

# The effects of $\beta$ -alumina on the production of $\text{Al}_2\text{O}_3/\text{Al}$ composites by the directed melt oxidation process

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Directed melt oxidation (DMOX) of pure aluminium has been used to produce  $\text{Al}/\text{Al}_2\text{O}_3$  composites by growth into a particulate alumina filler in the absence of any dopants apart from a  $\beta\text{-Al}_2\text{O}_3$  impurity in the filler. The microstructural development and mechanisms of growth of these composites have been investigated. It is shown that the  $\text{Al}_2\text{O}_3$  filler used in this work has both chemical and physical effects on the reaction process. The  $\beta\text{-Al}_2\text{O}_3$  impurity introduces sodium into the system; this increases the wettability of alumina (both filler and oxidation reaction product) by molten aluminium, and initiates DMOX reactions. In addition, the filler particle size has an effect on the directed oxidation reaction. If the particle size is too fine, no oxidation growth takes place. Filler particles limit the ingress of oxygen through the reaction front so that  $\text{AlN}$  instead of  $\text{Al}_2\text{O}_3$  may be formed in regions behind the main reaction front. Although such  $\text{AlN}$  production is seen when magnesium is used as a dopant to initiate DMOX reactions in the  $\text{Al}/\text{Al}_2\text{O}_3$  system, it is more marked with sodium, because the latter has a greater effect on the wettability of alumina by aluminium.

## 1. Introduction

Ceramic matrix composites (CMCs) have the potential to overcome low toughness which is one of the principle disadvantages of ceramics. One production route for CMCs is the directed melt oxidation (DMOX) process, which involves, under appropriate conditions, the directed growth of a ceramic reaction product from a molten parent metal by reaction of that metal with an oxidant (*e.g.* air). Growth proceeds outwards from the surface of the original metal block and produces an interconnected ceramic reaction product which contains either a few per cent residual metal or porosity. Reinforcements may be readily incorporated in the product by allowing it to grow through, and thereby embody, a preform.

Dopants are required to initiate and maintain the growth process and it is this feature which distinguishes the DMOX process from other ceramic reaction bonding processes. These dopants may be introduced by alloying with the pure parent metal or externally in the form of elemental or oxide powders. Growth is limited by the presence of inert (barrier) powders; these define the shape of the product and thus shaped products may be produced by DMOX growth into either a defined empty space or into a shaped region containing a preform comprised of a loosely packed filler or ceramic fibres and whiskers. In this paper we distinguish the two cases by referring to bodies produced by growth into free space as “unreinforced bodies” and to those produced by growth into a preform body as “reinforced bodies”.

Much of the published work [1–3] in this area has concentrated on the production of  $\text{Al}_2\text{O}_3/\text{Al}$  bodies grown from specially prepared aluminium alloys containing both magnesium and silicon as dopant elements. Initially, it was thought that both magnesium and silicon were necessary dopants in this system but more recent work has concluded that only magnesium is necessary to initiate and sustain the reaction process [4–6]. Magnesium may be incorporated via an aluminium alloy or externally as  $\text{MgO}$  [6] or spinel [7]. This work has concluded that the presence of magnesium in the system leads to the formation of a non-protective oxide layer of  $\text{MgO}$  on the surface of the product and that this layer is also instrumental in the dissolution and reoxidation process, resulting in a continuous supply of oxygen to the reaction interface. In addition to magnesium and silicon, some workers have focused on the effects of tin and sodium [8,9] on the production of  $\text{Al}_2\text{O}_3/\text{Al}$  composites by the DMOX process. The role of sodium is believed to be similar to that of magnesium although no sodium-containing oxide surface has been reported in the published literature [8]. The functions of silicon and tin are not well understood, although addition of silicon or tin apparently enhances the oxidation process in that, as the percentage of these elements is increased, the amount of unreacted aluminium remaining in the reaction system after a given reaction time is decreased [9].

It has been stated that for the production of reinforced bodies by the DMOX process the preform

TABLE I T-60 tabular alumina data (taken from Alcoa Industrial Chemicals Division product data sheet for tabular alumina T-60)

Grade	Open size	Chemical analysis (%)					
		Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	CaO	Others
T60A	8–14 mesh (1.18–2.36 mm)	99.4	0.01	0.003	0.36	0.05	0.177
T60B	14–28 mesh (0.600–1.18 mm)	99.4	0.04	0.009	0.36	0.08	0.111
T60C	28–48 mesh (0.300–0.600 mm)	99.4	0.04	0.010	0.36	0.08	0.110

should be inert so that it takes no part in the chemical reactions [10]; necessarily, however, any preform will have physical effects on the reaction. For example, the preform will restrict the flow of the oxygen and the molten metal to the reaction growth front; in addition, if the preform is non-wettable by the molten parent metal, the extent of the reaction will be severely limited [11]. To investigate the importance of such physical effects we have studied the growth of DMOX Al<sub>2</sub>O<sub>3</sub>/Al bodies into alumina preforms. Initially, coarse tabular alumina, which contained several per cent of sodium as  $\beta$ -Al<sub>2</sub>O<sub>3</sub> (NaAl<sub>11</sub>O<sub>17</sub>) as an impurity, was used. The presence of the  $\beta$ -Al<sub>2</sub>O<sub>3</sub> impurity has significant effects on the results obtained. These effects are described in more detail in this paper and some conclusions are drawn about the role of sodium in the production of Al<sub>2</sub>O<sub>3</sub>/Al bodies by the DMOX process.

