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Particle degradation during remelting of Al–1% Mg alloy reinforced with SiC_p coated with sol–gel-produced TiO_2

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TiO_2 coatings on SiC particles were produced by the sol–gel process to reduce the reinforcement degradation in Al–1 wt % Mg/SiC_p composites during remelting. The reaction kinetics of the degradation was followed using electron probe analysis and the microstructure of the interfaces was investigated by transmission electron microscopy (TEM). The results obtained clearly show that TiO_2 coatings reduce the degradation of the particles during remelting of composites at 700 °C. The degradation becomes detectable after 20 min for the uncoated particles and after 100 min for the TiO_2-coated particles. TiO_2 reacts during the fabrication of the composites to form MgO. Titanium does not have time to leave the interface and remains in the reaction layer during fabrication in the semi-solid state. The MgO/Ti reaction layer appears to be responsible for the protection of the particles. During remelting, titanium leaves the interface and aluminium diffuses into channels between the MgO crystals. MgO then transforms into spinel ($MgAl_2O_4$) leading, after remelting for 150 min, to a non-uniform reaction zone mainly composed of large spinel crystals. Particle degradation begins when the reaction zone becomes discontinuous and allows molten aluminium to reach the SiC particles.

1. Introduction

Optimum interface strength in metal matrix composites (MMC) must be sought to obtain the best combination of yield strength and fracture toughness [1]. It is considered that an intimate contact between the matrix and the reinforcement, as well as chemical stability of the reinforcement in the matrix, are necessary to obtain a strong interface. The choice of the reinforcement and the matrix often cannot satisfy these two requirements simultaneously [2]. It is difficult to achieve good reinforcement/matrix compatibility in aluminium matrix composites because aluminium does not wet the ceramic reinforcements and reacts easily with the reinforcements to form intermetallics [3]. In the Al/SiC system, aluminium reacts with SiC to form aluminium carbide (Al_4C_3). This reaction is accompanied by a rejection of silicon in the melt. The carbide formed is water soluble [4] and has detrimental effects on the properties of the composites [5].

Many investigations have been made on the wetting and the stability of SiC in aluminium. It has been shown that the chemical composition of the alloy can considerably affect these phenomena [4, 6]. In addition, coatings have been developed on SiC to improve their wetting and their stability in liquid aluminium. The use of coatings often allows more freedom in the choice of the alloy composition but increases the production cost of these materials. It is thus important to develop low-cost coating methods that are easily manufactured.

The sol–gel method is of interest because it allows surfaces to be coated with continuous and thin oxide films. The method is well adapted to coat particles because the deposition proceeds in a liquid environment. Liu *et al.* [7] and Teng and Boyd [8] developed oxide coatings by the sol–gel method and showed that these coatings delay the degradation of SiC during remelting of the Al/SiC composites.

Clement *et al.* [9] used TiO_2 coatings fabricated by the sol–gel process to protect graphite fibres during fabrication of aluminium matrix composites. The authors showed that a thin TiO_2 coating ($\approx$100 nm) improves wetting of the fibres and prevents the formation of Al_4C_3 during fabrication of the composite. Thanh and Suéry [10] studied the stability of

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TiO_2-coated SiC particles in a molten Al–1 wt % Mg alloy. The coating was discontinuous and constituted of small TiO_2 powders deposited on the SiC particles by dry mixing. Even though the coatings were not uniform, the coating delayed the degradation of the particles during remelting of the composite.

The aim of the present work was to study the degradation kinetics of SiC particles coated with a continuous TiO_2 film manufactured by the sol–gel method in an Al–1 wt % Mg alloy at 700 °C. This alloy was chosen because its composition is close to that of the widely used 6061 alloy. Moreover, it does not contain silicon, which allows the kinetics of the SiC degradation by electron probe microanalysis ($4Al + 3SiC \rightarrow Al_4C_3 + 3Si$) to be followed. Particular attention was paid to the morphology and phase identification of the reaction products at the interface by analytical transmission electron microscopy. A model of the mechanisms involved in the formation of these products is presented in the discussion.

2. Experimental procedure

2.1. Manufacture of the TiO_2 coatings

The sol preparation was based on the work of Takahashi and Matsuoka [11]. The preparation of the sol involved the combination of a solution of 0.8 mol l^{-1} titanium isopropoxide (Aldrich Chemical Company) in 4.3 mol l^{-1} isopropanol (ACP Chemicals) with a solution of 0.8 mol l^{-1} diethanolamine (Aldrich Chemical Company) in 2.2 mol l^{-1} isopropanol and a solution of 0.88 mol l^{-1} water in 2.2 mol l^{-1} isopropanol. The concentrations given are the final concentrations of the sol.

SiC particles (PRESI, France, average particle diameter 13 μm) were added to the sol and mechanically and ultrasonically mixed to ensure good contact between the surface of the particles and the sol. The suspension of SiC particles was then filtered to recover the particles. The product recovered was lightly ground. The loose particles were dried for 2 h at 70 °C and heat treated at 600 °C for 2 h in air. These operations were repeated three times to increase the thickness of the coating. The coating was characterized using a scanning Auger microscope (Jeol JAMP30). The characterization of the coating with selected-area diffraction (SAD), energy dispersive spectrometry (EDS) and dark-field imaging was done with a Jeol 2000FX transmission electron microscope. The amount of TiO_2 deposited was quantified with inductively coupled plasma atomic emission spectroscopy (ICP).

