

## Effect of Reinforcement Coating on the Oxidation Behavior of AA6061/SiC/20p Composite

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*The oxidation behavior of SiO<sub>2</sub>-active coatings on SiC reinforcement particles of an aluminium-matrix composite, AA6061/SiC/20p, was studied. In order to improve the processing behavior of the composites the SiC particles were coated prior to composite manufacture by a casting procedure, using the sol-gel technique. The oxidation resistance of the composites was analyzed to determine the influence of the manufacturing variables. Gravimetric tests were used to evaluate the oxidation kinetics at 500°C. The nature of the corrosion products before and after accelerated testing was analyzed by Scanning-Electron Microscopy (SEM), EDX and low-angle X-ray Diffraction (XRD), to determine the influence of the oxidation environment on micro-structural changes. Corrosion damage to the AA6061/SiC/20p composite was dependent on the manufacturing process and increased with the manufacturing temperature. Three corrosion products were detected  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, MgO and MgAl<sub>2</sub>O<sub>4</sub>. The corrosion resistance decreased slightly when the SiO<sub>2</sub> coating was used, and the matrix/SiC interfaces acted as preferential nucleation sites, but the intensity of the oxidation process was low. The use of active coatings on reinforcement particles is justified by the improvement in their wettability by molten aluminum, in spite of some slight loss of oxidation resistance.*

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**KEY WORDS:** oxidation; oxidation MMC; Al/SiC composites; sol-gel coatings.

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## INTRODUCTION

Metal-matrix composites (MMCs) reinforced with ceramic particles, whiskers, or fibers have received increasing attention due their potentially high fracture toughness and strength. Particle-reinforced, Al-base MMCs find potential applications in high-temperature environments, especially in automobile engine parts such as drive shafts, cylinders, pistons and brake rotors, and in aerospace applications.<sup>1-4</sup>

In particle-reinforced composites, the metallic matrix and the particles share the applied load with a volume fraction of particles usually in the region of 10–30%. The load transfers between the particles and the matrix, and is associated with the chemical and crystallographic behavior of the particle/matrix interface. Indeed, because the interfacial region between the reinforced particles and the metallic matrix is critical and often involves the formation of intermetallic compounds or a diffusion layer, complex chemical interactions may occur.<sup>5-7</sup>

The oxidation resistance of composites is determined by the properties of the surface-oxide products formed during exposure to an oxidizing environment. The nature composition, structure and thickness of the protective-oxide layer depend on the environmental conditions, the composition of the alloy and the behavior of the reinforced-particles/matrix interface. The presence of ceramic particles in the aluminum-matrix alloy break the continuity of the Al<sub>2</sub>O<sub>3</sub> protective layer and decrease the corrosion resistance of aluminum-composite materials. In order to design better composite components, the performance of the composites used should be fully evaluated in terms of their oxidation behavior at high temperature.<sup>8-11</sup>

The aim of this study was to determine the influence of active-SiO<sub>2</sub> coatings applied to reinforcement particles of SiC on the oxidation resistance of AA6061/SiC/20p composites exposed to 500°C for 80 days. The effect of manufacturing variables on the corrosion resistance was evaluated using gravimetric tests, Scanning-Electron Microscopy (SEM), EDX, and low-angle X-Ray Diffraction (XRD).

## EXPERIMENTAL PROCEDURES

### Sol-gel Coating Procedure

SiC particles used as reinforcement in the aluminum-matrix composite had an average diameter of 26.2 μm with an aspect ratio in the range 2:1 to 5:1. Particles, produced for abrasive applications, were supplied by Navarro S.A. SiO<sub>2</sub> coatings were applied on particle surfaces by dipping these in solutions of tetraethyl orthosilicate (TEOS), as a precursor, ethanol (C<sub>2</sub>H<sub>5</sub>OH or EtOH) and acidulate water. The pH of the solution

was controlled by the addition of HCl to produce acid catalysis. The H<sub>2</sub>O/TEOS and EtOH/TEOS molar ratios were 5 and 11, respectively, working with a sol concentration of 204 g/l. These coating conditions were optimized on the basis of previous research.<sup>12</sup>

After coating, the particles were vacuum-filtered and washed with C<sub>2</sub>H<sub>5</sub>OH to eliminate the mass of residual gel, which causes SiC particles to agglomerate. Sol-gel coatings were heat treated to eliminate any remaining water and ethanol by evaporation (drying stage at 120°C, 3 hr) and to consolidate the particle/coating bond (sintering at 500°C for 1 hr in air). SiO<sub>2</sub> sol-gel coatings on SiC particles were characterized by means of SEM, EDX and XRD.

