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Template formation of magnesium aluminate ($MgAl_2O_4$) spinel microplatelets in molten salt

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Abstract

Magnesium aluminate, $MgAl_2O_4$ (MA), microplatelets were synthesized using a molten salt technique. α-Alumina platelets partially decomposed from aluminium sulphate were reacted with either commercial magnesium oxide or magnesium nitrate in the molar ratio 1:1 to synthesize spinel platelets. Molten salts such as chloride, MCl (M = Li, Na, and K) and potassium sulphate were used for MA synthesis and the salt to oxide ratio was kept at 3:1 for all compositions. Reactants and molten salt mixes were fired in an alumina crucible for 3 h at from 800 to 1150 °C. XRD revealed complete MA without formation of any secondary phase for powders fired for 3 h at 1100 °C. Electron microscopy revealed the MA platelet morphology and size was the same as the α-alumina platelets indicating a 'template process' during molten salt synthesis.

Keywords: Molten salt synthesis; Platelets

1. Introduction

$MgAl_2O_4$ (MA) spinel offers a desirable combination of properties including high melting temperature,[1] good corrosion resistance[2] and high strength at elevated temperatures.[3] It is a good candidate material as a reinforcing phase to improve the strength and toughness of ceramic matrix composites (CMCs)[4] making them suitable for high temperature applications. Hence MA whiskers and/or platelets are excellent reinforcing phases in ceramic matrix composites. While MA whiskers may be synthesized by vapour phase reactions,[5] it is noteworthy that spinel grains do not easily adopt a platy morphology, even when using a liquid flux technique.[2] Previously, we reported the synthesis of MA platelets using α-alumina platelet and magnesium sulphate precursors,[6] but a reactant mass of $MgSO_4$ remained in the crucible after heating and 3% HCl was needed to dissolve it before washing the resulting platelets with distilled water. Hence, an improved process using molten salt synthesis (MSS) is adopted in the present work which does not involve an acid washing step.

Many novel methods have been developed over the last few years for the preparation of ceramic powders including sol–gel processing, hydrothermal synthesis, combustion synthesis, MSS and a variety of deposition techniques. Of late, MSS has attracted the interest of materials scientists for synthesis of ceramic powders with varying morphologies and as well as complex stoichiometry.[7] Generally, two reaction sequences for the product formation are considered in MSS. In the first case, the reactants dissolve in the molten salt, followed by formation of the product in the molten salt medium and finally precipitation of the product above its solubility limit. In the second case, one of the reactants dissolves in the molten salt and the dissolving component is transported to the outer surface of the other reactant and the product is formed on the latter surface. In our earlier report on synthesis of MA powder in molten salt,[8] we observed that MA formation of was predominantly through a template process mechanism. By taking advantage of the second MSS reaction sequence, we attempted to synthesize MA micro-

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platelets by reacting α-alumina platelets with MgO in molten chlorides or sulphate salts.

