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Effect of polymorphism of Al_2O_3 on the sintering and microstructure of transparent $MgAl_2O_4$ ceramics

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ABSTRACT

Transparent $MgAl_2O_4$ ceramics were fabricated by reactive sintering in air followed by hot isostatic press treatment using commercial Al_2O_3 powder (γ-Al_2O_3 or α-Al_2O_3) and MgO powder as raw materials. The densification rate, microstructure and optical properties of the ceramics were investigated. Densification temperature of the sample from γ-Al_2O_3/MgO was lower than that from α-Al_2O_3/MgO. However, in-line transmission (2 mm thick) of the sample from α-Al_2O_3/MgO at the wavelength of 600 nm and 1100 nm were respectively 77.7% and 84.3%, higher than those (66.7%, 81.4%) of the sample from γ-Al_2O_3/MgO. SEM observation revealed that the sample from α-Al_2O_3/MgO exhibited a homogeneous and pore-free microstructure, while, the sample from γ-Al_2O_3/MgO showed an apparent bimodal microstructure containing pores.

1. Introduction

Since the first appearance in the late 1960s [1], transparent magnesium aluminate spinel ($MgAl_2O_4$) ceramics have received a great deal of attention due to the excellent mechanical properties and high optical transmission (0.2–6 μm) [2,3]. Over the last ten years, with the improvement of fabrication technology and raw powder quality, $MgAl_2O_4$ ceramics with high optical quality and large size have been produced, which renders them suitable for transparent armor, domes and windows for ultraviolet (UV), visible (VIS), and infrared (IR) application [4–6].

Most of the transparent $MgAl_2O_4$ ceramics were produced by hot pressing (HP) [7,8], HP/HIP (Hot Isostatic Press) [9,10] or spark plasma sintering (SPS) [11–13] using $MgAl_2O_4$ powders doped with LiF or other sintering aids [1,7,14]. The powder characteristics including purity, particle size, size distribution, morphology obviously affect sintering process and properties of the ceramics. The limited availability and fairly high cost of high quality raw powder have restricted the widely application of transparent $MgAl_2O_4$ ceramics. In fact, reactive sintering using widely produced Al_2O_3 and MgO powders is a feasible method to prepare transparent $MgAl_2O_4$ ceramics. A few articles [15–17] have reported the production of transparent $MgAl_2O_4$ ceramics by solid-state reactive sintering and almost all of them choose α-Al_2O_3 as raw materials. It is known that γ-Al_2O_3 owns high activity which can promote the reaction and densification process, but it is barely reported to be used in producing transparent $MgAl_2O_4$ ceramics.

In the present work, transparent $MgAl_2O_4$ ceramics were fabricated by reactive sintering in air and further by HIPing, starting from commercial Al_2O_3 powder (γ-Al_2O_3 or α-Al_2O_3) and MgO powder. The effects of polymorphism of Al_2O_3 on the densification rate, microstructure and optical properties were investigated.

2. Experimental procedures

The raw powders were high-purity γ-Al_2O_3 (purity, 99.99%; particle size, 100 nm), α-Al_2O_3 (purity, 99.99%; particle size, 150 nm) and MgO (purity, 99.99%; particle size, 150 nm). The combinations of starting powders were γ-Al_2O_3 with MgO (γ-Al_2O_3/MgO) and α-Al_2O_3 with MgO (α-Al_2O_3/MgO). As the powders were easy bibulous, they were dried at 120 °C for 12 h before

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weighed. The powders were weighted according to the stoichiometry of $MgAl_2O_4$, and then mixed by ball milling for 12 h using ethanol as medium. The mixtures were dried at 60 °C for 12 h and then sieved through 80-mesh screen. After calcined at 800 °C for 6 h to remove the organic component, the powders were dry pressed at about 20 MPa, and then further cold isostatically pressed at 200 MPa. Relative density of the pellet from γ-Al_2O_3/MgO is about 35%, much lower than that from α-Al_2O_3/MgO (~50%). All pellets were pre-sintered in air up to a relative density of 95–98% followed by HIPing to obtain transparent samples. Finally, the resultant ceramics were double-sides polished for further tests.

The phase compositions of samples pre-sintered at different temperatures were analyzed by X-ray diffraction (XRD, D8, Bruker, Germany) in the range of $2\theta = 10–70°$. The shrinkage behavior of the green bodies was measured by a thermal dilatometer (DIL, 402E, Netzsch, Germany) and relative densities were measured by the Archimedes method. Thermally etched surfaces of the pre-sintered and HIPed samples were observed with Scanning Electron Microscopy (SEM, JSM-6390, JEOL, Japan). The in-line transmittance was measured by a UV–VIS–NIR spectrometer (Carry 5000 spectrophotometer, Varian, USA).

3. Results and discussions

The XRD patterns of the samples pre-sintered from 800 to 1200 °C are shown in Fig. 1. For the reason of peaks of γ-Al_2O_3 and $MgAl_2O_4$ overlap in XRD patterns, it's difficult to estimate the reaction from Fig. 1b alone. XRD patterns of γ-Al_2O_3 calcined between 800 and 1200 °C (Fig. 1a) were also measured for comparison. With the rise of temperature, the crystalline of γ-Al_2O_3 increased, leading to the increase of intensity of the diffraction peaks. γ-Al_2O_3 transformed to α-Al_2O_3 at 1100–1200 °C. For the mixture of γ-Al_2O_3/MgO, γ-Al_2O_3 firstly reacted with MgO directly which started at 1000 °C, when the temperature was above 1100 °C, the unconsumed γ-Al_2O_3 transformed to α-Al_2O_3 (Fig. 1b). For the sample from α-Al_2O_3/MgO, the onset of the reaction was located at 900 °C (Fig. 1c). It seems that the reactivity of α-Al_2O_3/MgO was a little higher than that of γ-Al_2O_3/MgO. This may be caused by the high relative density (50%) and large contact area between Al_2O_3 and MgO particles in the green body from α-Al_2O_3/MgO. With further increasing the temperature to 1200 °C, all the peaks of the samples from γ-Al_2O_3/MgO and α-Al_2O_3/MgO were indexed to $MgAl_2O_4$ (PDF#82-2424) and no other impurity was found.