### Composite Manufacturing

Composites were manufactured by controlled melting. The specimens were 13 mm in diameter × 5 mm thick, consisting of a homogeneous mixture of aluminum alloy powders (AA6061) supplied by *Aluminum Powder Company* (95.5% Al, 1.47% O, 1.23%Mg, 0.941% Si, 0.432% Cu, 0.387% Cr, 0.0623% Fe) and contained 20% SiC particles by volume. The powder mixtures were pressed at 520 MPa at ambient temperature followed by vacuum (10<sup>-4</sup>–10<sup>-5</sup> Pa) melting at preset temperatures and times (Table I). Both coated and uncoated particles were used in the manufacture of the composites tested.

### Oxidation study

The kinetics were studied using gravimetric measurements. The specimens were exposed to the non-flowing oxidizing laboratory atmosphere in a Carbolite furnace type EML 11/6 for 80 days at 500°C. The surface area of the sample was approximately 3 cm<sup>2</sup>. The surfaces were ground to

**Table I.** Manufacturing Conditions for the Composites Tested

Specimens	SiC <sub>p</sub> condition	Melting temperature (°C)	Holding time (min)
MC6-01-800-1 h	coated	800	60
MC6-Ini-800-1 h	uncoated	800	60
MC6-01-800-30 m	coated	800	30
MC6-Ini-800-30 m	uncoated	800	30
MC6-01-850-30 m	coated	850	30
MC6-Ini-850-30 m	uncoated	850	30
MC6-01-900-1h	coated	900	60
MC6-Ini-900-1h	uncoated	900	60

600 grit using a series of emery paper with water as the lubricant. Specimens were washed in acetone, dried, weighed and then subjected to oxidation tests. The oxidation kinetics was determined by measuring the weight changes as a function of time at regular intervals.

SEM was used to observe the reinforced composites before and after oxidation in order to study the morphology and evolution of the oxide products that formed on the material surface. EDX analysis was used to identify the elements in the oxide formed. The oxidation layer was examined by low-angle X-ray diffraction.

## RESULTS DISCUSSION

The nature of the as-received SiC particles (Fig. 1(a)) was characterized by sharp shapes with broken surfaces, where concave-fracture lines are visible. EDX microanalysis of the particle surfaces showed the absence of external oxidation films (Fig. 1(b)). The sol-gel coating partially reduced the rough surfaces by means of a homogeneous, uniform coating which gave a smoother appearance (Fig. 2(a)). The thickness of the SiO<sub>2</sub> coating, measured at fractured zones, averaged 0.7 μm for the given coating conditions. The presence of the coating on the SiC particle was revealed by EDX microanalysis through detection of the O energy peak which corresponds to the formation of a continuous SiO<sub>2</sub> layer (Fig. 2(b)). The XRD pattern of the sol-gel-treated particles also showed a wide peak at approximately 22° corresponding to the vitreous silica layer produced by sol-gel coating (Fig. 3).

The manufactured AA6061/SiC/20p composites presented a typical casting microstructure (Fig. 4), consisting of α-aluminum primary dendrites (A); minority AlSiCrFe intermetallic compounds (B); and characteristic geometrically-shaped SiC particles (C) homogeneously distributed in

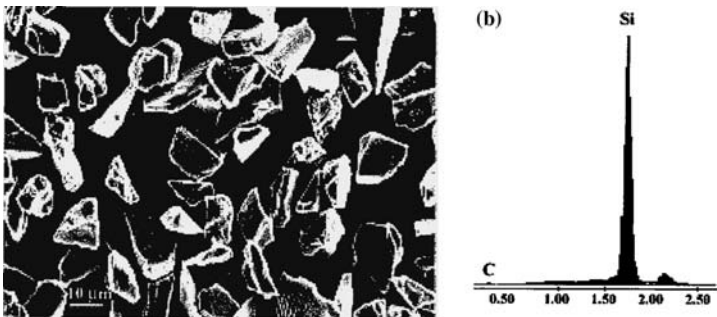


Fig. 1. (a) As-received SiC particle, (b) EDX microanalysis.

