Degradation of SiC particles in aluminium-based composites

G. CAROTENUTO, A. GALLO, L. NICOLAIS
Department of Materials and Production Engineering, University of Naples, Piazzale Tecchio, 80125 Napoli, Italy

The technological process used for the production and processing of metal matrix composites (MMCs) can require contact over extended periods of time between matrix and the ceramic reinforcement or at least the permanence at high temperature and pressure of the two parts in contact. During the contact a chemical interaction takes place in the interfacial zone as a consequence of the free-energy difference existing between ceramic compound and metal. Aluminium and aluminium alloys reinforced with silicon carbide are widely utilized materials. The chemical interaction between matrix and reinforcement is not very fast but the reaction equally occurs, and a harmful layer of interfacial compound (Al_4C_3) is developed after a sufficiently long time. At present, the degradation of the reinforcement produced by molten matrix is the major problem for some production technologies. This problem has only been solved partially by using a coating or changing the chemical nature of the matrix. In particular, the technological problem of interfacial reaction in the SiC–Al system can be solved by adding elemental silicon to the matrix to achieve the eutectic composition. However, this expedient gives rise to a consequent significant lowering of the melting point. The problem can be overcome and the production process improved without changing the characteristics of the material by the control of processing parameters. The interfacial reaction also produces elementary silicon and this has been found as aluminium–silicon eutectic segregated at the aluminium grain boundary. An accurate description of the kinetic process can be obtained by determining the silicon content present in the matrix by original derivations obtained by means of calorimetric analysis.

1. Introduction

Currently, silicon carbide/aluminium (SiC/Al) composites are very attractive for their properties, such as high modulus, high specific stiffness, high-temperature strength, low coefficient of thermal expansion, good wear resistance and good workability and isotropy. The high SiC–Al interface bonding strength is the main reason for their relatively high specific mechanical properties. The increased strengthening observed is due to the strength of the bonding at the interface between the matrix and the reinforcement. A sufficient bond is possible only when good wetting of the reinforcement by the matrix is obtained, and this is highly dependent on the surface properties of the two phases.

Unfortunately, the discontinuously reinforced aluminium (DRA) fabrication is still one of most crucial problems and the processing parameters have a remarkable effect on the corresponding mechanical property. When this material is fabricated by liquid-phase methods [1] (e.g. rheocasting, compocasting, squeeze casting) or the as-supplied composite billets are exposed to high temperatures for remelting and casting into near net-shape components, a gradient of chemical potential exists at the ceramic/metal interface which provides a driving force for chemical reactions. The development of interaction zone is detrimental to composite mechanical properties [2], be-

cause it gives rise to a brittle interfacial zone that cracks in servicing, under high applied force and thermal stress [3]. The microcracks formed reduce the local adhesion with a consequent degradation of the properties and the corrosion resistance. It has also been shown that the formation of aluminium carbide leads to a substantial increase in the viscosity of the melt; this makes it difficult to cast aluminium-based composites into net shapes. During the fabrication of DRA, the reaction depends on fabrication parameters such as temperature, atmospheric composition, pressure and chemical composition of both matrix and reinforcement. Thus, a study of the compatibility between the matrix and the reinforcement under conditions similar to those of the fabrication and processing is an important step in developing this material.

It is established that SiC can react with molten aluminium producing, under atmospheric pressure and from the aluminium melting point to about 1400 °C, Al_4C_3 and silicon, according to the following heterogeneous double decomposition

$$4Al_l + 3SiC_{(s)} \rightleftharpoons Al_4C_{3(s)} + 3Si_{(s)} \qquad (1)$$

As proposed by Viala *et al.* [4, 5], in this temperature range, kinetic factors impede the establishment of most stable equilibria, observed at higher temperatures by Oden and McCune [6], and because

Reaction 1 obeys the thermodynamics rules, it can be regarded as a metastable equilibria.

In particular, if the elemental silicon does not dissolve in the molten aluminium, but forms a pure solid phase, the free energy change of the reaction is positive over the entire temperature range and the reaction does not spontaneously proceed. Nevertheless, in accordance with the Al–Si phase diagram, the silicon dissolves into unreacted aluminium, giving rise to a binary liquid alloy, and the resulting free-energy change is negative for low activity values.

Therefore, the reaction can occur but because the amount of silicon in the liquid aluminium increases as the reaction proceeds, the silicon activity becomes larger, and the interaction tends to terminate rapidly.

Kinetically, the reaction between the aluminium and SiC involves the dissolution of SiC into aluminium and, with increasing carbon activity in it, the Al_4C_3 nucleates. At higher temperatures, ternary carbides (e.g. $Al_4C_3 \cdot SiC$ up to 1900 °C and $2Al_4C_3 \cdot SiC$ at still higher temperatures) form instead of Al_4C_3. Recently, many studies have been performed on this interfacial reaction [2, 4, 5, 7–10].

