# **Microstructural evolution of silicon carbide/aluminum oxide composites processed by melt oxidation***∗†*

# M. GUERMAZI $^{\ddagger}$ , R. A. L. DREW

McGill University, Department of Metallurgical Engineering, Montreal, QC, H3A 2B2, Canada E-mail: Robin@minmet.lan.mcgill.ca

The nucleation and growth mechanisms during high temperature oxidation of liquid Al-3 wt % Mg and Al-3 wt % Mg-7 wt % Si alloys were studied to provide a better understanding of the composite fabrication process, especially in the presence of SiC reinforcement.  $Al_2O_3$ -matrix composites with and without SiC particulates have been produced by directed oxidation of aluminum alloys. The microstructure consists of three interpenetrating phases: the SiC preform, a continuous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> matrix, and a network of unoxidized metal. The volume fraction of metal within the oxidation product decreases with increasing processing temperature. The preform does not show any evidence of degradation by the molten alloy, but the growth front tends to climb up the particles, increasing the oxidation area and therefore enhancing the rate of composite growth. The amount of porosity was found to increase with the Mg content in the alloy, from 2.0 vol % for 0.5 wt % Mg to 5.8 vol % for 3 wt % Mg. The role of magnesium and silicon in the growth process are discussed.  $\odot$  1998 Kluwer Academic Publishers

# **1. Introduction**

The directed oxidation process or  $\text{DIMO}X^{TM}$  process involves the formation of ceramic/metal composites by the directed oxidation of molten metal [1, 2]. The ceramic–metal matrix is formed by the partial oxidation reaction of a molten metal with an oxidant. Different metals can be used: aluminum, zirconium, titanium, etc., whereas both oxygen and nitrogen can be used as oxidants. The  $\text{DIMOX}^{\text{TM}}$  process involves the oxidation of a bulk molten metal by a gas to form a solid ceramic body using a directed growth process. The reaction product forms, initially, on the exposed surface of a molten metal pool and then grows outward.

The oxidation process is fed by the transport of additional metal through the ceramic product of the oxidation reaction between the parent metal and the gas phase oxidant. The amount of residual metal in the ceramic body therefore depends on the processing conditions and the starting material. Alternatively, particulatereinforced or fiber-reinforced composites can be produced by the  $\text{DIMOX}^{\text{TM}}$  process to achieve favorable structural properties [2–4]. In such cases, the reaction product grows into the filler material (particulates, fibers) to form the composite. The material consists of three-dimensionally interconnected ceramic phase and interconnected metal channels supplying the metal to the surface during the reaction. The filler material is

placed on top of the metal (in the direction of the oxidation growth process). The filler material is usually not displaced or disturbed during the matrix formation reaction [2].

Temperatures within a limited process envelope are typically in the range of 900 to  $1350\,^{\circ}\text{C}$ , depending on the dopant materials used, are also necessary for practical reaction kinetics [2]. When the appropriate process conditions are achieved, matrix growth in the  $Al_2O_3/Al$ system typically occurs at a constant rate (linear kinetics). It has been observed that the microstructure and properties of the matrix can be strongly influenced by the nature and amount of dopants present and the process temperature and time [5]. For instance, processing at a lower temperature tends to produce a matrix with a lower ceramic/metal phase ratio than matrices processed at higher temperatures. Once started under appropriate conditions, the  $\text{DIMOX}^{\text{TM}}$  process appears to grow a composite of uniform microstructure as along as (i) molten metal and oxidant are available to sustain the process, and (ii) the process temperature is maintained [1]. Similarly, the formation of unreinforced AlN/Al ceramic composite bodies by the directed oxidation of molten Al alloys in nitrogen has been demonstrated [6–9], and shows similarities with the  $Al_2O_3/Al$  system.

Previous authors have confirmed that composite growth is promoted by the addition of elements with

∗ Based in part on the thesis submitted by M. Guermazi for the Ph.D. degree in Metallurgical Engineering, McGill University, Montreal, Canada, 1997.

† Financial Support: NSERC, Canada.