2.2. Fabrication of the composites

The metal matrix composites ($\approx$200 g) were fabricated by incorporating 10 vol % coated or uncoated SiC particles in the semi-solid Al–1 wt % Mg alloy ($\approx$660 °C). The incorporation of the particles typically required 10 min. Fabrication of the composites and the remelting tests were carried out in a SiC/ graphite crucible (Morgan Thermic) heated by induction. An argon flux was maintained at the surface of the melt and the composites agitated (with a graphite agitator) during fabrication and remelting. After the incorporation of the particles, the temperature of the melt was increased to 700 °C for the remelting experiments. The time required to raise the temperature was about 1 min and there was no overshooting. The temperature was maintained at 700 °C during the remelting tests. Samples ($\approx$5 g) were taken at different times during remelting, and air-cooled. Two series of experiments were carried out with intermediate sampling times for the second series and the results were found to be reproducible. The samples were solution treated for 14.5 h at 520 °C, quenched in water and then aged at 175 °C for 10 h.

2.3. Degradation of the SiC particles

The silicon content of the alloy was measured with an electron microprobe (CAMEBAX-SX50) to evaluate the degradation kinetics of the SiC particles. Because the matrix of the composites did not initially contain silicon, the amount of silicon measured in the matrix after remelting of the composites is proportional to the extent of the degradation of the SiC particles [12]. The quantification was made using the ZAF corrections without standards and the results were normalized to 100%. The accelerating voltage used was 15 keV. X-ray maps were also obtained to determine the spatial distribution of magnesium, titanium, silicon and oxygen in the matrix as a function of remelting time.

The morphology and phase identification of the reaction products at the interfaces were studied by transmission electron microscopy (Jeol 2000FX). Energy dispersive X-ray microanalyses (EDS) and selected-area diffraction patterns (SADP) were used for phase identification. TEM samples were prepared by cutting 0.7 mm slices with a low-speed saw which were then mechanically polished to a thickness of 200 μm. Finally, 3 mm diameter discs cut by electroerosion (MPD-2 Electricspark cut off) from these slices were dimpled and ion milled with argon at an angle between 10° and 20° (6 kV, 2 mA).

3. Results

3.1. Characterization of the TiO_2 coatings

Scanning electron micrographs of the coated and uncoated SiC particles are shown in Fig. 1. Fig. 2 shows a TEM dark-field image of the coated particles with the corresponding SADP (annular) pattern. The grain size of the crystals in the coating is small ($\leq$30 nm). Indexation of the patterns was made based on the ratio of the first five diffraction vectors. The SAD pattern of Fig. 2b corresponds to that of the TiO_2 anatase phase. This is consistent with the EDS spectrum of the coating which shows the presence of titanium and oxygen, and with the Auger spectrum of Fig. 3. A large number of analyses were made in the scanning Auger microscope and the results show that the coating thickness is not uniform and can be quite small in certain areas. The results obtained with the

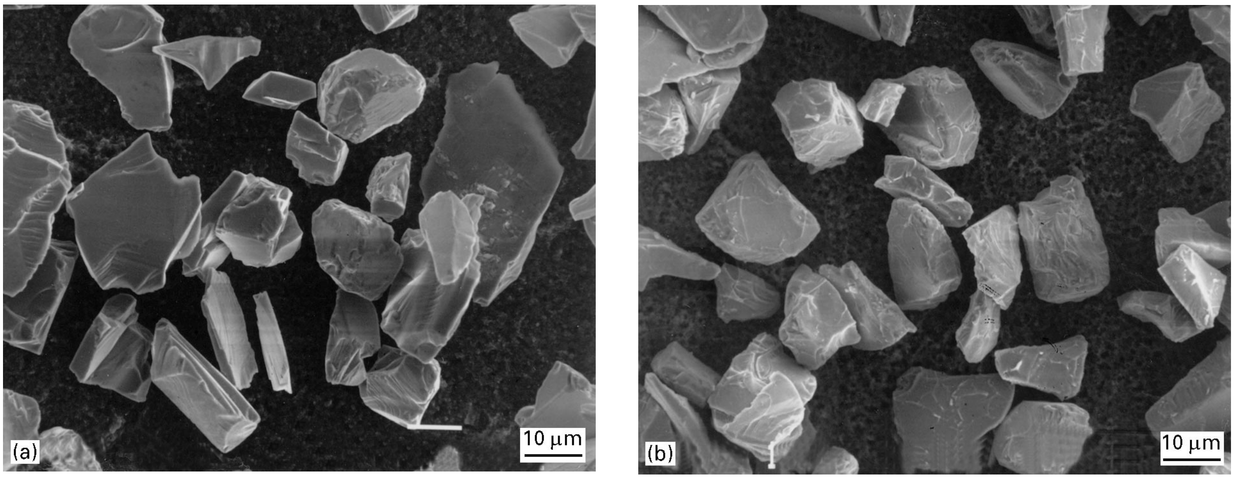

Figure 1 Scanning electron micrographs of the (a) uncoated and (b) TiO_2-coated SiC particles.