The extent of the reaction has been followed by measuring the intensity of the aluminium carbide and silicon X-ray peaks from the composite. The reaction can also be followed by chemical analysis of the composite and determining changes in the liquidus temperature. In this work, the interfacial reaction of SiC with aluminium is investigated by an alternative method founded on the determination of the heat of the invariant reaction ($\alpha + \beta \rightarrow$ eutectic liquid).

In this work, some physico-chemical considerations have been applied to derive the kinetic expression of the interfacial reaction in the α-SiC/Al discontinuously reinforced metal matrix composites. The kinetics of interfacial degradation is investigated at low and medium temperatures by differential scanning calorimetry (DSC) and by traditional optical metallography and scanning electron microscopy (SEM), and an useful relationship between the reaction conversion and thermal exposure time, for different heating temperatures, has been derived.

2. Experimental procedure
2.1. Materials and fabrication process
Two different composite materials were analysed in this work. The first was pure metallic aluminium (99.8 wt %) reinforced with SiC particles (15 vol %, grain size <13 µm) produced by sintering technology, the second was a silicon–aluminium alloy (with eutectic composition, 13 wt % Si), equally reinforced with SiC particles (15 vol %) and obtained by intrusive technology. Both materials were produced by TEMAV s.p.a. and provided, for this study, in the form of extruded rods.

2.2. Procedure
Samples with a weight of about 10 g were obtained from the rod and were put in a glass vial and sealed in a vacuum to limit oxidation reactions. The heat treat-

ment was carried out by heating the samples in a horizontal tubular furnace. The calibration of the furnace was obtained by reading the temperature values with a chromel P–alumel thermoelectric couple. At the end of the annealing, the samples were air-cooled. To avoid the segregation process the samples were annealed for few minutes to the eutectic melting point and then water-quenched.

Specimens were cut from the heat-treated samples and sections prepared for optical and scanning electron microscopy (SEM) were obtained by grinding and then polishing on successively finer grades of diamond abrasive, down to 1 µm particle size.

The microstructural evolution of the metallic matrix was analysed by examining diamond-polished sections of the samples by optical microscopy (OM). The best results for etching were obtained by an aqueous solution of sodium hydroxide (2 wt %) kept at room temperature for 2 min [11]. The formation and the development of interfacial zones were investigated by OM and SEM using diamond-polished sections not etched by the previous solution because a very soft etching with air dampness, was sufficient.

A Hitachi S-2300 scanning electron microscope was used; the examination was carried out at 25 kV and the specimens were coated with gold to reduce charging and to improve image quality.

The particle volume fraction was determined from specimen weight measurements [12]. Calorimetric analysis was performed by using a differential scanning calorimetry (Mettler TA3000-DSC apparatus) working from 25–700 °C under a dynamic nitrogen atmosphere (0.4 cm^3 min^{-1}). Specimens were encapsulated in standard high-purity aluminium sample pans. A similar aluminium sample pan was used as a reference. Runs were carried out at a heating rate of 5 °C min^{-1}, from 560–600 °C, using 5–8 mg samples.

2.3. Principles of the method
The composite matrix becomes, during the remelting, a ternary system Al–Si–C. Recently, Simensen [13] has established that the carbon solubility in molten aluminium, found experimentally by Oden and McCune [6], in the temperature range 1700–2156 °C, can be extended down to at least 960 °C. Because, below 900 °C, the carbon solubility is less than 2.34 p.p.m. (Fig. 1), the system Al–Si–C can be approximated with the well-known binary subsystem Al–Si.

At the eutectic point of the binary system Al–Si (577 °C) the β-crystals react with eutectic α-crystals to form the liquid alloy. The determination, by calorimetry, of eutectic phase melting-heat allows evaluation of the eutectic amount and the contained silicon. The remaining silicon, present in primary α-crystals, follows from stoichiometric consideration.

The elemental silicon, produced during the interfacial reaction, is allocated in the matrix between α-phase primary crystals and eutectic phase (secondary α-crystals and β-crystals). Thus, the total mass of the produced silicon is the addition of the silicon mass contained in the two phases. If the system is in thermo-
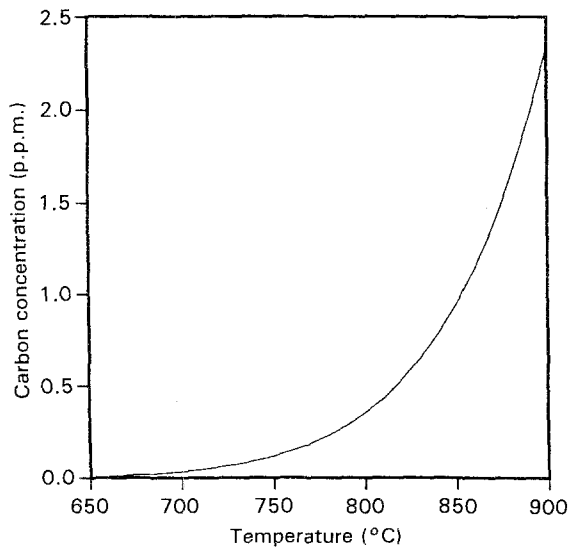
Figure 1 Carbide concentration as a function of temperature of the molten metal.

