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Densification and microstructure of magnesium aluminate spinel for adding method of Sc_2O_3

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ABSTRACT

The effect of adding method of Sc_2O_3 on the densification and microstructure of magnesium aluminate spinel prepared by co-precipitated method was investigated. Sintered products were characterized in terms of densification, phase analysis, quantitative elemental analysis, microstructure and flexural strength. Sintering additives were added in the form of Sc salt and in the form of scandium oxide, respectively. No matter in what way to add, sintering additives exist in the form of Sc_2O_3. Moreover, incorporating of Sc^{3+} into the spinel structure increases lattice parameters, which improves the diffusion, mass transfer, and densification. The microstructure of sintered samples with adding Sc salt as a sintering additive is more compact and the grain size distribution is more uniform although their grain size is larger compared with that of sintered samples with adding scandium oxide as a sintering additive. Moreover, the optimum flexural strength (97 MPa) of the sintered products is obtained on sintering at 1650 °C with the addition of Sc salt.

1. Introduction

Magnesium aluminate spinel (MAS) possesses a high melting point (2135 °C), a low thermal expansion, good mechanical strength and an excellent chemical resistance etc. [1,2]. Due to these desirable properties, MAS has been used for various applications, such as refractories, humidity sensors, and transparent ceramic materials and as an anode and sidewall material in aluminum electrolytic cells [3–7]. However, dense materials of stoichiometric composition with high purity characteristics are difficult to fabricate directly from mixtures of individual Al_2O_3 and MgO powders via solid-state technique, since the volume expansion (8%) accompanying the spinellization reaction [8] is detrimental to densification. It is well known that good properties of ceramics are the result of properly chosen formation processing and sintering conditions as well as the favorable properties of starting powder. As previous studies proved [9–11], there is good sintering performance of $MgAl_2O_4$ powders prepared by co-precipitation. However, there is hardly any method in which the MAS powder either commercially obtained or synthesized by following most of the commonly employed synthetic routes is fully densified into components without the help of sintering aids [8].

The effect of sintering aids on the densification of MAS has been reported [12–15]. For example, adding LiF can enhance spinel densification through liquid-phase sintering [12], and adding TiO_2 can improve spinel densification through Al_2O_3 exsolution and TiO_2 dissolution [13]. In ZnO addition, anion vacancy formation can induce spinel densification [14]. Satisfactorily densified spinel products are obtained after rare earth oxides are added. Dy_2O_3 prevents exaggerated grain growth and contributes to densification [15]. The sinterability of high-quality spinel increases in the presence of 5 wt% Y_2O_3 [16,17]. In our previous study [18], 96.17% densification in MAS is obtained using 4 wt% Sc_2O_3 as an additive, suggesting that incorporating Sc^{3+} into the spinel structure improves mass transfer and densification. However, few studies have focused on the effects of the addition of sintering additives on the densification and properties of MAS.

In this study, attempts have been made to study the effect of the method of adding Sc_2O_3 on the densification and properties of $MgAl_2O_4$ powders prepared by co-precipitated method.

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2. Experimental

$MgAl_2O_4$ powders were synthesized by co-precipitated method. The production of stoichiometric $MgAl_2O_4$ powders was described in detail in the study by Zawrah et al. [10]. Mixed solution of stoichiometric magnesium and aluminum chlorides with Mg^{2+}:Al^{3+} molar ratio 1:2 was prepared by dissolving the corresponding amount of magnesium and aluminum chlorides in 80 °C distilled water. After mixing the corresponding chlorides, these solutions were stirred with an excess of NH_4OH solution at pH 9.5–10.5. The gelatinous precipitate was finally dried overnight at 120 °C and then calcined at 1200 °C for 2 h with a heating rate of 3 °C/min. The XRD pattern and SEM micrograph of as-synthesized MAS powder by co-precipitated method was described in our previous study [19]. The mean crystallite size of the synthesized powder is 80 nm. The additions of Sc_2O_3 were carried out via scandium oxide (99.99% pure, SiO_2 < 0.005%, CaO < 0.012%, Fe_2O_3 < 0.05%) and Sc salts (Scandium chloride), respectively. Scandium oxides were directly added to the above $MgAl_2O_4$ powders at 4 wt % Sc_2O_3. Sc salts were introduced to aqueous slurries of $MgAl_2O_4$ powders; the slurries were gelled by adjusting their pH, then dried and recalcined to obtain $MgAl_2O_4$ powders containing 4 wt % Sc_2O_3 as additives. The batches are termed MAS, MSO, and MSL, respectively. All the batches were milled in isopropyl alcohol in a zirconia pot using zirconia grinding media for 3 h. Slurries thus obtained were dried at 120 °C, crushed to break the agglomerate and discs and bars were fabricated under a uniaxial pressure of 200 MPa. The pressed samples were then sintered at 1550 °C, 1600 °C, and 1650 °C for 3 h at peak temperature. Firing was conducted in a program-controlled electric furnace (KSL–1750X) and the heating rate was maintained at 3 °C/min.