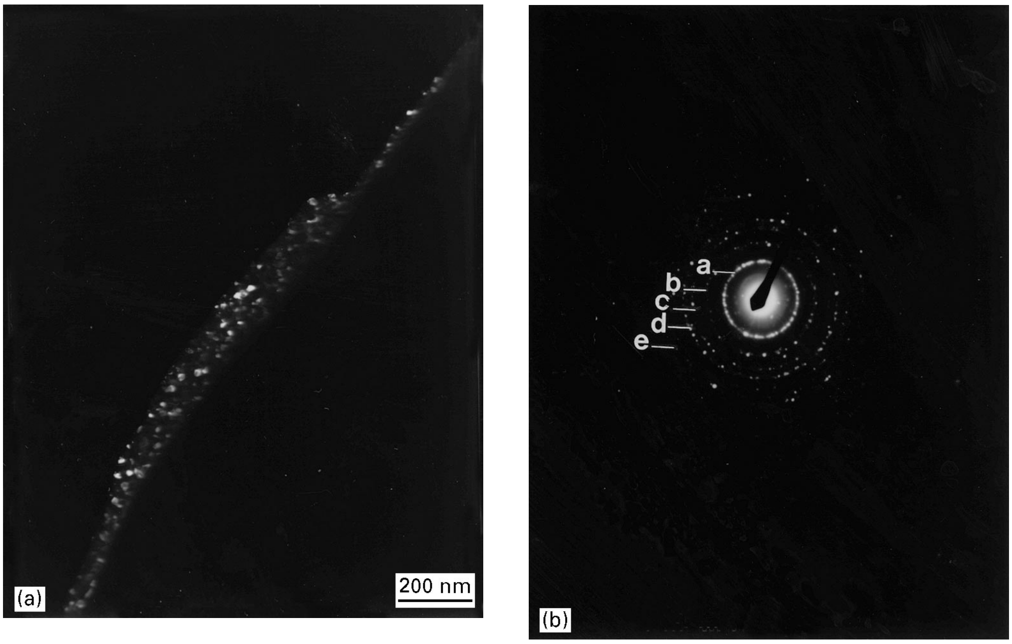

Figure 2 (a) TEM dark-field image of the coated particles; (b) SADP of the coating. a, (1 0 1); b, (1 0 3), (0 4 4), (1 1 2); c, (2 0 0); d, (1 0 5), (2 1 1); e, (2 0 4).

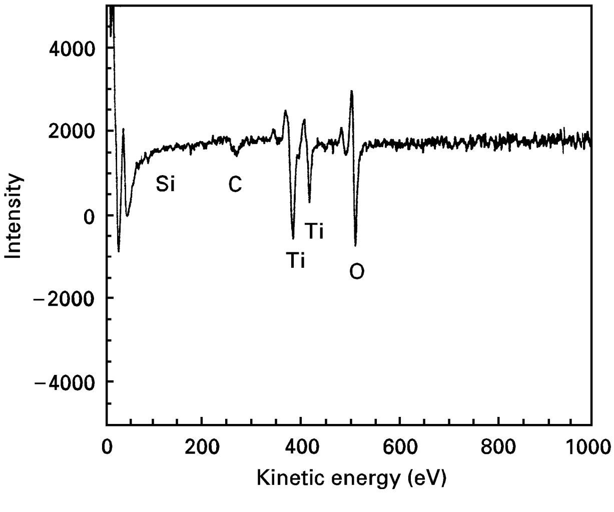

Figure 3 Auger spectrum from a TiO_2-coated SiC particle.

inductively coupled plasma atomic emission spectroscopy (ICP) show that the uncoated SiC particles are slightly oxidized (0.03 wt % SiO_2) and the amount of TiO_2 at the surface of the coated particles is 3.34 wt %. The amounts of SiO_2 and TiO_2 were calculated from the amounts of silicon and titanium, assuming that all the silicon and titanium were combined with oxygen as SiO_2 and TiO_2, respectively.

3.2. Evaluation of the degradation of the particles

As mentioned previously, the amount of silicon rejected in the matrix is proportional to the degradation of the SiC particles. The variation of the silicon content in the matrix of the composites reinforced with the coated and uncoated SiC particles during remelting at 700 °C is shown in Fig. 4. The analyses show that silicon is uniformly distributed in the matrix and that the silicon content in the matrix after fabrication is about 0.1 wt %. The silicon saturation observed at about 1 wt % in Fig. 4 is caused by the attainment of the solubility limit of silicon in the matrix. The degradation proceeds beyond 1 wt % but the technique used (microprobe) is only suited to evaluate the silicon

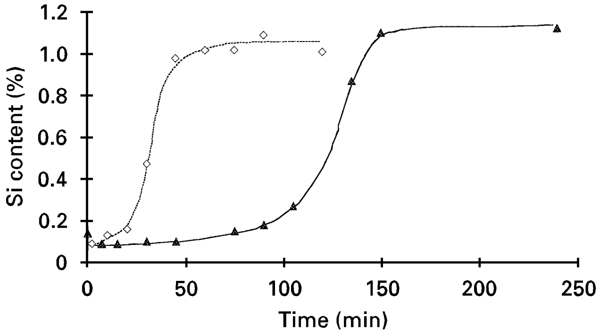

Figure 4 Variation of the silicon content in the matrix of composites reinforced with (◇) uncoated and (▲) TiO_2 coated particles as a function of remelting time at 700 °C.

content in a non-saturated matrix (i.e. the beginning of the degradation of SiC).