dynamic equilibrium, the chemical composition of the phases assumes a definite value, provided by the aluminium–silicon binary phase diagram [14]. Therefore, denoting by r_α and r_β the silicon fractions contained in the two respective phases, we have

$$m_{Si} = r_\alpha m_\alpha + r_\beta m_e \qquad (2)$$

where m_α and m_e are, respectively, the mass of α-phase (primary crystals) and eutectic phase, contained in the matrix at time t. In addition, by denoting with m_{Al} and m_{Si}, respectively, the aluminium and silicon mass, we have

$$m_\alpha = m_{Al} + m_{Si} - m_e \qquad (3)$$

Now, substituting Equation 3 into Equation 2 gives

$$(1 - r_\alpha)m_{Si} - r_\alpha m_{Al} = (r_\beta - r_\alpha)m_e \qquad (4)$$

Because

$$m_{Si} = \frac{M_{Si}}{M_{SiC}}m_c r\alpha \qquad (5)$$

and

$$m_{Al} = m_c\left(1 - r - \frac{4}{3}\frac{M_{Al}}{M_{SiC}}r\alpha\right) \qquad (7)$$

where m_c is the composite mass, M_i are the atomic and molecular weights, r is the weight fraction of reinforcement (SiC) in the matrix and α the reaction conversion, Equation 4 can be rewritten

$$(1 - r_\alpha)\frac{M_{Si}}{M_{SiC}}m_c r\alpha - r_\alpha m_c\left(1 - r - \frac{4}{3}\frac{M_{Al}}{M_{SiC}}r\alpha\right)$$
$$= (r_\beta - r_\alpha)m_e \qquad (8)$$

from where, deriving α we obtain

$$\alpha = \left[1 - r + \left(\frac{r_\beta}{r_\alpha} - 1\right)\left(\frac{m_e}{m_c}\right)\right]\bigg/\left\{\frac{r}{M_{SiC}}\left[\left(\frac{1}{r_\alpha} - 1\right)M_{Si} + \frac{4}{3}M_{Al}\right]\right\} \qquad (9)$$

Replacing the values of numerical constants, we have, for a composite with a SiC content of 15 vol %, as the

examined material

$$\alpha = 0.113 + 0.905\left(\frac{m_e}{m_c}\right) \qquad (10)$$

So, the reaction conversion can be determined by the evaluation of the eutectic amount in the matrix.

The amount of eutectic phase contained in the matrix, for unit weight of composite, can be estimated calorimetrically, by calculation of its melting heat, ΔH_f, without system alteration, because the melting occurs at a temperature (577 °C) lower than the starting point of the reaction (650 °C).

The eutectic phase mass is

$$m_e = \frac{\Delta H_f}{\overline{\Delta H_f}} \qquad (11)$$

where $\overline{\Delta H_f}$ is the specific melting heat.

The calorimetric tests provide the thermal flux per gram of composite, ΔH_s. Therefore, Equation 10 becomes

$$\alpha = 0.113 + 0.905\left(\frac{\Delta H_s}{\overline{\Delta H_f}}\right) \qquad (12)$$

The specific melting heat of the eutectic Al–Si has been evaluated calorimetrically on an Al/Si eutectic cast alloy (13 wt % Si) and the resulting value is

$$\overline{\Delta H_f} = 439.8\,J\,g^{-1} \qquad (13)$$

Therefore, knowing, from calorimetric thermograms, the melting heat for unit weight of composite, of specimens remelted, for a certain period, at different temperatures, is possible to obtain, from Equations 12 and 13, the interfacial reaction conversion.

2.4. Method limitations

The developed method assumes the presence in the matrix of the eutectic phase and, moreover, a silicon content lower than eutectic composition. The conversion, α, is related to silicon weight fraction contained in the matrix, τ, by the relation

$$\alpha = \left(1 - \frac{1}{r}\right)\bigg/\left[\frac{M_{Si}}{M_{SiC}}\left(1 - \frac{1}{\tau}\right) - \frac{4}{3}\frac{M_{Al}}{M_{SiC}}\right] \qquad (14)$$

Because, for the eutectic appearance, τ should be larger than 0.0165 (α-phase composition), α must be larger than 0.113 (for the used material). Therefore, up to $\alpha = 0.113$, the method is inapplicable and α must be linearly extrapolated (see Section 3.3).

Viala *et al.* [4] found the silicon content in the liquid phase in equilibrium with Al_4C_3 and SiC and they established that, below 1000 °C, this is even lower than eutectic composition (a result independent of composite composition and particle size).

3. Results

3.1. Microstructure after thermal exposure

The microscopic characterization of heat treated α-SiC_p/Al and α-SiC_p/(Al–13 wt % Si) samples provided the following results.

