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Al_2O_3/Al composites produced by directed melt oxidation using Zn containing external dopants

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Al_2O_3/Al composites have been produced by the directed melt oxidation of Al with externally applied Zn containing dopants. Zn, ZnO and $ZnAl_2O_4$ are all shown to be capable of initiating the directed melt oxidation of Al without any Mg being present. The external surfaces of the reaction products were covered with a layer of ZnO overlaying a layer of $ZnAl_2O_4$, however, no Zn was observed within the composite bodies. Doping with ZnO or $ZnAl_2O_4$ resulted in a fine, dense ceramic microstructure and the amount of growth increased with increasing firing time and increasing ZnO or $ZnAl_2O_4$ content. Doping with Zn resulted in significantly less dense composites to those produced using ZnO or $ZnAl_2O_4$ and thus in the Zn system oxide and spinel dopants offer a significant advantage over using metallic Zn. *© 2001 Kluwer Academic Publishers*

1. Introduction

Alumina matrix composites can be produced by the directed melt oxidation of aluminium. Early work on directed melt oxidation involved the oxidation of molten Al-Mg-Si alloy to form Al_2O_3/Al composites and initially it was thought that the presence of both Mg and Si in the alloy was necessary for the reaction process to occur [1, 2]. Subsequent studies have shown that it is only necessary to have Mg present to initiate the growth process by the formation of non-protective $MgAl_2O_4$. Mg also controls the supply of oxygen to the reaction front [3–5]. Complex Al-Mg alloys containing elements such as Zn, Ge, Sn, Pb have also been studied [4] and additional elements such as Si have been shown to enhance the growth rate of dense composites [1, 3, 6, 7]. More recently it has been shown that Al-Zn alloys also result in directed melt oxidation composite formation [8] although some authors suggest that Al-Zn alloys will only result in oxidative growth when a trace of magnesium is present to create a surface layer of MgO [9].

Use of external dopants, whether in the metallic elemental or oxide form, which are placed on top of the metal reservoir greatly simplifies the preparation of directed melt oxidation reaction systems as no special alloy preparation is involved. It has previously been shown that Mg, Li and Na supplied externally can initiate the reaction process [10–12]; the current work considers the use of Zn and Zn containing external dopants. The dopant has been supplied as Zn, ZnO or $ZnAl_2O_4$ because previous work on the Mg, Li and Na doped systems indicates that external dopants can successfully be introduced into the reaction system in the metallic, oxide or mixed oxide form [10–12].

2. Experimental procedure

Composites were prepared by externally doping pure Al (99.15%; see Table I) with either Zn (99.8%; Aldrich), ZnO (99.9%; Aldrich) or $ZnAl_2O_4$. The $ZnAl_2O_4$ was prepared by mixing 50 wt% ZnO (99.9%, Aldrich) and 50 wt% (99.8%, AlCOA) in a ball-mill with alumina balls for 1 hour. The mixture was pressed into a pellet and fired to 1300°C for 12 hours. The fired pellet was crushed, sieved to 8 μm and refired to 1300°C for a further 12 hours. $ZnAl_2O_4$ formation was confirmed by powder X-ray diffraction.

Between 2 and 7 wt% of the dopant (Zn, ZnO and $ZnAl_2O_4$) based on the weight of Al, was placed on a polished, cleaned surface of a block of Al and a defined space was created on the top of the block (see Fig. 1). The oxidation reactions were conducted in an air atmosphere in a muffle furnace. The rate of heating was 200°C/hour to a soaking temperature of 1180°C which was maintained for 36 hours, after which the samples were cooled to room temperature inside the furnace. During firing, the temperature of the samples was monitored by using thermocouples placed adjacent to the samples.

Fired samples were cross-sectioned parallel or perpendicular to the oxidation growth and either cold mounted in epoxy resin or hot mounted in bakelite. The samples were then ground and diamond polished to a 1 μm finish. Qualititative phase analysis of both the starting powders and the fired specimens was undertaken using X-ray diffraction (XRD) (Phillips PW1050 diffractometer, CoKα radiation). Microstructural characterisation was carried out using optical microscopy and, after carbon coating, scanning electron microscopy (SEM) (JEOL JSM 6400) coupled with

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TABLE I Chemical analysis of aluminium metal used in this work (ICP)

Element	Weight % (±0.02%)
Al	99.15
Fe	0.60
Zn	0.10
Si	0.08
Cu	0.08
Ti	0.02
Cr	<0.02
Mg	<0.02
Mn	<0.02
Ni	<0.02
Ca	<0.001