At the beginning of the remelting test at 700 °C, the silicon rejection is low for the composites reinforced with uncoated particles. Rapid degradation of the uncoated particles follows after 20 min remelting and rapidly reaches the saturation point (after about 50 min). For composites reinforced with coated particles, the silicon rejection is very low for the first 100 min remelting. After 100 min, particle degradation proceeds more rapidly and saturation is reached after 150 min remelting. The coating thus delays by about 80 min the beginning of the degradation. The rate of degradation (slope of the %Si versus *t* curves) appears to be lower for the coated particles.

X-ray maps of magnesium from the composites reinforced with coated and uncoated particles are shown in Fig. 5. Fig. 5a and b show that magnesium segregates at the matrix/particle interface during fabrication and that segregation of magnesium is more important in composites reinforced with coated particles. After 240 min remelting, the magnesium is still at the interface (Fig. 5c).

Fig. 6 which represents the variation of the magnesium content in the matrix as a function of remelting time for both types of composites clearly shows that the magnesium content in the matrix after fabrication is not the same in the composites reinforced with coated and uncoated particles. After fabrication, the magnesium content in the matrix is lower for the composites fabricated with the coated particles. Segregation therefore appears to be affected by the chemical composition of the surface of the particles. The measured concentration of magnesium in the matrix of the composite fabricated with the uncoated particles decreases after 20 min remelting (Fig. 6). This variation is probably caused by the decrease of the magnesium solubility limit as the silicon content in the matrix increases (beginning of the SiC degradation). The maximum (around 100 min remelting) of the %Mg versus time curve of the composite fabricated with coated particles may be associated with a reaction which rejects magnesium. This will be discussed later in the discussion.

The spatial distribution of titanium in the composites reinforced with the coated particles is shown in Fig. 7. After fabrication, titanium is located around the particles (Fig. 7a). Microprobe analyses showed that the titanium content in the matrix is as low as 0.02 ±0.01 wt % after fabrication. After 45 min remelting at 700 °C, however, titanium is no longer present in large quantities at the interface indicating that titanium diffused away from the interface during remelting (Fig. 7b).