(i) Under atmospheric pressure, the heterogeneous binary mixture Al–SiC was stable at every temperature up to 10 °C lower than the aluminium melting point (i.e. up to 650 °C) and no interfacial chemical interaction was observed even when the annealing treatment time was very long. The DRA structure is completely unchanged and remains precise: the ceramic particles are dispersed in a single-phase matrix of pure aluminium, their interface was free from reaction products and the reinforcement outlines were always sharp (see Fig. 2).

(ii) The remelting, in the temperature range from 660 °C (melting point of pure aluminium) to 1000 °C, changed the microstructure of the composite significantly, confirming that α-SiC particles reacted with molten metal producing Al_4C_3 and elemental silicon. Their amounts increased with the remelting temperature and holding time.

The metal matrix had the typical appearance of a hypoeutectic Al–Si die-cast alloy, i.e. large dendrites of primary α-phase cemented by a fine Al–Si eutectic phase (Fig. 3). When the remelting time is short, the morphology of the eutectic silicon, solidified in the primary aluminium interdendritic region (around the dendrite boundaries), is exclusively acicular, but on increasing the temperature or the reaction time, the eutectic phase contains large, blocky primary grains of elemental silicon with their idiomorphic shape, in addition to small and thin platelets, as shown by Fig. 4. The carbon amount in the matrix is very low and consequently graphite trails were not found.

The α-SiC particles appeared segregated in the interdentritic regions because they were pushed by the primary aluminium dentrite to the least freezing eutectic liquid. Because the size of the SiC particles, in the present case, is more than the dendrite arm spacing of
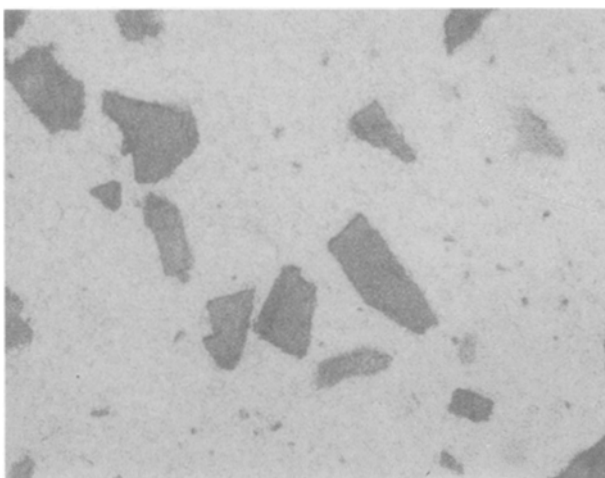

Figure 3 Optical micrograph of an etched SiC–Al sample, heat treated at 700 °C for 23 h under vacuum, showing an ipoeutectic Al–Si matrix, × 504.

Figure 4 Optical micrograph of an etched SiC–Al sample, heat treated at 900 °C for 19 h under vacuum, showing an ipoeutectic Al–Si matrix, × 1008.

Figure 2 Metallograph of an etched SiC–Al sample, heat treated at 600 °C for 22 h under vacuum, showing the unchanged matrix structure, × 1008.

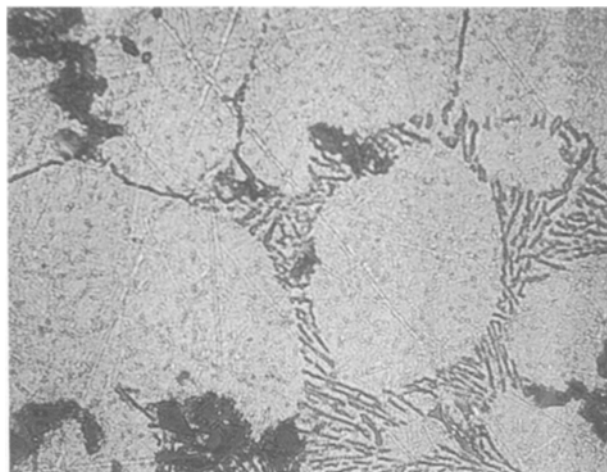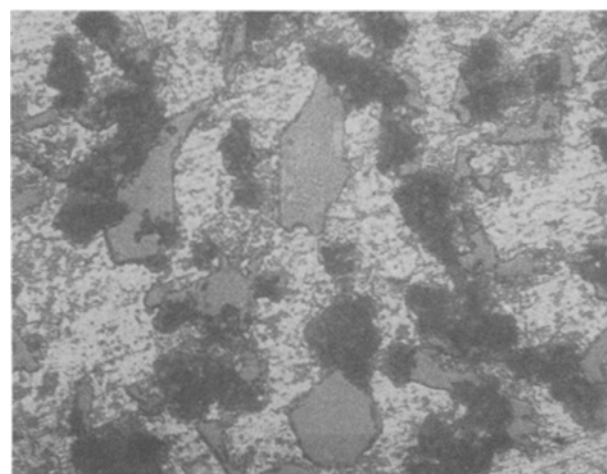primary aluminium, entrapment of the SiC particles in the interdentritic region was ruled out. The ceramic particles with originally sharp corners, become partly rounded after remelting, with jagged outlines. The average size was reduced and cracks were sometimes found; it is considered that the cracks were formed because of the difference in the thermal expansion between aluminium and SiC.