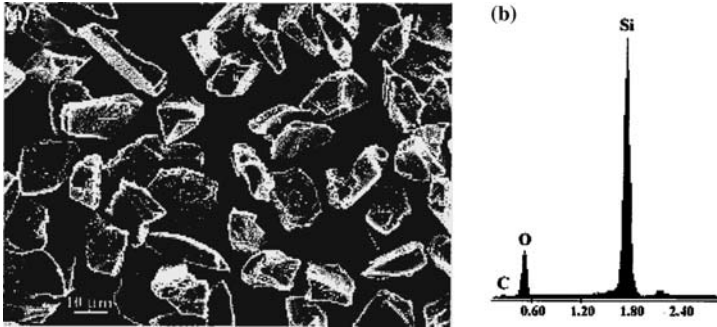


Fig. 2. (a) Sol-gel-treated SiC particle, (b) EDX microanalysis.

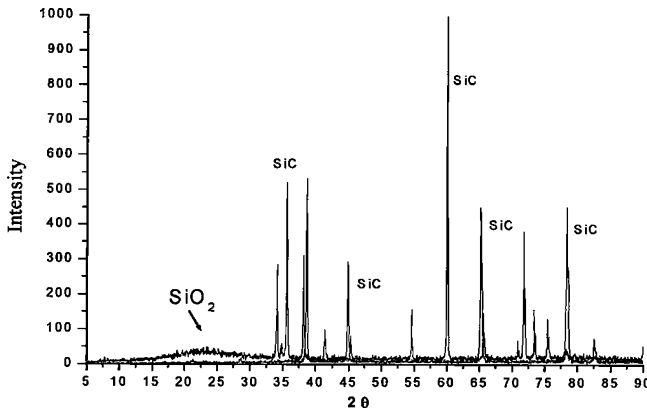


Fig. 3. XRD pattern of sol-gel-treated SiC particles showing the formation of a wide peak corresponding to the  $\text{SiO}_2$  coating.

the metallic matrix. However, significant differences were observed between composites reinforced with uncoated and coated SiC particles. The former presented a high degree of direct interaction between the particles and molten aluminum which occurred during manufacture of the composite, and formation of (dark)  $\text{Al}_4\text{C}_3$  aggregates (D) at the SiC/Al interfaces (Fig. 5(a)). Composites with sol-gel-treated reinforcement had a very low proportion of  $\text{Al}_4\text{C}_3$ , but enrichment by free Si aggregates (E) was detected around SiC particles (Fig. 5(b)). The Si enrichment is associated with the reaction between the  $\text{SiO}_2$  coating and the molten aluminum, which the present authors have described elsewhere.<sup>13</sup>

Figure 6 shows the surface morphology and X-ray maps of an AA6061/SiC/20p composite manufactured at 800°C, 30 min, before

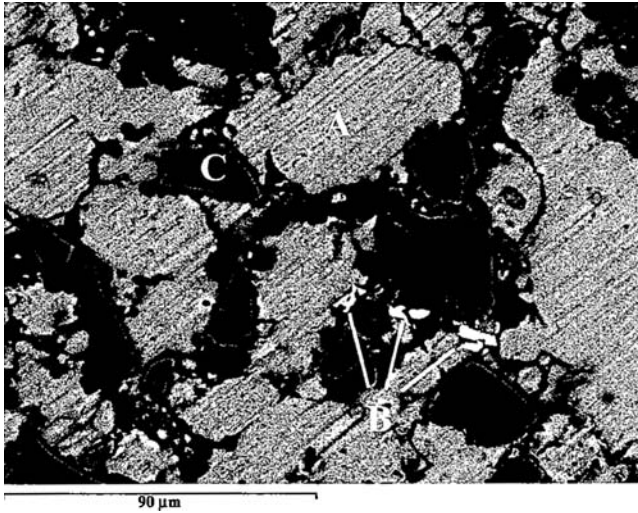


Fig. 4. BSE image of MC6-Ini-800-30 m material.