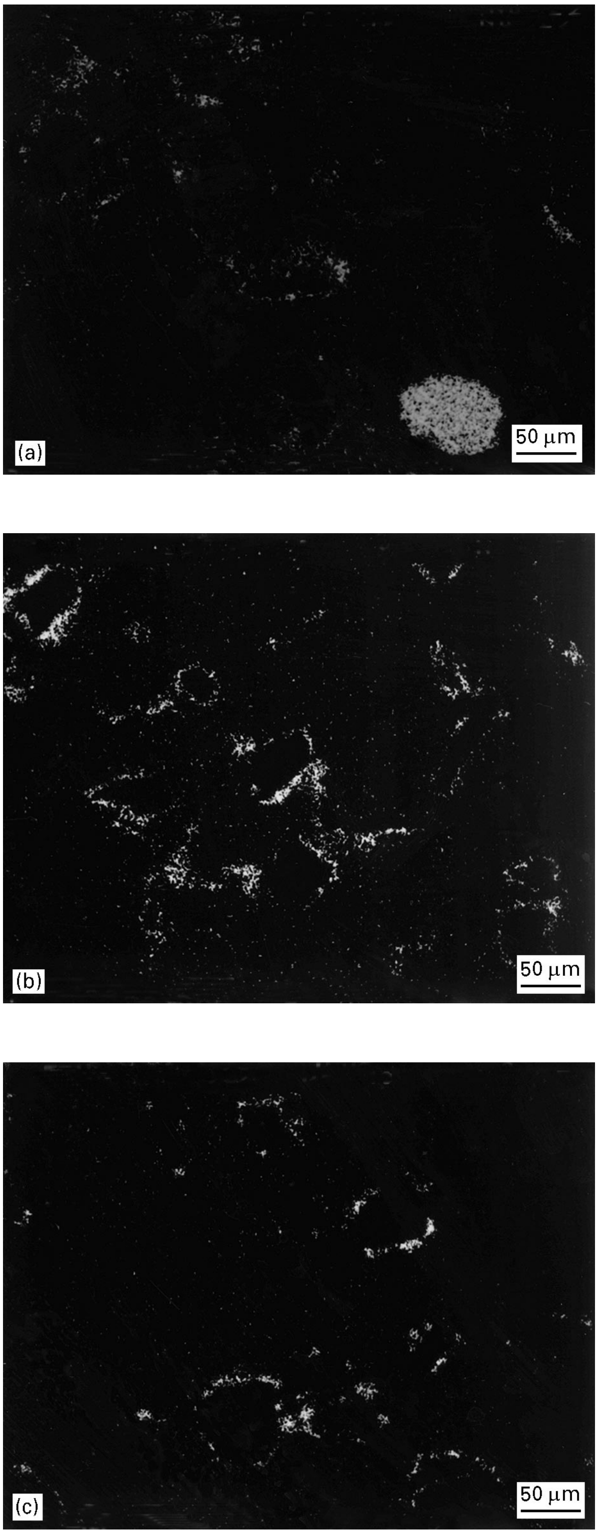

Figure 5 X-ray maps of magnesium from composites reinforced with (a) uncoated particles after fabrication, (b) TiO_2 coated particles after fabrication, (c) TiO_2 coated particles after 240 min remelting at 700 °C. The very magnesium rich particle in (a) is probably an oxide film entrapped during fabrication.

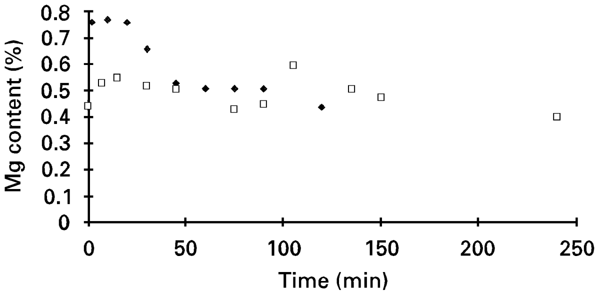

Figure 6 Magnesium variation in the matrix of composites reinforced with (◆) uncoated and (☐) TiO_2 coated SiC particles as a function of time during remelting at 700 °C.

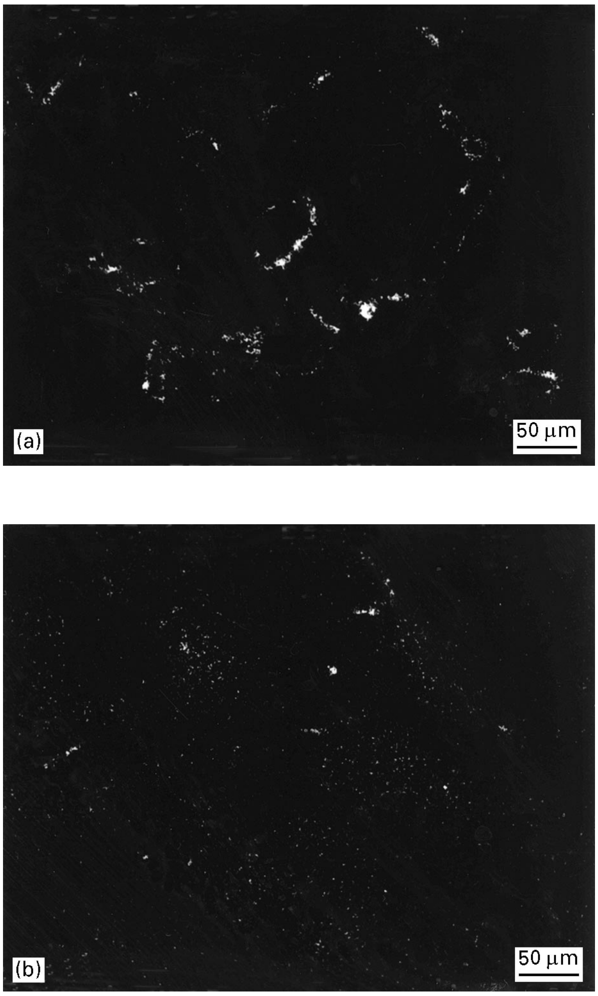

Figure 7 X-ray maps of titanium from composites reinforced with coated particles, (a) after fabrication, and (b) after 45 min remelting at 700 °C.

3.3. Characterization of the interfaces

A bright-field transmission electron micrograph of a matrix/SiC interface after fabrication of a composite reinforced with coated SiC is shown in Fig. 8a. The reaction layer appears to be uniform. A SAD (annular) pattern from the reaction layer shows that MgO crystals are present at the interface (Fig. 8b). There is no evidence for the presence of titanium, TiO_2 or Mg–Al–Ti–O compounds in the diffraction pattern from the interface. The MgO crystals are quite small and have a size similar to that of the TiO_2 crystals of the coating before the incorporation of the particles in the alloy (Fig. 2a). EDS analyses show that there is still a large amount of titanium at the interface after fabrication.