A thin and uneven reaction layer surrounded each α-SiC particle (Fig. 5). The thickness was irregular and its average size changed considerably with remelting temperature and heating time, ranging from a few isolated particles, for short remelting time at low temperature, to a complete coverage, for long remelting times. The layer was discontinuous because it was constituted of distinct Al_4C_3 crystallites (Figs 6 and 7). These crystallites were closely linked to the SiC surface and the morphology was easily detectable by optical metallography by their dark-grey colouring. The outline was that of hexagonal platelets and the size was not finely crystalline, but only a few, large,
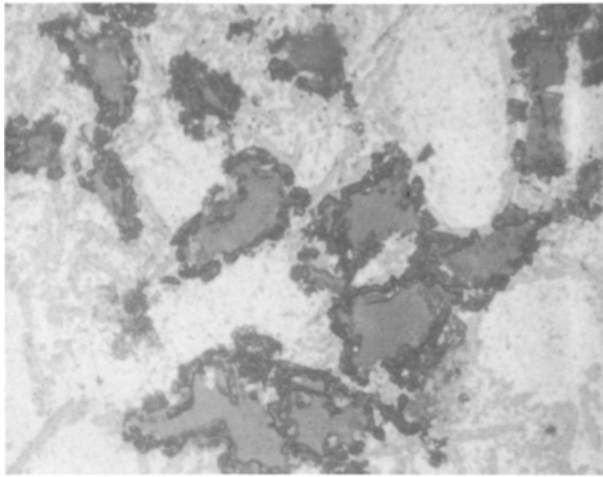
Figure 5 Microstructure of an SiC–Al sample heat treated at 800 °C for 48 h under vacuum (as-polished sample, × 1008). The Al_4C_3 forms on the surface of SiC (dark-grey particles) a non-uniform layer of well-faceted dark crystallites.
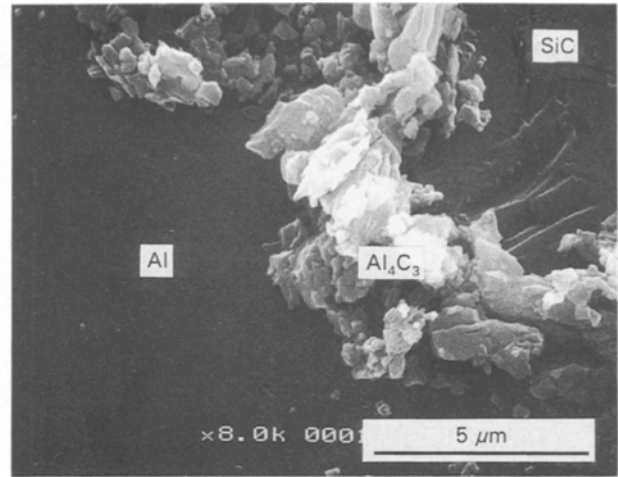

Figure 7 Scanning electron micrograph of the SiC/Al interface in a sample heat treated at 900 °C for 6 h under vacuum. The high-magnification view show the discontinuous layer of aluminium carbide (back-scattered electrons on polished and gold-coated sample).
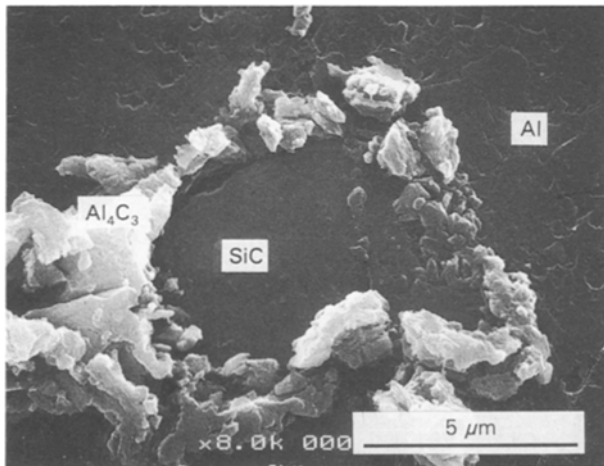

Figure 6 Secondary electron image of the interface in a SiC/Al sample heat treated at 900 °C for 5 min under vacuum. This high-resolution micrograph shows faceted traces of hydrated Al_4C_3 crystals.

well-faceted crystallites, that tend to join together, appeared. The size of these aggregates was of the order of 0.1–3 μm.

From SEM observations it appears that the aluminium carbide does not grow as a continuous layer (i.e. layer by layer) on the SiC substrate and it cannot be suggested that Al_4C_3 nucleates at specific sites; it is evident, though, that several small crystals are formed at an early stage and later these crystals coalesce and form aggregates of minute Al_4C_3 precipitates.