<sup>‡</sup> *Present address*: Ecole Polytechnique de Montreal, CIREP, Montreal, QC, H2M 2N9, Canada, E-mail: Mohamed.Guermazi@Polymtl.ca

relatively high vapor pressures (e.g. Mg or Zn) which form surface oxides that prevent the passivation of the melt and control the supply of oxygen to the reaction front [1, 10, 11]. Nagelberg [10] investigated the growth of  $Al_2O_3/Al$  composites from a complex aluminum alloy at temperatures ranging from 1273 to 1473 K in atmospheres of 20 to 100 vol %  $O_2$  (balance Ar or  $N_2$ ) using  $SiO<sub>2</sub>$  as an initiator. Nagelberg found a continuous ZnO layer ( $\sim$ 1  $\mu$ m) at the outer surface, and reported an activation energy of ∼89 kJ/mol, which is significantly lower than values reported for other alloys [11, 12], which range from 270 to 400 kJ/mol.

The present study examined the nucleation and growth mechanisms responsible for the formation of  $Al_2O_3/Al$  alloy composites by oxidation of Al-3 wt % Mg and Al-3 wt % Mg-7 wt % Si alloys in air. One composition contains both alloying elements used for this study, while the other contains only Mg, thus allowing some conclusions to be drawn on the role of Si in the microstructural development (Mg is essential to the formation of these composites, i.e. if absent no reaction occurs). All composites in this investigation were reinforced with 240-grit SiC particles and composites produced without preforms were used for comparison. The present experiments were conducted at an intermediate temperature (1150 $\degree$ C) to facilitate the study of the early stages of the process. The study includes extensive microstructural characterization of the oxidation reaction products. Mechanisms are proposed based on these observations that explain the high temperature nucleation and growth phenomena leading to the conversion of the majority of the bulk Al into  $Al_2O_3$ .

# **2. Experimental**

The two main alloys used in these studies were prepared starting from pure metals: Al, Mg, and Si. Melting of the alloys was carried out using an induction furnace. The crucibles for melting were machined from a high purity graphite block which was baked at 800 ◦C to remove volatiles. The alloys were induction melted in 500 g batches in the baked crucible. Initially, Si pieces were placed at the bottom of the crucible and then Al shot was loaded on top. Once the aluminum and silicon were molten and mixed, the temperature of the induction furnace was lowered to about  $650^{\circ}$ C. The magnesium pieces, wrapped in aluminum foil, were then added to the melt to minimize oxidation and loss of magnesium. Once the magnesium had dissolved in the alloy, the temperature was raised back to  $740^{\circ}$ C to ensure complete mixing. The molten alloys were cast into a cylindrical graphite mold 20 cm in length and 2.4 cm inner diameter. After filling the mold, the remaining melt was cast into a small copper mold to obtain samples for spectrochemical analysis. The chemical composition of the two cast alloys was quantified using emission spectroscopy. The analysis is given in Table I, where  $(a/b)$  designates an alloy having  $a \le x \le \text{Si}$  and *b* wt % Mg. The cast ingots were then sectioned into discs 5–6 mm in thicknesses.

The composites were grown into loosely packed  $\alpha$ -SiC particulate preforms with an average particle size



of 44.5  $\mu$ m (standard grit size #240). The SiC powder was oxidized in air for a period of 48 hours at 1400 ◦C prior to composite fabrication, according to

$$
2SiC + 3O_2 \rightarrow 2SiO_2 + 2CO^{\uparrow} \tag{1}
$$

The specific surface area of the powder was also measured by the single point Brunauer, Emmett and Teller (BET) method, using a Quantachrome system (Quantasorb Sorption) and yielded a value of 0.13 m<sup>2</sup>/g.

For composites grown without SiC filler material, cylindrical alloy specimens approximately 2.4 cm in diameter and 0.5 cm high were cut from the castings, degreased and placed in a slip-cast  $Al_2O_3$  crucible fabricated in house. The weight of the crucible and the alloy were noted prior to composite fabrication. When a filler material was used to grow the composites, SiC powder was placed on top of the alloy in the  $Al_2O_3$  crucible and tapped level using a vibrating table to ensure reproducible tap densities (Fig. 1a). The weight of the crucible, alloy and SiC powder were noted prior to composite fabrication. The growth of the molten Al-Mg and Al-Mg-Si alloys in air was studied by interruption of the growth process at intermediate times during the isothermal soak. For this purpose, a TGA-furnace setup (Fig. 1b) was used which allowed the lowering of the sample into the hot zone without any previous heating, and also enables air quenching of the sample from the furnace after a given soak time. The crucibles were strong enough to withstand the thermal shock. Composite growth was carried out at a  $1150\degree C$  in air to allow monitoring the different stages of the growth process.