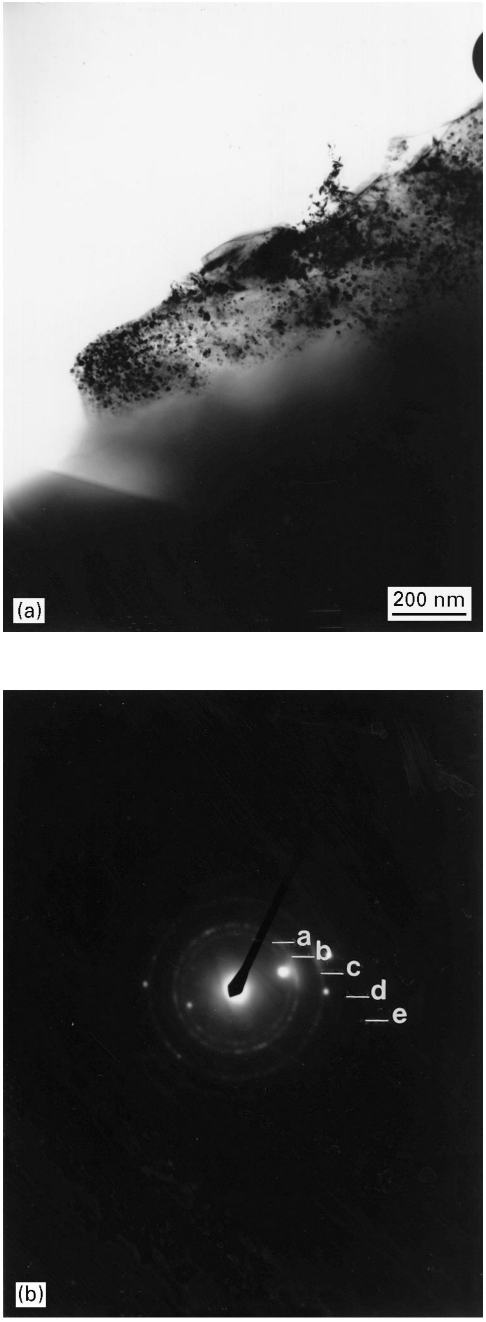

Figure 8 (a) Bright-field transmission electron micrographs of a matrix/SiC interface of a composite reinforced with coated SiC after fabrication, (b) SAD annular pattern from the reaction layer: a, (1 1 1); b, (2 0 0); c, (2 2 0); d, (2 2 2); e, (4 2 0).

Observations of the matrix/particle interface of the composites reinforced with coated particles after 150 min remelting were also made. The TEM bright-field micrograph in Fig. 9a shows that the reaction layer is no longer uniform with the presence of large crystals at the interface (≈400 nm). These crystals are identified as $MgAl_2O_4$ from SAD patterns (Fig. 9b). SAD (annular) patterns from other parts of the interface show that there is still a small amount of MgO crystals at the interface (Fig. 9c). On the other hand, EDS analyses (Fig. 9d) show that titanium is present