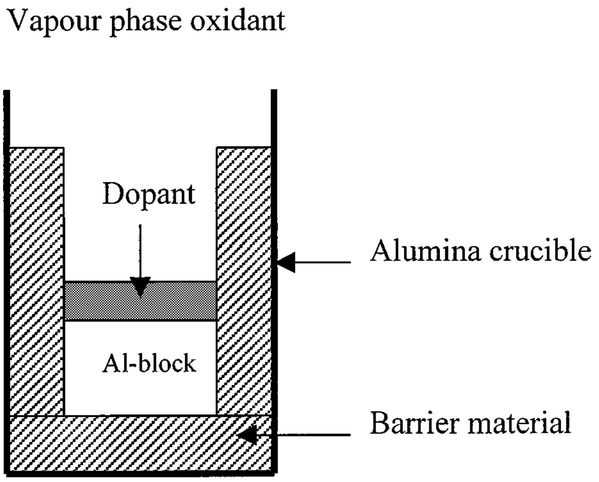

Figure 1 Experimental set-up for the directed melt oxidation of pure Al externally doped with Zn containing dopants.

energy dispersive spectroscopy (EDS) (LINK Analytical 6276) for elemental analysis. Optical image analysis (PC_Image for Windows) of the phases was also undertaken.

3. Results

3.1. Samples doped with Zn metal

In the samples doped with 2 or 7 wt% Zn, complete oxidation of Al occurred on firing at 1180°C for 36 hours. The growth developed not only outward from the top of Al reservoir but sideways into the barrier material in both cases and the outer surfaces of the products were covered by a thin layer of a yellow compound. There was no free Zn left after the firing in either case.

Powder XRD (Fig. 2) shows that the products contained α-Al_2O_3, Al and $ZnAl_2O_4$. No Zn or ZnO was detected in the bulk of the growth products however XRD of the yellow surface layer indicated that this layer mainly consisted of ZnO with a small amount of $ZnAl_2O_4$ (Fig. 3). In the 7 wt% Zn doped sample, EDS supported the identification of the outer layer as ZnO; the layer immediately beneath the ZnO layer contained Al, O and Zn and was therefore presumed to be the $ZnAl_2O_4$ detected by XRD (Fig. 4). The ZnO layer was found to be discontinuous and in some regions only a $ZnAl_2O_4$ layer was found. For samples doped with 2 wt% Zn, only the $ZnAl_2O_4$ layer was detected on the outer surface of the growth.

SEM examination (Fig. 5) showed that the growth contained interspersed dense and porous regions. Optical image analysis showed that the products contain between 25–30 vol% porosity (see Table II) and

TABLE II Volume fractions of porosity, residual Al metal and alumina matrix in the Al_2O_3/Al composites produced by doping with Zn containing phases

Volume fraction (%)	Zn		ZnO		$ZnAl_2O_4$	
	2 wt%	7 wt%	2.5 wt%	8.7 wt%	7 wt%	19.6 wt%
Porosity	22 ± 6	24 ± 7	7 ± 3	4 ± 1	5 ± 2	2 ± 1
Al metal	8 ± 4	8 ± 3	9 ± 2	13 ± 3	12 ± 1	1 ± 0.2
Alumina matrix	65 ± 10	62 ± 7	84 ± 6	81 ± 5	81 ± 4	97 ± 1