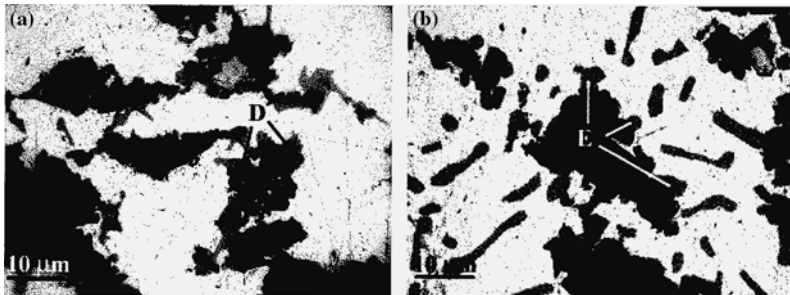
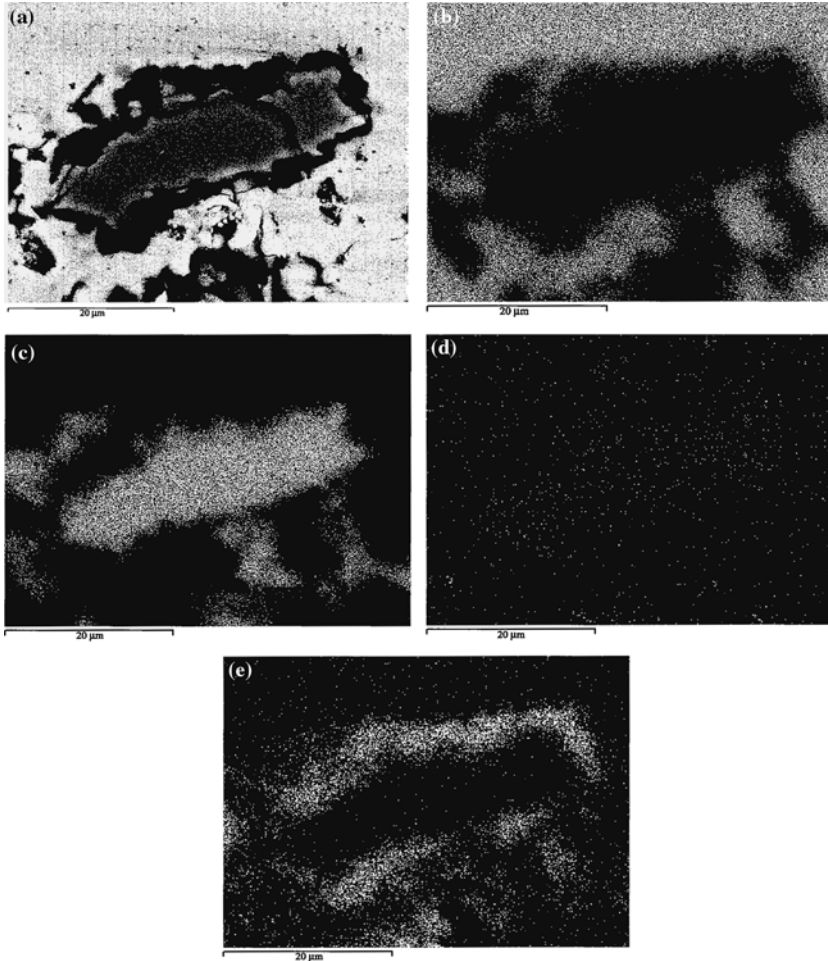


Fig. 5. Microstructures of the AA6061/SiC/20p composites manufactured at 800 °C, 30 min: (a) uncoated particles, (b) coated particles.

coming into contact with an oxidizing atmosphere. The SiC particles were not greatly affected by the oxidation products. The oxidized products presented two different zones of coloring: one darker zone surrounding the SiCp, rich in Al and oxygen, and a lighter zone corresponding to a matrix containing Al and Mg, probably in the form of  $\text{Al}_2\text{O}_3$  and MgO. The matrix/SiCp interface favored the nucleation and growth of  $\text{Al}_2\text{O}_3$ .

Figure 7 shows the weight gain versus time for oxidation of the materials tested at 500 °C for 80 days. The materials exposed to the oxidizing atmosphere presented exponential kinetics with a low weight gain due to growth of a protective layer. The mass gain augmented with increases in



**Fig. 6.** (a) BSE image of a detail for MC6-Ini-800-30 m material; X-ray maps of: (b) Al, (c) O, (d) Mg and (e) Si.

the manufacturing temperature and the materials reinforced with  $\text{SiO}_2$ -coated particles. However, the mass gains of all the materials tested was similar.

The oxidation kinetic laws were calculated from the gravimetric data. The mass-gain dependence was determined as an exponential type  $y = at^b$  (Table II). The kinetics constants and exponents were low. This indicates the formation of a stable oxide layer after 80 days of exposure to an oxidizing atmosphere at  $500^\circ\text{C}$ .