The Al_4C_3 crystallites arose from a recrystallization process, interpretable as follows. When the surface of the SiC particles came into contact with molten aluminium, it slowly dissolved, producing silicon and carbon ions. These left the interface and migrated to the matrix by liquid-phase diffusion.

$$SiC_{(s)} \rightarrow Si^{4+} + C^{4-} \qquad (15)$$
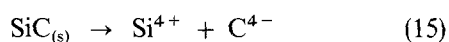
Because of the high diffusivity and low solubility of carbon in the liquid aluminium, the matrix was

quickly carbon-saturated and the Al_4C_3 precipitation started. The first formed Al_4C_3 crystals again recrystallized, to produce, at the end of remelting, large and flawless crystallites

$$4Al^{3+} + 3C^{4-} \rightleftharpoons Al_4C_{3(s)} \qquad (16)$$

The new phase was crystallized at the surface of the SiC particles because the nucleation was promoted there.

A high sensitivity of the carbide to moisture in the air was also experienced in this study. Figs 6 and 7 show faceted traces of hydrated Al_4C_3 crystals. Likewise, the growth of silicon crystals was promoted on the SiC uncoated surface because of the epitaxial development that is possible there; so clusters of silicon and aluminium carbide crystals sometimes appear at the interface. The free silicon crystals observed to be enclosed by the aluminium carbides indicate, as expected, that the (Al–Si) eutectic, from which silicon precipitated upon cooling, was "trapped" between grown Al_4C_3 crystals.

(iii) The interfacial chemical interaction was also experimentally studied for composites with Al–Si matrix by means of optical microscopy. By alloying the aluminium matrix with silicon up to the eutectic composition (13 wt % Si), ceramic degradation was fully prevented. The interface did not exhibit a jagged outline and was also free from interfacial reaction layers after extended remelting.

3.2. Calorimetric analysis

The quantitative investigation of the reaction kinetics behaviour on α-SiC$_p$/Al and α-SiC$_p$/(Al–13 wt % Si) systems, was carried out by DSC in the temperature range 500–700 °C. A minimum of two DSC scans was performed on each sample.

Both cooling and heating thermograms were sometimes executed, finding completely coinciding results.

The thermograms obtained on heating showed:

(i) the α-SiC$_p$/Al system as-received or annealed below 650 °C evinced only one endothermic peak at 660 °C;

(ii) the α-SiC$_p$/Al system variously remelted up 600 °C evinced one endothermic peak at 577 °C, produced by eutectic melting, plus a large endothermic peak produced by monovariant transformation;

(iii) the α-SiC$_p$/(Al–13 wt % Si) system evinced only the endothermic peak at 577 °C produced by eutectic melting.

A systematic investigation was carried out on the α-SiC$_p$/Al heat-treated samples in the as-quenched condition. The value conversions are shown in Fig. 8 and the simulated behaviour of microstructural features concentration as a function of heat-treatment time at 800 °C is plotted in Fig. 9.

3.3. Kinetics of reaction

The interaction between α-SiC particles and molten aluminium includes the following steps:

(I) silicon carbide dissolution;

(II) diffusion of silicon and carbon away from the interface into the bulk liquid metal;

(III) the reaction between dissolved carbon and aluminium with precipitation of Al$_4$C$_3$, when the solubility product is exceeded.

Either dissolution or silicon diffusion can be the rate-determining step in the kinetic behaviour of the reaction.

As proposed by Lin [15], the silicon diffusion in molten aluminium is fast (i.e. the absence of a silicon concentration gradient in the aluminium matrix) and the chemical dissolution rate of solid SiC controls the interaction rate. The kinetics of a solid dissolving in a liquid phase is (in a first approximation) a zero-order reaction and, neglecting the reverse reaction, the con-
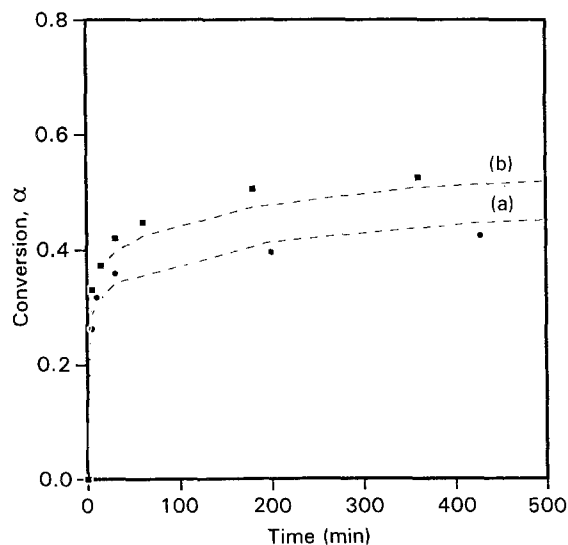

Figure 9 Behaviour of microstructural feature concentration as a function of the heat-treatment time at 800 °C. $(---)$ m_{SiC}/m_c, $(-\cdot-)$ m_{Si}/m_c, $(\underline{\qquad})$ $m_{Al_4C_3}/m_c$.

version increases linearly with time at constant temperatures.