Microstructural characterization of the composites included primarily optical metallography and scanning electron microscopy (SEM). Metallographic samples were mounted in a cold setting epoxy resin. They were then ground using two diamond "ultra-prep" grinding discs of 45  $\mu$ m followed by 15  $\mu$ m. The samples were later polished with a diamond paste and an ethylene glycol lubricant, using a diamond grit of  $6 \mu$ m down to a 1  $\mu$ m finish. Ultrasonic cleaning was carried out after each polishing step. Optical micrographs were taken on a Zeiss Neophot 21, fitted with an oil immersion lens  $(x 2000)$ .

The polished samples were sputter coated with Au-Pd and examined on a Jeol JSM-840A SEM equipped with an ultra-thin window light-element X-ray detector (Al,  $0.1 \mu m$  thick) A Tracor Northern (Model TN-96-606E3/513) system was used to carry out (a Energy Dispersive Spectroscopy (EDS), (b) X-ray mapping, and (c) image analysis using a compatible software package.

The surface microtopography of the composites was examined on high-resolution replicas by TEM (Model Jeol CX100). The replicas consist of a thin



*Figure 1* Experimental set-up (a) for composite fabrication using a filler material and (b) to measure the composite growth rate.

platinum/carbon (Pt/C) film (95Pt/5C wt % and 1–2 nm thick) and a supporting carbon film (15–20 nm thick). Polished cross sections of the composites were mounted on a flat substrate using double-sided adhesive tape, with the surface of interest parallel to the substrate. The shadowing and replication procedure was performed in a freeze-etch unit (Balzer 400) under high vacuum  $(1.333 \times 10^{-4} \text{ Pa})$  and at room temperature. The replica was cleaned by dissolving the composite adhering to the replica using a 10% HF solution, rinsed with de-ionized water and transferred onto a 200 mesh TEM grid.

#### **3. Results**

Fig. 2 is a typical TGA curve showing the several stages of the oxidation behavior of these alloys in the temperature range where composites can be grown [13]. A limited weight gain occurs initially representing the incubation period with variable length depending on several parameters. After this incubation period, the bulk  $Al_2O_3$ -matrix composite forms. The growth ends rather abruptly, although some further oxidation of the alloy continues at an exceedingly slow rate. It has been suggested [1] that the sudden drop in growth rate



*Figure 2* Typical oxidation behavior for Al-containing Mg alloys in air or oxygen at temperatures in the range of 1100–1300 ◦C.

corresponds to the exhaustion of the bulk metal reservoir, with the additional slow weight gain resulting from the oxidation of residual metal in the microchannels of the composite only. However, the current TGA results indicate that in some cases composite growth ceases long before the bulk metal is totally consumed.

#### 3.1. Initial oxidation and incubation period

The general features during initial oxidation of the alloys in the presence of SiC particles are similar for both the Al-3 wt % Mg and Al-3 wt % Mg-7 wt % Si. After 2 minutes of exposure at  $1150^{\circ}$ C, the exposed surface of the alloy becomes porous and  $MgAl<sub>2</sub>O<sub>4</sub>$  rings appear around the surface pores, as shown in Fig. 3a. Cross sections of the samples do not reveal any traces of either  $MgAl<sub>2</sub>O<sub>4</sub>$  or  $MgO$ . This is due to the fact that the MgAl<sub>2</sub>O<sub>4</sub> rings are small (1–5  $\mu$ m) and it is difficult to intercept them during sectioning of the samples. Fig. 4 shows that after 5 minutes the exposed surface is completely covered by a continuous dense  $MgA<sub>2</sub>O<sub>4</sub>$  layer but contains metal channels. New MgO crystallites nucleated on the outer  $MgAl<sub>2</sub>O<sub>4</sub>$  surface with an average grain size of  $3-4 \mu m$  and grow favorably on the SiC particles, as shown in Fig. 3b. The MgO crystallites quickly cover the  $MgAl<sub>2</sub>O<sub>4</sub>$  surface and form a locally continuous layer between the SiC particles (Fig. 3c). The MgO then starts to dissociate upon arrival of the metal to the  $MgAl<sub>2</sub>O<sub>4</sub>/MgO$  interface and composite nodules start forming on the exposed surface as seen in Fig. 3d. The composite nodules nucleate between the SiC particles, and can actually nucleate on the surface of the SiC, as shown in Fig. 5.