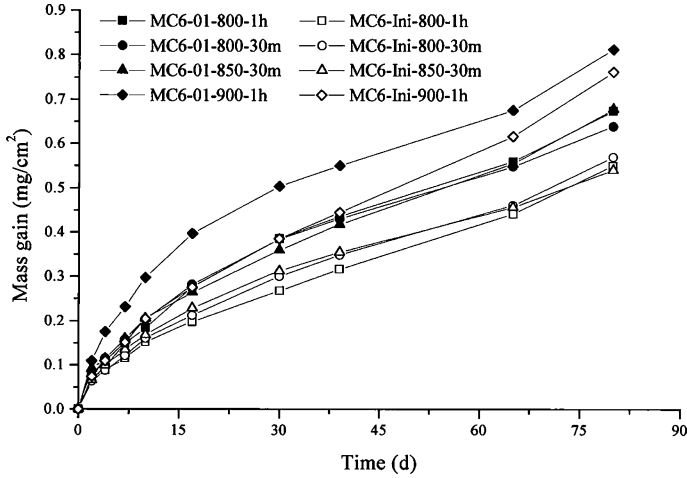


Fig. 7. Weight gain vs. time for materials tested for 80 days in a non-flowing oxidizing atmosphere.

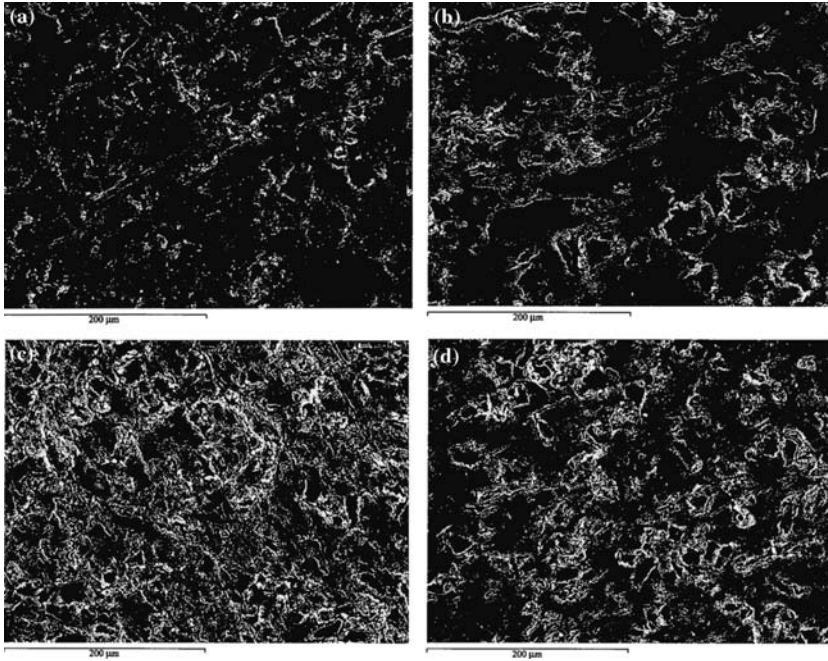
Table II. Kinetics Laws of the Gravimetric Test in Non-flowing Oxidizing Atmosphere at 500°C for 80 days

Specimens	Kinetic law ( $y = \text{mg}/\text{cm}^2$ ; $t(\text{days})$ )	$R$
MC6-01-800-1 h	$y = 4.78 \times 10^{-2} t^{0.599}$	0.971
MC6-Ini-800-1 h	$y = 3.33 \times 10^{-2} t^{0.628}$	0.973
MC6-01-800-30 m	$y = 5.71 \times 10^{-2} t^{0.549}$	0.966
MC6-Ini-800-30 m	$y = 3.71 \times 10^{-2} t^{0.615}$	0.972
MC6-01-850-30 m	$y = 5.08 \times 10^{-2} t^{0.582}$	0.969
MC6-Ini-850-30 m	$y = 4.64 \times 10^{-2} t^{0.555}$	0.967
MC6-01-900-1h	$y = 9.29 \times 10^{-2} t^{0.448}$	0.960
MC6-Ini-900-1h	$y = 4.31 \times 10^{-2} t^{0.646}$	0.974

Figure 8 shows the morphology of the AA6061/SiC/20p surface after oxidation at 500°C for 80 days. As the figure shows, the oxidation process was of low intensity, and the grinding lines were still visible. The specimens manufactured at 900°C showed just a slight degradation.