2. Experimental

Aluminum sulphate hydrate ($Al_2(SO_4)_3 \cdot 14$–$18H_2O$, Kishida Chemical Co. Ltd., Osaka, Japan) and sodium sulphate (Na_2SO_4, Kishida Chemical Co. Ltd., Osaka, Japan) of reagent grade were used as raw materials for preparing α-Al_2O_3 platelets. Calcined MgO (Cerac, Grade-M1016, purity 99.14%, Milwaukee, Wisconsin, USA), and $Mg(NO_3)_2 \cdot 6H_2O$ (Aldrich, Gillingham, UK, purity >99%), were used as source materials for MgO for preparing MA platelets using LiCl, KCl, NaCl and K_2SO_4 (Aldrich, Gillingham, UK, purity >99%) as molten salts. α-Al_2O_3 platelets were prepared from partially decomposed $Al(SO_4)_3$ using Na_2SO_4 flux, as reported elsewhere.[9] ($Al_2(SO_4)_3 \cdot 14$–$18H_2O$) was first calcined in air for more than 12 h at 300 °C to form $Al_2(SO_4)_3$ and it was reheated in air for 3 h at 900 °C to form γ-Al_2O_3. The powder mixture of γ-Al_2O_3 and Na_2SO_4 (approximately 10 g) was placed into an alumina crucible covered with a lid and then fired for 1 h at 1000 °C. A reactant mass, remaining at the bottom of the crucible was soaked in 1 N HCl at 70–80 °C for 0.5–1 h. After washing the reactant with water and drying, hexagonal α-Al_2O_3 platelets were obtained. An equimolar composition of MgO or $Mg(NO_3)_2$ and α-Al_2O_3 platelets was homogeneously mixed in acetone medium using an agate mortar, without disrupting the α-Al_2O_3 platelets morphology, and dried. The dried powder was later mixed with molten salt; the salt/oxide weight ratio was kept at 3:1. The powder mixture was placed in an alumina crucible covered with an alumina lid, heated to a given temperature and held for 3 h. After furnace-cooling to room temperature, the reacted mass was repeatedly washed with hot distilled water to remove salts. The resulting oxide powders were oven-dried prior to further characterization. For comparison, MA was also prepared via a conventional mixed oxide synthesis (CMOS) method using the same heating schedules. Phases and extents of reaction were identified by powder X-ray diffraction (XRD) analysis using a Philips PW 1825/00 X-ray diffractometer, UK. Spectra were recorded at 30 mA and 40 kV, using Ni-filtered Cu Kα radiation. JCPDS cards used for identification were MgO (45–946), Al_2O_3 (71–1123) and MA (75–1796). Microstructural analyses were carried out using a high resolution FEG-SEM (FEI Sirion, UK) operated at a voltage between 10 and 15 kV with secondary electron imaging.

3. Results and discussion

As-synthesized α-Al_2O_3 platelets were made to react with either calcined MgO or $Mg(NO_3)_2$ in stoichiometric ratio (Al_2O_3 to MgO mole ratio is 1:1) in molten salts such as LiCl, KCl, NaCl and K_2SO_4 by heating for 3 h at various temperatures from 800 to 1150 °C. The experimental conditions and corresponding crystalline phases after heating the reactants at different temperatures are given in Table 1, samples are identified by MA-*x* where *x* corresponds to the batch number. XRD from MA prepared in different molten salts reveals that the formation of MA (MA-3) is complete after 3 h at 1100 °C in molten LiCl compared to 1150 °C in molten KCl and NaCl salts. This is attributed to two factors: the molten salt melting temperature and the solubility of reactants in the respective salts. The melting point of LiCl is 615 °C compared to 774 °C for KCl and 801 °C for NaCl.[10] Fig. 1 shows the XRD patterns of samples heated at 800 and 900 °C in different molten salts. Although the melting points of these salts are well below or around 800 °C, XRD of MA composition powder mixes heated 3 h at 800 °C (Fig. 1(a)) reveals that LiCl has facilitated formation of MA to much greater degree than the other salts. However, XRD of MA composition powder mixes fired 3 h at 900 °C (Fig. 1(b)) shows that MA starts to form also in KCl and NaCl salts. It is suggested that α-Al_2O_3 is sparingly or not soluble in chloride salts[10] and that the only dissolving reactant species is MgO.

Table 1
Experimental conditions and respective crystalline phases after firing in molten salts

S.ID.	Tempature (°C)	Reactants		Molten salt	Salt to oxide ratio	Crystalline phases
MA-21	800	Al_2O_3	MgO	LiCl	3:1	C, P, $MA_{(m)}$
MA-1	900	Al_2O_3	MgO	LiCl	3:1	C, P, $MA_{(m)}$
MA-2	1000	Al_2O_3	MgO	LiCl	3:1	C, P, MA
MA-3	1100	Al_2O_3	MgO	LiCl	3:1	MA
MA-30	800	Al_2O_3	MgO	NaCl	3:1	C, P
MA-31	900	Al_2O_3	MgO	NaCl	3:1	C, P, $MA_{(m)}$
MA-4	1100	Al_2O_3	MgO	NaCl	3:1	MA, $C_{(m)}$
MA-22	1150	Al_2O_3	MgO	NaCl	3:1	MA
MA-32	800	Al_2O_3	MgO	KCl	3:1	C, P
MA-33	900	Al_2O_3	MgO	KCl	3:1	C, P, $MA_{(m)}$
MA-12	1100	Al_2O_3	MgO	KCl	3:1	MA, $C_{(m)}$
MA-23	1150	Al_2O_3	MgO	KCl	3:1	MA
MA-11	1100	Al_2O_3	MgO	K_2SO_4	3:1	MA, $C_{(m)}$
MA-24	1150	Al_2O_3	MgO	K_2SO_4	3:1	MA
MA-6	1100	Al_2O_3	$Mg(NO_3)_2$	KCl	3:1	MA
MA-5	1100	Al_2O_3	$Mg(NO_3)_2$	K_2SO_4	3:1	MA, $C_{(m)}$
MA-25	1150	Al_2O_3	$Mg(NO_3)_2$	K_2SO_4	3:1	MA