## 2. Experimental procedure

Aluminium blocks (99.8% pure, Alcan) were placed on a bed of fine alumina powder contained in an alumina crucible. Above the aluminium block a defined space was created using fine alumina (99.9% pure; Alcoa A17) as a barrier material. Tabular alumina (Alcoa T-60) particles were placed on the surface of the aluminium block. Three different sizes of particles have been used; their chemical analyses and open sizes are shown in Table I. X-ray diffraction (XRD) of this filler showed that it mainly consists of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and a small amount of  $\beta$ -Al<sub>2</sub>O<sub>3</sub> which accounts for the sodium identified in the chemical analyses shown in Table I.

The experimental arrangement is shown in Fig. 1. The prepared systems were heated in air at 200 °C h<sup>-1</sup> in a muffle furnace to a soaking temperature of 1180 °C. This temperature was maintained for 5, 15, 24 and 35 h, after which the samples were cooled to room temperature inside the furnace.

Qualitative phase analysis of both the starting materials and fired specimens was undertaken by X-ray diffraction (XRD) (Philips PW 1050 diffractometer with CoK<sub>α</sub> radiation). 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).

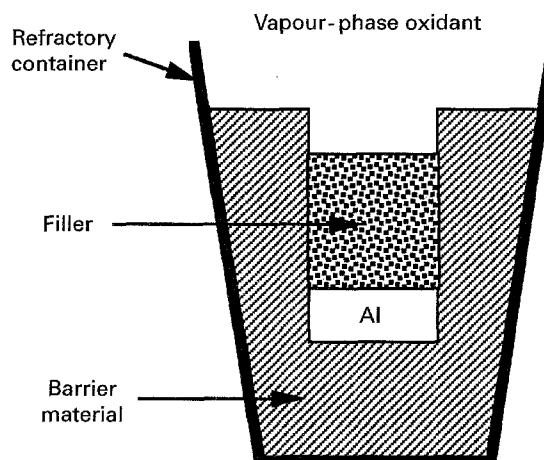


Figure 1 Experimental arrangement used in the DMOX process.

## 3. Results

Although the three filler grades differ only marginally in terms of their chemical analysis, significantly different results were obtained with the three different grades. With the finest grade (T60C), no directed oxide growth took place, no matter how long a soaking time at the reaction temperature of 1180 °C was used. When the coarser grades (T60A and T60B) were used, oxide products were formed in both cases. Growth rates into T60A are greater than those into T60B. After 5 h at 1180 °C, the aluminium block was completely consumed for a T60A reinforced body (Fig. 2a) and the growth product encapsulated all the filler particles. With T60B (Fig. 2b), however, some unreacted aluminium remained in the reservoir after 5 h and a portion of the filler had not been embedded by the DMOX growth. After 15 h at 1180 °C, in both cases, the aluminium blocks were totally consumed; however, the growth with T60A (Fig. 3a) is much denser than that with T60B (Fig. 3b).

Cross-sections show that aluminium has infiltrated the regions between the filler particles and that some of it has been oxidized to form DMOX Al<sub>2</sub>O<sub>3</sub> which surrounds the filler particles. The growth is more extensive and uniform towards the edges of the sample than in the centre of the samples. The distribution of filler particles is quite uniform, showing that the reaction product grows through the filler mass without displacing and disturbing the filler, although some large holes are present, especially towards the growth base. The reaction products were also analysed by