Figure 9 shows the morphology and X-ray maps of the AA6061/SiC/20p surface after oxidation at 500°C for 80 days. As the figure shows, oxidation started at the SiC/matrix interface, and oxidation products formed mainly on the aluminum matrix. The SiC particles were not greatly affected. The oxidation products contained high concentrations of Mg and Al, probably  $\text{Al}_2\text{O}_3$  and MgO or even the spinel  $\text{MgAl}_2\text{O}_4$  from the oxidized surface. This may be related to the fact that oxidation is confined



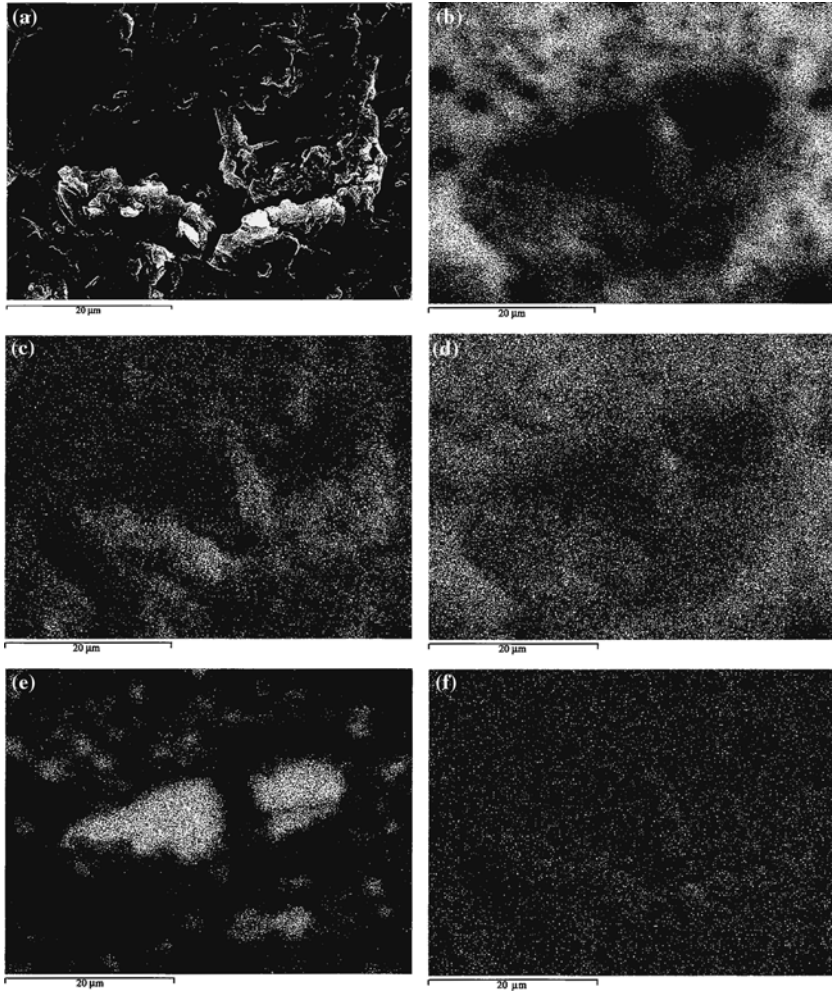


**Fig. 8.** Morphology of the corrosion layer for the materials tested: (a) MC6-Ini-800-1 h, and (b) MC6-01-800-1 h, (c) MC6-Ini-900-1 h and (d) MC6-01-900-1 h.

almost exclusively to the matrix and is associated with nucleation and growth of aluminum and magnesium oxides on the metal matrix.

On analysis of the matrix/SiCp interface in composites with coated reinforcements oxidized at 800°C for 80 days, none of the original SiO<sub>2</sub> coating was detected after corrosion (Fig. 10). Previous studies of this type of interface have shown that there is an interfacial reaction between the molten aluminum and the SiO<sub>2</sub> coating, with the formation of glassy aluminosilicate phases.<sup>12</sup> These new interfacial products do not appear to have a detrimental effect on the corrosion behavior of the composite in an oxidizing atmosphere. However, the matrix in contact with the SiCp is rich in Mg, Al and oxygen, probably Al<sub>2</sub>O<sub>3</sub> and MgO, or MgAl<sub>2</sub>O<sub>4</sub>.

