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The Production of Reinforced Aluminium/Alumina Bodies by Directed Metal Oxidation

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Abstract

Both unreinforced and model filler reinforced aluminium/alumina bodies have been produced by directed metal oxidation from pure aluminium parent metal blocks externally doped with magnesium. It is shown that there are some differences between the growth processes in the two cases and that in particular the presence of the filler in the production of reinforced bodies restricts the supply of oxygen to the reaction front and that an oxygen-depleted atmosphere may arise locally, leading to areas where aluminium nitride is produced rather than alumina.

1 Introduction

The production of ceramic materials by the directed metal oxidation process developed by the Lanxide Corporation, Delaware, USA, has received increasing attention recently. The process involves the oxidation of a bulk molten metal by a gas through a directed growth process to produce an interconnected ceramic reaction product, that may contain several percent of residual metal. Reinforcements may be readily incorporated in the ceramic/metal body by allowing the oxidation reaction product to grow through, and thereby incorporate, a filler material such as ceramic particles, platelets or fibres. Dopants are required to initiate and maintain the growth process and it is this feature that distinguishes it from other reaction bonding processes. Growth is limited by the presence of inert (barrier) powders which may used to define the shape of the desired product.

Much of the published work[1–3] in this area has concentrated on the production of unreinforced Al_2O_3/Al bodies grown from specially prepared aluminium alloys containing both Mg and Si as dopant elements. Nagelberg[4] has studied directed growth from an Al–Mg alloy, but in this case initiation required scratching the initial oxide scale to expose the molten Al alloy directly to the air atmosphere. Xiao and Derby[5,6] have shown that MgO may be used as an external dopant to initiate growth with pure Al.

In this paper, we concentrate on the effects of reinforcement on the production of Al_2O_3/Al bodies from pure Al with Mg as an external dopant element. To this end both unreinforced and model reinforced bodies have been produced. The model reinforced bodies were produced by growth into coarse alumina fillers (this filler could be readily distinguished from the alumina reaction product generated by the oxidation process). The microstructural development and the relationships between the growth mechanisms for both unreinforced and reinforced directed metal oxidation bodies have been investigated and are discussed below in some detail.

2 Experimental Procedure

99·8% pure Al (Alcan) blocks were placed on a bed of fine alumina powder (A17, Alcoa) contained within a mullite crucible. A mullite tube was placed on top of the Al block and further fine alumina was packed round the outside of this tube. Powdered reagent-grade Mg (5 wt%, Fisons) was either placed inside the tube directly on the surface of the Al block as a dopant (in the production of unreinforced bodies) or mixed with coarse tabular alumina (8–14 mesh, Alcoa) and the mixture placed in the tube above the Al block (to produce model reinforced bodies). In either case the tube was then withdrawn leaving the arrangements are shown in Fig. 1.

The prepared systems were heated in air at 200°C per hour in a muffle furnace to a soak temperature of 1180°C. This temperature was maintained for 15 or 24 h, after which the samples were cooled to room temperature inside the furnace.

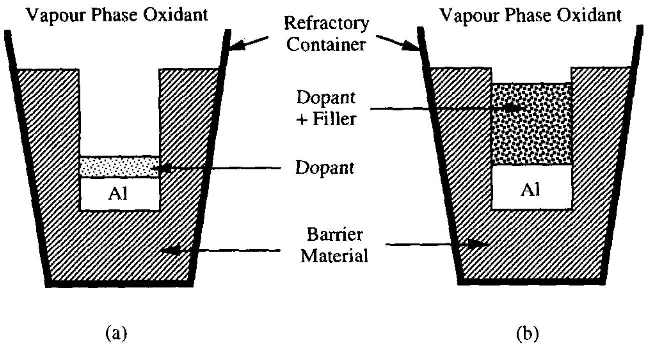


Fig. 1. Experimental arrangements used; (a) unreinforced body system: dopant directly placed on Al block, (b) reinforced body system: dopant mixed with filler and mixture placed above Al block.

Qualitative phase analysis of both the starting materials and fired specimens was undertaken by X-ray diffraction (XRD). Fired samples were sectioned parallel or perpendicular to the growth direction and the different regions analysed by XRD. These samples were subsequently mounted in epoxy resin, ground and diamond-polished to 1 μm, before carbon coating for examination with both scanning electron microscopy (SEM) (Jeol JSM 6400) and energy dispersive spectroscopy (EDS) (Link Analytical 6276).

3 Results

3.1 Unreinforced Al_2O_3/Al composites

After 24 h oxidation at 1180°C, the Al-block was partially consumed; the reaction product had an irregular shape with a smooth surface. Cross sections of this reaction product showed that it contained substantial amounts of aluminium in wide channels 3–5 μm in diameter, it is clear that the oxidation process was not completed. XRD showed that the product was predominantly Al and $MgAl_2O_4$, (magnesium aluminium spinel) with some Al_2O_3 present (Fig. 2).

SEM and EDS indicated the presence of several regions within the sample. The bulk of the sample consisted of unoxidised aluminium interspersed with a ceramic phase that contained both Al and Mg and which was presumed to be spinel (Fig. 3) as XRD failed to detect either Mg or MgO. On the outer surface of the product, there was a denser Mg-containing layer, which was about 10 μm thick; the lack of Mg or MgO detected by XRD indicated that this was also spinel (Fig 4).

