JOURNAL OF MATERIALS SCIENCE 30 (1995) 1903–1911

Review

Role of magnesium in cast aluminium alloy matrix composites

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Wetting between the dispersoid and the matrix alloy is the foremost requirement during the preparation of metal matrix composites (MMC) especially with the casting/liquid metal processing technique. The basic principles involved in improving wetting fall under three categories: (i) increasing the surface energies of the solids, (ii) decreasing the surface tension of the liquid matrix alloy, and (iii) decreasing the solid/liquid interfacial energy at the dispersoid matrix interface. The presence of magnesium, a powerful surfactant as well as a reactive element, in the aluminium alloy matrix seems to fulfil all the above three requirements. The role played by magnesium during the synthesis of aluminium alloy matrix composites with dispersoids such as zircon ($ZrSiO_4$), zirconia (ZrO_2), titania (TiO_2), silica (SiO_2), graphite, aluminium oxide (Al_2O_3) and silicon carbide (SiC), has been analysed. The important role played by the magnesium during the composite synthesis is the scavenging of the oxygen from the dispersoid surface, thus thinning the gas layer and improving wetting and reaction-aided wetting with the surface of the dispersoid. The combinations of magnesium and aluminium seem to have some synergistic effect on wetting.

1. Introduction

Metal matrix composite (MMC) is one of the important innovations in the development of advanced materials. Among the MMC systems developed, the aluminium alloy matrix composites (AMC) have reached the industrial production stage. The early work on AMC was concentrated on continuous fibre-reinforced composites whose use was limited by the high cost of reinforcements, the complex fabrication route, and limited fabricability to aerospace structures only in a limited way. The development of discontinuous dispersoid-reinforcement composites, particularly with short fibres, whiskers and particulates synthesized by the casting route, has made AMC an economically viable material of the present and future [1–4]. In the casting route, the dispersoids are uniformly dispersed in a semi-solid or in a fully liquid matrix material and the resulting composite slurry is cast into components, ingots, etc. For uniform dispersions, wetting between the dispersoid and the matrix alloy is a foremost requirement during the preparation of the composite by the casting route [1–4]. Over the years, several techniques have been developed to improve the wetting, based on the following principles: (i) increasing the surface energy of the dispersoid solids, (γ_S), (ii) decreasing the surface tension of the matrix liquid metal, (γ_L), during synthesis; and (iii) decreasing the solid–liquid interfacial energy, (γ_{SL}), [2–5] of the dispersoid–matrix interface.

Generally, it has been observed that the dispersoid surface is normally covered with a gas layer. This prevents molten matrix material coming into contact with the surface of the dispersoid. In addition, when the dispersoid concentration in the melt reaches a critical level, these gas layers can form a bridge, leading to total rejection of dispersoids from the melt [6]. Hence, it is essential that these gases from the surface of the dispersoids are desorbed prior to composite synthesis. By coating the surface of the dispersoid with metals/alloys/compounds, one can remove the adsorbed layer of gases from the surface of dispersoids. Copper and nickel coatings over the carbon fibres helped in introducing them into aluminium alloy matrix with ease and less interaction [7, 8]. Similarly, chemical and ultrasound treatments [9] and heat treatments [10] helped in introducing uncoated carbon fibre and graphite particles into aluminium alloy matrices. On the other hand, additions of (i) reactive elements such as hafnium, zirconium or titanium in the nickel matrix helped in wetting AlN [11], (ii) phosphorus in aluminium improved wetting of graphite [12]; and (iii) titanium, chromium, zirconium and magnesium in copper-based alloys aided in graphite dispersion [13]. In Al alloys the most widely used wetting element is Mg [14–17]. In addition to the above, some of the above-mentioned alloying elements can also decrease the solid–liquid interfacial energy.

This review looks into the role played by magnesium during the synthesis of different aluminium alloy matrix composites prepared by the casting/solidification route. The composite systems investigated are aluminium-zircon, aluminium-zirconia,

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aluminium-titania, aluminium-silica, aluminium-graphite, aluminium-alumina and aluminium-silicon carbide.

2. Composite synthesis

Excellent reviews on composite synthesis are already available [1–5], hence only relevant processing aspects are dealt with here. The casting route is also called the solidification route or sometimes the molten metal processing route. A few of the important methods followed are given below.

2.1. Mixing method

This is also called the liquid metallurgy or vortex method [3, 18]. This is one of the oldest and most popularly used methods for synthesizing cast MMCs. The process essentially consists in stirring the molten metal using a specially designed impeller, and introducing the pretreated dispersoids into the vortex. After mixing, the composite is cast as for conventional alloys. The smooth transfer of the dispersoids into the melt, impeller design, mixing and casting conditions are the important steps involved for the uniform dispersion of the dispersoids apart from wetting. Most of the syntheses reported earlier were carried out under an ambient atmosphere without the cover of an inert atmosphere. Gas entrapment and related problems are common in this method. A patented process developed by the Alcan Aluminium Corporation [19] could introduce SiC and Al_2O_3 particles (10 μm size and above) in aluminium alloy melts. Composites are now commercially produced in 6800 kg batches by this method [19]. Two other companies, Hydro Aluminium AS [20] and Comalco are also producing AMC by the molten metal mixing route.