MA, $MgAl_2O_4$; C, corundum; P, periclase; m, minor phase.

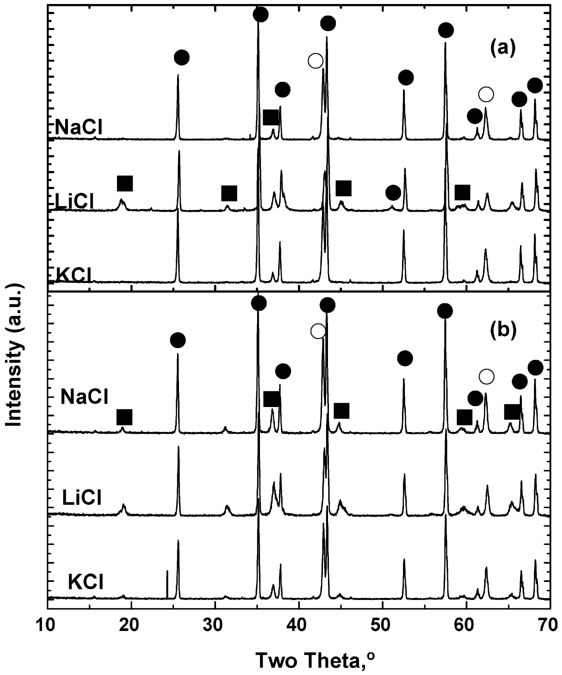

Fig. 1. XRD of MA composition powder heated in different salts: (a) 800 °C/3 h and (b) 900 °C/3 h; (■) MA spinel, (●) Al_2O_3 and (○) MgO.

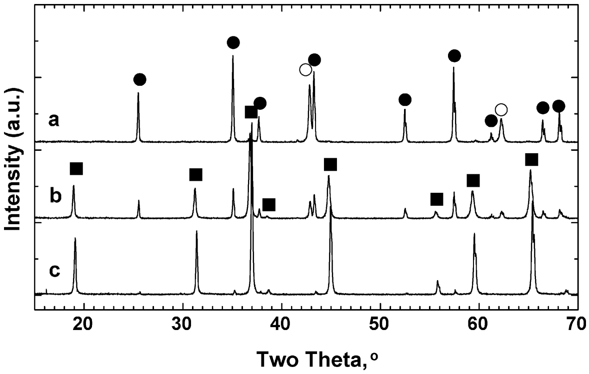

Fig. 3. XRD of MA composition powder heated at different temperatures by CMOS method: (■) MA spinel, (●) Al_2O_3 and (○) MgO; (a) 900 °C/3 h, (b) 1100 °C/3 h and (c) 1300 °C/3 h.

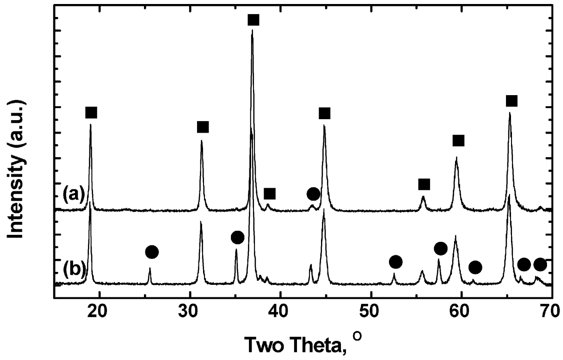

Fig. 2. XRD of MA composition powder heated in KCl at 1100 °C/3 h: (a) Al_2O_3 + $Mg(NO_3)_2$ and (b) Al_2O_3 + MgO; (●) Al_2O_3, (■) MA spinel.