3.2 Reinforced Al_2O_3/Al bodies

On heating the system with filler to 1180°C for 15 h, a small amount of growth product was obtained. Macroscopic inspection of a cross-section of the growth product showed that although infiltration of the filler/dopant mixture by the molten metal occurred during the initial stages of the oxidation reaction, it was limited in extent and most of the mixture (filler and dopant) remained unimpregnated by either metal or ceramic. XRD (Fig. 5) showed that the unimpregnated mixture contained Al_2O_3, $MgAl_2O_4$ and MgO but no free Mg. In the growth product, although both α-Al_2O_3 and Al were present, the filler was the main source of α-Al_2O_3; Mg and $MgAl_2O_4$ were also present; again no MgO was detected.

Microanalysis of the oxidised sample provided further confirmation that Al infiltrated into the base of the filler mass close to the metal reservoir (Fig. 6). Within the metallic phase, inclusions containing Al, Mg and O were observed by EDS, which again suggested that they consisted of $MgAl_2O_4$. In the upper region of the growth product, ceramic

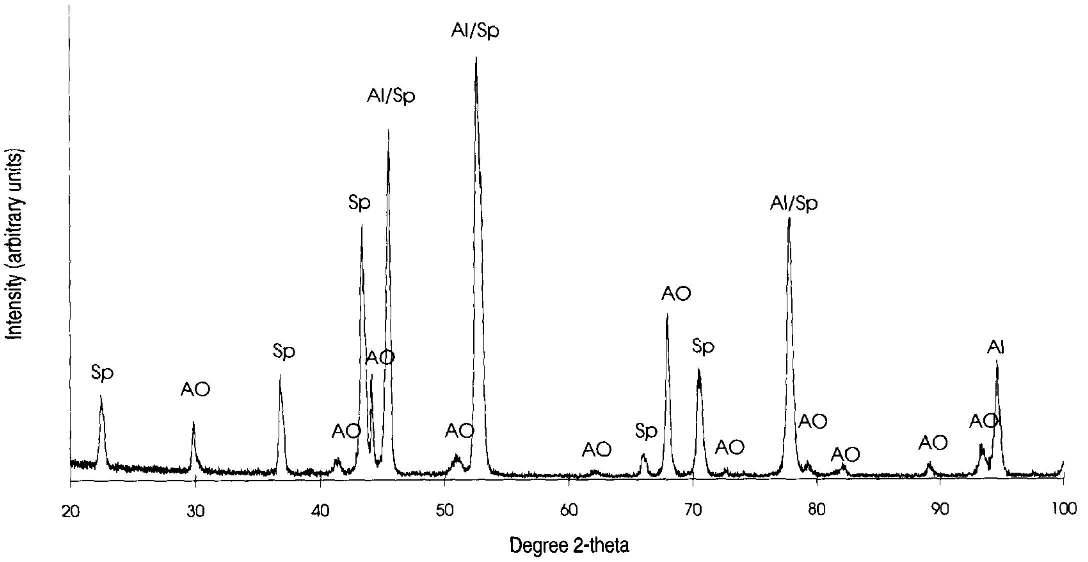
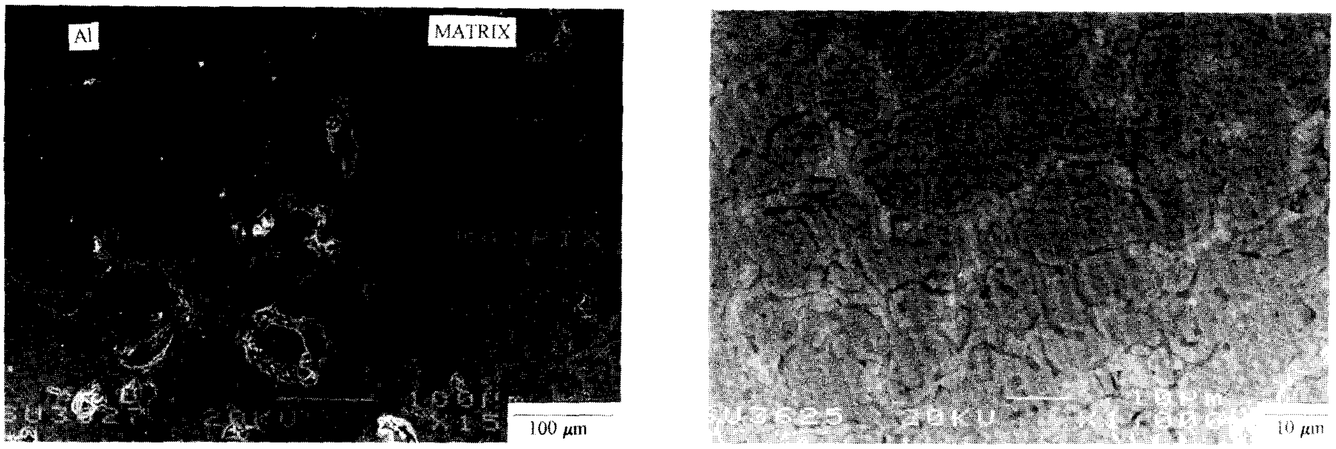


Fig. 2. XRD pattern from unreinforced body produced by firing for 24 h at 1180°C AO: Al_2O_3; Sp: $MgAl_2O_4$.