#### 3.2. Bulk oxidation: composite growth

Initial examination of the composite surface after careful removal of the uninfiltrated portion of the preform reveals a slightly undulated front covered by a continuous MgO layer between the SiC particles, as shown in Fig. 6. Thus, the proposed growth mechanism involving formation and dissolution of the MgO surface layer seems to be essentially preserved within the preform. The surface roughness in Fig. 6 is not sufficiently different from the unreinforced composite to suggest



(b)

*Figure 3* Top views of the surface oxides on the (0/3) alloy with SiC held at 1150 ℃ for various times (a) 2 minutes, (b) 10 minutes, (c) 15 minutes and (d) 30 minutes. (*Continued*)

a substantial increase in the surface area of oxidation. However, the cross section of the same specimen in Fig. 7 shows that the profile of the oxidation front is much more convoluted than that suggested by the top surface view. The front is rather porous and extends over a scale of several particle diameters with the volume fraction of the  $Al_2O_3/$ alloy reaction product increasing inward from the surface. It was also found that a layer of SiC particles immediately above the visible surface oxide remained attached to the composite when the crucible was turned upside down and tapped to remove the uninfiltrated portion of the preform. These particles appeared to be lightly sintered, suggesting that neck formation is aided by some form of condensation (presumably MgO) from the vapor phase ahead of the oxidation front [14].

The case for secondary nucleation and growth from the particles is supported by observations of the grain structure in the final composite. It is well established that oxidation in the absence of a preform leads to columnar  $Al_2O_3$  grains tens of micrometers across, growing with the same crystallographic orientation over hundreds of micrometers [1, 11]. Unreinforced composites grown from the present alloy also clearly showed a preferred orientation of the  $Al_2O_3$  grains parallel to the growth direction. In contrast, grain boundaries (revealed by changes in channel pattern orientation) were often found between particles in the



(c)



(d)

*Figure 3* (*Continued*).

SiC-bearing composites, suggesting that the preform tends to refine the  $Al_2O_3$  grain size and produce a more randomly oriented microstructure.

The nucleation of  $Al_2O_3$  on the preform particles could arise from the reaction of Al in the spreading melt with the protective oxide layer typically present on SiC, especially after lengthy exposure of the preform to air at high temperature, according to

$$
4(A1) + 3SiO2 \rightarrow 2Al2O3 + 3(Si)
$$
 (2)

This phenomenon is illustrated in Fig. 8, where the composite nodules are shown to be nucleating on the exposed surface of the SiC particles. Fig. 9 shows a composite nodule nucleating on the surface of the alloy

during the early stages of the composite formation. This would tend to promote more random nucleation of the  $Al_2O_3$  grains within the microstructure.

#### **4. Discussion**

The presence of SiC preforms in the composites did not affect their overall microstructures which still consisted of 3D interconnected ceramic phase  $(Al<sub>2</sub>O<sub>3</sub>)$  and 3D interconnected residual metal channels as well as isolated metal pockets (Fig. 10). However, the presence of SiC disrupted the columnar growth of the ceramic phase although there is some local orientation of the  $Al_2O_3$  phase in the direction of growth. Overall, the introduction of SiC preform in the composite resulted in



*Figure 4* Cross section of the (0/3) alloy surface after 5 minutes of oxidation.



*Figure 5* Top views of the surface on the (0/3) alloy with SiC held at 1150 ℃ for 30 minutes.

refinement of the composites, that is the metal channels became finer compared to the unreinforced composites.