For very low conversion, this interpretation appeared to agree with the experimental results of this study. Nevertheless, as the growing interface reaches a particular thickness, the growth mechanism changes from dissolution to diffusion-controlled, i.e. the carbide coating deposited on the SiC particles acts as a diffusion barrier and the conversion follows the following relation

$$\alpha = kt^{1/2} \qquad (17)$$

The reaction kinetics equation may be expressed in a general form by

$$\alpha = kt^n \qquad (18)$$

where k and n are constants associated with the mechanism of the reaction. Equation 18 can be transformed to

$$\log \alpha = \log k + n \log t \qquad (19)$$

Substituting the measured data of conversion for α and the corresponding time for t, and regressing the equation with the data, the constants can be obtained: the values of k and n are given in Table I. Considering that the thermal variation of k follows an Arrhenius-type rate equation in the 800–900 °C temperature range

$$k = k_0 \exp\left(-\frac{Q}{RT}\right) \qquad (20)$$

where the pre-exponential factor, k_0, and the activation energy, $Q(\text{kJ mol}^{-1})$ are material constants, T is the absolute temperature and R is the gas constant $(R = 8.3144 \text{ J K}^{-1}\text{mol}^{-1})$, the values obtained for k_0 and Q, for low conversion, were

$$k_o = 0.78 \qquad (21)$$

$$Q = 24 \text{ kJ mol}^{-1} \qquad (22)$$

Figure 8 Comparison between (■, ●) experimental and $(---)$ calculated molar ratio, α, of SiC converted to Al$_4$C$_3$, for SiC–Al samples, as a function of the heat-treatment time, at two test temperatures: (a) 800 °C, (b) 900 °C.
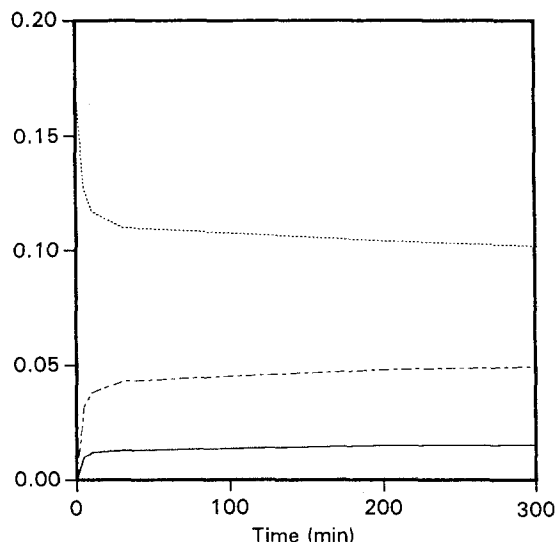
TABLE I Values of the coefficients in Equation 18 and the resulting standard deviations

$T(^\circ C)$	$k \pm 0.01$	$n \pm 0.01$	σ_α
800	0.24	0.10	± 0.02
900	0.28	0.11	± 0.01

The comparison between experimental and calculated conversions are shown as a function of the heat-treatment time, at two test temperatures, in Fig. 8.

3.4. Thermodynamic considerations

The suppression of aluminium carbide formation can be analysed by thermodynamic considerations. The free energy change, $(\Delta\mu)$, for the transformation

$$4Al_{(l)} + 3SiC_{(s)} \xrightarrow{Al_{(l)}} Al_4C_{3(s)} + 3(Si\text{-}Al)_{(l)} \quad (23)$$

is

$$\Delta\mu = [\Delta\mu_f^0(Al_4C_3) - 3\Delta\mu_f^0(SiC)]$$
$$+ 3RT \ln\{Si\} \quad (24)$$

where $\Delta\mu_f^0(Al_4C_3)$, $\Delta\mu_f^0(SiC)$ are the free energy of formation of two carbides and $\{Si\}$ is the silicon activity in the molten aluminium.

At equilibrium, $\Delta\mu = 0$ and (from thermodynamic data [15]) the equilibrium silicon activity becomes

$$\{Si\}_{eq} = 1.936 \exp\left(-\frac{41\,660}{T}\right) \quad (25)$$

Silicon addition up to the equilibrium activity prevents the interaction (below T). Nevertheless, this work establishes that in practice the inhibition is achieved with eutectic matrix composition (i.e. 13 wt % Si).

A comparison of free energy of formation data indicates that several metallic carbides are more thermodynamically favourable than aluminium carbide (see Fig. 10). Titanium and zirconium carbides are the most promising in eliminating the formation of aluminium carbide. These compounds are chemically stable and not subject to dissolution in water.