(a) (b)

Fig. 3. SEM image from unreinforced growth body fired for 24 h at 1180°C. (a) Secondary electron image of product which consists of both unoxidised Al closest to metal reservoir and ceramic matrix growth; (b) back-scattered image of matrix region which contains connected ceramic (dark) inter-spersed with metal (light) channels.

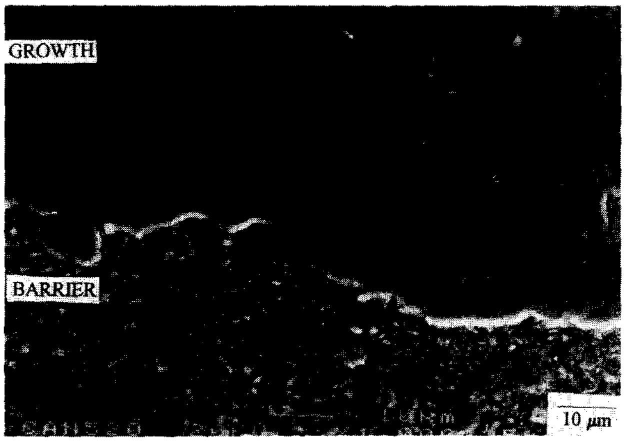


Fig. 4. SEM image of top region of unreinforced growth body fired for 24 h at 1180°C; the outermost layer in the product is spinel.

particles were developing within the metallic phase. The oxidation front was rather porous and extended over a scale of several particle diameters, with the extent of the reaction product increasing towards the central axis of the sample. It appears that layers of matrix grew outwards from the surface of the filler particles (Fig. 7a). The growth matrix contained unoxidised aluminium channels and was covered by a Mg-containing layer thought to be $MgAl_2O_4$ (Fig. 7b).

By comparison, after 24 h at 1180°C the Al-block was totally consumed, and the resultant reaction product encapsulated the filler particles. It was also observed that, in the completely oxidised sample, the distribution of Al_2O_3 filler particles was quite uniform, although some large holes

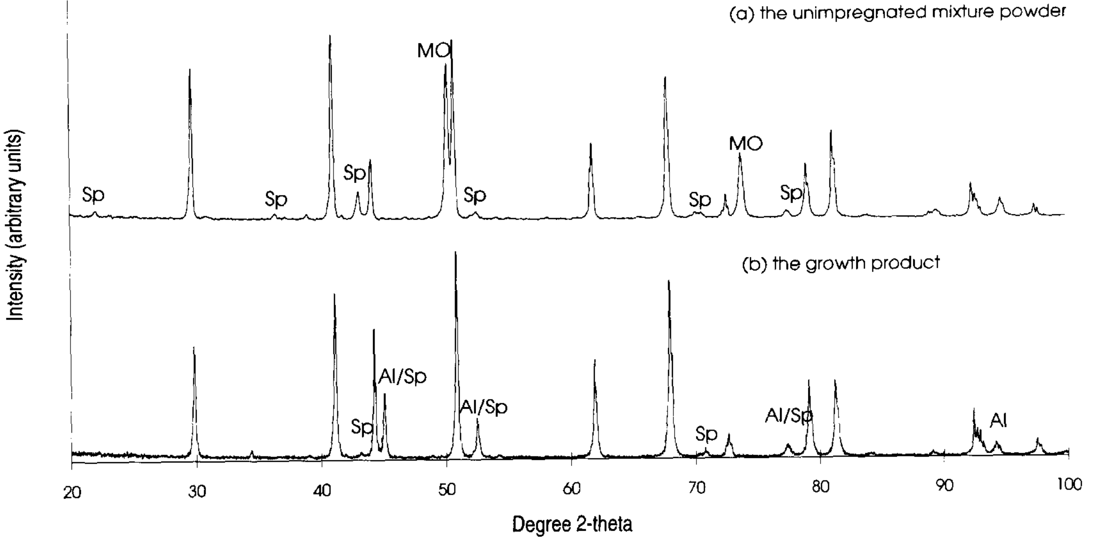


Fig. 5. XRD pattern from reinforced body system fired for 15 h at 1180°C. (a) Unimpregnated mixture powder, (b) growth product. Al: aluminium, Sp: $MgAl_2O_4$, spinel; MO: MgO; unlabelled peaks are Al_2O_3.