2.2. Semi-solid casting

This is also called rheocasting/compocasting [21, 22]. The matrix alloy is isothermally held within the freezing range and stirred using a mechanical impeller to give a non-dendritic slurry. The pretreated dispersoids are added and mixed and the composite slurry is cast. The high viscosity and thixotropic nature of the composite slurry demand pressurizing during casting. The lower operating temperatures and minimization of gravity segregation of the dispersoids during preparation and subsequent solidification are the attractive features of the process.

2.3. Infiltration process

The molten metal is pressurized through a packed bed of reinforcements [23] in the pressure infiltration technique, whereas in the pressure infiltration technique, a reactive molten metal, such as Al–Mg alloy, is used to percolate through a bed of ceramic reinforcements [24].

2.4. Spray deposition

The process involves the incorporation of fine ceramic dispersoid particles in atomized droplets of molten metal and subsequent codeposition over the substrate. Further densification may be required for applications [25].

2.5. XD™ process

The patented process developed by Martin Marietta Corporation [26] consists of adding to a solvent metal, such as molten aluminium, a compound which will react isothermally to produce the required refractory particle internally.

The essential difference in the above processes for synthesizing composites is in the approaches used for the incorporation of dispersoids in the melt. In all cases, the wetting between the dispersoid surfaces and the molten metal matrix plays a key role.

3. Magnesium in aluminium alloys

Magnesium is one of the important alloying elements in aluminium alloys. In Al–Si casting alloys (356/357), as well as in wrought alloys (6XXX series alloys), Mg_2Si is the key phase for alloy strengthening [27]. The strength achievable in these alloys is very sensitive to the magnesium concentration, namely in A 356 alloy ± 0.1 wt % change in the magnesium level with a nominal concentration of 0.3 wt % can change ultimate tensile strength by ± 25%. Magnesium addition to aluminium reduces its casting fluidity [28] at the same time as it reduces the surface tension of the aluminium sharply (e.g. 860 dyn cm^{-1} to 650 dyn cm^{-1} with 1 wt % Mg addition). The above surface tension reduction is very sharp for the initial 1 wt %Mg addition; however, with further increase in magnesium content, the reduction is very marginal [28]. On the other hand, magnesium can also act as a powerful surfactant in aluminium alloys [29]. This also implies that it moves to the free surface and can be readily oxidized to form MgO

$$2\,Mg_l + O_{2(g)} \longrightarrow 2\,MgO_{(s)} \qquad \Delta F_{1000\,K} = -498\ \mathrm{kJ\,mol^{-1}} \quad (1)$$

This also means that if an oxygen-containing surface comes into contact, there is a likely chance of oxygen becoming scavenged, depending upon the thermodynamic and kinetics conditions.

The aluminium has the tendency to form Al_2O_3 in the presence of oxygen. However, in pure molten aluminium the Al_2O_3 forms an impervious oxide layer over the surface, and further oxidation is reduced. On the other hand, in Al–Mg alloys, magnesium has the tendency to reduce Al_2O_3 and to form MgO, according to the reaction

$$Al_2O_{3(s)} + 3Mg_{(l)} \longrightarrow 3\,MgO_{(s)} + 2\,Al_{(l)} \qquad \Delta F_{1000\,K} = -76.63\ \mathrm{kJ\,mol^{-1}} \quad (2)$$

The thermodynamic stabilities of Al–Mg oxides have been well studied [30]. Fig. 1 gives the stabilities of MgO, $MgAl_2O_4$ and Al_2O_3 as a function of temperature and magnesium concentration. According to this, a low concentration of 0.02 wt % Mg in the melt can destabilize Al_2O_3 to form $MgAl_2O_4$ spinel, and higher concentrations of magnesium (> 0.06) give

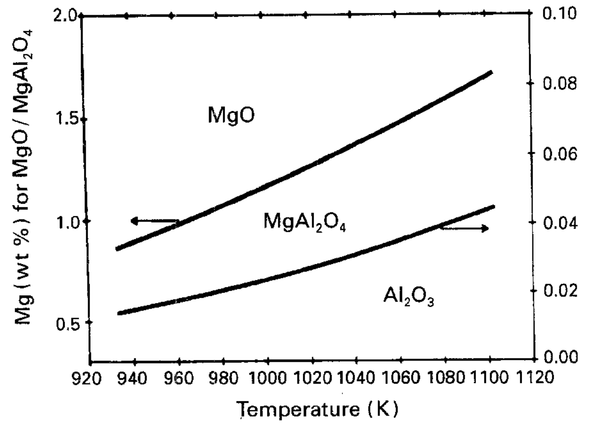

Figure 1 Thermodynamic stabilities of Al–Mg oxides in Al–Mg alloys [30].

MgO at 1000 K. The other possible reactions in this context are

$$3\,Mg_{(l)} + 4\,Al_2O_{3(s)} \longrightarrow 3\,MgAl_2O_{4(s)} + 2\,Al_{(l)}$$

$$\Delta F_{1000\,K} = -76.6\,kJ\,mol^{-1} \qquad (3)$$

$$MgO_{(s)} + Al_2O_{3(s)} \longrightarrow MgAl_2O_{4(s)}$$

$$\Delta F_{1000\,K} = -47\,kJ\,mol^{-1} \qquad (4)$$

In addition, magnesium can also form a series of compounds and intermetallics with other alloying elements present in aluminium alloys, the thermodynamics and kinetics of which are not well worked out.

