EFFECT OF Li_5AlO_4 ADDITIONS ON THE SINTERING AND PROPERTIES OF MAGNESIUM ALUMINATE SPINEL

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Abstract

Magnesium aluminate spinel ($MgAl_2O_4$) with high transparency has been wildly used in various applications because of its high mechanical strength and good optical properties. The aim of this work is to evaluate the effects of an additive, Li_5AlO_4, on the sinterability of $MgAl_2O_4$. The concentrations of Li_5AlO_4 focused in this study were 1, 5, and 10 wt%. An aqueous solution of Li_5AlO_4 was prepared by the reaction between high purity lithium nitrate and aluminium nitrate. Under the magnetic stirring at 60°C, $MgAl_2O_4$ powder (Baikalox, S30CR) was homogeneously added into the solution. The obtained viscous slurries were then dried, ground, sieved, and uniaxially pressed under 50 MPa. The green bodies were sintered in air at atemperature of 1600°C. It was found that, for the 1 wt% Li_5AlO_4 added specimens sintered at 1600°C, the relative density reached up to 99.47%. The pre-sintered specimens were subjected tohotisostaticpressingat 1500°C for 1 h. Phase compositions, microstructures, and bulk densities of the sintered and HIP specimens were also characterized and discussed.

Keywords: Magnesium aluminate spinel, Li_5AlO_4, hot isostaticpressing, sintering

Introduction

Nowadays, transparent ceramics are widely used in many applications. They are used as window glass and decoration for the construction industries and are used as lenses for specific work whenoptical properties are necessary. Including military usage as an application for transparent armour, transparent ceramics have been of interestwhen there is a requirement for excellent optical properties, high chemical stability, and good mechanical strength.

Many kinds of transparent ceramics, such as aluminum oxynitride (AlON) (Clay *et al*., 2006; Frage *et al*., 2007), alumina, and yittria alumina garnet (YAG) (Li *et al*., 2012) have been widelydeveloped and used in various engineering fields. One of the most suitable materials for transparent ceramics is magnesium

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aluminate spinel ($MgAl_2O_4$ spinel) because of its high mechanical strength, good optical properties, and beinglighter than metal (Goldstein *et al.*, 2008). $MgAl_2O_4$ spinel has excellent optical properties with useful transmission from about 0.2 nm in the UV through the visible range to about 6.0 nm in the near-IR,while its cubic structure allows it to be made transparent, even at a considerable thickness, while maintaining decent mechanical properties (Dericioglu and Kagawa, 2003; Krell *et al.*, 2010). $MgAl_2O_4$ spinel and sapphire are bothcandidates for transparent armor systems. $MgAl_2O_4$ spinel has the advantage of easier processing and a lower cost than sapphire.

Relatively expensive powders and high finishing costs prevent the wide-spread use of sapphire. The present research investigated the use of commercial spinel powder as the primary component in the starting powders and hypothesized thata sintering additive, such as lithium aluminate (Li_5AlO_4) with a melting point of 1055°C would aid in densification via transient liquid phase sintering. A beneficial side effect of using lithium aluminate as a transient liquid phase is that it can be removed from the sintered specimens by evaporation at a higher temperature (over 1300°C) due to its high vapor pressure. The aim of this work is to evaluate the effect of Li_5AlO_4 as a sintering additive on the sinterability of $MgAl_2O_4$ spinel.

Materials and Methods

Preparation of Specimens

Various fabrication technologies were developed (Goldstein *et al.*, 2009). In this paper we used 2 stages of heat treatment, air sintering and hot isostatic pressing (HIP) (Krell *et al.*, 2010; Benameur *et al.*, 2011). An aqueous solution of Li_5AlO_4 was prepared by a reaction between high purity lithium nitrate (Fluka 98.0%, Sigma-Aldrich Corp., St. Louis, MO, USA) and aluminium nitrate nanohydrate (QRëCTM grade AR) that wereused as starting materials for the sintering additives. An aqueous solution of nitrate precursors was prepared by magnetic stirring. The concentrations of Li_5AlO_4 to the spinel powder in this study were 1, 5, and 10 wt%. Commercial $MgAl_2O_4$ spinel powder (SCR30, 99.0%, Baikarox) was homogeneously added into the prepared nitrate solution. The viscous slurries that were obtained had been heated andstirred until dried at about 100°C. The mixtures were then dried again at 100°C in an oven, ground, and sieved through a 100 mesh. The sieved powders were uniaxially pressed at 50 MPa into pellet shapes with a 2.5 mm in diameter. The pellet green bodies were sintered in an electrical box furnace at the temperature range 1100-1600°C for 2 h. After the air sintering stage,HIP was performed at 1500°C/1 h (Ar, 200 MPa). The flow chart of the preparation is shown in Figure 1.