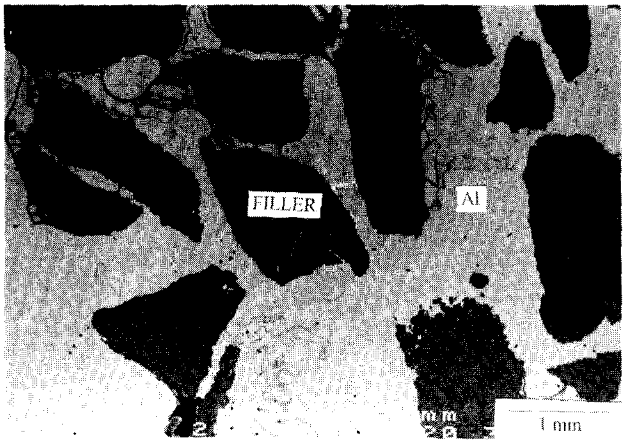
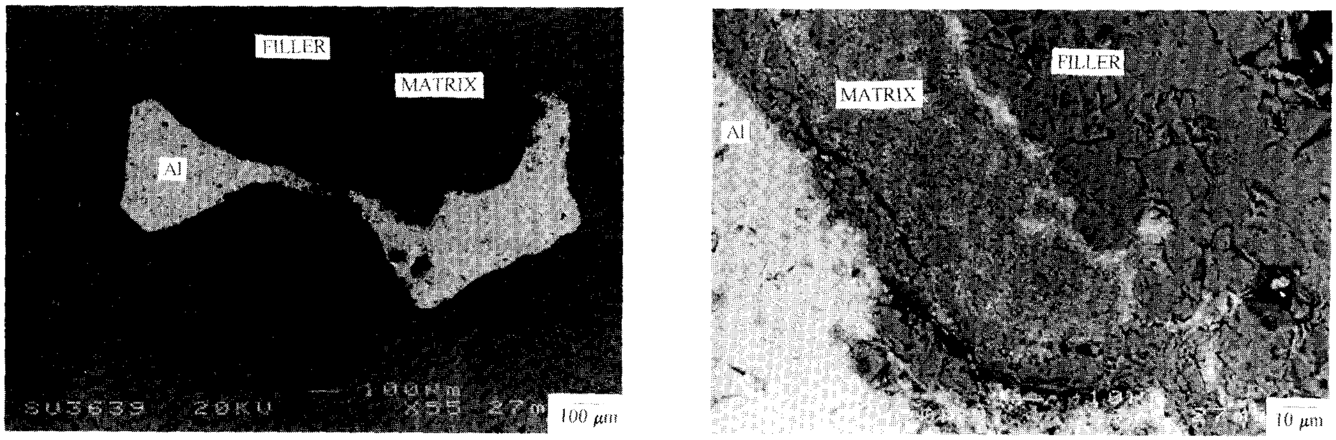


Fig. 6. SEM image from bottom region of reinforced growth body fired for 15 h at 1180°C showing aluminium (white) infiltrated into filler mass (dark) and some ceramic traces (grey) formed within metallic phase.

were present, especially towards its base. In this case XRD (Fig. 8) showed that Al, α-Al_2O_3 and $MgAl_2O_4$ were all present but there was still no MgO and there was also no longer any free Mg. Significantly, aluminium nitride, AlN, was also detected by XRD in this sample.

Microanalysis of the sample fired for 24 h at 1180°C showed that it consisted of an Al_2O_3/Al matrix with some $MgAl_2O_4$. In the middle of part of the product, AlN instead of Al_2O_3 matrix could be observed (Fig. 9). Three different structures could be clearly distinguished. The first was filler particles; whilst the second, close to the filler, was the matrix growth, which consisted of Al_2O_3 with a surface layer about 5 μm thick, of $MgAl_2O_4$. The third structure which was immediately next to the $MgAl_2O_4$ layer, consists of needles which EDS indicates contain both Al and N and which were



(a) (b)

Fig. 7. SEM image from upper region of reinforced growth body fired for 15 h at 1180°C showing (a) that matrix grew outwards from individual filler particles and (b) metal channels covered by a $MgAl_2O_4$ layer.

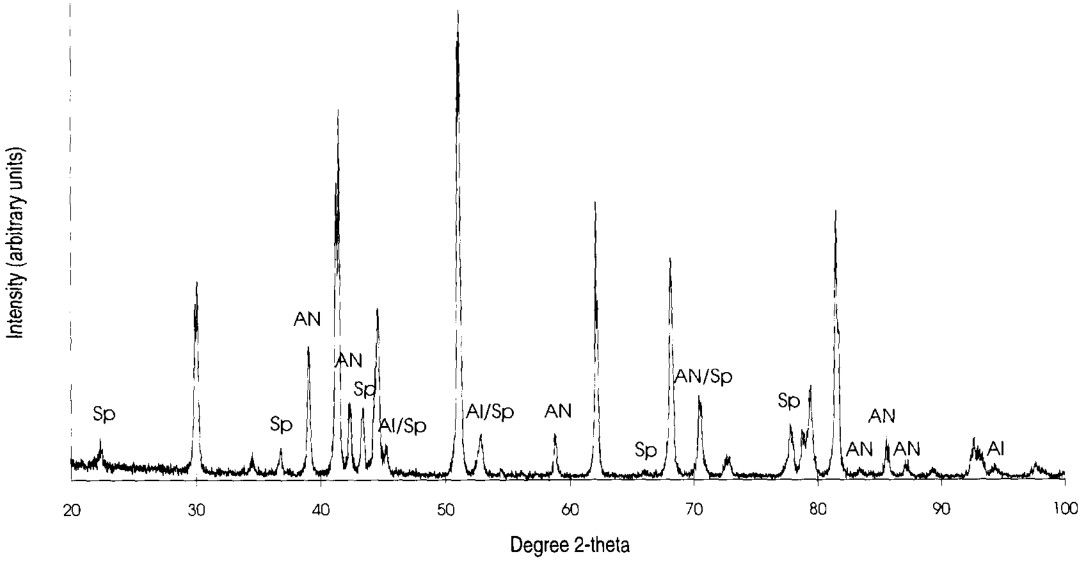


Fig. 8. XRD pattern from reinforced body system fired for 24 h at 1180°C. Al: aluminium; AN: aluminium nitride; Sp: $MgAl_2O_4$ spinel; unlabelled peaks are Al_2O_3.