In short, the presence of magnesium in aluminium alloy matrix during composite fabrication, not only strengthens the matrix but also scavenges the oxygen from the surface of the dispersoid, leading to an increase in the surface energy (γ_S), of the dispersoids. It can reduce Al_2O_3, either to form Al, $MgAl_2O_4$ or MgO depending upon its concentration. Magnesium, being a powerful surfactant, reduces the surface tension of the aluminium alloy melt. It can reduce the solid–liquid interfacial energy by aiding the reaction at the surface of the dispersoid and forming new compounds at the interface. Hence, magnesium can perform all three roles to produce a composite with better properties.

4. Composite systems and the role of magnesium

The work carried out by researchers on synthesizing aluminium alloy matrix composites with different dispersoid systems and magnesium addition by the casting route is examined.

4.1. Zircon ($ZrSiO_4$)

Banerjee *et al.* [17] reported the dispersion of zircon particles in pure aluminium and Al–11.8 Si alloy matrices with and without the addition of magnesium. It was observed that without magnesium additions, a maximum of about 5 wt % zircon could be introduced in both the matrices, whereas with magnesium addition, higher amounts can be incorporated. With 5 wt % Mg additions, about 30% zircon was introduced. There was no reaction zone around the particles in all the composites prepared with and without magnesium. However, a higher concentration of silicon was observed around zircon particles in the case of Al–11.8 Si alloy matrix which was absent in pure aluminium matrix composites. It was interpreted and proposed [17] that the high silicon content was due to the reduction of SiO_2 from zircon according to the reaction

$$SiO_{2(s)} + 2\,Mg_{(l)} \longrightarrow 2\,MgO_{(s)} + Si_{(s)}$$

$$\Delta F_{1273\,K} = -256\,kJ\,mol^{-1} \qquad (5)$$

The absence of such higher silicon concentrations around zircon particles in pure aluminium alloy matrix composites clearly suggests that the proposed Reaction 5 has not taken place. It can only be due to the precipitation from the silicon-rich eutectic liquid around them, because the zircon particles with low thermal diffusivity acted as a thermal centre. This is further substantiated by the observations made by the authors in pressure die-cast Al–7 Si–3 Mg–15 zircon composites [31] namely the absence of an interfacial reaction or preferential segregation of silicon (Fig. 2). Hence it can be concluded that in this system the presence of magnesium improves the wetting between the particle and the matrix only by thinning down the gas layer, i.e. mainly by scavenging the oxygen rather than reaction-induced wetting.

4.2. Zirconia (ZrO_2)

Banerjee and Rohatgi [32] reported incorporation of higher amounts of ZrO_2 in Al–11.8 Si–1 Mg in the presence of magnesium. Higher magnesium concentration at the particle interface was observed than in the bulk of the matrix. However, there was no evidence for reduction of ZrO_2 according to the reaction

$$ZrO_{2(s)} + 2\,Mg_{(l)} \longrightarrow 2\,MgO_{(s)} + Zr_{(s)}$$

$$\Delta F_{1000\,K} = -158\,kJ\,mol^{-1} \qquad (6)$$

These results once again suggest that in this system also the role of magnesium is to scavenge the oxygen

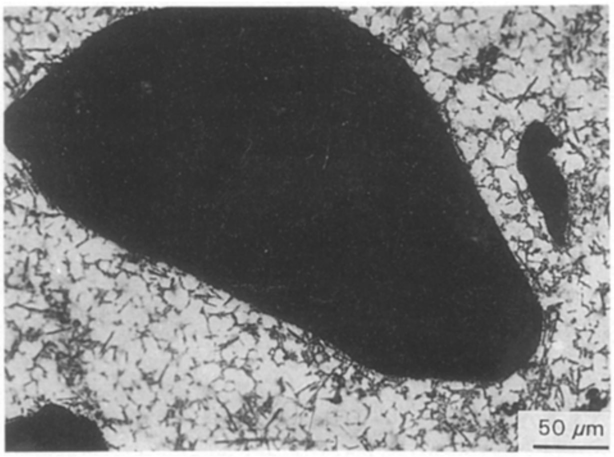

Figure 2 The particle–matrix interface in pressure die-cast Al–7Si–3 Mg–15 zircon composite.

from the surface of the particles and thus improve wetting.