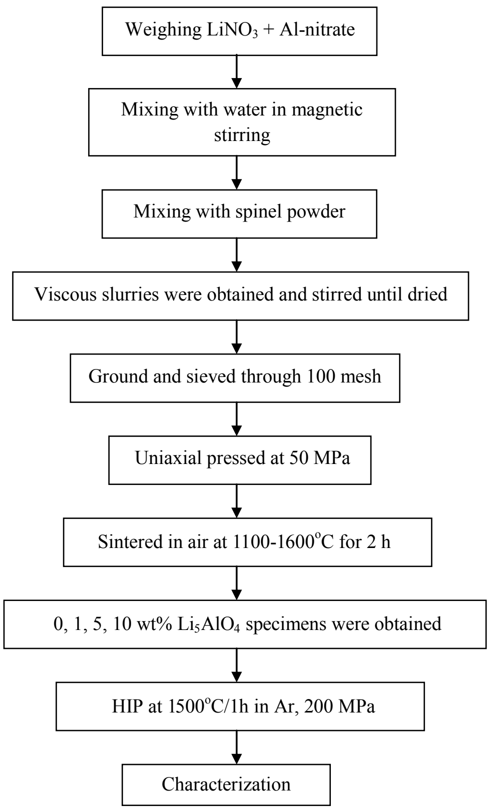

Figure 1. The flow chart of preparations

Characterization

The bulk density and water absorption were measured by the standard method according to the American Society of Testing and Materials (ASTM C373-88 (2006)). Shrinkage and weight loss were measuredby length and weight before and after firing.The crystalline phases were investigated by X-ray diffraction (XRD) (D8-Advance, Bruker Corp., Billerica, MA, USA)using Cu-Kα radiation, and the diffraction data were collected over the 2θ range from 5 to 60^o with a step size of 0.02^o. The microstructures were investigated by optical microscope (Olympus BX60M, Olympus Corp., Tokyo, Japan) and scanning electron microscopy (SEM)(JSM 6480 LV, JEOL Ltd., Tokyo, Japan).

Results and Discussion

The firing shrinkage of 4 different concentrations of Li_5AlO_4 is shown in Figure 2. The firing shrinkage in percentage increased with the increased temperature. The sample without the additive has higher shrinkage than that of the other concentrations.

The water absorption of the specimens after firing from 1100 to 1600^{o}C is shown in Figure 3. It indicated that water absorption was less than 0.03% in the 1 wt% added specimen.

In addition, Figure 4 presents the percentage of weight loss of the $MgAl_2O_4$ spinel specimens after sintering which are dependent on the temperature and concentration of Li_5AlO_4 added.

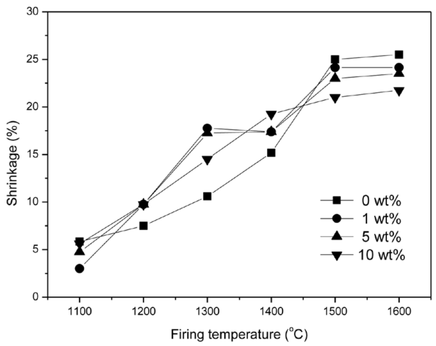

Figure 2. Effect of Li_5AlO_4 additions on firing shrinkage of $MgAl_2O_4$ spinel

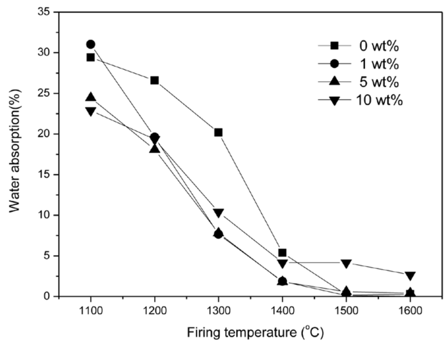

Figure 3. Effect of Li_5AlO_4 additions on water absorption of specimens

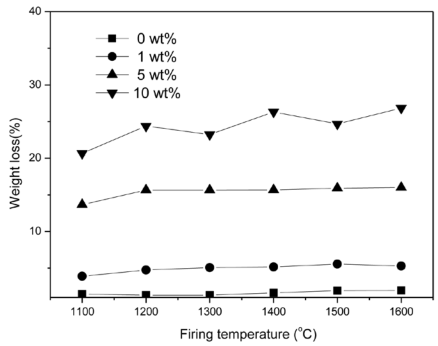

Figure 4. Effect of Li_5AlO_4 additions on weight loss

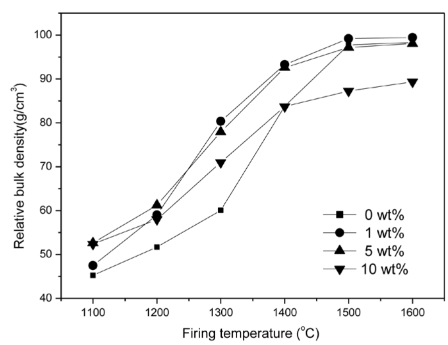

Figure 5. Effect of Li_5AlO_4 additions on bulk density

The bulk density of the samples is shown in Figure 5. The bulk density increased when the temperature increased. The highest bulk density was found in the 1 wt% added, which reached up to 99.47% when sintered at 1600°C. However, all of the specimens were still not transparent.