#### 4.1. Incubation period

It is evident that the presence of SiC preform in the composites affected the microstructural evolution of the composites, and resulted in much shorter incubation times (compared to composites without SiC preforms). In some composites, the growth started immediately after introduction of the sample into the furnace. Besides the fact that the SiC preform provides a skeleton upon which the reaction product grows, the surface of the SiC particles seems to play a key role. It is well established that Al and Al-Mg alloys wet SiC at temperature >1100 °C [15–17]. As soon as the alloy is molten and is in contact with the SiC particles, spreading of the alloy occurs over the edges of the SiC particles that are in contact with the melt. Between the SiC particles, the same process occurs as in the unreinforced composites, where the surface of the alloy is initially covered by MgAl2O4 and MgO layers (see Fig. 11). However, during the incubation period, nucleation of  $MgAl<sub>2</sub>O<sub>4</sub>$ takes place on the surface of the SiC particles due to the evaporation of Mg accompanied by spreading of the aluminum melt. Mg and Al both react with oxygen from the atmosphere and through the dissolution of the  $SiO<sub>2</sub>$ passivation layer surrounding the SiC particles and the



*Figure 6* Top view of a SiC reinforced composite.



*Figure 7* Optical micrograph showing a cross-section of the top of the composite.

new products (MgO and MgAl<sub>2</sub>O<sub>4</sub>) are deposited on the outer surface of the alloy, according to [18]

$$
2SiO2 + (Mg) + 2(Al) \rightarrow MgAl2O4 + 2(Si)
$$
 (3)

Therefore the SiC surface is a preferential nucleation site for both the  $MgAl<sub>2</sub>O<sub>4</sub>$  and  $MgO$  layers.

The present investigation clarifies the microstructural evolution of the composites in relation to the role of the surface oxide layers (MgO and  $MgAl<sub>2</sub>O<sub>4</sub>$ ) in both the absence and the presence of SiC preforms. These two layers start appearing as soon as the alloy is in contact with oxygen at the processing temperature, and they persist until the growth process is completed. Therefore

these two oxides are responsible for the continuous oxidation process responsible for composite formation.

From the microstructural observations of the unreinforced composites, the Al-Mg and Al-Mg-Si alloy surfaces are covered by two oxide layers: MgO and MgAl2O4. Salas *et al*. [19] performed experiments where they covered the surface of the alloy with a thin  $SiO<sub>2</sub>$  layer prior to oxidation. They concluded that the  $SiO<sub>2</sub>$  shortens the incubation period by providing sites wherein the dense  $MgAl<sub>2</sub>O<sub>4</sub>$  layer (which seal off the metal channels) is prevented from forming. It is documented that the reaction between Al-Mg alloys and  $SiO<sub>2</sub>$  involves the reduction of  $SiO<sub>2</sub>$  to form  $MgAl<sub>2</sub>O<sub>4</sub>$ according to Equation 3 [18], which indicates that the



*Figure 8* Nucleation of composite nodules on the exposed surface of the SiC particles.



*Figure 9* Cross section of a composite nodule containing SiC particles.

transition from  $SiO<sub>2</sub>$  to MgAl<sub>2</sub>O<sub>4</sub> is accompanied by a volume contraction of ∼14%, leading to the formation of channels filled by the molten metal [19]. Unlike Mg, however, the released Si is not reoxidized but gradually diffuses back into the bulk melt. However, our experimental observations do not fully agree with the above studies. If the presence of  $SiO<sub>2</sub>$  is the only factor responsible for the shortening or elimination of incubation, then Al-Mg-Si alloys should have no incubation period, or at least a very short one. This is not the case since Al-Mg-Si alloys typically exhibit an incubation period of up to 4.5 hours at  $1350\,^{\circ}$ C [13]. On the other hand, with a SiC preform, the incubation period remained the same  $(1-1.5$  hours) and did not vary with the change in alloy content of either Mg or Si. The

 $MgAl<sub>2</sub>O<sub>4</sub>$  that forms during the incubation period in the SiC–reinforced composites grows between the SiC particles and composite growth soon follows.

According to Equation 3, free silicon is released into the melt. It was observed that in composites grown from Al-Mg alloys, silicon is present in the metal channels of the composite. If the length of the incubation period is solely dependent on the presence of Si in the alloy, then it should be expected that the length of the incubation period in the Al-Mg alloys should be of approximately the same magnitude as in the Al-Mg-Si alloys, which is in good agreement with our experimental observations, as shown in Fig. 12.