4.3. Titania (TiO_2)

The observation of no interfacial reaction between the TiO_2 particles and the matrix Al–11.8 Si–1 Mg alloy matrix [32] suggests once again the role of magnesium only as a surface scavenger of gases to improve wetting. However, substantial layers of reaction products were observed at the particle matrix interface in stir-cast Al–4.5 Zn–2.2 Mg–5 TiO_2 composite systems [33]. The X-ray analysis across the dispersoids, as well as selected-area diffraction patterns of the composites, showed the presence of titanium, TiO_2 and $MgTi_2O_5$. The possible reactions identified are

$$4\,Al_{(l)} + 3\,TiO_{2(s)} \longrightarrow 2\,Al_2O_{3(s)} + 3\,Ti_{(s)}$$

$$\Delta F_{1100\,K} = -422.5\,kJ\,mol^{-1} \quad (7)$$

$$2\,Mg_{(l)} + TiO_{2(s)} \longrightarrow 2\,MgO_{(s)} + Ti_{(s)}$$

$$\Delta F_{1100\,K} = -218.5\,kJ\,mol^{-1} \quad (8)$$

$$MgO + 2\,TiO_2 \longrightarrow MgTi_2O_5$$

$$\Delta F_{1100\,K} = -26.9\,kJ\,mol^{-1} \quad (9)$$

The absence of entrapped Al_2O_3 at the interface, as well as in the matrix, led to the conclusion that Reactions 8 and 9 are probably the dominant ones in these conditions. The $MgTi_2O_5$ was exclusively found around larger agglomerates of TiO_2 particles (Fig. 3). The domination of the reaction-aided wetting could be due to the presence of higher amounts of magnesium in the base alloy. Because zinc has not participated in the reaction, its role in these cases is not known.

4.4. Silica (SiO_2)

Quartz particles were dispersed in a pure aluminium matrix with varying (0.5–5 wt %) amounts of magnesium additions [15]. In the absence of magnesium it was not possible to disperse SiO_2 in pure aluminium. A higher amount of SiO_2 incorporation was observed with higher amounts of magnesium. There was no interfacial reaction when the composite was synthesized at temperatures below 1273 K. In these cases, higher amounts of Mg/(MgO) were observed at the interface than in the bulk of the matrix, suggesting the scavenging effect of magnesium. When the melt temperature exceeded 1273 K, cuboids of silicon were observed at the particle–matrix interface, suggesting the reduction of SiO_2 to silicon according to Reaction 5

$$3\,SiO_{2(s)} + 4\,Al_{(l)} \longrightarrow 2\,Al_2O_{3(s)} + 3\,Si_{(s)}$$

$$\Delta F_{1273\,K} = -813\,kJ\,mol^{-1} \quad (10)$$

In the absence of detailed chemical analysis of the interface, it is very difficult to conclude which reaction is dominant, Reaction 5 or 10. The base alloy being pure aluminium, the fact that the silicon has increased after dispersions, clearly suggests that the reduction of SiO_2 takes place at 1273 K and above.

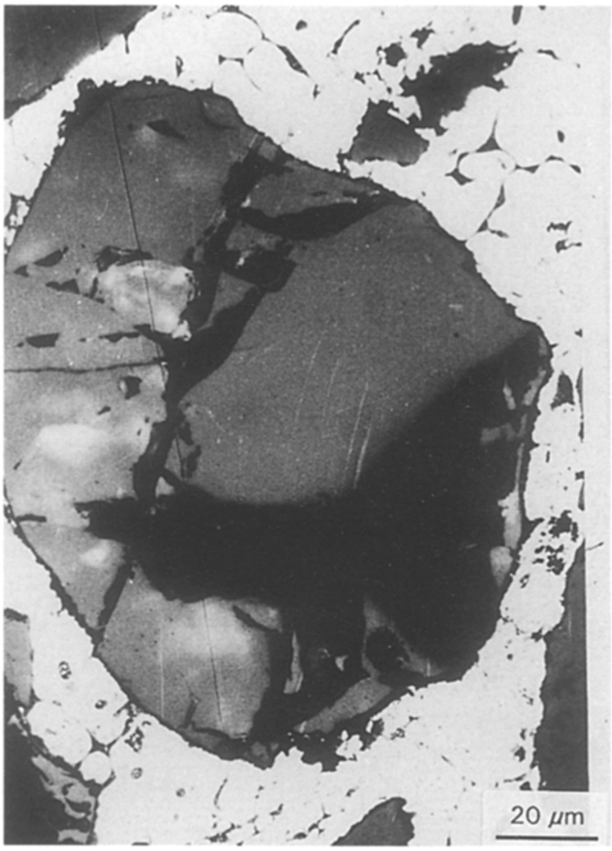

Figure 3 The presence of $MgTiO_5$ reaction product around an agglomerate of TiO_2 particles.

4.5. Graphite

Particulates of graphite could be introduced in molten Al–Si alloys without the addition of magnesium to the melt by heating the alloys prior to dispersion [10]. However, for consistent and reproducible results it was essential to add about 1 wt % Mg to the melt prior to dispersion [34]. Graphite can form aluminium carbide when it comes into contact with molten aluminium alloys at temperatures exceeding 900 K. No evidence for the formation of aluminium carbide according to Reaction 11 was reported during the dispersion of electrode-grade or natural graphite particles

$$4\,Al_{(l)} + 3\,C_{(s)} \longrightarrow Al_4C_{3(s)} \quad (11)$$

However, short carbon fibres have exhibited a severe reaction tendency with the molten aluminium when the melt temperature exceeded about 900 K. Graphite particles have shown discontinuous reaction products at the interface at melt temperatures exceeding 1023 K and at contact times exceeding 4–6 h [35].