Bulk density and apparent porosity of the sintered products were measured by liquid displacement method using Archimedes' principle. XRD (X'Pert Pro, Philips, Eindhoven, Netherlands) was conducted to identify the phase compositions of the fired samples using filtered Cu-$K\alpha$ radiation (1.54056 Å). For $MgAl_2O_4$ spinel, the strongest diffraction peak corresponds to the (311) plane [20]. The lattice parameter a was calculated from the characteristic XRD peaks of the spinel phase using the following equation [21].

$$a = \frac{\lambda}{2\sin\theta}\sqrt{(h^2+k^2+l^2)} \quad [1]$$

where a is the lattice parameter; λ is the radiation wavelength; θ is the Bragg's angle; and h, k, and l are the corresponding Miller indices. Fracture surfaces of dense spinel ceramics were observed with a scanning electron microscope (SEM, Nova NanoSEM 230). Quantitative elemental analysis of the selected grain was done by EDAX. The samples were examined after mounting them on araldite platform, chemically etched (phosphoric acid at 150 °C for 6 min), and gold coated for conductivity [22,23]. Samples chopped into prisms of 5 × 5 × 30 mm were used for the three-point bending test with a span of 16 mm. The flexural strength was measured using a CSS-44100 type universal tester with a loading rate of 0.5 mm/min. Flexural strength (σ) was calculated from the following equation.

$$\sigma = \frac{3PL}{2bh^2} \quad [2]$$

where P, L, b and h represent maximum load of sample damage (N), the length of the support span (mm), width (mm) and thickness (mm), respectively.

3. Results and discussion

X-ray diffraction pattern of MSL batch is shown in Fig. 1. X-ray analysis shows that the presence of spinel and Sc_2O_3 phase for MSL batch and indicates that the phase composition of MSL batch is the same as that of MSO batch.

Fig. 2 shows the increase in the sintered density and the decrease in the apparent porosity of the sintered products termed S_{MAS}, S_{MSL} and S_{MSO} with increasing sintering temperature. These trends can be explained by a large driving force for sintering at the high sintering temperature. Fig. 2(a) shows that the bulk density of the S_{MAS} samples increases from 3.02 g/cm^3 to 3.4 g/cm^3 when the sintering temperature increases from 1550 °C to 1650 °C. Composition without additive results in a low density during sintering at 1550 °C, whereas density increases sharply as sintering temperature increases. However, the bulk density of the S_{MSL} (3.3 g/cm^3) and S_{MSO} (3.15 g/cm^3) samples sintered at 1550 °C is greater than that of S_{MAS} samples sintered at 1550 °C. So Sc_2O_3 can improve the density sharply, and increasing the temperature to 1650 °C yields 99% densification possibly because scandium ion with characteristics similar to aluminum ion can substitute aluminum ion in a spinel due to their similar characteristics. Moreover, incorporating scandium ion into the spinel structure causes strain in the lattice (because of ionic size variation), which improves the diffusion, mass transfer, and densification. MSL batch shows (Fig. 2) much greater sinterability than the MSO batch. Sintering at 1550 °C is insufficient to obtain high densification in samples with Sc_2O_3 additive added in the form of oxide. This result is attributed to the partial poly or missing of sintering additives among $MgAl_2O_4$ powders when sintering additives are directly added in the form of oxide.

Fracture surface profiles of each sample are shown in Figs. 3–5. The microstructures of the additive-free S_{MAS} samples sintered at 1550 °C, 1600 °C, and 1650 °C for 3 h conducted by SEM are shown in Figs. 3(a), 4(a) and 5(a), respectively. It can be seen that the grain size of the spinel increases as sintering temperature increases. As shown in Fig. 5(a), a higher sintering temperature (1650 °C) causes an exaggerated grain growth in final-stage sintering. Although a higher relative density product can be obtained, coarse and non-uniform microstructures adversely influence the flexural strength. Figs. 3(b), 4(b) and 5(b) are the photomicrograph of the S_{MSO} sample with 4 wt % Sc_2O_3 sintered at 1550 °C, 1600 °C, and 1650 °C for 3 h, respectively. Sc_2O_3 has entered in the spinel grains and it is observed as white shiny dots on the grains. The lattice strain generated by replacing Al^{3+} with Sc^{3+} enhances mass transfer, resulting in higher densification. However, a non-uniform

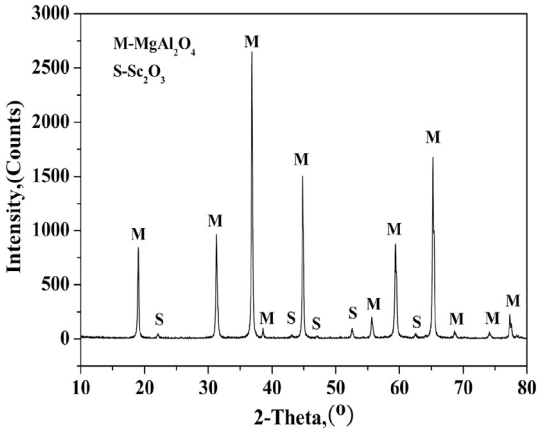

Fig. 1. X-ray analysis of MSL powders.