The dissolution start temperature for MgO in molten chlorides[10] clarifies the MA formation temperature; in LiCl it is 688 °C but 900 °C in KCl and NaCl salts. As a result LiCl is more effective than KCl and NaCl in decreasing the synthesis temperature of MA. However, when $Mg(NO_3)_2$ is used instead of MgO as the reactant source for MgO, nearly complete transformation to MA was obtained using KCl salt when fired for 3 h at 1100 °C (Fig. 2). This indicates that a nitrate MgO source is better than an oxide for achieving complete MA formation. $Mg(NO_3)_2$ whose melting point is 90 °C, is expected to become more fluid with increasing temperature.[11] The low viscosity of the $Mg(NO_3)_2$ at high temperature,[11] enables easy spreading of liquid throughout the reactant mix wetting all α-Al_2O_3 platelets. This ensures homogeneous mixing of the reactants which at high temperature assists rapid diffusion of Mg^+ ions into α-Al_2O_3 platelets in KCl. To illustrate the effect of MSS, XRD data for MA synthesized by CMOS are given in Fig. 3. The global reaction for the formation of MA through a solid-state reaction can be expressed as follows:

$$Al_2O_3(s) + MgO(s) \rightarrow MgAl_2O_4(s)$$

The standard free energy change ΔG° of this reaction is −24.145 kJ at 25 °C and −26.676 kJ at 950 °C[12] suggesting that MA formation is possible by solid-state reaction of alumina with magnesia from room temperature. However, XRD of solid-state synthesis of MA (Fig. 3) indicates that the kinetics of this solid-state reaction are too slow to produce MA sufficiently even when the mixture has been at 900 °C for 3 h. The kinetics of this reaction are a strong function of particle size and degree of mixing as well as temperature. Nevertheless comparing XRD data for MSS and CMOS reveals that the extent of reaction at 1100 °C in some salts is similar to that by CMOS at 1300 °C, indicating that the synthesis temperature of MA can be decreased by $\sim$200 °C in MSS.

Fig. 4(a) shows an SEM micrograph of α-Al_2O_3 platelets that are used as template particles for preparing MA platelets by MSS in different molten salts. MA platelets with an average edge length of $\sim$5 μm and average thickness of $\sim$1 μm were observed (Figs. 4 and 5). The synthesized MA grains have an overall platy morphology and retain the morphology and size of the original α-Al_2O_3 platelets. SEM observation revealed the MA grains synthesized after 3 h at 1100 °C in LiCl salt (Fig. 4(b)) have a platy morphology with much rougher surface than the original α-Al_2O_3 platelets. This is attributed to mild dissolution of MA in LiCl (unlike the other molten salts) thereby forming small MA crystals on the surface of MA platelets with blunt edges. However, the MA platelets synthesized after 3 h at 1150 °C in molten KCl and NaCl are platy with sharp edges as shown in Fig. 4(c) although the MA platelet surfaces appear roughened.

Fig. 5(a)–(c) show that MA platelets synthesized in combination with $Mg(NO_3)_2$ or K_2SO_4 have retained the typical hexagonal platy morphology; in particular, the MA platelets prepared using $Mg(NO_3)_2$ are smooth compared to the rough MA platelets synthesized using MgO in molten chloride salts. The insert shows EDS analysis confirming the stoichiometric ratio of MgO and Al_2O_3 in MA platelets. Previous studies on MSS of oxide powder[13,14] reveal that the salt species significantly affect the final product morphologies, probably due to differences in