In graphite–dispersed Al–Mg alloy matrix composites with varying magnesium contents (0–10 wt %), the magnesium concentration at the interface was around 2–3 wt %, irrespective of the quantity of magnesium present in the bulk of the matrix. The magnesium was basically in the form of MgO [36]. This clearly suggests that in this composite system too, magnesium thins down the gas film around the particles by forming MgO. Because the adsorbed gas layer thickness is expected to be the same, the amount of MgO formed is also the same and this supports the observation. As magnesium has no tendency to form magnesium carbide, no reaction-aided wetting at the interface with magnesium will take place. Similar results were also observed with coconut shell char dispersed composites [37].

Hence, it can be said that in graphite particle-dispersed aluminium alloy matrix composites, the role of magnesium is to reduce the thickness of the gas layer and thus to improve the wetting.

4.6. Aluminium oxide (Al_2O_3)

This is considered to be one of the ideal dispersoids in pure aluminium matrix owing to its good interfacial compatibility with aluminium and also there is no possibility of degradation of the dispersoid surface with molten aluminium. However, the presence of magnesium in the aluminium matrix changes the situation. Even though extensive literature is available on structure property correlations in Al–Al_2O_3 composite system prepared by the liquid metal processing route [38–40], a few papers only discuss the role of magnesium on synthesis, which is discussed here.

The composites prepared by the stir casting route [14] at 1123 K in pure aluminium and Al–Cu–Si alloy as matrices with varying amounts of magnesium (0–14.5 wt %) showed (i) a higher retention of particles with increasing magnesium content, (ii) higher amounts of retained Al_2O_3 particles in pure aluminium compared to the Al–Cu–Si alloy system under similar magnesium levels, (iii) a higher concentration of magnesium at the interface, and (iv) partial reduction of Al_2O_3 in many cases and total reduction at the higher concentration of magnesium (nearly 14.50%). These results clearly indicate that all three types of wetting conditions take place during synthesis. At lower concentrations, magnesium only acts as a scavenger of gaseous oxygen from the surface of the dispersoid, beyond which it begins to interact with the Al_2O_3 surface, according to Reaction 3, to form spinel. The magnesium can also reduce the surface of Al_2O_3 according to Reaction 2 to form spinel according to Reaction 4. However, because this reaction takes place in the solid state only, the probability of the domination of Reaction 3 will be greater. The effectiveness of the freshly added magnesium over pre-alloyed magnesium in the melt during composite synthesis can be explained on the basis that the freshly added magnesium is likely to be retained at the top because of its lower density and it can thus come into contact with the particles more readily than in the pre-alloyed condition. The higher rotation station speeds of the impeller can also help in thinning down the adsorbed gas layer from the surface of the dispersoid [41] and thus result in greater incorporation.

In compocast composites with Al–Mg as matrix with α-Al_2O_3 fibre as reinforcement [42], a void-free intimate bond between the dispersoid and the matrix was reported. The interaction zone contained fine α-Al_2O_3 and $MgAl_2O_4$ in alloys containing less than 4 wt % Mg and exclusively MgO when the magnesium content in the matrix exceeded 4 wt %. Further, the fibres did not show any degradation. The results could be explained on the basis of the formation of Al_2O_3 which could be the result of the Reaction

$$4\,Al_{(l)} + 3O_{2(g)} \longrightarrow 2\,Al_2O_{3(s)}$$
$$\Delta F_{1000\,K} = -1743\ \mathrm{kJ\,mol^{-1}} \quad (12)$$

where the oxygen comes from the adsorbed gas layer on the surface of the dispersoid. The $MgAl_2O_4$ could be the result of Reaction 3. When the magnesium concentration exceeds 4 %, it takes all oxygen from the surface as in Reactions 1 and 3, including the reduction of nascent Al_2O_3. Because the composite was synthesized at lower temperatures (< 900 K) no fibre degradation took place. The surface treatment [43] reduced the tendency for magnesium attack over the Al_2O_3 particle surface and, in such cases, only a limited reaction product will be seen at the interface.

In silica binder-coated alumina fibre-reinforced Al–2.5 Mg and 6061 Al alloy composites, MgO and free silicon were observed at the interface [44]. In infiltrated composites, progressive depletion of the magnesium in the matrix alloy [45] with the infiltration distance was observed along with the formation of silicon and MgO, suggesting the possibility of Reaction 5 occurring with the binder. Even though the alloying elements, such as cerium, are powerful oxygen scavengers, their effect is not as good as magnesium [46].

The kinetics of the growth of $MgAl_2O_4$ spinel at the particle interface in 15 vol % Al_2O_3-dispersed Al–1 Mg, was studied [30] in detail in the temperature range 948–1073 K. The growth kinetics followed a decelerating growth mechanism. During the spinel growth, depletion of magnesium in the region was observed and a model was proposed for predicting its loss. The analysis concludes that for minimizing the spinel formation, the magnesium content in the matrix should be as low as possible.