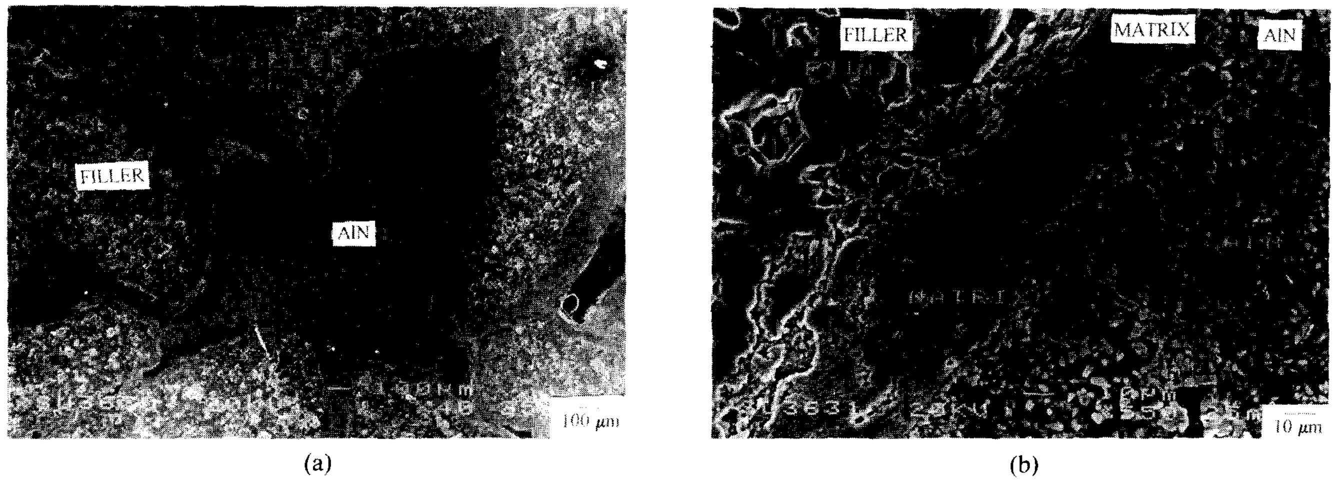


Fig. 9. SEM image from middle region of reinforced growth body fired for 24 h at 1180°C showing (a) AlN instead of Al_2O_3 formed amongst filler particles; (b) enlargement of part of (a).

thus identified as the aluminium nitride detected by XRD in this sample.

4 Discussion

In the current work, directed metal oxidation from a pure aluminium block with a surface doping of Mg particles has been studied, rather than growth from an aluminium alloy which has been reported elsewhere. Differences in microstructure between these two types of system have been observed, implying that there are differences in growth mechanism between Al–Mg alloy systems and an externally doped pure Al system.

Some mechanisms have been proposed to explain the directed oxidation of the Al–Mg–Si alloy system.[4,7,11] These are, in general, based on the initiation of the reaction sequence in the aluminium/alumina system by magnesium. For example, Xiao and Derby reported that when pure MgO was placed on the surface of a commercial-purity Al alloy (>99·5%) and oxidised at 1200°C for 7 h, a reaction occurred. Nagelberg[4] pointed out that oxidation product can also be obtained from the Al–Mg alloy; however, the initiation of composite growth required the mechanical disruption of the protective oxide formed during initial heating to the growth temperature.

When aluminium is exposed to oxygen in the atmosphere, a persistent oxide film is soon formed by the following reaction:

$$2Al(s) + \frac{3}{2} O_2(g) \rightarrow Al_2O_3(s). \qquad (1)$$

However, if Mg is present on the surface of the Al-block then, according to the Ellingham diagram,[12] Mg is oxidised first. For example, Bahadur[13] reported that the addition of 0·9 wt% Mg to pure Al at temperatures of more than 500°C caused the formation of MgO at the surface instead of α-Al_2O_3. In addition Al–Mg alloys favour the formation of both MgO and $MgAl_2O_4$ for Mg concentrations above 0·02% and thus Mg is thought to prevent the normal passivation of aluminium by the formation of aluminium oxide film. Haginoya[14] demonstrated by XRD that during the initial oxidation of Al–Mg alloys, the amount of MgO first increased and then decreased with time, while the $MgAl_2O_4$ content increased continuously with time as bulk depletion of Mg in the alloys results in the eventual conversion of nearly all the MgO to $MgAl_2O_4$.

In the present study MgO was not observed, but EDS has shown that most of the Mg was found in regions which also contained Al and these regions are thereby presumed to be the $MgAl_2O_4$ identified by XRD. This is the case even for reaction products formed by heating to 1180°C followed immediately by furnace cooling. Those workers who have observed MgO have air-quenched their samples. This difference in cooling rate implies that $MgAl_2O_4$ is more stable than MgO for alloy compositions containing 5% Mg. This is in agreement with the thermodynamic calculations of Xiao and Derby,[5] which show that spinel ($MgAl_2O_4$) is the most stable oxide in contact with liquid aluminium alloys containing greater than about 0·5 wt% Mg.

Based on these observations the following growth mechanisms for both unreinforced and reinforced bodies are proposed. In the following argument all the thermodynamic data has been calculated using the SGSUB database in the MT-DATA package.