Figure 11 shows a low-angle XRD study of the materials tested. The manufacturing process did not influence the oxidation products. As the figure shows, the oxidation products were basically Al<sub>2</sub>O<sub>3</sub>, MgO and MgAl<sub>2</sub>O<sub>4</sub>. The oxidation process favored growth of the oxidation layer by the formation of these oxides. For longer exposure times, different thermal-expansion coefficients may produce cracking of the oxidized layer,



**Fig. 9.** (a) Morphology of the corrosion layer for MC6-01-800-30 m; X-ray maps of: (b) Al, (c) O, (d) Mg, (e) Si and (f) C.

favor the access of oxygen to the metal alloy and lead to slow degradation of the material.<sup>14,15</sup>

## CONCLUSIONS

1. All the materials tested presented high oxidation resistance when exposed to an oxidizing atmosphere at 500°C for 80 days.

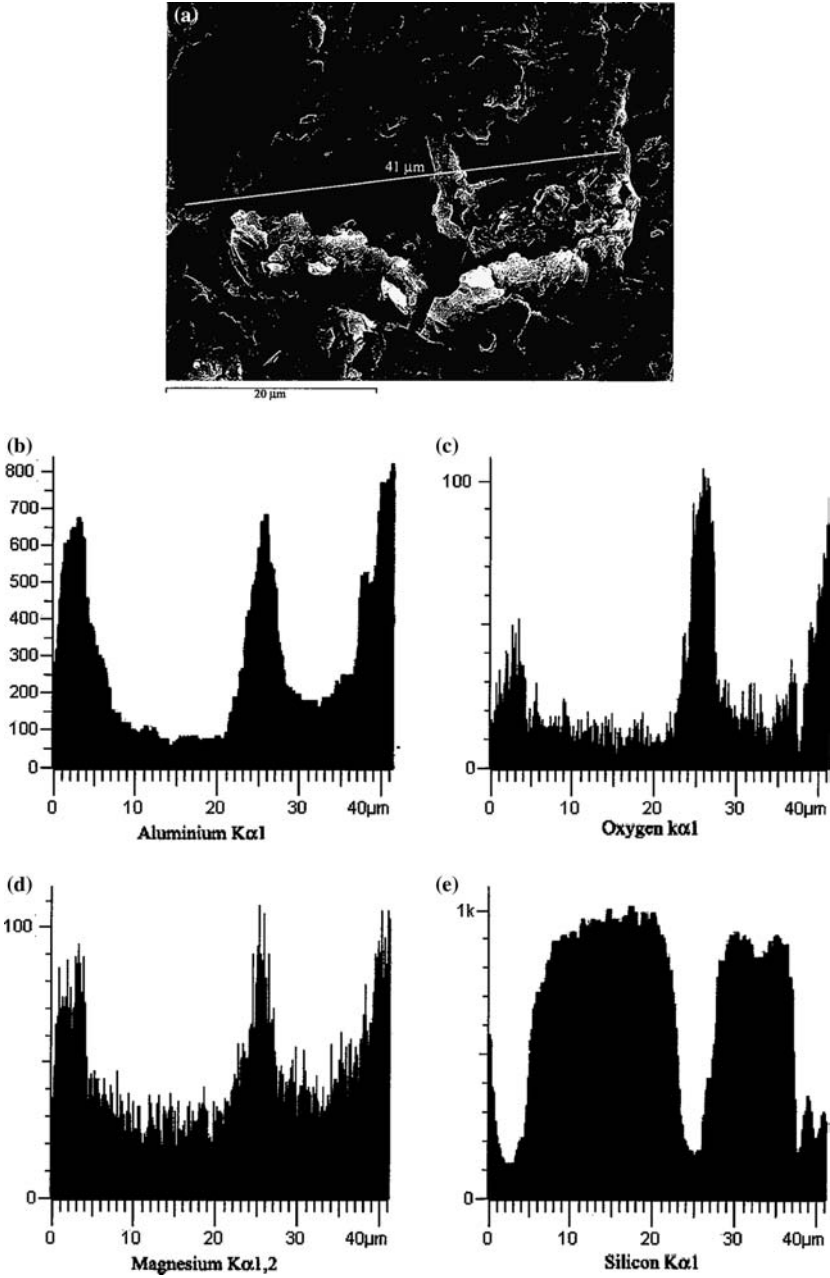


Fig. 10. (a) Morphology of the corrosion layer for MC6-01-800-30 m; Profile-line of: (b) Al, (c) O, (d) Mg and (e) Si.