When a SiC preform is used as a reinforcement upon which the composite grows, dissolution of the  $SiO<sub>2</sub>$ 





(b)

*Figure 10* (a) Microstructure of a composite grown from a (7/3) alloy at 1150 °C with a 240-grit SiC particles and (b) TEM replica showing the interconnectivity of the metal channels.

layer surrounding the SiC particles leads to the formation of  $MgAl<sub>2</sub>O<sub>4</sub>$ , i.e. recall that the SiC powder was preoxidized prior to the growth process. Another important observation is that even if the SiC powder was not preoxidized, the composite growth process started immediately after a brief incubation period. This implies that the role of the SiC particles is not limited to the presence of a thick  $SiO<sub>2</sub>$  layer, but also the fact that the particles are disrupting the formation of the two oxides on the alloy surface. MgO and MgAl<sub>2</sub>O<sub>4</sub> layers can be thought of as passivating layers that prevent the alloy

from oxidation when in contact with air. The areas of contact between the particles and the alloy surface are actually shielded (relatively speaking) from the oxygen. Consequently the portion of the particles that is in contact with the alloy is transformed into  $MgAl<sub>2</sub>O<sub>4</sub>$  and the other side of the particles is in contact with oxygen and it reacts only with the evaporated Mg/Al mixture. The triple points (intersection of the SiC particles, the alloy surface and the oxygen) are sites where the alloy can be withdrawn upwards to the oxidizing environment (by wetting of SiC).



*Figure 11* Schematic of the evaporation and redeposition process after oxidation of Mg/Al.



*Figure 12* Weight gain vs. time curves into SiC preforms (240-grit) showing the effect of changing of Si content on the incubation time  $(1350 °C)$ .

Nagelberg [20] grew composites starting from Al-3 wt % Mg and Al-3 wt % Mg-10 wt % Si alloys at temperatures ranging from 1100 to 1250  $\degree$ C. On some of his samples, he scratched the surface of the molten alloy during the incubation period and concluded that this resulted in the growth of  $Al_2O_3/metal$  composites along the scratches. He also observed that the sizes of the nodules along the scratch were proportional to the elapsed time following surface scratching and appeared to be independent of the presence or absence of Si in the alloy. The role of SiC preform in decreasing or nearly eliminating the incubation period is therefore attributed to the disruption of the outer passivating oxide layers (i.e.  $MgO/MgAl<sub>2</sub>O<sub>4</sub>$ ). The two-layer structure still exists on the outer surface of the alloy in the presence of the SiC preform, but this layer is continuous only between the preform particles. Under the SiC particles, the layer is discontinuous which would serve as a mechanical disruption to promote growth initiation sites, as was observed in our experiments, where the growth initiation of the  $MgAl<sub>2</sub>O<sub>4</sub>$  occurs on the SiC particle surfaces.

### 4.2. Composite formation

Cracking of the  $MgAl<sub>2</sub>O<sub>4</sub>$  layer is a common occurrence observed in the composites. The thicker the initial oxide layer on the alloy, the more susceptible it becomes to cracking under growth stresses. Since the oxide layers grow faster in the Al-Mg-Si alloy than in the Al-Mg alloy, cracks would develop sooner in the Al-Mg-Si alloy indicating a shorter incubation period than for the Al-Mg alloy. When a SiC preform is used, the  $MgAl<sub>2</sub>O<sub>4</sub>$ layer grows very thick in a significantly shorter time.

The MgO layer covering the composite nodules has a texture similar to that of a sponge, and in some locations it is never observed. This leads to the conclusion that MgO is dissolved and then re-precipitated on the outer surface. The reaction starts around the SiC particles, and the product grows outward from the SiC surface. Further reaction results in the coalescence of the  $Al_2O_3$ nodules originating from the different SiC particles. The reaction on the preform surface is enhanced by wetting of the SiC by aluminum and its alloys and is even further promoted by the presence of the  $SiO<sub>2</sub>$  layer around the SiC. Manor *et al*. [14] suggested that the nucleation of the  $Al_2O_3$  on the preform particles could arise from the reaction of Al in the spreading melt with the  $SiO<sub>2</sub>$  layer typically present on the SiC. This might occur after lengthy exposure of the preform to air at high temperature, according to Equations 1 and 2 [14].