4.1 Unreinforced directed metal oxidation

In this case the system is pure aluminium with a surface layer of 5 wt% of powdered Mg. Initially Mg powder is oxidised by the air to form MgO (this occurs before the aluminium melting temperature is reached):

$$2\mathrm{Mg}(s) + \mathrm{O}(g) \Leftrightarrow 2\mathrm{MgO}(s). \qquad (2)$$

An interdiffusion reaction between the MgO so formed and the layer of alumina that will be present on the aluminium surface can then convert the MgO layer to spinel:

$$\mathrm{MgO}(s) + \mathrm{Al_2O_3}(s) \Leftrightarrow \mathrm{MgAl_2O_4}(s) \qquad (3)$$

This spinel layer is non-protective and because it is easily wetted by aluminium permits infiltration by aluminium. At the aluminium melt surface, the oxygen partial pressure is determined by the equilibrium between Al and $\mathrm{Al_2O_3}$:

$$\mathrm{Al}(l) + \frac{3}{2}\mathrm{O_2}(g) \Leftrightarrow \frac{1}{2}\mathrm{Al_2O_3}(s)$$

for which $\Delta G = 1{\cdot}21842 \times 10^6$ J mol^{-1} at 1453 K. Thus, assuming that condensed materials have unit activity, the partial pressure of oxygen in this region is fixed and low at about $9{\cdot}064 \times 10^{-30}$ atm. The spinel in this region will be in equilibrium with magnesium and alumina. Considering the following equilibrium:

$$\mathrm{MgAl_2O_4}(s) + 2\mathrm{Al}(l) + \mathrm{O_2}(g) \Leftrightarrow 2\mathrm{Al_2O_3}(s) + \mathrm{Mg(g)} \qquad (4)$$

for which $\Delta G = -7{\cdot}27010 \times 10^5$ J mol^{-1} at 1453 K. Again, taking the condensed materials to be at unit activity, this gives an equilibrium constant of $K = P_{\mathrm{Mg}}/P_{\mathrm{O_2}} = 1{\cdot}36458 \times 10^{26}$ and thus the partial pressure of magnesium at the aluminium melt interface is $1{\cdot}237 \times 10^{-3}$ atm. This is sufficient to move magnesium away from the melt interface to a region with a higher partial pressure of oxygen, where it will recombine to form magnesia:

$$\mathrm{Mg}(g) + \frac{1}{2}\mathrm{O_2}(g) \Leftrightarrow \mathrm{MgO}(s). \qquad (5)$$

At 1453 K $\Delta G = -4{\cdot}33283 \times 10^5$ J mol^{-1} for this reaction, and thus using $\Delta G = -RT\ln K$ the equilibrium constant is:

$$\mathrm{K} = \frac{1}{P_{\mathrm{Mg}}P_{\mathrm{O_2}}^{1/2}} 3{\cdot}76703 \times 10^{15}.$$

Recombination will therefore occur when the magnesium reaches a region where the oxygen partial pressure is greater than $4{\cdot}6068 \times 10^{-26}$ atm. As the partial pressure of magnesium drops, a proportionately higher oxygen partial pressure will be required to cause the formation of magnesia. The magnesia formed by this reaction will subsequently react with the Al that reaches it by penetrating the non-protective spinel layer that lies immediately beneath it.

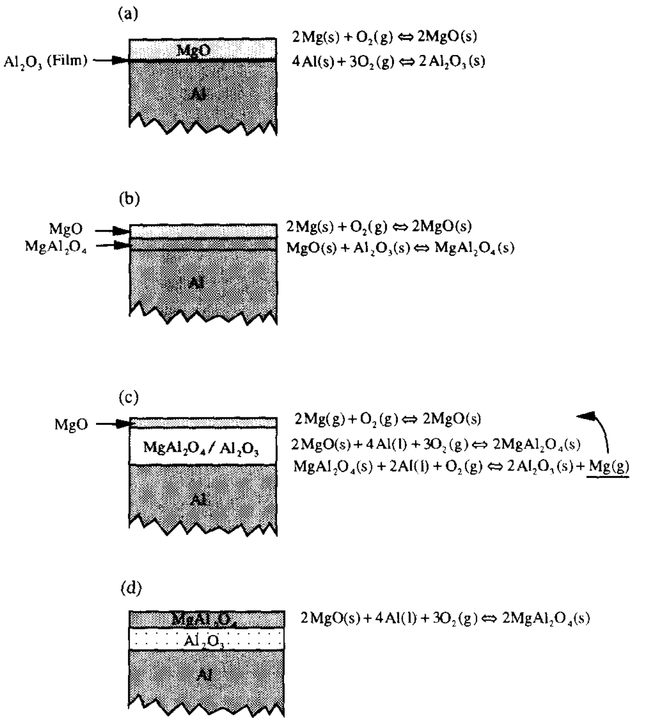


Fig. 10. Schematic diagram of development of cyclic reaction sequence in unreinforced DMOX bodies (time increases from (a)–(d)).

Removal of magnesium from the melt interface will favour the decomposition of the spinel to form alumina and thus a reaction system is set up with a thin magnesia layer overlaying a spinel layer, which in turn overlays an alumina layer. The spinel layer is continually being decomposed at its lower surface to form the next layer of alumina and it is continually being replenished at its upper surface by the reaction of the lower surface of the magnesia layer. The upper surface of the magnesia layer is in turn being replenished. The reaction process, which is shown schematically in Fig. 10, agrees in essence with that given elsewhere.[7,9,10]

Although this reaction sequence implies the existence of a magnesia layer on the growth surface, this was not seen in this work, although it has been reported elsewhere on air-quenched samples. Air-quenching will tend to freeze the sample in the high-temperature state, whereas during furnace cooling there is sufficient time for lower-temperature equilibria, which favour the formation of spinel from magnesia, to develop.