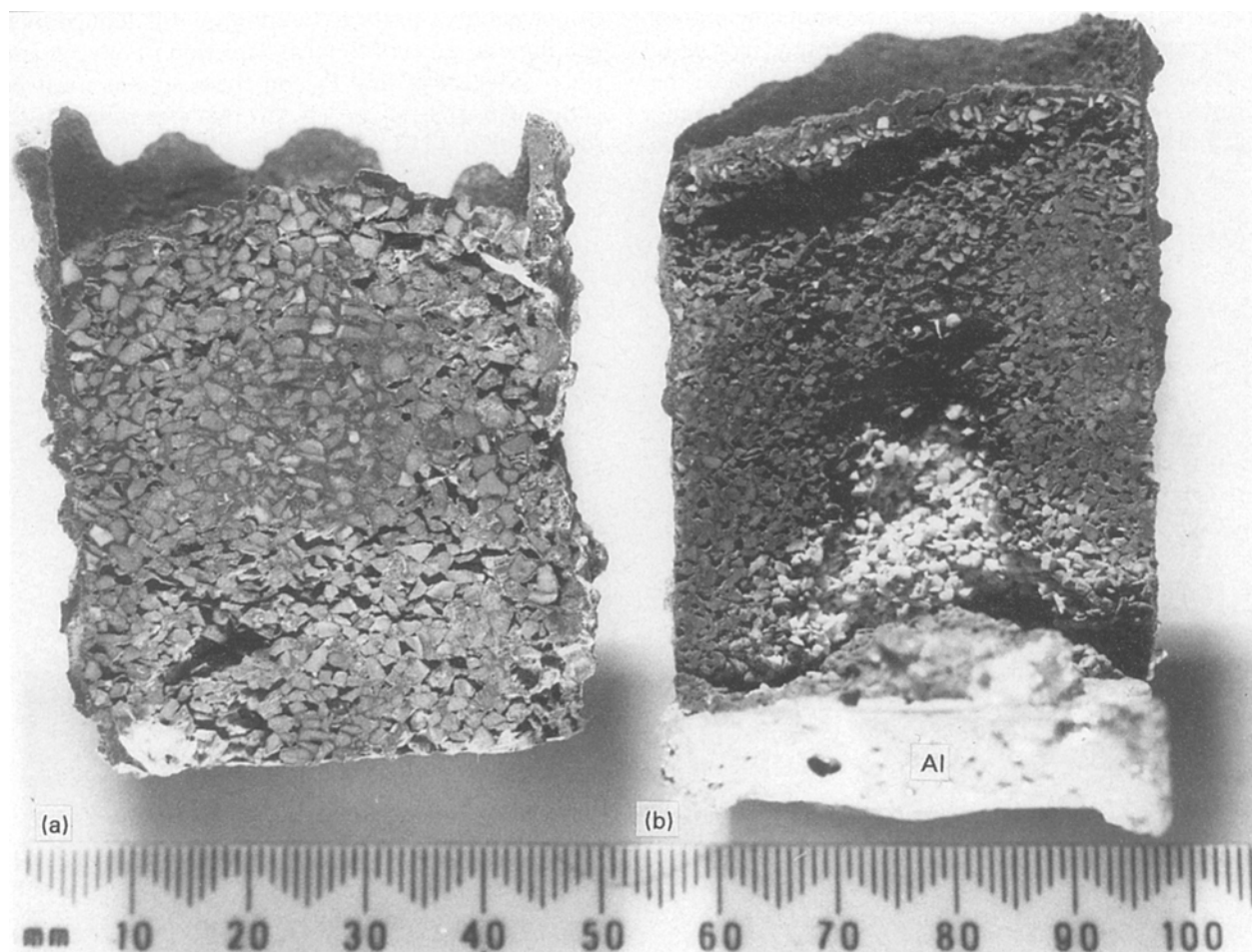


Figure 2 Cross-sections of the products with (a) T60A, and (b) T60B, by firing for 5 h at 1180 °C.

XRD.  $\alpha$ - $\text{Al}_2\text{O}_3$ , aluminium and a small amount of  $\beta$ - $\text{Al}_2\text{O}_3$  are present. Significantly, some AlN was also detected in some products fired for more than 15 h at 1180 °C. More AlN is seen at longer soaking times (Fig. 4a) and with larger filler particle sizes (Fig. 4b).

With the arrangements described here, the process leads to the presence of  $\alpha$ - $\text{Al}_2\text{O}_3$  from two different sources: filler  $\text{Al}_2\text{O}_3$  and DMOX  $\text{Al}_2\text{O}_3$  formed by the oxidation of pure aluminium. In the  $\text{Al}_2\text{O}_3/\text{Al}$  composites produced, several different structures can be clearly observed.

At the base of the growth region (Fig. 5) the filler is embedded in aluminium with a thin interlayer of DMOX alumina; this suggests the filler used in this work is highly wettable by liquid aluminium and that the DMOX reactions occur post-infiltration by liquid metal. After long firing times, aluminium in this region is oxidized, forming a DMOX  $\text{Al}_2\text{O}_3$  layer on the filler particles and large holes appear between coated particles (Fig. 6a). The DMOX matrix therefore grows outward from the surface of the filler particles. In addition, unoxidized aluminium regions containing small particles of  $\text{Al}_2\text{O}_3$  can be found (Fig. 6b). In the central region of the growth product (Fig. 7), filler particles are encircled by double layers: the inner layer is DMOX  $\text{Al}_2\text{O}_3/\text{Al}$ ; and the outer layer is a metallic phase comprised of unoxidized aluminium interspersed with a ceramic phase that EDS indicated contains both aluminium and nitrogen and which is thus iden-

tified as the AlN detected by XRD. In products fired for longer times, the aluminium in this mixed Al–AlN layer is completely converted to AlN (Fig. 8). Within the upper region, which is just below the main reaction front (Fig. 9), only DMOX  $\text{Al}_2\text{O}_3$  and filler particles with no interphases could be found.

On the outermost surfaces (top and sides) of the growth product, sodium containing layers were identified by EDS (Fig. 10). This phase is presumed to be the  $\beta$ - $\text{Al}_2\text{O}_3$  detected by XRD. In the central region of growth, it was also found that a sodium-containing phase is present in the holes between the filler particles (Fig. 11). However, EDS can detect no sodium, either in the  $\text{Al}_2\text{O}_3/\text{Al}$  growth or in the filler particles, although it can detect sodium in the unfired alumina filler. This indicates that the sodium initially present in the filler has been removed, or at least substantially reduced, during the firing process.

#### 4. Discussion

Preform bodies are used to reinforce ceramics produced by the DMOX process. However, they effect the physics of the growth process by disrupting growth patterns and may also modify the chemistry if they contain available elements that can affect the DMOX reactions.

The introduction of filler into the composite results in several additional effects on the composite growth

rate and microstructure. Loose filler limits the ingress of oxygen to the growth surface and results in a more tortuous path for the wicking of molten metal to the growth surface. The oxidation reactions occur round each filler particle so that growth proceeds outwards

from each filler particle. In addition, the limited oxygen ingress can lead to local depletion of oxygen and thus the effect of low  $P_{O_2}$  on the reactions must be considered. Assuming, as in the experiments described, that air is used as the oxidizing atmosphere



Figure 3 Cross-sections of the products with (a) T60A, and (b) T60B, by firing for 15 h at 1180 °C.