In most of the liquid metal processing route where Al–Mg alloy was used for the matrix, $MgAl_2O_4$ spinel, crystal growth was observed at the interface [38–40]. The detailed interfacial studies [47] on 10% Al_2O_{3p}-dispersed 6061 Al alloy matrix-cast Duralcan composites (W 6 A 10) showed the presence of $MgAl_2O_4$ crystals over Al_2O_3 particles. The thickness of these crystals was of the order of 1 μm. In addition, higher concentrations of silicon were observed near the interface than in the bulk of the matrix. For spinel formation, in addition to Reactions 3 and 4, Reactions 13 and 14 were also proposed

$$Mg_{(l)} + 2\,Al_{(l)} + 2\,O_{2(g)} \longrightarrow MgAl_2O_{4(s)} \quad (13)$$

$$2\,SiO_{2(s)} + 2\,Al_{(l)} + Mg_{(l)} \longrightarrow MgAl_2O_{4(s)} + 2\,Si_{(s)}$$
$$\Delta F = -442\ \mathrm{kJ\,mol^{-1}} \quad (14)$$

Detailed morphological analysis of the spinel was carried out [47] and it was suggested that the most probable reaction for spinel formation could be Reactions 3 or 14. The presence of higher amounts of silicon at the interface led the authors [47] to suggest that Reaction 14 is the most probable reaction, by assuming that free silicon in the melt becomes oxidized to SiO_2 leading to Reaction 14. Because aluminium has a higher potential for oxygen than silicon, it is unlikely to have SiO_2 in the melt rather than Al_2O_3. The higher silicon concentration can also come from the solidification of eutectic-rich silicon liquid around the particles, because Al_2O_3 particles can act as thermal centres. It is also interesting to note that in these composites, no free MgO or Al_2O_3 was observed at the interface as observed in the earlier cases. This may be due to the absence of a gas film around the particles, because of the special treatments given to the particle surface and also the mixing technique used by M/s. Duralcan during the processing of the composites. Thus, in general, the presence of magnesium in the matrix alloy has the tendency to destabilize the Al_2O_3 at the interface to form $MgAl_2O_4$ spinel.

4.7. Silicon carbide (SiC)

Al–SiC is one of the well-studied composite systems and has enormous potential for a large number of industrial applications. Despite the use of SiC in the form of whiskers, short fibres and particulates as reinforcements, the particulate form is the most popular one. SiC is unstable in molten aluminium at melt temperatures exceeding about 1000 K. It dissociates [48, 49] into Al_4C_3, rejecting metallic silicon in the matrix according to the reaction

$$4\,Al_{(l)} + 3\,SiC_{(s)} \longrightarrow Al_4C_{3\,(s)} + Si_{(s)}$$

$$\Delta F_{1000\,K} = -51.3\ \mathrm{kJ\,mol^{-1}} \qquad (15)$$

However, the above dissociation tendency can be reduced by having a higher silicon content in the matrix [50]. Fig. 4 gives the minimum amount of silicon required in the matrix to suppress the interfacial Reaction 15 at the interface, as a function of melt temperature. For most of the aluminium alloy casting, a melt temperature of about 1015 K is desired to have good fluidity. Thus, to have a composite casting with SiC reinforcements, a minimum silicon content of 7–8 wt % is required in the matrix to prevent this reaction. A well-studied composite system is A 356 matrix with 10, 15 and 20 vol % SiC particle reinforcement. Duralcan, USA, is synthesizing these composites by the liquid metal processing method [19] and has commercialized them. These composites can be remelted and cast at temperatures below 1015 K without appreciable degradation of SiC_p. The base alloy contains 0.4–0.6 wt % Mg, which helps the matrix strengthening by precipitation hardening. In addition, magnesium has no reaction with SiC_p.

The composites prepared with oxidized SiC_p and A 356 [51] or 6061 [52] matrices, showed precipitation of $MgAl_2O_4$ spinel at the interface. These alloys contain < 1 wt % Mg, whereas in 2124 alloy containing 1.5 wt % Mg, both MgO and $MgAl_2O_4$ were observed at the interface [53]. With further increase in the magnesium content (> 5% Mg) even though both MgO and Al_2O_3 are observed at the interface, the MgO formation is more predominant.

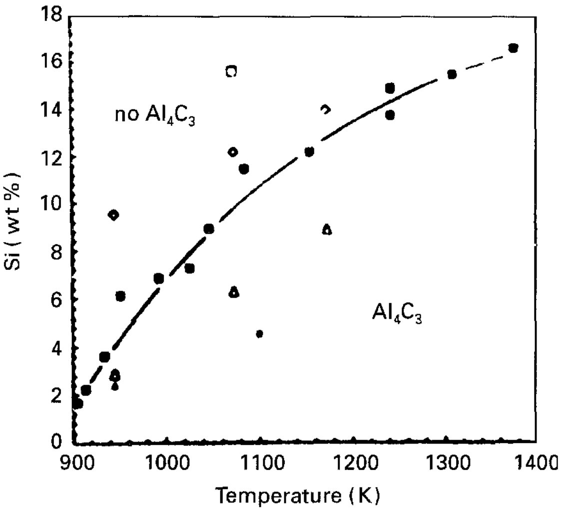

Figure 4 The silicon levels required in the matrix to prevent the formation of aluminium carbide as a function of melt temperature [54].