It should be noted that the process of formation of  $Al_2O_3$  nodules occurs in a similar manner to that of  $MgAl<sub>2</sub>O<sub>4</sub>$  and MgO layers, i.e. formation starts on the surface of the SiC particles and grows away from them.

## 4.3. Porosity formation in the composites Two types of porosity were observed in these composites:

1. Micro-pores are voids within the metal network, as shown in Fig. 13a. They originate primarily from the





(b)

*Figure 13* Optical micrographs showing (a) microporosity and (b) macroporosity.

solidification shrinkage and are also related to the gas evolution, e.g.  $H_2$  during solidification.

2. Macro-pores are empty of both metal and ceramic on a scale much larger than the microchannels, e.g. Fig. 13b. They are found in most of the composites whether with or without preforms and originate from the spreading of the oxidation front.

The primary advantages of the  $\text{DIMOX}^{\text{TM}}$  process include its ability to form relatively complex, fully dense composite net shapes. From the micrographs showing the microstructure of different composites, it is clear that the composites are fully dense and contain little porosity.

However, if the composite is still subjected to the processing temperature after all of the alloy has been consumed, some porosity starts to develop as can be seen in Fig. 14. In such a case, after the majority of the metal from the reservoir has been oxidized to form the ceramic matrix with residual metal channels, further exposure at the oxidation temperature results in a continued oxidation of the aluminum from the metal channels with a concurrent increase in the metallic Si content. Moreover, the aluminum from the metal channels oxidizes preferentially and leaves behind residual porosity. As aluminum is consumed, the metal becomes richer in Si at the reaction temperature and crosses into the Si-rich semi-solid region of the Al-Si phase diagram. Consequently, primary Si precipitates at the reaction temperature within the channels.

The amount of porosity was found to increase with the Mg content in the alloy, from 2.0 vol % for 0.5 wt %



Pores  $20 \mu m$ (b)

*Figure 14* Microstructure of various composites grown from a (7/3) alloy and subjected to processing at 1250 °C after all of the alloy has been consumed (30 hours).

Mg to 5.8 vol % for 3 wt % Mg (measured by means of image analysis). This is in agreement with the results of Manor *et al.* [14] who found an increase in porosity from 1.8 to 5.2% for an increase in Mg content from 0.17 to 2%. Similarly, the growth rate was found to increase by a factor of two (especially in the case of composites without reinforcing SiC particles) when the Mg content was raised from 0.5 to 3 wt %.

# **5. Conclusions**

1. It has been shown that  $Al_2O_3$  matrix composites containing SiC particles and an interpenetrating network of metal can be grown by directed oxidation of Al-Mg and Al-Mg-Si alloys at temperatures ranging from 1150 to 1350 ◦C. The presence of the SiC preform disrupted the columnar growth of the  $Al_2O_3$  matrix, but the composite still remains a three dimensionally interconnected network.

2. In the SiC-free composites, the initial oxidation event corresponds to the formation of  $MgAl<sub>2</sub>O<sub>4</sub>$ , followed by the evolution of the MgO on the outer surface during the incubation period. Initially the  $MgAl<sub>2</sub>O<sub>4</sub>$  and MgO layers thicken continuously with time. However, at 1150 ◦C, the MgO layer becomes thinner towards the end of the incubation period. Melt wicking via the metal channels created in the  $MgAl<sub>2</sub>O<sub>4</sub>$  layer increases at the end of the incubation period where the melt comes into direct contact and reacts with the MgO layer and therefore setting the stage for the formation of  $Al_2O_3/Al$ nodules.

3. The  $SiO<sub>2</sub>$  layer on the SiC particles plays a key role in the composite formation process by its reaction with the Al alloy to form  $MgAl<sub>2</sub>O<sub>4</sub>$  and  $Al<sub>2</sub>O<sub>3</sub>$  during the composite growth process and therefore enhances the formation of the composites.

4. The amount of porosity was found to increase with the Mg content in the alloy, from 2.0 vol % for 0.5 wt % Mg to 5.8 vol % for 3 wt % Mg. Similarly, the growth rate was found to increase significantly when the Mg content was raised from 0.5 to 3 wt %.