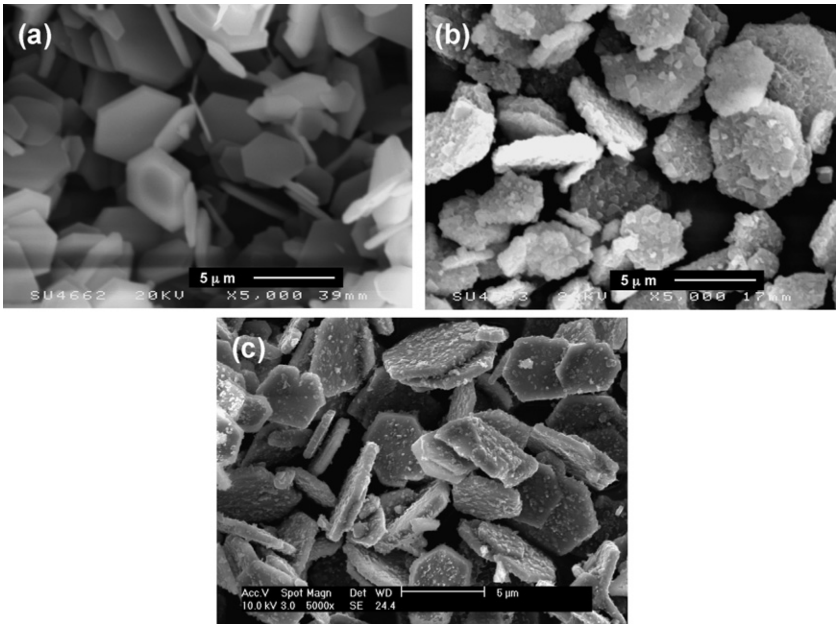

Fig. 4. SEM micrographs of (a) α-Al_2O_3 platelet (p) and MA platelets (b–c) synthesized at different conditions: (b) α-Al_2O_3 (p) + MgO, LiCl, 1100 °C/3 h; (c) α-Al_2O_3 (p) + MgO, KCl, 1150 °C/3 h.

anion sizes of the salts, and the solubilities of the constituent oxides in the salt fluxes. High resolution FEG SEM of these MA platelets (Fig. 6) indicates different size MA crystallites growing on the surface of polycrystalline MA platelets. MA platelets synthesized using MgO in the chloride salts (Fig. 6(a) and (c)) have significant numbers of submicron MA particles on their surface with gaps between them (Fig. 6(c)) revealing the polycrystalline nature of the underlying MA platelet (Fig. 6(a)) causing the surface to be rough. However, for MA platelets synthesized using $Mg(NO_3)_2$ (Fig. 6(d)), nano crystalline particles (<100 nm) form on the platelet surfaces at higher density than with MgO and hence the surfaces are smoother (Fig. 6(b)). The difference in size of crystalline MA particles appearing on the MA platelets could be accounted for by the viscosity of the molten reactants. When MgO dissolves in molten chlorides, the viscosity of the molten salt is higher compared to when $Mg(NO_3)_2$ dissolves in molten chloride or sulphate.[15] With highly fluid molten liquid, the wettability is higher and the reaction is quicker leading to the nano-crystalline particles detected because many more nuclei could be formed at an early stage in a short duration whereas the