Fig. 2 shows the shrinkage curves of the green bodies between 20 °C and 1650 °C. For the sample from γ-Al_2O_3/MgO, its shrinkage started at ~1000 °C and ended at ~1400 °C without any expansion (Fig. 2a). Generally, 5%–8% volume expansion will happen during the reaction process, because of the different densities of MgO (3.58 g/cm^3), Al_2O_3 (3.98 g/cm^3), and $MgAl_2O_4$ (3.58 g/cm^3). The reason why no expansion happened in the present case may include two aspects: one is that the expansion by reaction was lower than the shrinkage by sintering; the other is the quite low relative density of the green body from γ-Al_2O_3/MgO which can offset the expansion caused by reaction. In contrast, the shrinkage of the sample from α-Al_2O_3/MgO started at 1400 °C and it demonstrated a slight expansion between 1100 °C and 1300 °C (Fig. 2b) which was caused by the reaction of Al_2O_3 and MgO.

The relative density and grain size of the pre-sintered samples as a function of sintering temperature are shown in Fig. 3. For the sample from γ-Al_2O_3/MgO, the relative density increased rapidly to 98.5% with the temperature rising to 1400 °C, then showed little change when the temperature continued to rise (Fig. 3a), it is corresponding to the shrinkage curve (Fig. 2a). In contrast, the grain size of the sample grew slowly before 1400 °C, and when the temperature was above 1400 °C, the rapid grain growth happened

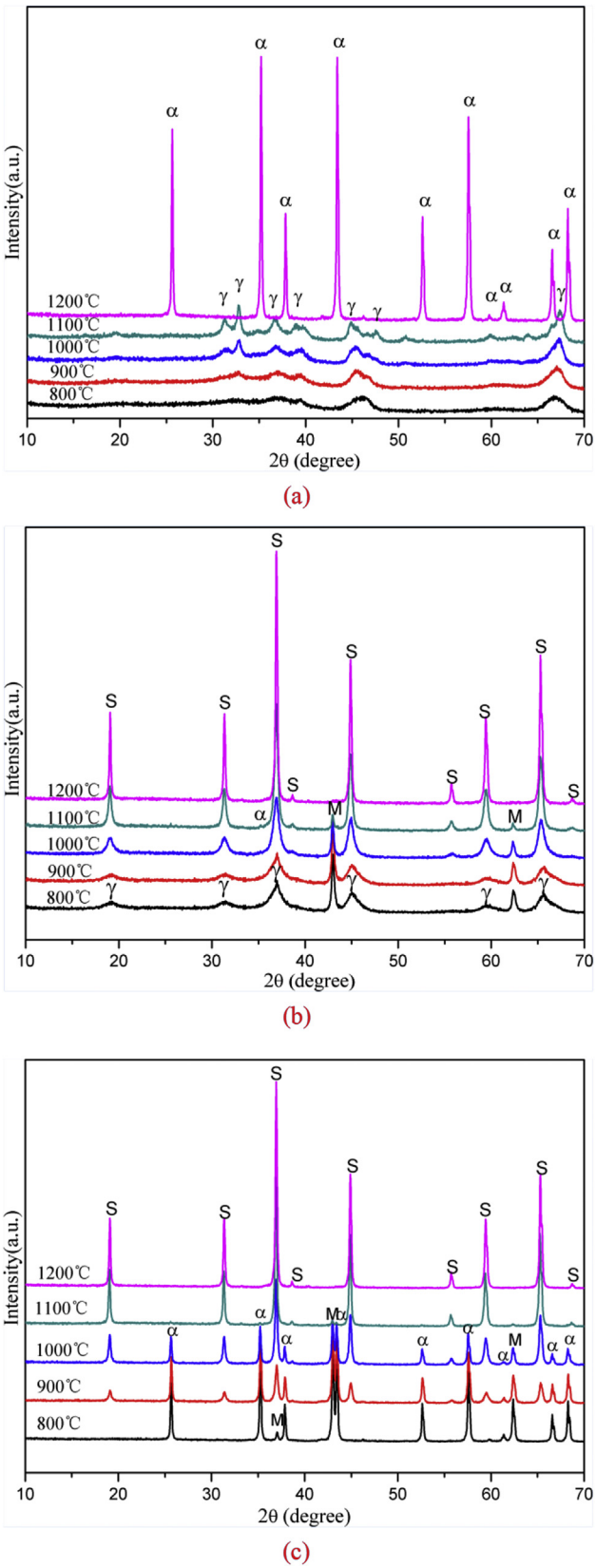

Fig. 1. X-ray patterns of the samples from (a) γ-Al_2O_3, (b) γ-Al_2O_3/MgO and (c) α-Al_2O_3/MgO pre-sintered at different temperatures. (γ: γ-Al_2O_3, α: α-Al_2O_3, M: MgO, S: $MgAl_2O_4$).

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