#### **Acknowledgements**

The authors would like to thank Dr. H. Vali of the Electron Microscopy Center, McGill University for his help with sample preparation for TEM using an advanced Pt/C replication technique.

#### **References**

- 1. M. S. NEWKIRK, A. W. URQUHART, H. R. ZWICKER and E. BREVAL, *J. Mater. Res.* **1**(1) (1986) 81–89.
- 2. M. S. NEWKIRK, H. D. LESHER, D. R. WHITE, C. R. KENNEDY, A. W. URQUHART and T. D. CLAAR, *Ceram. Eng. Sci. Proc.* **8**(7/8) (1987) 879–885.
- 3. C. A. ANDERSSON and M. K. AGHAJANIAN, "The fracture toughening mechanism of ceramic composites containing adherent ductile metal phase."
- 4. C. A. ANDERSSON, P. B. ANTOLIN, A. S. FAREED and G. H. SCHIROKY, in Proceedings of the International Conference on Whisker- and Fiber-Toughened Ceramics (ASM International, Metals Park, OH, (1988) pp. 209–215.
- 5. <sup>S</sup> . LEE and D. K. KIM, *Ceram. Eng. Sci. Proc.* **11**(7/8), (1990) 795–805.
- 6. E. BREVAL, *J. Amer. Ceram. Soc.* **76**(7), (1993) 1865–1886.
- 7. D. K. CREBER, S. D. POSTE, M. K. AGHAJANIAN and T. D. CLAAR, *Ceram. Eng. Sci. Proc*. **9**(7/8) (1988) 975–983.
- 8. H. LEHUY and S. DALLAIRE, in Proceedings of the International Symposium on Ceramics and Metal Matrix Composites, CIM, edited by H. Mostaghaci (Pergamon Press, New York, 1989) Vol. 17, pp. 302–311.
- 9. H. SCHOLZ and <sup>P</sup> . GREIL, *J. Mater. Sci.* **26** (1991) 669–677.
- 10. A. <sup>S</sup> . NAGELBERG, *Solid State Ionics* **32/33** (1989) 783–788.
- 11. O. SALAS, H. NI, V. JAYARAM, K. C. VLACH, C. G. LEVI and R. MEHRABIAN, *J. Mater. Res.* **6**(9) (1991) 1964– 1981.
- 12. K. C. VLACH, O. SALAS, H. NI, V. JAYARAM, C. G. LEVI and R. MEHRABIAN, *ibid* **6**(9) (1991) 1982–1995.
- 13. M. GUERMAZI and R. A. L. DREW, "Growth kinetics of silicon carbide/aluminum oxide composites processed by melt oxidation," *J. Amer. Ceram. Soc.* in press.
- 14. E. MANOR, H. NI, C. G. LEVI and R. MEHRABIAN, *J. Amer. Ceram. Soc.* **76**(7) (1993) 1777–1787.
- 15. A. ALONSO, A. PAMIES, J. NARCISO, C. GARCIA-CORDOVILLA and E. LOUIS , *Metallurgical Trans. A* **24A** (1993) 1423–1432.
- 16. V. LAURENT, D. CHATAIN and N. EUSTATHOPOULOS, *J. Mater. Sci.* **22** (1987) 244–250.
- 17. J. GOICOECHEA, C. GARCIA-CORDOVILLA, E. LOUIS and A. PAMIES , *ibid* **27** (1992) 5247–5252.
- 18. D. A. WEIRAUCH and G. E. GRADDY, Jr., in Proceedings of the International Symposium on Advances in Refractories for the Metallurgical Industries, Winnipeg, Canada, August 1987, edited by M. A. J. Rigaud (Pergamon Press, New York, 1988) pp. 251–266.
- 19. O. SALAS, V. JAYARAM, K. C. VLACH, C. G. LEVI and R. MEHRABIAN, *J. Amer. Ceram. Soc.* **78**(3) (1995) 609– 622.
- 20. A. <sup>S</sup> . NAGELBERG, *J. Mater. Res.* **7**(2) (1992) 265–268.

*Received 3 September and accepted 18 September 1998*