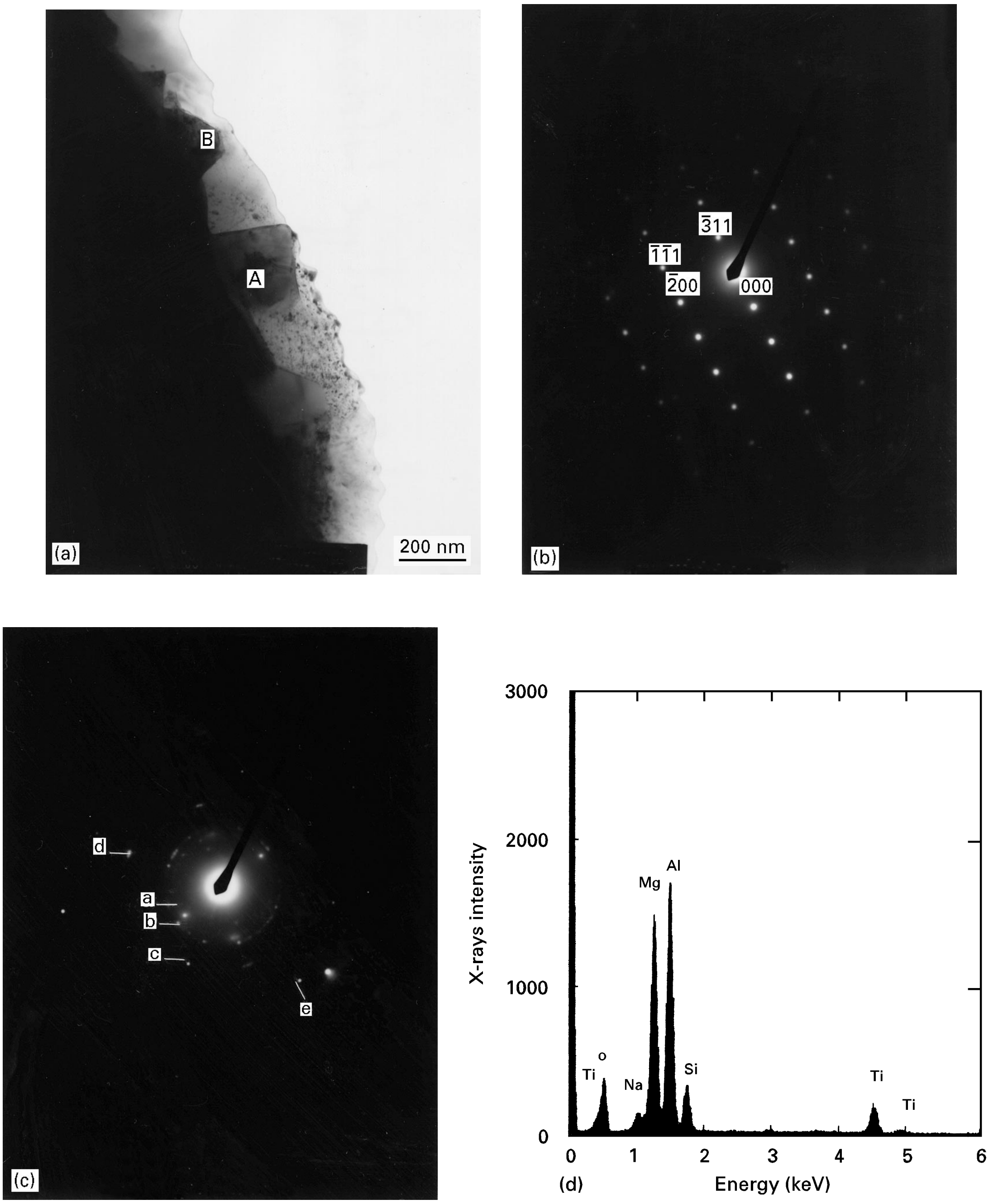

Figure 9 (a) TEM bright-field micrograph of the matrix/SiC interface of a composite reinforced with TiO_2 coated particles after 150 min remelting; (b) diffraction pattern from area A; (c) SAD annular pattern from area B (a, (1 1 1); b, (2 0 0); c, (2 2 0); d, (2 2 2); e, (4 2 0)); (d) EDS spectrum from area B.

in areas where MgO crystals are observed, while titanium is not detected in other parts of the interface. A model of the mechanism of transformation of the reaction layer is presented in the next section.

4. Discussion

4.1. Reaction zone at the particle/matrix interface after fabrication

Magnesium X-ray maps of the as-fabricated samples show that there is some magnesium segregation at the the particle/matrix interfaces for composites reinforced with both the uncoated and coated particles (Fig. 5). However, as shown in Fig. 6, this segregation is more important for composites reinforced with the coated particles.

For the composites fabricated with the uncoated particles, the variation of the magnesium concentration from the initial value of 1% to about 0.8% is probably associated with both magnesium loss during remelting and segregation at the particle/matrix interface. Some of the magnesium can then react with residual SiO_2 to form MgO

$$2[\mathrm{Mg}] + \mathrm{SiO}_{2(s)} \rightarrow 2\mathrm{MgO}_{(s)} + [\mathrm{Si}] \qquad (1)$$

This reaction has already been reported in the case of oxidized SiC particles in contact with a magnesium-rich alloy [13]. Indeed, during fabrication of the composites by compocasting, the SiC particles come in contact with an enriched liquid having a magnesium content larger than 1% thus leading to the formation

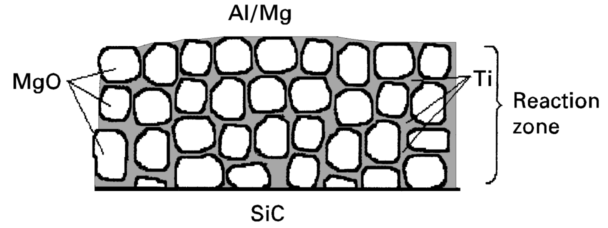

Figure 10 Structure of the reaction zone after fabrication of the composites reinforced with coated SiC.

of MgO rather than $MgAl_2O_4$ as predicted by thermodynamic calculations [14].

The additional segregation of magnesium observed in the case of the composite reinforced with coated particles is due to the transformation of TiO_2 into MgO according to the reaction

$$2[Mg] + TiO_{2(s)} \rightarrow 2MgO_{(s)} + [Ti] \quad (2)$$

This reaction consumes 0.24% Mg to transform entirely the TiO_2 present around the particles (3.34% of the weight of the particles). This value is close to the difference observed in the magnesium concentration between the composite with the uncoated and that with the coated particles. The occurrence of Reaction 2 is confirmed by the presence of MgO crystals and titanium at the particle/matrix interface. No other compounds are found in the diffraction patterns of the interfacial region confirming that the reaction has been completed during fabrication of the composite. In addition, titanium is not detected in the matrix (only 0.02 wt %) and $TiAl_3$ particles are not observed. Titanium should therefore be located at the interface in between the MgO crystals both in solid solution and in the form of $TiAl_3$ according to the phase diagram and the amount of titanium rejected.

The previous discussion allows a schematic representation of the particle/matrix interfacial region after fabrication to be proposed, as shown in Fig. 10. An important aspect is that Reaction 2 is associated with a volume expansion of 58.5% which contributes to the compact character of the layer and thus to the protection against attack by liquid aluminium.