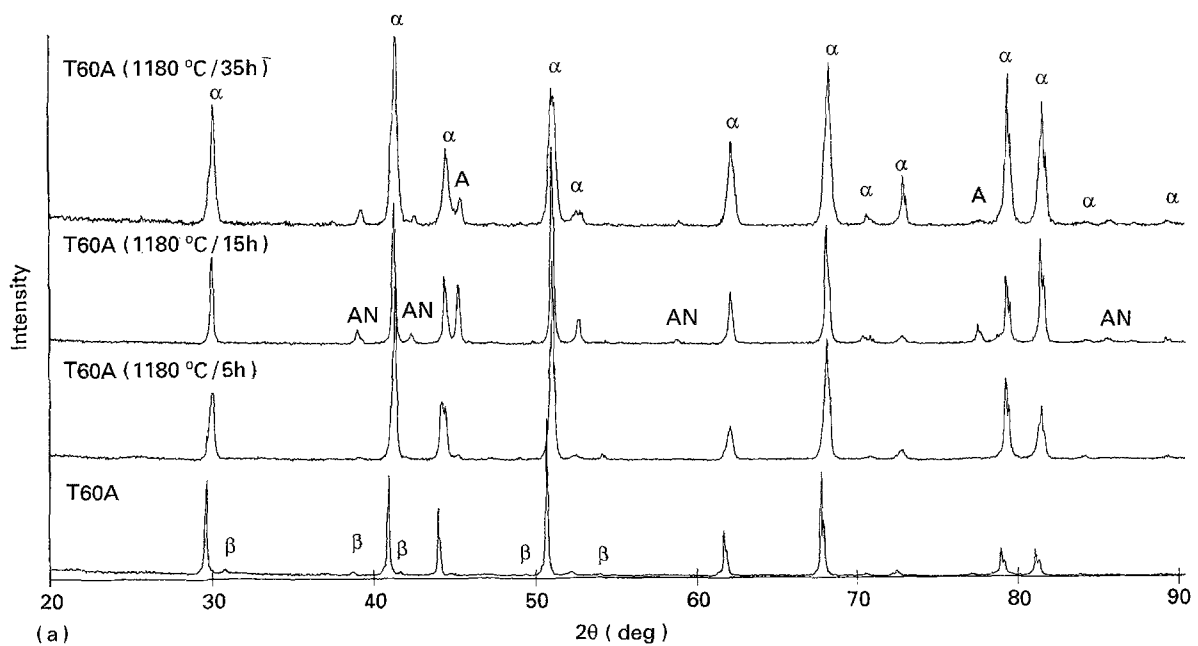


Figure 4 XRD pattern from (a) unheated T60A (lowest trace) and T60A reinforced products fired for 5, 15 and 35 h at 1180 °C; and (b) T60A and T60B reinforced products fired for 15 h at 1180 °C.  $\alpha$ ,  $\alpha$ - $Al_2O_3$ ;  $\beta$ ,  $\beta$ - $Al_2O_3$ ; A, Al; AN, AlN.

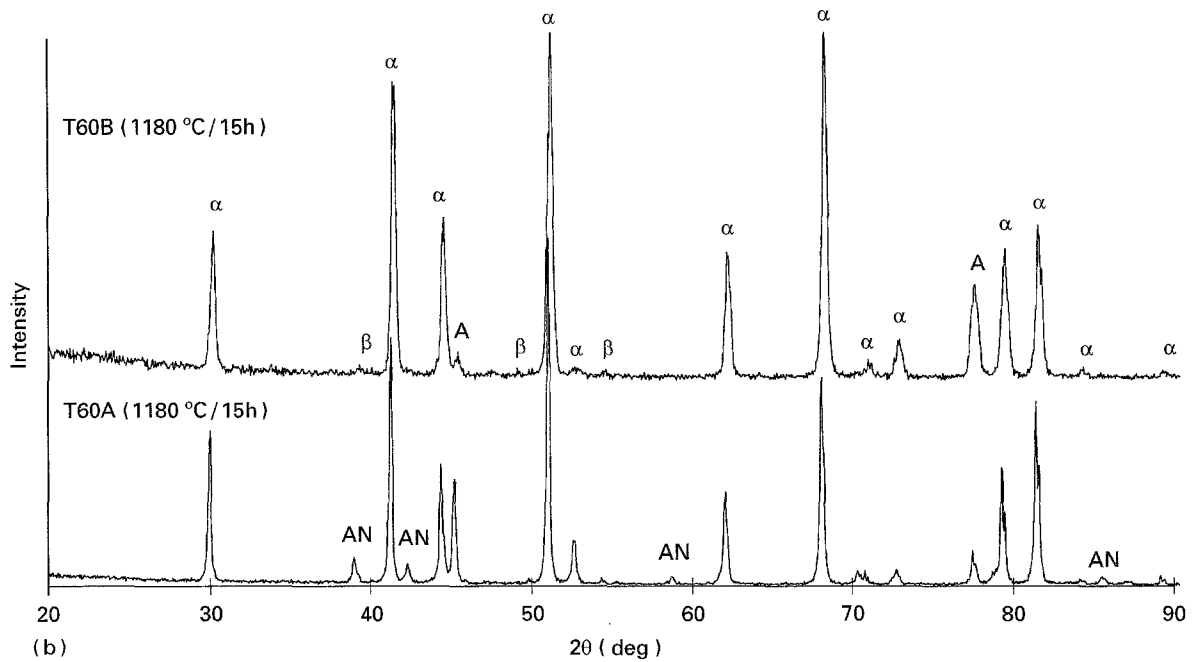


Figure 4 (Continued).

