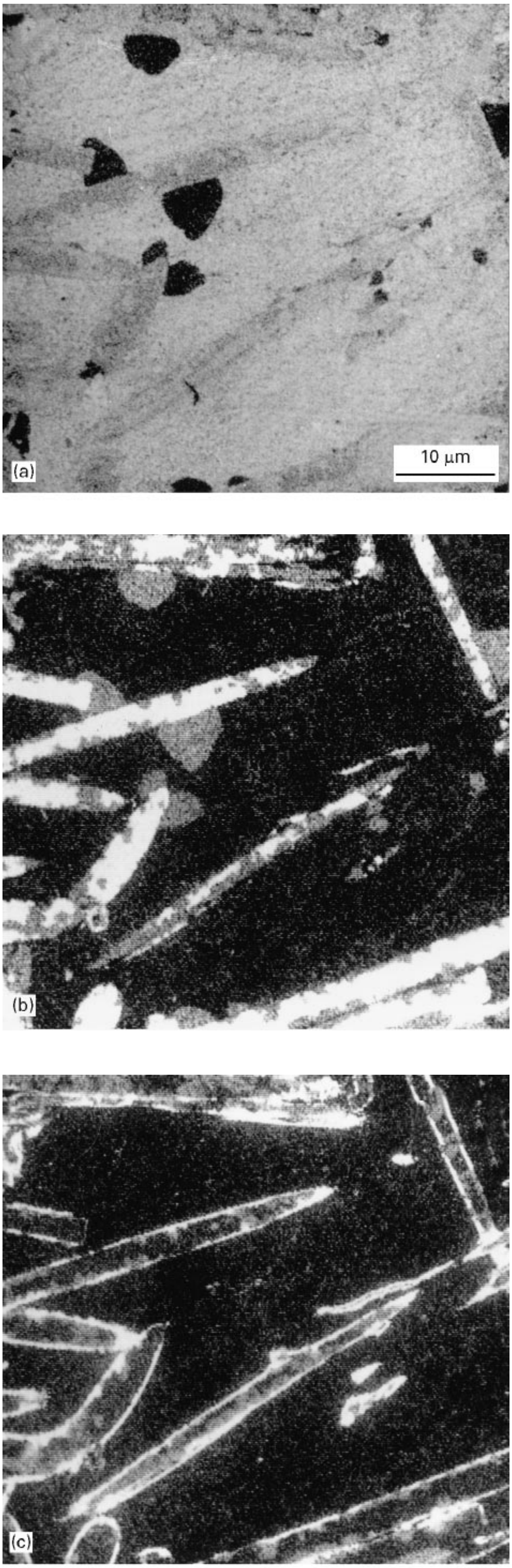


Figure 6 Correlative SIMS maps of sample D: (a) Al^+, (b) Si^+, and (c) Mg^+. The fibre preform was calcined at 1200 °C and the composite was given a T6 heat treatment. The binder is completely reduced and the fibres are partially attacked.