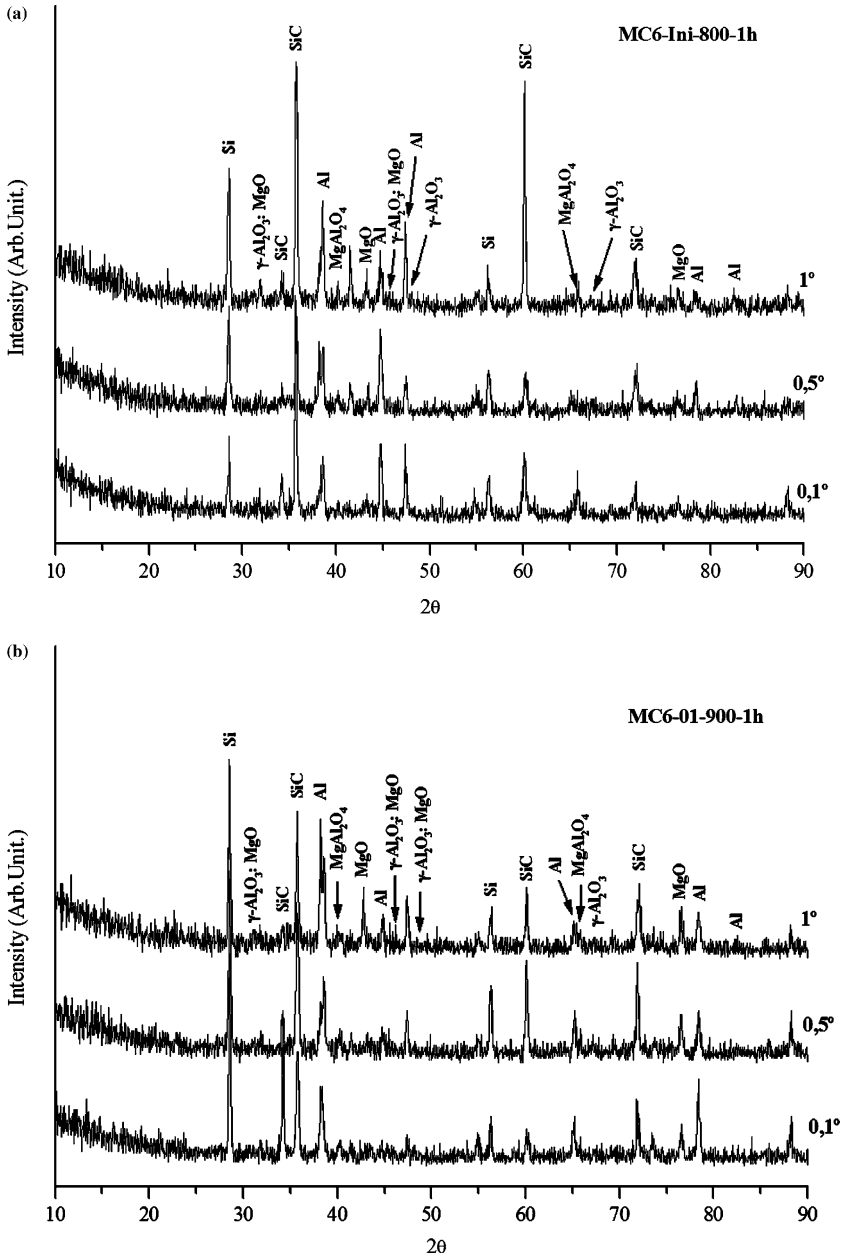


Fig. 11. Low-angle XRD study of materials: (a) MC6-Ini-800-1 h and (b) MC6-01-900-1 h.

Protection of SiC<sub>p</sub> with a SiO<sub>2</sub> sol-gel coating does not significantly affect the oxidation process, even in manufacturing at high casting temperatures.

2. The use of a SiO<sub>2</sub> coating on the reinforcement more effectively improves the oxidation resistance of the composites studied where manufacturing conditions are less reactive (800°C and 30 min), because it more effectively controls the direct reaction between the SiC and the molten aluminum.
3. Material degradation is associated with the formation of Al<sub>2</sub>O<sub>3</sub>, MgO and MgAl<sub>2</sub>O<sub>4</sub> oxides.
4. SiO<sub>2</sub> coating of SiC particles by the sol-gel route is worth considering in that it improves the processing of aluminum/SiC composites without the loss of chemical resistance in the resultant interface.

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