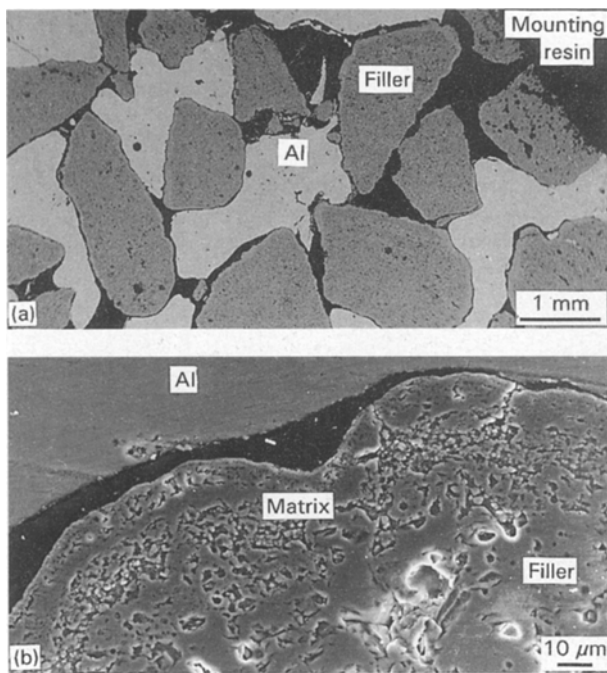


Figure 5 SEM image of the bottom of a T60A reinforced body fired for 5 h at 1180 °C. (a) Filler particles surrounded by a thin layer of DMOX matrix and embedded in aluminium; (b) enlargement of a part of (a).

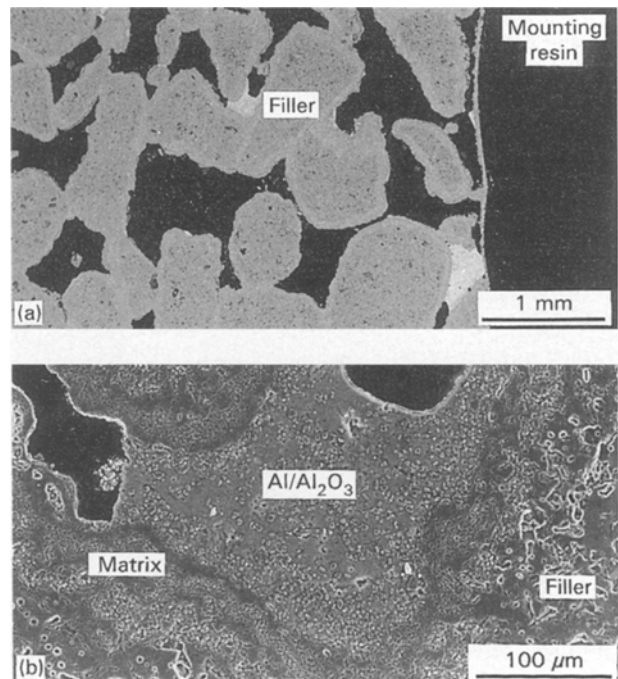


Figure 6 SEM image of the bottom of a T60B reinforced body fired for 24 h at 1180 °C. (a) Large holes and small unoxidized regions of aluminium are present between DMOX  $\text{Al}_2\text{O}_3$ -coated filler particles; (b) enlargement of a part of (a), showing small  $\text{Al}_2\text{O}_3$  particles in unoxidized aluminium.

when the oxygen content is sufficiently low, aluminium liquid reacts with the residual nitrogen to form AlN amongst the filler particles. As long as the  $P_{\text{N}_2} : P_{\text{O}_2}$  ratio is greater than  $1:3.07 \times 10^{-20}$ , AlN and  $\text{Al}_2\text{O}_3$  can co-exist [12]. Thus AlN, as well as  $\text{Al}_2\text{O}_3$ , can be readily produced in reinforced DMOX “alumina” products.

Filler particle size affects both the supply of oxygen and aluminium to the growth surface, with finer fillers leading to reductions in the supply of both elements. Thus bodies reinforced with larger particles grow

more quickly than ones reinforced with smaller particles. When the finest filler grade, T60C, was used, no growth occurred at all.