4.2. Degradation of the coated particles during remelting at 700 °C

The main difference between the as-fabricated composites and the composites remelted for 150 min is the modification of the interfacial layer around the particles which consists of large $MgAl_2O_4$ crystals. The MgO crystals present after fabrication have thus been transformed into $MgAl_2O_4$ according to the reaction:

$$2[Al] + 4MgO_{(s)} \rightarrow MgAl_2O_{4(s)} + 3[Mg] \quad (3)$$

This reaction is expected, owing to the low magnesium concentration in the melt during remelting [14]. It leads to magnesium rejection which is probably the reason for the increase of the magnesium content in the matrix observed in Fig. 6 after about 100 min remelting. In parallel to this transformation, titanium diffuses in the matrix, as demonstrated by the absence of titanium in the interfacial layer when MgO is no longer present. In fact, this diffusion is almost completed within 45 min of remelting at 700 °C, because titanium is found to be uniformly distributed in the matrix after this remelting time, as shown in Fig. 7.

The transformation of fine MgO crystals ($\approx$30 nm) leads to the formation of large $MgAl_2O_4$ crystals ($\approx$400 nm) which do not completely cover the SiC particles (Fig. 9). The discontinuous character of the coating can be explained by the 11 vol % contraction associated with Reaction 3. As a consequence, channels become available between the $MgAl_2O_4$ crystals allowing liquid aluminium to come into contact with the bare SiC surface and therefore to form Al_4C_3. Fig. 11 shows schematically the change of the morphology of the interfacial layer with increasing remelting time.

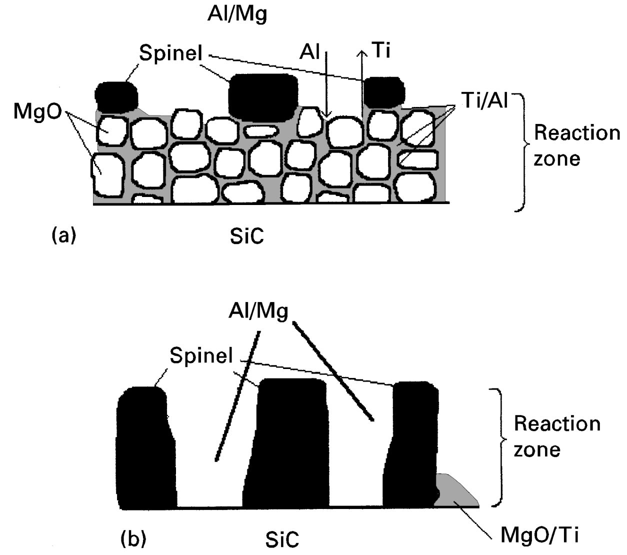

Figure 11 (a) Illustration of the evolution of the microstructure of the matrix/SiC interface of TiO_2-coated SiC during remelting at 700 °C, (b) interface after 150 min remelting.

It follows from the above discussion that the protection of the SiC particles could be more effective for thicker TiO_2 coating and (or) larger magnesium concentrations in the alloy. Indeed, a thicker TiO_2 coating would lead to a comparatively thicker MgO layer thus increasing the time for this layer to be transformed into $MgAl_2O_4$. This conclusion was confirmed by experiments carried out with SiC particles which underwent the elementary coating procedure for six times rather than three times as in the present investigation [15].

For sufficiently high magnesium concentrations, remelting would not transform MgO into $MgAl_2O_4$ [14]. The contraction associated with this reaction would not, therefore, take place, thus limiting the diffusion of aluminium towards the SiC particles. In fact, this diffusion would nevertheless occur as a consequence of the diffusion of titanium initially present in the MgO layer towards the aluminium melt. Remelting experiments of Al–Mg alloys reinforced with SiC particles coated with a complex Sn/Sb oxide support this explanation; degradation of the SiC particles being delayed by increasing the magnesium concentration in the alloy [16].

MgO or $MgAl_2O_4$ coatings rather than TiO_2 would probably be more effective in protecting the SiC particles in the Al–Mg alloy studied here. Because MgO is more stable in high magnesium-content alloys, it is probable that a MgO coating would be more effective in these alloys. $MgAl_2O_4$ would be more effective in low magnesium content alloys. It is possible, however, that the growth of spinel crystals during remelting of $MgAl_2O_4$-coated particles would eventually lead to a non-uniform layer. In fact, spinel crystals observed at the interfaces in aluminium composites reinforced with Al_2O_3 or SiC (coated with oxides) are generally large crystals that do not entirely cover the reinforcement surface.

5. Conclusion

TiO_2 coatings on SiC particles are effective in delaying the degradation of the particles in Al–1 wt % Mg alloys during remelting at 700 °C. Rapid degradation of uncoated particles begins after 20 min whilst it begins after 100 min for TiO_2-coated particles.

TiO_2 is not stable in Al–1 wt % Mg alloys and is transformed into MgO during fabrication of the composites at 660 °C. During remelting, titanium diffuses away from the reaction layer and MgO is transformed into $MgAl_2O_4$. After 150 min remelting, the reaction layer is mainly constituted of large spinel crystals. The reaction layer is then non-uniform and allows aluminium to reach SiC and to react with it.

Increasing the coating thickness and (or) the magnesium concentration in the alloy would certainly further delay the SiC degradation by the melt. The transformation of TiO_2 coatings into MgO suggests that direct MgO coatings would be more effective to protect SiC particles in relatively high magnesium-content alloys, whereas $MgAl_2O_4$ would be more stable in low magnesium-alloys.

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