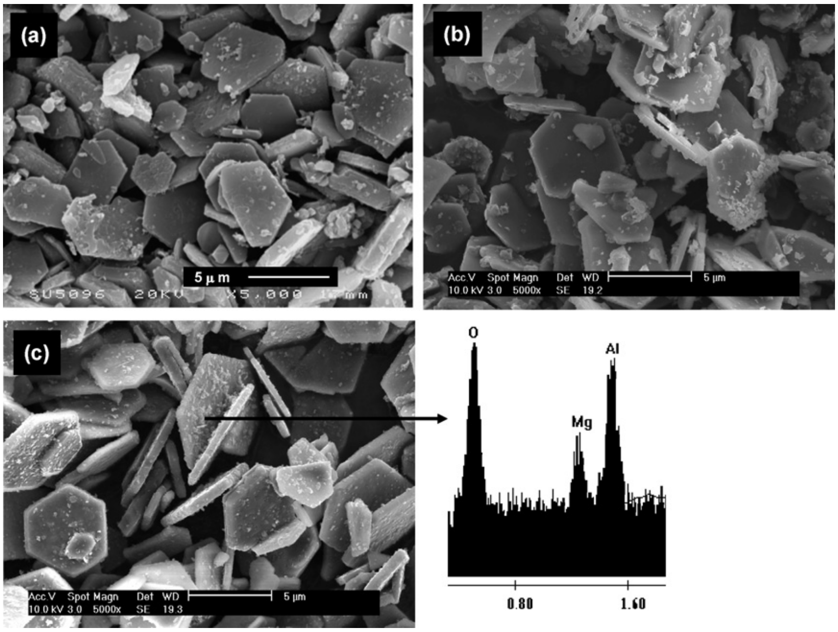

Fig. 5. SEM micrographs of MA platelets synthesized at different conditions: (a) α-Al_2O_3 (p) + $Mg(NO_3)_2$, KCl, 1100 °C/3 h; (b) α-Al_2O_3 (p) + $Mg(NO_3)_2$, K_2SO_4, 1100 °C/3 h, and (c) α-Al_2O_3 (p) + MgO, K_2SO_4, 1150 °C/3 h.

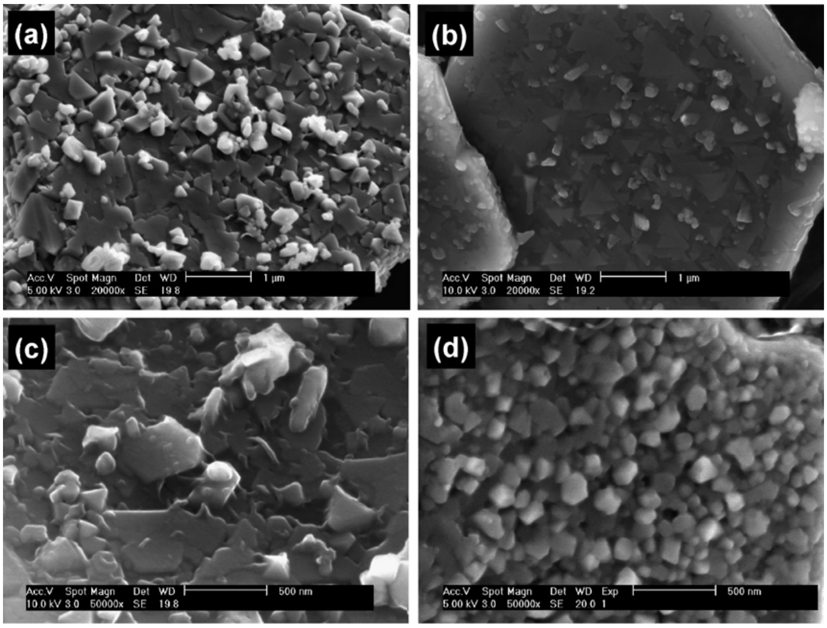

Fig. 6. High resolution FEG SEM micrographs of MA platelets: (a and c) α-Al_2O_3 + MgO in KCl, 1100 °C, 3 h; (b and d) α-Al_2O_3 + $Mg(NO_3)_2$ in KCl, 1100 °C, 3 h.

growth of these nuclei is constrained for a given time. In a high viscosity system, only a low number of nuclei will form. Hence the nuclei have sufficient space for growth leading to formation of large (0.5 μm) particles and can be seen clearly in Fig. 6(c).

Overall the MSS template mechanism involves: (i) reactant dissolution, (ii) reactant transport through the melt, (iii) nucleation of the product and (iv) growth of the product on existing nuclei.

4. Conclusion

MSS was effective in preparing MA platelets by the template formation mechanism. These results indicate that MgO is the fast dissolving component of the constituent oxides in the selected molten salts and that the formation of MA initiates on the Al_2O_3 platelet surfaces. All spinel grains develop a platy morphology confirming the template mechanism but the size and surface topography of the MA platelets differs depending on many factors such as differences in anion sizes of the salts, the solubilities of the constituent oxides in the salt fluxes, and viscosity of the molten salt containing the molten reactants. MA synthesized using $Mg(NO_3)$ yielded smooth hexagonal platelets while MA synthesized with MgO in chloride salts yielded rough hexagonal platelets.

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