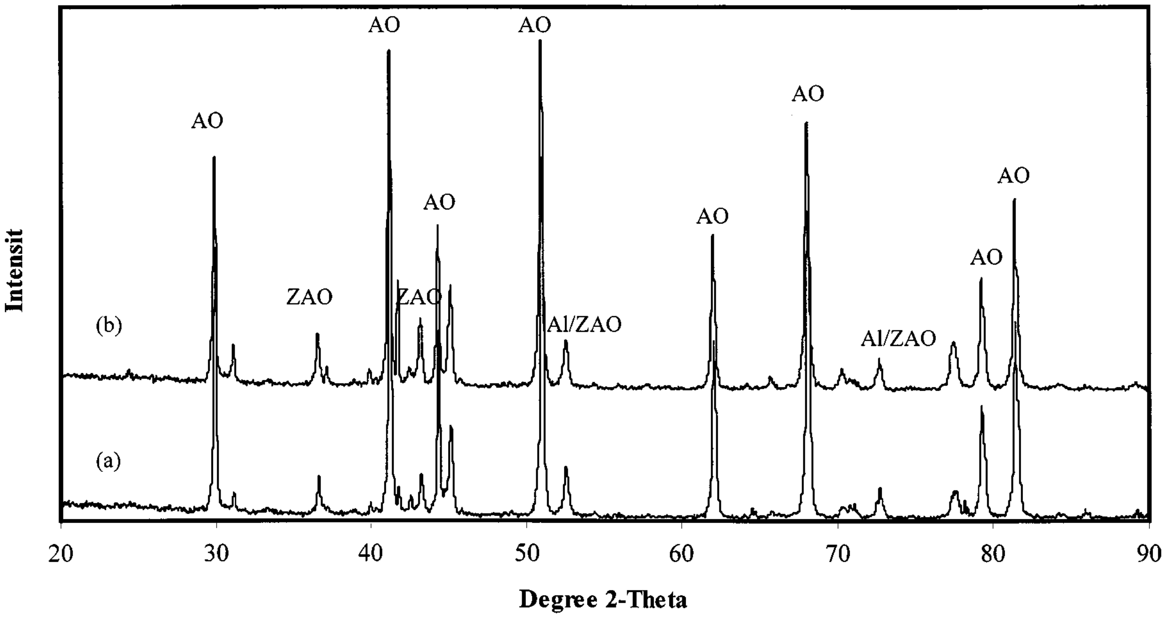

Figure 2 Powder XRD patterns of crushed Zn doped products (a) 2 wt% and (b) 7 wt% Zn, fired to 1180°C for 36 hours [AO-α-Al_2O_3, Al-aluminium and ZAO-$ZnAl_2O_4$].

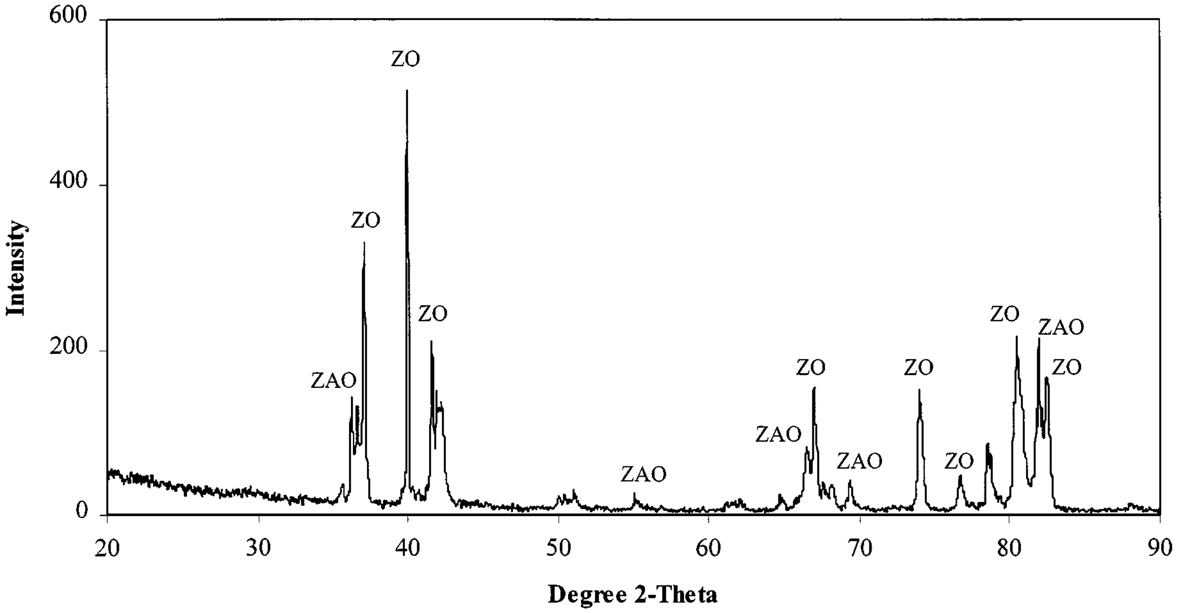

Figure 3 XRD of the yellow compound on the surface of a Zn doped sample [Zo-ZnO and ZAO- $ZnAl_2O_4$].