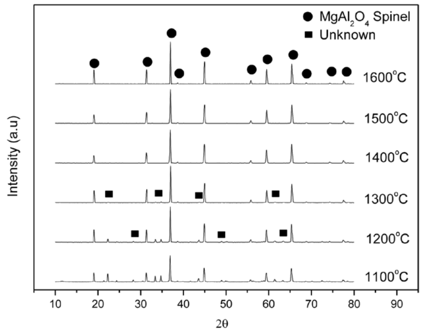

Figure 6. XRD patterns of 10 wt% Li_5AlO_4 specimens sintered at temperature range of 1100-1600°C

The XRD patterns of the crystalline phases ofthe specimens are shown in Figure 6. In the temperature range between 1100-1300°C, there are 2 phases, $MgAl_2O_4$ spinel and an unknown phase found as a secondary phase. At the higher temperature range of 1400-1600°C, the secondary phase has disappeared due to the higher sintering temperature. Only 1 phase, $MgAl_2O_4$ spinel, remained. According to Figure 5, using Li_5AlO_4 as the sintering additive can increase the bulk density and it can be eliminated at over 1400°C.

Figure 7, from left to right, presents the microstructure of the specimens sintered at 1600°C (a) without additive, (b) 1 wt%, (c) 5 wt%, and (d) 10 wt% of the Li_5AlO_4 additions, respectively. At 1600°C, a suitable

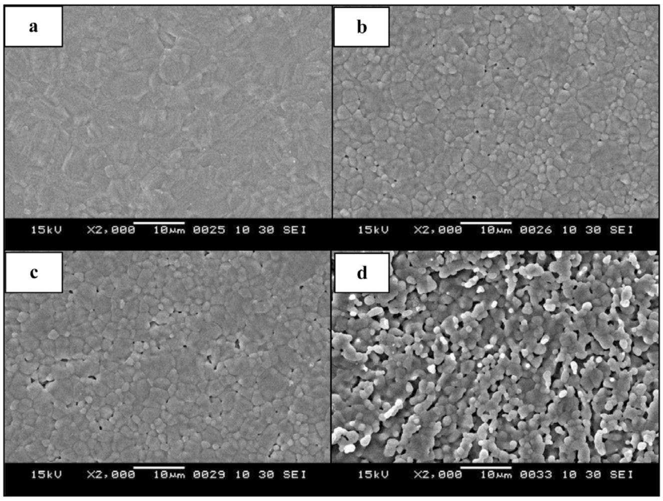

Figure 7. SEM micrographs of spinel specimens after sintering at 1600°C; (a) without additive, (b) 1 wt%, (c) 5 wt%, (d) 10 wt% of Li_5AlO_4

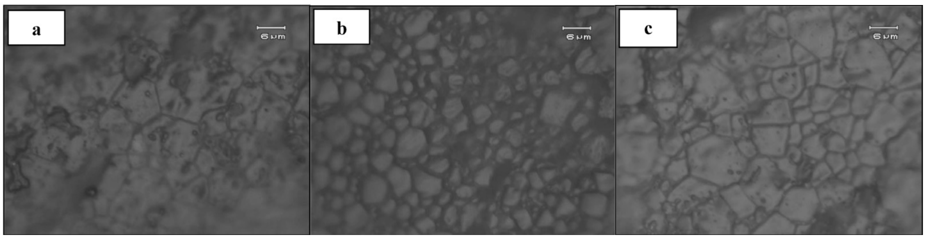

Figure 8. Optical micrographs of spinel specimens after sintering at 1600°C; (a) without additive, (b) 1 wt%, (c) 5 wt%

concentration of Li_5AlO_4 was 1 wt% that not only decreased the grain size, but also increased the densification. A 1 wt% addition was related to the result of the water absorption in Figure 3. And in Figure 7(d) the highestaddition made an increase in porosity because of the evaporation of the lithium compound.

Conclusions

In summary, the effect of the Li_5AlO_4 additions on the sintering of $MgAl_2O_4$ spinel showed that a small grain size, low firing shrinkage, and high densification at 1600°C were obtained by using 1 wt% of Li_5AlO_4 addition. On the other hand, weight loss was increased.

Acknowledgments

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