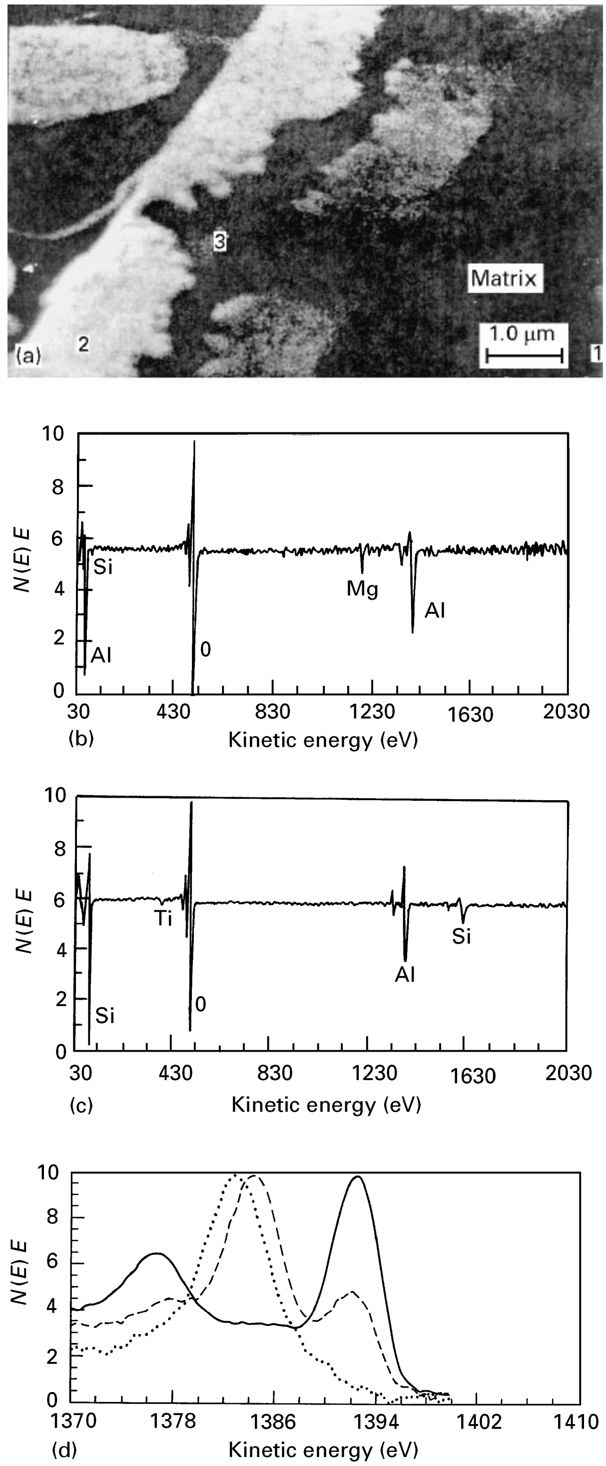


Figure 7 (a) Secondary electron micrograph of a cross-sectioned Fiberfrax® fibre in an MMC. This sample contained 20 vol% fibres calcined at 850°C and the MMC was T6 heat treated (similar to sample A, but with higher fibre volume fraction). (b, c) Auger spectra from (b) the reaction zone (point 2) and (c) the central unreacted core (point 3) of the fibre shown in (a). The reaction zone contains magnesium and no silicon, whereas the unreacted core of the fibre still contains silicon with trace of magnesium. (d) Aluminium Auger peaks from (——) points 1 (aluminium alloy matrix), (- - -) 2 (reaction zone) and (···) 3 (unreacted core) shown in the secondary electron micrograph (a). The peak from the reaction zone contains signatures of both aluminium oxide and elemental aluminium.

3.4. Mechanical properties of the composites

Fig. 8 shows the effect of preform calcining temperature on the yield and ultimate tensile strengths of the composites that were T5-treated. The measurements were made at room temperature and at 260 °C. At a given test temperature, the yield and ultimate tensile strengths improved as the firing temperature of the preform was increased. Strengths values were reduced at the higher test temperature.

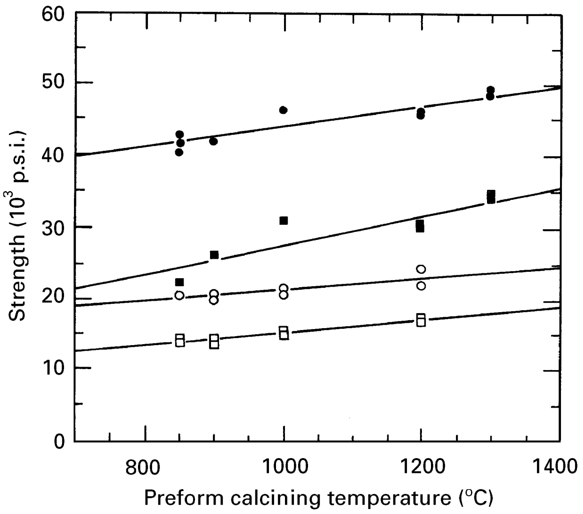


Figure 8 (■, □) Yield and (●, ○) ultimate tensile strengths of aluminium alloy/Fiberfrax® MMCs plotted as a function of the preform calcining temperature. The MMC samples were T5 heat treated. Strength values were determined at both (●,■) room temperature, 24 °C and (○,□) 260 °C (10^3 p.s.i. = 6.89 N mm^{-2}).

4. Discussion

The diffusion of magnesium into the porous silica binder occurs during both the squeeze infiltration and the T5 heat treatment. SIMS analysis of similar composites in the as-cast condition (with fibres calcined at 1200° C) was discussed previously [8, 10]. Migration of magnesium and aluminium from the matrix into the binder was detected in these studies. This observation implies that even a short period of contact between the fibres and the matrix during squeeze infiltration is sufficient to cause chemical interaction between these two constituents. Magnesium is present in the binder as MgO according to the following reaction

$$SiO_2 + 2Mg = Si + 2MgO \qquad (1)$$

However, the amount of magnesium consumed in this reaction during squeeze casting is very small and does not drastically change the microstructure of the matrix with respect to the alloy in its virgin state.

During heat treatments following squeeze casting, the matrix/binder/fibre chemical interactions are accelerated depending on the temperature and time [9, 15, 16]. These heat treatments are necessary to homogenize and age-harden the alloy matrix. Unfortunately, some of these treatments exacerbate the chemical reactions between the fibre and the matrix. These chemical effects must be understood, so that fabrication parameters and component materials can be properly chosen. In Al–Mg alloys reinforced with silica-containing fibres and binder, the reduction of silica by magnesium and aluminium is inevitable. The extent of this reaction depends on the temperature and duration of the thermal treatment. The Fiberfrax® fibres employed in this study contain alumina and silica in nearly equal amounts and undergo partial crystallization to form mullite at temperatures above 900 °C. It has been demonstrated that the fibre preforms calcined at 1200 °C undergo less attack from aluminium and magnesium because of the formation of mullite and the consolidation of the silica binder. The effect of calcining temperature is dramatic, particularly during T6 treatment. The porous binder (for low calcining temperature) is easily consumed by reaction with magnesium and also permits rapid diffusion of magnesium and aluminium to the fibre surface.