4.2 Reinforced directed metal oxidation $\mathrm{Al_2O_3}$/Al

The introduction of a filler has several effects on both the process reactions and the microstructure of the product. For growth to be possible, the filler must both be wettable by the molten metal and allow matrix growth through the pores amongst its particles. If there were no wetting of the filler particles by the matrix, the effective reactive surface area of the growing matrix would be reduced in proportion to a volume fraction of the filler. Conversely, if the filler is easily wetted by the growing matrix, the matrix/atmosphere surface area can be increased significantly and this should give enhanced growth rates. The coarse filler used in this work has a very rough surface texture, which according to the Wenzel model implies a high degree of wettability of the filler by molten Al.[15]

In this work, filler particles mixed with magnesium powder are placed on the Al-block. During firing, within the mixture, Mg powder is firstly oxidised to form MgO (reaction (1) above). As well as reacting with the protective alumina layer on the aluminium reservoir surface Mg may also react with the Al_2O_3 filler surface to form $MgAl_2O_4$ by either:

$$MgO(s) + Al_2O_3(s;\ \text{filler}) \Leftrightarrow MgAl_2O_4(s), \quad (6)$$

$$Mg(s) + Al_2O_3(s;\text{filler}) + \frac{1}{2}O_2(g) \rightarrow MgAl_2O_4(s). \quad (7)$$

This is in agreement with the observation of Hitchcock *et al.*[15] who reported that in the wetting of alumina by Al–Mg alloys, the interface was characterised by formation of spinel, which considerably enhanced the wettability of aluminium liquid for alumina.

As described above, the Al-rich melt may also dissolve Mg from spinel to nucleate Al_2O_3 (reaction (4) above), thereby releasing magnesium and thus setting up the same basic reaction sequence that is outlined above. A reaction front will thus gradually propagate through the filler body, leading to the encapsulation of filler in the alumina product.

This time, however, the gas phase reaction between Mg and O_2 can also lead to the deposition of magnesia on the surface of the alumina filler. This magnesia then reacts with the filler to produce spinel. Molten aluminium will react with the spinel layer to produce alumina, thereby freeing magnesium, and the cycle of reactions can proceed locally round each filler particle so that growth proceeds outwards from each filler particle.

This process will, however, deplete oxygen locally; this is especially significant if the filler particles in question are behind the main reaction front. The presence of the filler limits the ingress of oxygen to the growth surface. As a result, when the matrix grows and wetting of the filler proceeds upwards, unreacted regions may remain between filler particles where the oxygen content is very low (shown schematically in Fig. 11). If the oxygen content is sufficiently low, with nitrogen (in air) as the diluent, Al liquid reacts with nitrogen to form AlN amongst the filler particles:

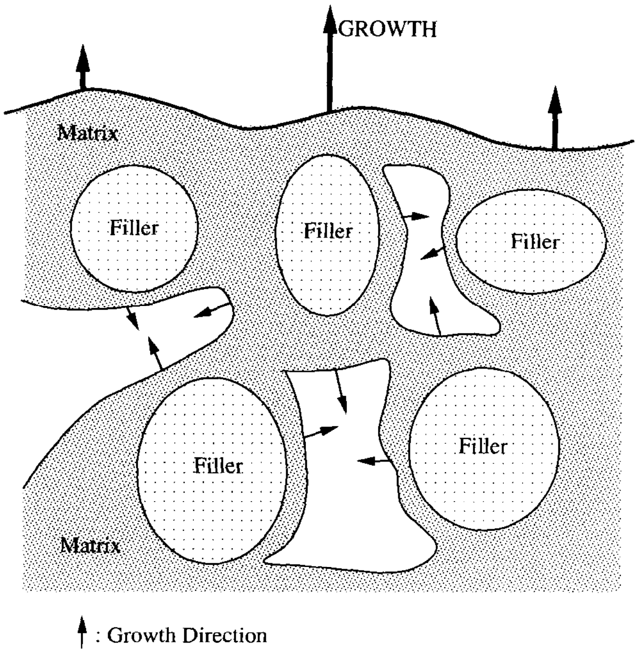


Fig. 11. Schematic diagram of growth mechanism in reinforced DMOX bodies.

$$Al(l) + \frac{1}{2}N_2(g) \Leftrightarrow Aln(s). \quad (8)$$

In fact, high-purity AlN can be prepared by complete nitridation of molten Mg–Al alloys[17] at temperatures above the boiling point of magnesium (1363 K). Scholz and Claussen[17] suggested that magnesium plays a similar role in the nitridation of aluminium as it does in the oxidation, it prevents the formation of a dense nitride layer and thus turns a surface reaction into a volume reaction. For the pure alumina, a threshold oxygen-to-nitrogen ratio exists, above which the oxide and below which the nitride become stable, according to the reaction:

$$2AlN(s) + \frac{3}{2}O_2(g) \Leftrightarrow Al_2O_3(s) + N_2(g). \quad (9)$$

For this reaction at 1453 K $\Delta G = -8{\cdot}94725 \times 10^5$ J mol^{-1} and as long as the $P_{N_2} : P_{O_2}$ ratio is greater than $1:3{\cdot}07 \times 10^{-20}$, then the nitride formed by reaction (8) will not be converted to alumina. This condition is achieved because of the tortuous oxygen diffusion path and the removal of oxygen from the local atmosphere within the filler body as either alumina or spinel. Hence both Al_2O_3 and AlN are observed in the central region of the final product. Enough oxygen reaches the top of the reaction product to ensure that only Al_2O_3 or spinel is seen in this region.