In compocast A 356, 6061, Al–1 Mg and Al–5 Mg matrix SiC_p composites [54], with as-received SiC_p dispersions, no Al_4C_3 was observed at the interface. This was mainly attributed to the presence of SiO_2 (0.1–0.2 wt %) over SiC_p in the as-received condition. The SiO_2 reacted with the magnesium present in the matrix alloy to form $MgAl_2O_4$ according to Reaction 14. The $MgAl_2O_4$ crystallites were discontinuous and were of the order of 100 nm in size. It was also observed that the reaction of SiO_2 with the melt was very rapid, while formation of $MgAl_2O_4$ was a slow process. In the case of SiC oxidized (approximately 4 wt % SiO_2) under controlled conditions, the crystallite layers were continuous, having about 200 nm thickness. With increasing magnesium content in the base alloy, along with $MgAl_2O_4$, MgO also began to form in certain regions. At higher oxidation levels of SiO_2 in addition to $MgAl_2O_4$ crystallites, Mg_2Si phase was also present at the interface in Al–1 Mg matrix alloy. By increasing the magnesium in the matrix, the Mg_2Si crystallite become coarser. The remelting studies with oxidized SiC_p composites showed lower degradation of SiC with molten aluminium compared to that of unoxidized SiC_p-dispersed composites. It was also observed that the $MgAl_2O_4$ spinel is not continuous over the SiC surface. In the discontinuous regions, the molten aluminium can directly come into contact with the SiC surface to form silicon and Al_4C_3. However, in these regions, when the local silicon concentration reaches the equilibrium silicon concentration, the reaction ceases. The studies on the age-hardening behaviour of these composites showed that the formation of $MgAl_2O_4$ and Mg_2Si at the interface reduced the magnesium concentration in the matrix, resulting in a lower response for the strengthening. By adding 1 wt % extra magnesium in the base alloy during composite synthesis, magnesium depletion from the matrix in both A 356 and 6061 alloy systems could be compensated.

The composite prepared by the liquid metal processing technique [55] with 80–100 μm size SiC_p in 356 alloy matrix, showed the presence of a gas layer

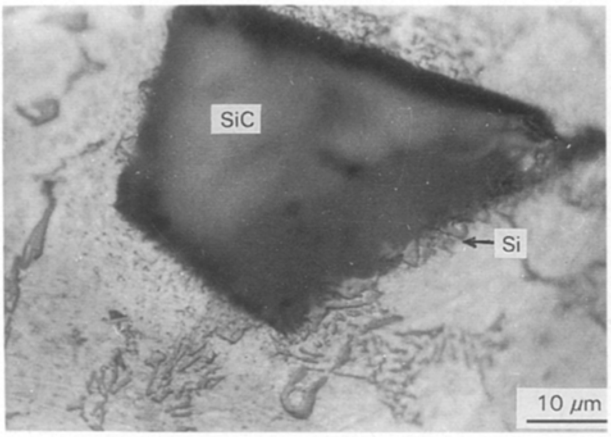

Figure 5 Microstructure Al–7Si–Mg 15 SiC_p composite showing higher concentrations of silicon at the particle–matrix interface.

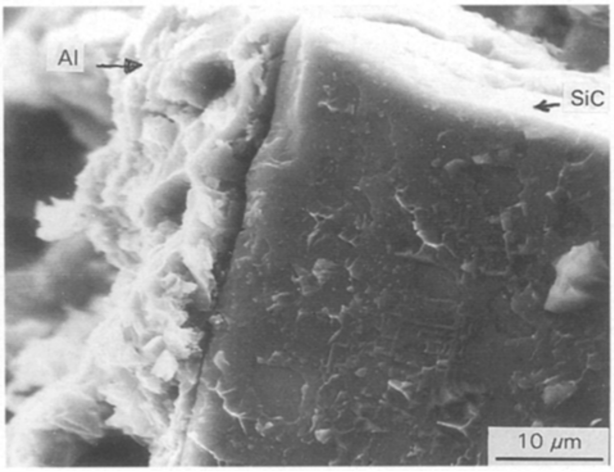

Figure 6 The fracture surface 356–SiC_p composite prepared with untreated particles.

over the SiC_p and the addition of magnesium helped in thinning the gas layer. The fractured surface of the composite showed a discrete reaction of SiC_p at the surface (Fig. 5) with untreated particles. With 356 and 6061 alloy melts [56], using preoxidized SiC_p as dispersoid, $MgAl_2O_4$ was observed at the interface and MgO was present in traces only. By preoxidation of SiC_p, higher amounts of silicon was observed at the interface (Fig. 6). This could be due to the rejection of silicon to the interface according to Reaction 14. Secondly, a part may also be due to the segregation of the eutectic silicon in the vicinity of the particles during solidification of the composites, because the particles can act as thermal centres due to their lower thermal diffusivity than the matrix. It was also seen by the authors [57] that some of the magnesium goes to the interface to form $MgAl_2O_4$ resulting in depletion of magnesium in the matrix. In addition, with the increase in particle loading, the amount of magnesium depletion also increased. This also supports earlier findings.