The reduction of silica in the binder and the fibre can also occur when aluminium from the matrix reacts as follows

$$3\,SiO_2 + 4\,Al = 2\,Al_2O_3 + 3Si \qquad (2)$$

The reduction of silica may occur by magnesium and aluminium simultaneously, leading to the formation of Al_2MgO_4 spinel as

$$2SiO_2 + 2Al + Mg = Al_2MgO_4 + 2\,Si \qquad (3)$$

Alternatively, the formation of spinel could be expressed by the following reaction

$$Al_2O_3 + MgO = Al_2MgO_4 \qquad (4)$$

During casting and T5 treatment, it has been observed that the attack by magnesium and aluminium remains limited up to the binder/fibre interface.

Silicon released on reduction of silica diffuses into the matrix and may form elemental silicon phases and/or may combine with magnesium in the matrix to form Mg_2Si; the latter is, however, unlikely because the alloy used in this study already contains 9.5 wt% Si. The formation of Mg_2Si, as a consequence of silicon rejection into the alloy, has been reported to occur in Al–Mg alloys that contain little or no silicon [15]. Large particles of silicon form in the composites that received T6 heating, samples C and D (see Figs 5b and 6b). These silicon particles differ from the eutectic silicon precipitates in their morphology and location in the matrix: the silicon particles produced by the reduction reactions are coarse and rounded, whereas the eutectic silicon precipitates are usually fine and needle-shaped. Also, these silicon particles embrace the fibre surface, in contrast to the uniform distribution of eutectic silicon in the matrix. During the T6 treatment, the composite containing amorphous fibres (C) is completely depleted of silica but the sample with partially crystallized fibres (D) retains a significant amount of silica. This difference in the severity of reaction is reflected in the size of the free silicon particles in the aluminium matrix: sample C has much larger particles than sample D. The amount of silicon released is very small during T5 treatment, because only a part of the silica binder is reduced. The location of this silicon in the matrix cannot be easily established, although fine precipitates of silicon border the fibres in the SIMS and X-ray maps of samples A and B.

The penetration of magnesium in the fibres can also reduce alumina as follows

$$Al_2O_3 + 3Mg = 3MgO + 2Al \qquad (5)$$

The presence of elemental aluminium in the reacted part of the fibres, as detected by scanning Auger analysis, is probably the result of the above reaction and/or diffusion of aluminium from the matrix. The elemental aluminium produced by this reaction may participate in Reaction 2 or 3.

The magnesium loss from the alloy causes the decrease in mechanical properties of the composite, because the magnesium depletion causes the Mg_2Si and Al_2CuMg precipitates to be dissolved; these precipitates are necessary for precipitation strengthening of the alloy.

The interfacial reactions are most intense during T6 heating of amorphous fibres. The effect of preform calcination on mechanical properties can be understood in terms of the changes caused in binder and fibre. In MMCs formed with preforms fired at 850 °C, the porous areas of unconsolidated binder provide points of easy failure. The fibres treated at 1200 °C suffer less attack from magnesium and aluminium because of the formation of mullite and a dense protective binder. Mollins *et al.* [16] studied interfacial phenomena in mullite-reinforced aluminium alloy (6061) containing (wt%) 1Mg, 0.25Cu, and 0.6Si as main alloying elements. These researchers found that the mullite fibres were less reactive than Al_2O_3 fibres. They also detected Al_2MgO_4 spinel at the interface in composites heat treated at 535 °C for 50 h. Observations made in the present study regarding the reduced reactivity of mullite and the formation of spinel are in agreement with the results reported by Mollins *et al.* [16].

5. Conclusions

1. Calcination of the fibre preform is essential to improve composite properties. When the preform is calcined above 1000 °C, the Fiberfrax® fibres partially crystallize into mullite and the silica binder densifies.

2. The silica binder is reduced by magnesium from the alloy leading to MgO formation during T5 treatment. Magnesium loss is less severe when a preform fired at high temperature (1200 °C) is used because the dense silica layer retards the migration of magnesium to the fibres. Consequently, the composite formed with these preforms exhibits better mechanical properties than that made with fibres fired at low temperature (850 °C).

3. Intense reactions occur between the matrix and the fibres during T6, irrespective of the preform treatment temperature. Silica, both in the binder and fibres, is reduced by magnesium and aluminium from the alloy. The products of these reactions include spinel (Al_2MgO_4) in the fibres and large particles of elemental silicon in the matrix. Preforms fired at low temperature (850 °C) undergo a complete loss of silica, whereas a small amount of silica is retained by fibres pretreated at high temperature (1200 °C).

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