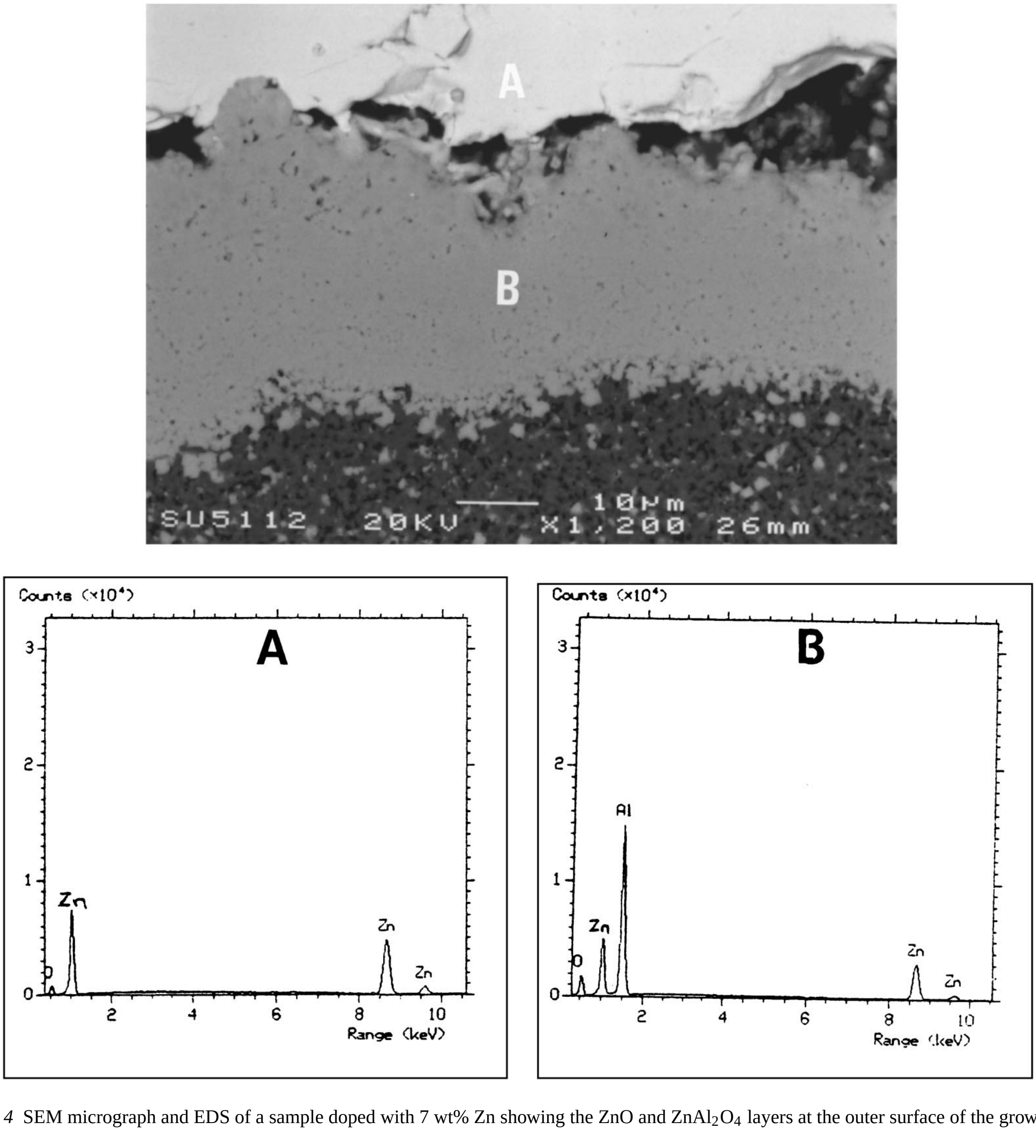

Figure 4 SEM micrograph and EDS of a sample doped with 7 wt% Zn showing the ZnO and $ZnAl_2O_4$ layers at the outer surface of the growth.

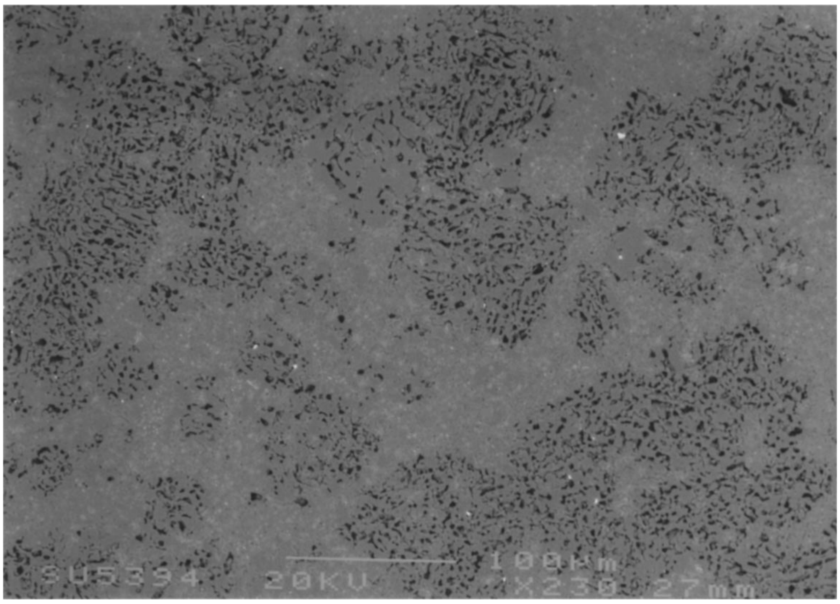

Figure 5 SEM micrograph of a sample doped with 7 wt% Zn showing the alternating dense and porous regions developed within the matrix.

it appeared that the size of the pores was larger in the sample doped with 7 wt% Zn than in that doped with 2 wt% Zn. Similarly although the residual Al content is around 10 vol% in both cases, it appeared to be present as larger particles in the 7 wt% Zn case.