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 was no wetting of the filler particles by the matrix, the effective reactive surface area of the growing matrix would be reduced in proportion to volume fraction of the filler. Conversely, if the filler is easily wetted by the growing matrix, the matrix/atmosphere surface area



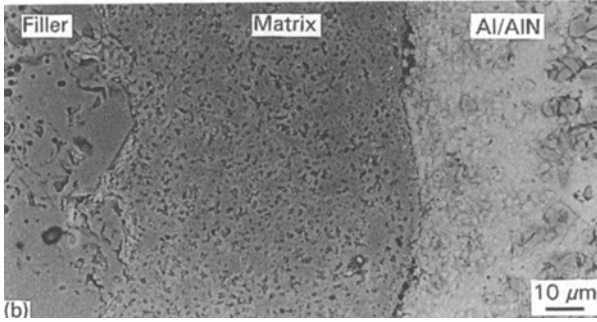
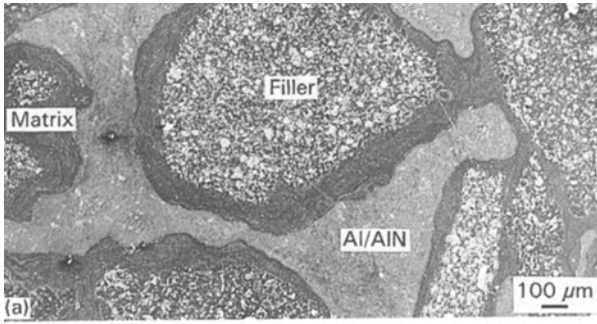


Figure 7 SEM image of the middle of a T60B reinforced body fired for 24 h at 1180 °C. (a) Filler particles surrounded firstly by a layer of DMOX matrix and secondly by unoxidized aluminium interspersed with AlN; (b) enlargement of a part of (a).

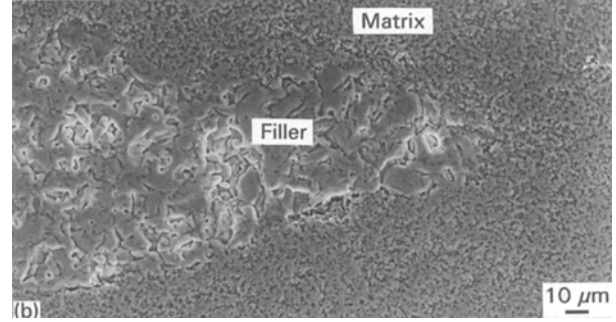
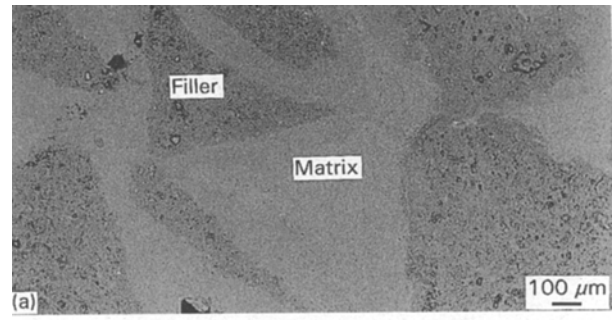


Figure 9 SEM image of the upper region of a T60B reinforced body fired for 15 h at 1180 °C. (a) Filler particles surrounded by DMOX Al<sub>2</sub>O<sub>3</sub>/Al matrix; (b) enlargement of a part of (a).

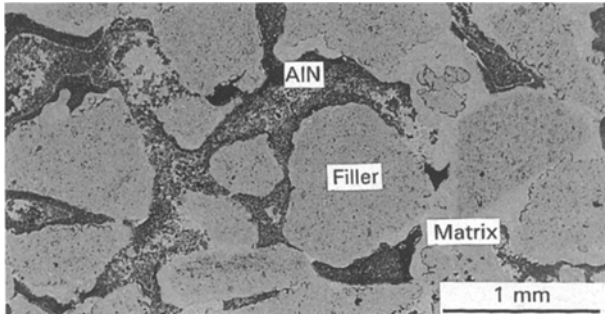


Figure 8 SEM image of the middle of a T60B reinforced body fired for 35 h at 1180 °C. All residual aluminium has been converted to AlN.

can be increased significantly and this should give enhanced growth rates. One of the relevant physical factors is that the wetting of a surface by a liquid is affected by its roughness, as shown by the Wenzel equation [13]

$$\cos \theta_R = W_R \cos \theta_0 \quad (1)$$

where  $W_R$  is the roughness area ratio (true area/nominal area), and  $\theta_R$  and  $\theta_0$  are the contact angle of sessile drops on rough and smooth horizontal surfaces, respectively. The Al<sub>2</sub>O<sub>3</sub> fillers used in this work have a very rough surface texture which enhances wettability of Al<sub>2</sub>O<sub>3</sub> filler particles by liquid-aluminium and thus promotes matrix growth.

In the Al<sub>2</sub>O<sub>3</sub>/Al system, the stable oxide film that protects aluminium from corrosion reduces wetting. Molten pure aluminium does not wet Al<sub>2</sub>O<sub>3</sub> even at 900 °C [14]. Two main approaches have been adopted to improve wettability: (i) alloying additions that either promote reaction at the interface or modify the