In Al–SiC composites, the presence of magnesium in the matrix alloy (i) scavenges the oxygen from the surface of the SiC if present, and (ii) helps in reducing the SiO_2 layer to form $MgAl_2O_4$ spinel, by combining with Al_2O_3 if SiC_p is oxidized. Otherwise, magnesium has no specific role during composite synthesis because SiC has no direct reaction with magnesium

5. Discussion

Most of the initial syntheses of the composite by the liquid metal processing route were carried out under an ambient atmosphere. The particles were transferred from air to the molten metal. During this processing the gas film retained over the dispersoid surface prevented it from becoming wetted by the liquid metal. The presence of magnesium in the molten melt helped in scavenging the oxygen from the dispersoid surface. The presence of higher amounts of magnesium in the melt thus helps in retaining higher amounts of dispersoid. In such cases, for a given volume percentage, there will be an optimum amount of magnesium, and finer sized particles should require a larger amount of magnesium. This was found to be true in the case of graphite particles dispersed in Al–Si alloys [6, 36, 58]. Hence the role of magnesium in graphite particle-dispersed composites can only be partial surface cleaning of the particles, thus aiding wetting and dispersion. At lower magnesium concentrations and lower synthesizing temperature (< 1000 K), this was also found to be true in the case of ZrO_2, $ZrSiO_4$, SiO_2 and Al_2O_3 particles. In addition, the MgO formed at the surface of the particles by reacting with surface oxygen can also improve wetting [59].

Thermodynamically, MgO is a stable oxide at 1000 K and above, compared all other oxides used as dispersoids in the present context. Hence, an intimate contact of magnesium with these oxides could reduce them to metal and form MgO. The kinetics of the reaction was dependent on the contact conditions, such as time and temperature. No reaction products were formed by ZrO_2 and $ZrSiO_4$ because the kinetics did not favour the reaction. On the other hand, TiO_2, SiO_2 and Al_2O_3 were partially or completely reduced. The reduction of the surface can expose a fresh nascent surface to the molten metal. In the case of partial wetting, the reaction product will also have better wetting. In the case of SiC, the SiO_2 formed by the pre-oxidation treatment is reduced completely, allowing a fresh surface to come into contact with $MgAl_2O_4$ spinel. The spinel protects the SiC from further attack for some time and also aids wetting. In all these cases the presence of magnesium in the base alloy assists reaction-aided wetting. The other alloying elements present in the matrix alloy do not seem to have any significant effect. Additions of oxygen scavengers such as titanium, cerium, etc. [60] during synthesis, only improved the quality of the dispersion, but they could not replace magnesium partially or totally. Thus the uniqueness of magnesium addition during aluminium alloy matrix composite synthesis comes from the fact that it reacts with Al_2O_3 even at very low concentrations (0.02 wt %) [30] to form $MgAl_2O_4$ spinel, thus allowing a fresh aluminium surface to come into contact with dispersoid surface [29]. Depending on the kinetics, both aluminium and magnesium can react with the dispersoid surface to give a $MgAl_2O_4$ spinel. When the magnesium concentration exceeds about 4%, the magnesium dominating reaction becomes prominent, forming MgO.

The role of magnesium in aluminium alloys in reducing its surface tension is well known [36]. However, this role seems to be less important during composite synthesis. For example, alloying elements such as lead, bismuth and lithium were found to reduce the surface tension of liquid aluminium more sharply than magnesium in lead- and bismuth-doped Al–Si alloys, even though the surface tension was less, graphite particles could not be introduced [36]. However, in lithium-doped aluminium alloys, graphite dispersion was possible, but it was very much less consistent compared to magnesium-doped aluminium alloys.

6. Conclusions

The presence of magnesium in aluminium alloy matrix composites not only has the beneficial effects of alloying and reduction of surface tension, but also aids in better wetting and dispersion. The major contributions of magnesium addition are as follows.

1. Being a powerful scavenger of oxygen, magnesium reacts with the oxygen present in the surface of the dispersoid, thinning the gas layer, and thus improving wetting and reducing the agglomeration tendency.
2. Because magnesium is a highly reactive element, it can form a thermodynamically stable oxide by reducing the oxide-based dispersoids at the composite synthesizing temperatures. The extent of the reaction depends on the kinetics. The reaction and resulting reaction products at the interface help the wetting.
3. Magnesium reduces the aluminium oxide film present in the melt, as well as that formed at the dispersoid–matrix interface, as the result of reaction between the adsorbed oxygen and aluminium. This allows fresh molten metal to come into contact with the dispersoid surface, to give better wetting. The $MgAl_2O_4$ spinel formation at the interface also promotes wetting.
4. Magnesium can also interact with alloying elements such as silicon and change the heat-treatment response of the matrix in the composite.

Thus magnesium is a vital element in aluminium alloy matrix composites playing a very important and unique role during the synthesis of the composite via the liquid processing route.

Acknowledgements

The authors thank Dr A. D. Damodaran, Director, Regional Research Laboratory, Trivandrum for encouragement, the MMC group members for their support during the preparation of this manuscript, Mr Hari Krishna Bhat for help with the thermodynamic calculations, and Mr A. V. Philip for assistance with the typing.

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Received 9 December 1993
and accepted 19 August 1994