3.2. Samples doped with ZnO

In the samples doped with 2.5 wt% or 8.7 wt% of ZnO (equivalent to 2 and 7% Zn, respectively) complete oxidation was observed after firing to 1180°C for 36 hours. Again the surface of the growth was covered by a thin yellow compound. No dopant was left at the end of the firing. This result is in contrast with that of Xiao and Derby [13], who observed no growth when ZnO was used to dope the surface of a commercial purity Al alloy.

Bulk XRD (Fig. 6) showed that in both cases the products contained α-Al_2O_3, $ZnAl_2O_4$ and residual Al metal. Neither Zn nor ZnO was detected in the bulk of the growth product. The yellow compound on the outer surface was again identified as being predominantly ZnO, in addition to some $ZnAl_2O_4$. Optical image analysis shows that ZnO doped samples contained less porosity compared to Zn doped samples; 2.5 wt% ZnO led to a volume porosity of $\sim$7% and 8.7 wt% ZnO led to a volume porosity of $\sim$4%. SEM examination revealed that ZnO doped samples had a typical directed melt oxidation microstructure (Fig. 7) and the alternating dense and porous regions seen in the Zn doped system were not observed.

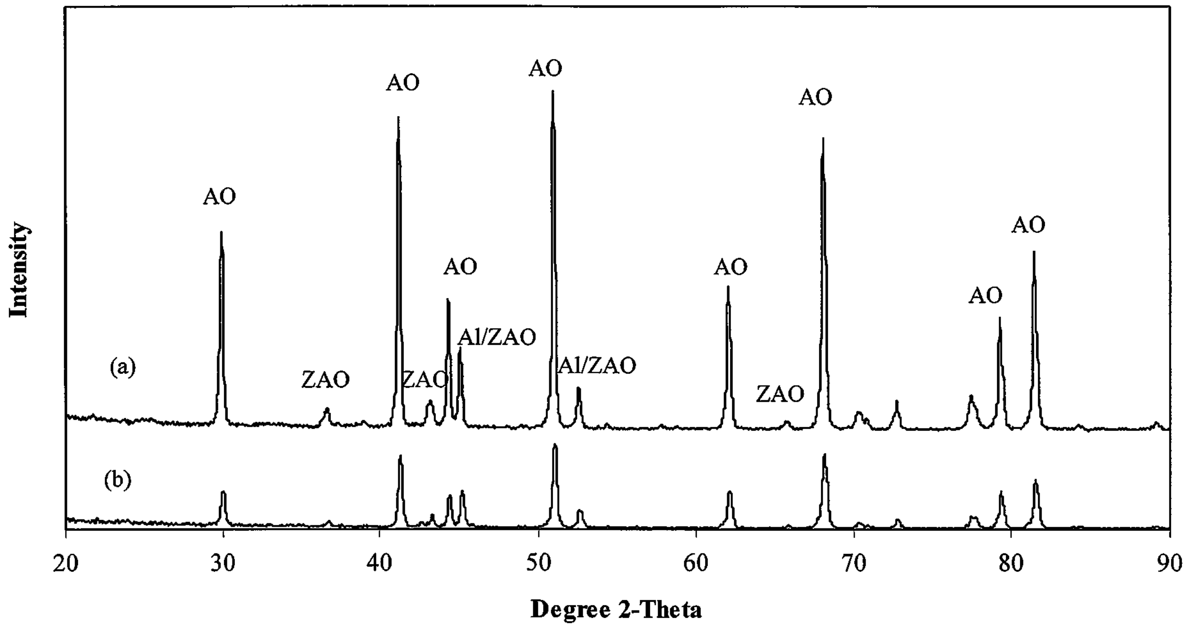

Figure 6 XRD pattern of samples doped with (a) 2.5 wt% ZnO and (b) 8.7 wt% ZnO fired to 1180°C for 36 hours [AO-α-Al_2O_3, ZAO-$ZnAl_2O_4$ and Al-aluminium].