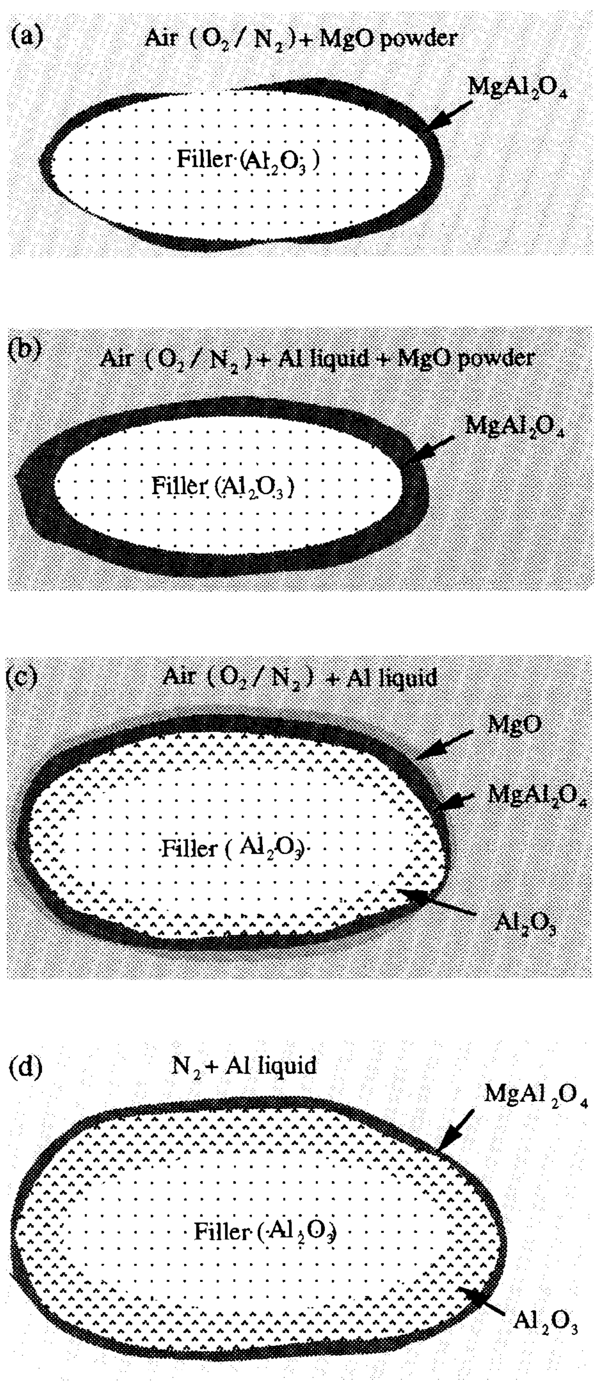


Fig. 12. Schematic diagram of stages of growth with time around filler particles in reinforced DMOX bodies (time increases in going from (a)–(d)).

Thus, although the presence of a filler does not change the overall reaction sequence in the Mg doped Al/Al_2O_3 system, it can give rise to local reaction sequences behind the main reaction front. The local growth mechanism is shown schematically in Fig. 12.

5 Conclusions

The directed metal oxidation growth of both unreinforced and reinforced Al_2O_3/Al bodies from pure Al with an external dopant of Mg has been investigated. The role of the dopant Mg is to promote the formation of a non-protective oxide layer at the surface of the reaction product. This layer is instrumental in developing the subsequent cyclic reaction sequence.

The proposed mechanism is consistent with the experimental results observed, and has the following stages: firstly, $MgAl_2O_4$ is formed via the reaction between MgO which is produced by oxidation of Mg dopant and the passive Al_2O_3 layer which is present on the surface of the Al-block. This ruptures the stable oxide film Al_2O_3; as it thickens, some of the $MgAl_2O_4$ is dissolved by Al melt, and Al_2O_3 is subsequently nucleated. Mg produced via the decomposition of $MgAl_2O_4$ moves to regions of higher oxygen partial pressure, where it forms magnesia and subsequently reacts with Al to reform $MgAl_2O_4$. The cyclic reaction sequence results in the observed product growth.

In the case of reinforced Al_2O_3/Al composite, the filler bed placed on the parent metal affects both reactions and microstructure. With an alumina filler, the magnesia formed during the reaction sequence may react with either aluminium metal or with the filler itself to form spinel. The latter reaction locally consumes oxygen and as the filler limits the ingress of oxygen to oxidation growth reaction fronts that are between the filler particles and behind the main reaction front, oxygen may become locally exhausted, leading to the formation of AlN instead of Al_2O_3. Thus the presence of a filler preform has led to changes in the observed reaction products. The details of such changes obviously depend upon the material used, but they should be considered in the production of ceramic matrix composites by this route.

Acknowledgments

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