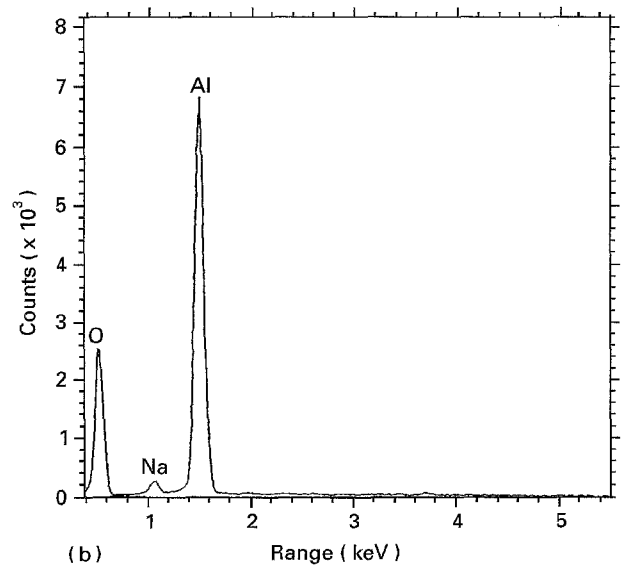
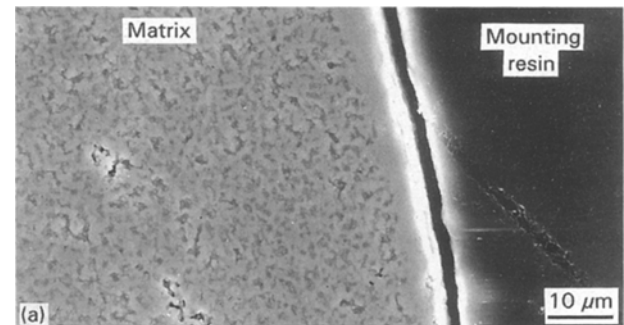


Figure 10 (a) SEM image and (b) EDS of the outer surface of a T60B reinforced body fired for 24 h at 1180 °C. A sodium-containing layer is present on the outer surface (next to the mounting resin).

characteristics of the oxide layer that covers the surface of liquid aluminium, or (ii) coating of the reinforcement with a material that will react either with the molten metal or with oxide layer.

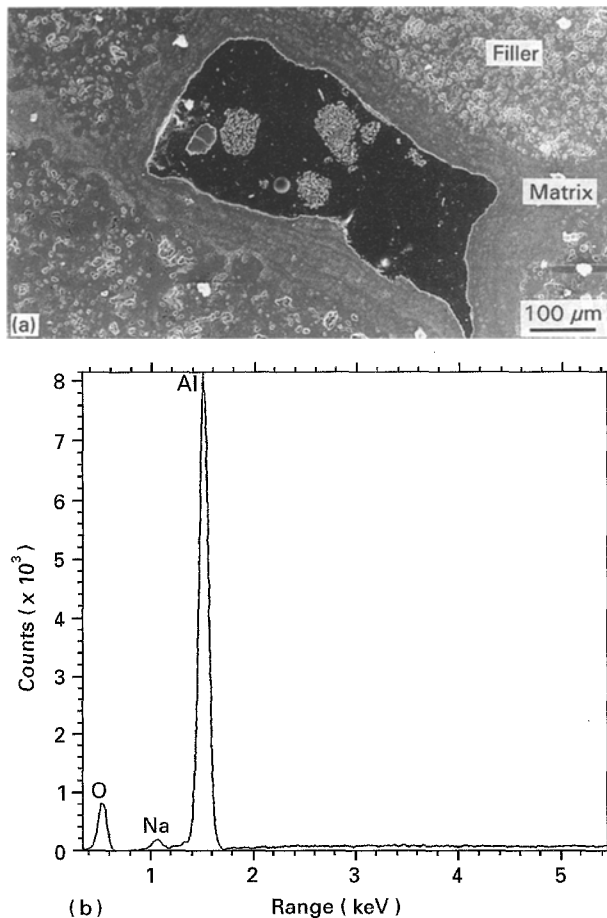


Figure 11 (a) SEM image and (b) EDS from a T60B reinforced body fired for 24 h at 1180 °C. A sodium-containing phase is present in the voids between the filler particles.

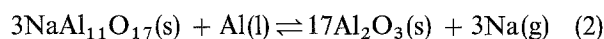
In the DMOX process, magnesium-containing aluminium alloys have commonly been used as the parent metal. In the production of reinforced  $\text{Al}_2\text{O}_3/\text{Al}$  DMOX composites, magnesium may react with the reinforcement; Lee and Subramanian [15] reported that  $\text{MgAl}_2\text{O}_4$  grew at the surface of reinforcing  $\text{Al}_2\text{O}_3$  particles. In our previous work [12], in which magnesium was used as external dopant and mixed with  $\text{Al}_2\text{O}_3$  particle filler and the mixture placed on a pure aluminium block, an  $\text{MgAl}_2\text{O}_4$  layer was found to cover the  $\text{Al}_2\text{O}_3$  particle filler. The  $\text{MgAl}_2\text{O}_4$  layer not only enhanced the wettability of alumina filler by aluminium liquid, but also resulted in DMOX reactions proceeding locally around each filler particle.

In the present work, although no dopant, either alloyed with aluminium or externally applied, has been used, the filler contains  $\beta\text{-Al}_2\text{O}_3$ , which means sodium is introduced into the system via  $\text{NaAl}_{11}\text{O}_{17}$ . There are some similarities between magnesium and sodium; specifically, both have a high vapour pressure at elevated temperature, and this is necessary to set up the cyclic reactions which are a feature of the DMOX process [9].  $\beta\text{-Al}_2\text{O}_3$  is a non-stoichiometric compound which can accommodate up to 25% excess soda. The crystal structure consists of  $\text{Al}^{3+}$  and  $\text{O}^{2-}$  ions in spinel-like blocks with  $\text{Na}^{1+}$  and  $\text{O}^{2+}$  ions loosely packed between these spinel blocks. As a consequence of the structure,  $\text{Na}^{1+}$  ions have a high diffusivity in  $\beta\text{-Al}_2\text{O}_3$  [16]. This behaviour is

similar to that of magnesium in  $\text{MgAl}_2\text{O}_4$  spinel structure.