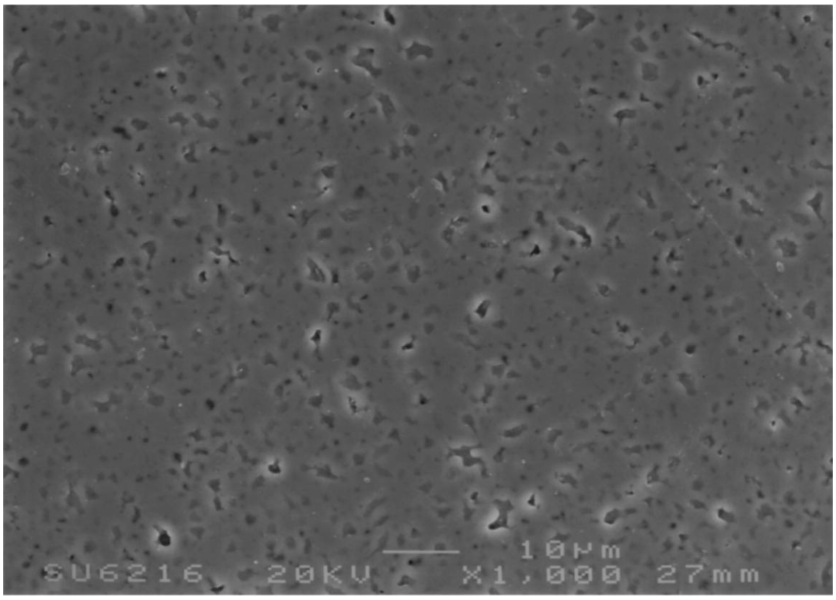

Figure 7 SEM micrograph of a sample doped with 8.7 wt% ZnO fired to 1180°C for 36 hours.

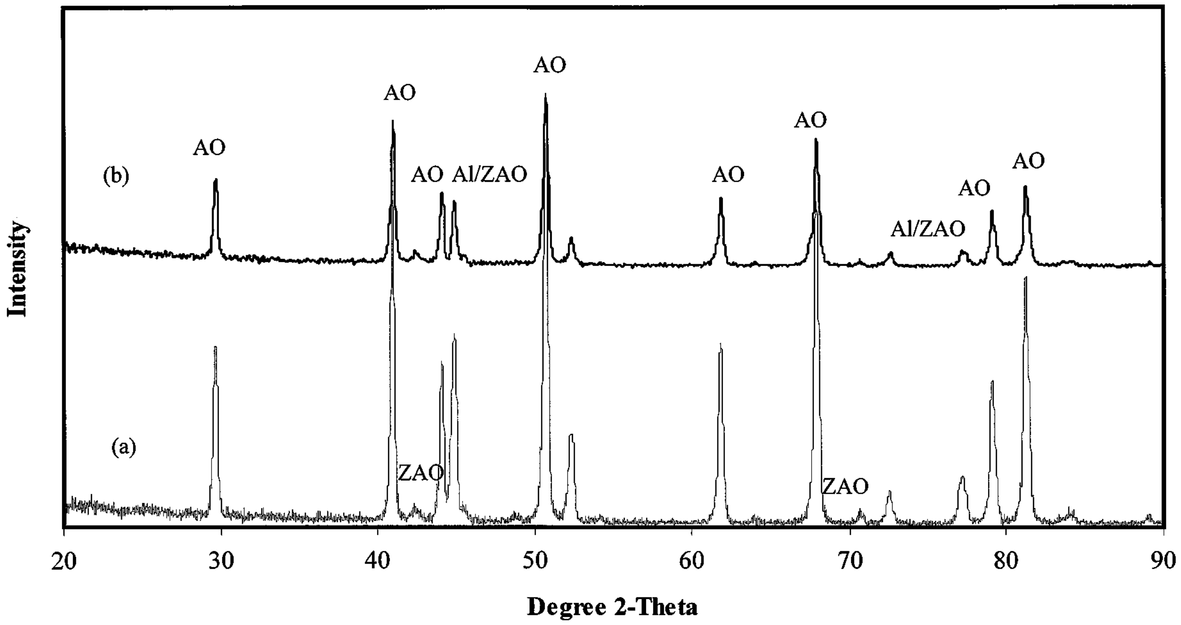

Figure 8 XRD patterns of samples doped with (a) 7 wt% and (b) 19.6 wt% $ZnAl_2O_4$ fired to 1180°C for 36 hours [AO-α-Al_2O_3, ZAO- $ZnAl_2O_4$ and Al-aluminium].

3.3. Samples doped with $ZnAl_2O_4$

Doping with 7 and 19.6 wt% $ZnAl_2O_4$ (equivalent to 2.5 and 7 wt% Zn respectively) resulted in oxidative growth at 1180°C. The reaction process was incomplete when only 7 wt% $ZnAl_2O_4$ was used however on increasing the $ZnAl_2O_4$ content to 19.6 wt% complete oxidation occurred after firing at 1180°C for 36 hours. In all cases, a yellow compound on the outer growth surface again covered the oxide growths similar to that seen with the other two systems.