4. Discussion

The first feature, resulting from the observations on the matrix microstructure, is that the high concentration of the two harder and, consequently, brittler micro-constituents (Al_4C_3 and silicon crystallites), among the primary grains of α-phase (first nucleated), provides the material with some easy routes for crack propagation. As soon as the cracks initiate, they propagate radially and a catastrophic failure of the composite results. Furthermore, the high brittleness of Al_4C_3 crystals also provides an easy source of cracks, because when external stress is applied, these brittle phases fracture first, therefore acting as crack initiators. In addition, the resulting silicon crystals are coarse, as in ordinary β-crystals of a ipoeutectic die-
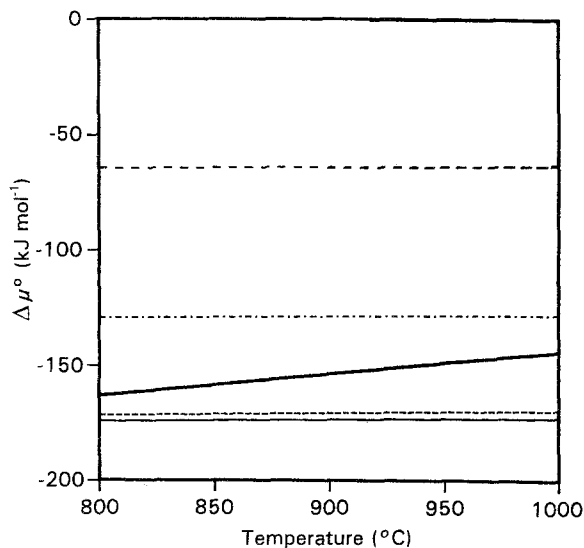

Figure 10 Free energy of formation for various metallic carbides as a function of temperature. $(- - -)$ SiC, $(-\cdot-)$ NbC, (———) Al_4C_3, (---) TiC, (———) ZrC.

cast Al–Si alloy, and together with Al_4C_3, reduce the size of the primary α-grains and consequently the matrix ductility. These features combine to produce a material which is extremely brittle such that a crack, once initiated, rapidly propagates across the entire piece to leave the planar fracture surfaces which characterize the material failure.

Further detrimental effects, due to these phases, are that Al_4C_3 has a strong tendency to hydrolyse, according to $Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4$ [16], thus a severe stress-corrosion crack failure mechanism can result and, at the same time, the corrosion resistance of the composite is, accordingly, rather poor. So the nature and arrangement of these phases were wholly detrimental to the composite mechanical property and corrosion resistance. In addition, if the SiC/Al interface, at which Al_4C_3 is present, is considered for use at high temperatures or wet atmospheres, then a barrier between the carbide and the atmosphere will be necessary.

It has also been pointed out that the reaction rate is not raised, but for the low solubility of carbon in the melted aluminium and for its high diffusivity in this temperature range, the Al_4C_3 crystallites grow at a high rate and a large fragile phase is formed even when the specimen is heat treated for a short time. This is a consequence of the crystal relationships between Al_4C_3 and SiC that produce a fast nucleation stage at the beginning of epitaxial growth.

The development of the interfacial reaction occurs for a large number of composite materials by a subsequent layer process, so that a growing diffusion barrier is rapidly formed to stop definitely the reinforcing degradation. The SiC–aluminium interaction occurs by a different physical process: Al_4C_3 crystallites grow from the solution and appear crowded near the SiC surface; the crystallites are separated from one another and constantly subject to a recrystallization process. Iseki *et al.* [17] have proved the presence of metallic aluminium among the Al_4C_3 particles. There-

fore, during remelting, the SiC surface is not efficiently protected from further consumption. As the SiC is constantly exposed to aluminium attack, the reaction can advance until it achieves equilibrium conditions. It had been found [4] that, when the extent of reaction has satured, a very large amount of Al_4C_3 is formed in the composites.

There are two possible solutions to prevent the chemical interaction in the metal–ceramic interface responsible for the degradation of the mechanical properties and the corrosion resistance of the material. In the first place, the reaction extent becomes remarkably smaller when silicon is added to the aluminium and the alloyment up to eutectic composition completely prevents the interaction, as seen. Unfortunately, this method significantly changes the properties of the materials, particularly the melting point that is lowered by 83 °C. Otherwise, the control of processing parameters of the SiC_p/Al composite fabrication technique, using the kinetics expressions obtained above, can be suitably achieved.

5. Conclusions

1. The SiC–Al interface is chemically stable at temperatures below 650 °C, therefore at service temperatures, very long annealing does not change the two starting phases of the matrix.

2. α-SiC_p reacts with aluminium during the remelting process, as in fabrication, and Al_4C_3 and silicon are formed in the composite. The extent of the interaction increases with increasing time and temperature of the casting operation.

3. Aluminium carbide forms as a discontinuous layer on the SiC substrate and free silicon precipitates in between the carbide crystals.

4. The dissolution of SiC in molten aluminium is the rate-determining step in the kinetic mechanism.

5. A semi-empirical relationship between the conversion and thermal exposure time have been derived from experiment results. The apparent activation energy for the interfacial reaction is about 24 kJ mol^{-1}.

6. If silicon is added to the molten aluminium, the reaction is inhibited up to very high temperatures.

In this work, the experimental data are limited to essential ones, but an extensive experimental programme to deduce the relationship between conversion and thermal exposure time at various temperatures is suggested for industrial application.

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