Xiao and Derby [8] have studied NaOH as surface dopant in the DMOX process. They have indicated that directed oxidation of aluminium occurs in the temperature range 850–1200 °C and nucleates growth both on the top surface of the parent aluminium and along the crucible wall. They observed a significant loss of sodium from the oxidizing system and, in contrast with the results presented here, did not find sodium concentrated on the surface of the growth product. The presence of  $\text{Al}_2\text{O}_3$  filler particles on the parent aluminium block makes it more difficult to lose sodium by long-distance gas-phase transport and thus the growth product obtained here is more uniform than that described by Xiao and Derby [8].

When molten aluminium comes into contact with  $\beta\text{-Al}_2\text{O}_3$  in the alumina filler at high temperature, the following reaction can occur



Sodium released by this reaction will migrate to the reaction front where the aluminium liquid is just infiltrating the filler. Here it will combine with oxygen to reform  $\beta\text{-Al}_2\text{O}_3$ . A  $\beta\text{-Al}_2\text{O}_3$  layer is therefore created on the surface of the aluminium. The base of this layer will continuously react with the aluminium to generate alumina and the resulting sodium will migrate to the top of the layer and react with oxygen thus replenishing the layer. These cyclic reactions therefore lead to progressive DMOX growth.  $\beta\text{-Al}_2\text{O}_3$  thus plays an analogous role in the DMOX growth of  $\text{Al}/\text{Al}_2\text{O}_3$  composites to the magnesia and spinel layers in the magnesium-doped DMOX system.

As well as chemically interacting in the DMOX system  $\beta\text{-Al}_2\text{O}_3$  promotes the wettability of alumina filler particle by molten aluminium. As a result, above the melting point of aluminium (660.4 °C), molten aluminium readily wicks by capillary action through the channels between the filler particles and encapsulates the filler. Some holes may be left between filler particles towards the base if there is insufficient aluminium to fill all the vacant spaces between the filler particles. Meanwhile, the gaseous oxidant (in air) also permeates through the filler mass, thus directed oxidation takes place not only globally on the main reaction front, but also locally around individual filler particles. Thus, around each filler particle, DMOX  $\text{Al}_2\text{O}_3$  is formed outwardly from the filler particle surface. However, as the diffusion of oxygen to points behind the main reaction front will be extremely limited, due to the low diffusion coefficient of oxygen in alumina, oxygen will probably be locally depleted in these regions. In these cases, once the oxygen content is sufficiently low, with nitrogen (in air) as the diluent, aluminium liquid will start to react with nitrogen to form AlN grains in the unoxidized aluminium left amongst the filler particles (Fig. 7). If the reaction time is long enough, all the remaining aluminium liquid in these regions will be consumed to form AlN instead of  $\text{Al}_2\text{O}_3$  (Fig. 8). Although production of AlN was observed in the magnesium-doped system [12], it was less extensive. This is because magnesium has a smaller

effect on the wettability of alumina by aluminium than sodium, and thus less unreacted aluminium gets trapped in oxygen-deficient regions behind the main reaction front.

## 5. Conclusion

A  $\beta$ - $\text{Al}_2\text{O}_3$  containing  $\text{Al}_2\text{O}_3$  filler was used in the production of reinforced  $\text{Al}_2\text{O}_3/\text{Al}$  DMOX composites. Pure aluminium without dopants was used. Normally the lack of dopants results in no DMOX reactions, thus as products were produced in this case, the presence of  $\beta$ - $\text{Al}_2\text{O}_3$  in the filler can initiate DMOX reactions. This is because  $\beta$ - $\text{Al}_2\text{O}_3$  introduces available sodium into the DMOX system; post-firing the sodium content of the filler is reduced below the limits of detection, whilst sodium concentrations are found on the top and sides of the reaction product. Sodium promotes the formation of a sodium-containing non-protective  $\beta$ - $\text{Al}_2\text{O}_3$  layer on the surface of the aluminium liquid. A similar layer is generated on the surface of the reaction product. Sodium also improves wettability of alumina by aluminium liquid. The initial infiltration of the molten metal into the filler body is thus very rapid and behind the main reaction front regions are developed where oxygen is locally depleted but unreacted aluminium remains. In these regions, AlN is formed instead of  $\text{Al}_2\text{O}_3$ . Although production of AlN has been seen in the magnesium-doped system, it is more extensive in the sodium-doped system.

The production of DMOX composites requires dopant(s) that produce a non-protective oxide layer and promote wettability of the filler (alumina, in this case) by aluminium. Sodium (introduced as  $\beta$ - $\text{Al}_2\text{O}_3$ ) can fulfil this role. However, sodium-doped systems produce lower quality mixed oxide/nitride products compared to the corresponding magnesium-doped ones. This is thought to be because of the greater enhancement of the wettability of alumina by aluminium by sodium, leading to the production of AlN in

oxygen-deficient regions behind the main reaction front.

## Acknowledgements

This work was carried out while one of us (XG) was in receipt of a University of Sheffield Scholarship.

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Received 12 January

and accepted 7 June 1995