XRD (Fig. 8) result of the sample doped with 7 and 19.6 wt% $ZnAl_2O_4$, fired to 1180°C for 24 and 36 hours shows that the oxide growths consist of α-Al_2O_3, Al and $ZnAl_2O_4$. No free Zn or ZnO was detected in either case. The oxide growth had a similar density to the ZnO doped samples and thus had a higher ceramic matrix content and lower porosity than the Zn doped samples. The greater $ZnAl_2O_4$ doping level resulted in less porosity in the oxide growth; $\sim$2 vol% porosity in the 19.6 wt% $ZnAl_2O_4$ doped sample compared $\sim$5 vol% porosity on the 7 wt% $ZnAl_2O_4$ doped sample (see Table II).

Again the oxidation products had the typical directed melt oxidation microstructure with ceramic interspersed with Al metal; the alternating porous and dense regions seen in the Zn doped samples were not observed (Fig. 9). EDS again indicated that the outer yellow layer was ZnO layer overlaying a $ZnAl_2O_4$ layer. Beneath these two layers only Al_2O_3 and homogeneously distributed residual Al metal were found.

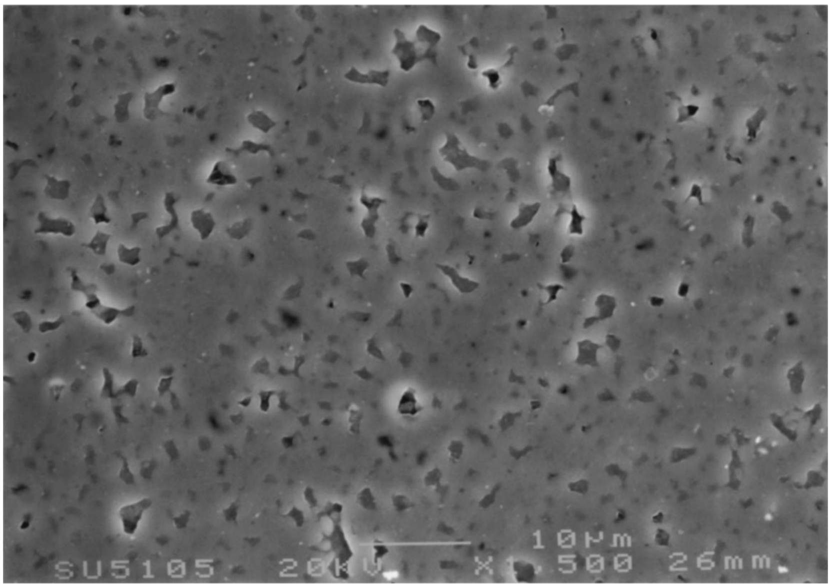

Figure 9 SEM micrograph of a sample doped with 19.6 wt% $ZnAl_2O_4$ fired to 1180°C for 36 hours.

4. Discussion

Zn has been introduced as an element, an oxide and also as a mixed oxide as an initiating dopant for the fabrication of directed melt oxidation ceramic composites. In contrast to some previous results [9, 13], in all cases Zn was found to be capable of initiating directed melt oxidation. Hanabe *et al.* [8] discovered that 1% Zn in the Al-alloys was insufficient to produce an oxide growth and they only observed growth when the Zn content was increased to between 5 and 8 wt% Zn, however in the present work, oxidative growth was observed when only 2 wt% Zn was present. This difference can be attributed to the fact that the local Zn content at the main reaction front will tend to be higher when externally applied dopants are used than when the dopant element is alloyed with the aluminium. Hanabe *et al.* [8] also found a ZnO layer at the surface, but they found that it was separated from the underlying alumina matrix by a metal layer. These results are noticeably different to the present study where the ZnO layer on the external growth surface was separated from the matrix by a $ZnAl_2O_4$ layer.

Growth rates were found to be dependent on the percentage of Zn added to the system and, in particular, to depend on whether Zn was supplied elementally, as an oxide or as a mixed oxide. Different zinc containing dopants (Zn, ZnO or $ZnAl_2O_4$) resulted in different initiation times and growth rates but the same general oxidation behaviour was observed once the process had commenced. It is believed that the basic reaction sequence is similar to the cyclic reaction sequences that have been suggested for other dopants such as Mg. Thus with the Zn doped system the Zn reacts with oxygen to form ZnO:

$$2Zn_{(g)} + O_{2(g)} \rightarrow 2ZnO_{(s)}. \tag{1}$$

The ZnO subsequently reacts with the molten Al and oxygen to form spinel:

$$2ZnO_{(s)} + 4Al_{(l)} + 3O_{2(g)} \rightarrow 2ZnAl_2O_{4(s)}. \tag{2}$$

The lower regions of the spinel layer that is formed in this fashion reacts with more molten Al to produce solid alumina which releases gaseous Zn [8]:

$$3ZnAl_2O_{4(s)} + 2Al_{(l)} \rightarrow 4Al_2O_{3(s)} + 3Zn_{(g)}. \tag{3}$$

The Zn vapour diffuses away from the newly created alumina (which is in a region of low oxygen partial pressure) towards the top of the system where there is a higher oxygen partial pressure and the Zn can re-oxide to form ZnO. Gu *et al.* [15] have shown that the Zn partial pressure under these conditions is $\sim 10^{-1}$ atm. Similar processes are expected to occur in the ZnO and $ZnAl_2O_4$ doped samples. This mechanism would result in a ZnO layer overlying a $ZnAl_2O_4$ layer as seen in this study. It does not explain the metal layer beneath the ZnO layer as seen by Hanabe *et al.* [8].

It is clear from Table II that the lowest porosity products were produced when $ZnAl_2O_4$ was used as a dopant and the least dense products were obtained when Zn was used as a dopant. Furthermore in the $ZnAl_2O_4$ doped system the porosity and residual metal content decreased when the dopant concentration was increased from 7 wt% to 19.6 wt%. Gu *et al.* [15] have demonstrated thermodynamically that the dopant partial pressure generated with 2.5 wt% Zn doping is significantly higher than that generated in other directed melt oxidation systems such as the Mg doped system; similarly Hanabe *et al.* [8] note that a high partial pressure of Zn is generated over an Al-5 wt% Zn alloy. In the reaction sequence outlined above sufficient dopant partial pressures need to be generated to give vapour phase transport of the dopant from above the surface of the newly formed alumina to the reaction front where it can react to form the dopant oxide. However if the dopant partial pressure is too great then the dopant will have an increasing tendency tend to travel beyond the main reaction front before the gas phase reaction to form dopant oxide occurs. If the dopant oxide is formed reasonably close to the main reaction system the cyclic reactions can continue but the product will be highly porous because the next cycle of the reaction process starts in a region adjacent to, but not at, the existing reaction front. However if the dopant oxide is formed well away from the main reaction system a dopant oxide deposit will be found but no further reaction will occur because this deposit is not accessible to the remaining aluminium; such ZnO deposits have been observed away from the main reaction product by Hanabe *et al*. [8] Thus in the metallic Zn system the observed high porosities are believed to arise from the high Zn partial pressure.

However as indicated above less porous products were obtained when ZnO and $ZnAl_2O_4$ rather than Zn were used as dopants. This suggests that when Zn is supplied via an oxide or a spinel phase that the Zn is less readily vapourised and thus the vapour pressures of Zn are lower. As outlined above this would mean that Zn is less readily transported away from the main reaction front and therefore the reaction product is denser. Given that the basic elements and compounds involved in all three systems are the same it is not immediately obvious why these differences in vapour pressure arise. However as the system is not at equilibrium it is most likely that in the Zn doped system some of the initial Zn content does not participate directly in the reaction sequence and instead remains in metallic form throughout much of the process. This metallic Zn leads to the continuing generation of high Zn partial pressures during the reaction process. In the oxide and spinel doped systems however some of the dopant remains as oxide or spinel throughout most of the process thereby generating lower Zn partial pressures at any stage thus helping to retain Zn within the reaction system. The spinel doped system apparently least readily releases Zn to participate in the reaction cycle because greater $ZnAl_2O_4$ contents are required for complete oxidation of the original Al reservoir.

5. Conclusions

Zn can be used as an external dopant to initiate the directed melt oxidation of aluminium. In contradiction to previously reported results directed melt oxidation has been successfully initiated using ZnO and $ZnAl_2O_4$ as well as Zn as external dopants without any Mg being present in the system. In all cases the outer surfaces of the reaction products were found to be covered with a layer of ZnO overlaying a layer of $ZnAl_2O_4$. This suggests that the same type of cyclic reaction sequence as that observed in the Mg, Li and Na doped systems occurs in the Zn doped system.

Denser products were obtained using ZnO or $ZnAl_2O_4$ rather than Zn as a dopant. This suggests that when Zn is supplied elementally it is relatively easily volatilised compared to when it is supplied as ZnO or $ZnAl_2O_4$ and that therefore the gas phase reaction to produce ZnO takes place well away from the main reaction front giving a reaction product contains significant porosity. Therefore external doping with oxide and spinel dopants not only works, but in the case of Zn containing dopants it leads to better products than external doping with metallic Zn.

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