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Microstructure and properties of transparent $MgAl_2O_4$ ceramic fabricated by aqueous gelcasting

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ABSTRACT

A nontoxic, water-soluble copolymer consisting of isobutylene and maleic anhydride (PIBM) was used as both dispersant and gelling agent to mold $MgAl_2O_4$ green body by gelcasting at room temperature in air. In this paper, $MgAl_2O_4$ slurries with solid loadings from 43 vol% to 50 vol% were prepared by adding PIBM. The rheological properties of the slurries were investigated. As the solid loadings increased from 43 vol% to 50 vol%, the linear shrinkage in the drying and pre-sintering process decreased from 6.9% to 2.8% and from 16.0% to 14.7%, respectively. The bending strength of the green body with 50 vol% solid loading can reach 2.62 MPa. The in-line transmission of the $MgAl_2O_4$ ceramics gradually increased from 61% to 86.9% (1100 nm) with the solid loadings increasing.

1. Introduction

Magnesium aluminate spinel ($MgAl_2O_4$) transparent ceramic has various potential applications such as high-energy laser windows, lightweight armor, and transparent domes due to its high hardness, well thermal shock resistance, high chemical resistance, and broad transmittance range from UV–Visible to mid-infrared wavelength [1–4]. The traditional routes to molding transparent ceramic green body include cold isostatic pressing, injection molding, and slip casting [5–8]. Unlike these methods, gelcasting is a novel near net technique used for shaping advanced ceramics. Gelcasting methods have various advantages over other methods, such as lower fabrication costs, higher green body strength, and flexibility for preparation of large ceramics with complex shapes [9–12]. However, up to now, there have been very few reports on fabrication of $MgAl_2O_4$ transparent ceramic by gelcasting. A. Krell et al. [13] reported the fabrication of $MgAl_2O_4$ spinel transparent ceramic using nano-scaled spinel powder as the raw materials. High transparency spinel ceramics with fine grain size and good mechanical performance had been fabricated successfully. I. Ganesh et al. [14] reported the traditional gel system of methacrylamide (MAM), methylenebisacrylamide (MBAM) and n-vinylpyrrolidinone (NVP) to fabricate dense $MgAl_2O_4$ spinel ceramic. In their work, six kinds of organics were used. In gelcasting, to minimize defects such as deforming and cracking during the drying and pre-sintering process, it is extremely important to prepare stable slurry with high solid loadings [15,16].

Recently, a novel spinel gel system using a copolymer of isobutylene and maleic anhydride (PIBM) at room temperature in air was developed [17]. Unlike the traditional gel system, PIBM functioned both as the dispersant and the gelling agent, and no more other additives were needed. This new gel system greatly simplified the gelcasting process [18–23]. In this paper, gelcasting process of $MgAl_2O_4$ green body with different solid loadings was investigated. Highly transparent $MgAl_2O_4$ ceramics were fabricated by vacuum sintering and hot isostatic pressing (HIP) post-treatment.

2. Material and methods

A commercial $MgAl_2O_4$ powder (TSP-20, Taimei, Nagoya, Japan), with an average particle size of 0.27 μm and BET surface area of 18.9 m^2/g, was used as starting material. A water-soluble co-

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polymer named PIBM (Isobam600AF (Ib600) and Isobam104 (Ib104), Kuraray, Osaka, Japan) served as both dispersant and gelling agent. First, an appropriate amount of PIBM containing different concentrations of Ib600 and Ib104 was dissolved in deionized water, and then $MgAl_2O_4$ powder was gradually added. Then the mixed slurries were ball-milled for 1 h. Then, the slurries were degassed in a vacuum mixer (ARV-310, Thinky, Tokyo, Japan) and cast into molds at room temperature in air. After 12 h, the wet $MgAl_2O_4$ green bodies were demolded and dried at room temperature. Then the green bodies were debindered at 800 °C for 2 h in a muffle furnace with a heating rate of 1.0 °C/min. Finally, all the samples were pre-sintered in vacuum at 1600 °C for 6 h and then HIPed at 1800 °C for 4 h.

The rheological behaviors of the $MgAl_2O_4$ slurries were characterized by a stress-controlled rheometer (physical MCR301, Anton Paar, Graz, Austria) at a shear rate ranging from 0.01 to 1000 s^{-1} at 25 °C. The gelling behaviors (storage modulus G') of the slurries were also tested using the rheometer in oscillatory mode. The microstructures of the green bodies with different solid loadings were observed using field emission scanning electron microscopy (FE-SEM, SUPRA55, Zeiss, Germany). The bending strength of the green bodies was tested using three-point bending on bars of 10 mm × 10 mm × 50 mm at a crosshead speed of 0.5 mm/min (Instron5566, Norwood, MA, U.S.). The bulk density of the debindered bodies was measured using Archimedes' method. Linear shrinkage of the debindered and pre-sintered $MgAl_2O_4$ ceramic was tested by measuring variations in the length with Vernier calipers. The fracture surfaces of the final spinel ceramics were observed by scanning electron microscopy (SEM, JSM-6360LV, JEOL, Tokyo, Japan). The in-line transmittance of the $MgAl_2O_4$ ceramics with a thickness of 1.0 mm was measured using a UV/VIS/NIR spectrometer (Lambda 950, Perkin–Elmer, Waltham, U.K.).

3. Results and discussion

Fig. 1(a) shows rheological properties of the $MgAl_2O_4$ slurries with different solid loadings and PIBM contents. All the $MgAl_2O_4$ slurries showed shear-thinning character with the increasing of shear rate. When the solid loading of the slurry was 47 vol%, the viscosity of the slurries increased with the addition of larger amounts of Ib104, which is due to the insufficient dissolution of Ib104 in water or the incompletely extended "brush" of the Ib104 molecular chain [19]. As shown in Fig. 1(b), results indicated that the gelation ability of Ib104 was stronger than that of Ib600. The molecular chain of Ib104 is longer than that of Ib600, which would increases the opportunity of ionic interaction between Ib600 and −OH group on the spinel particles. It also can be seen from the Fig.1(b) that the G' of the slurry will be too low for the following operation, if only Ib 600 is used for the slurry preparation [17]. Considering both dispersing ability and gelling rate, in this work, spinel slurry with 50 vol % solid loading was prepared using 0.1 wt % Ib 104 and 0.7 wt % Ib 600.

Fig. 2 shows microstructures of the fracture surfaces of the $MgAl_2O_4$ green bodies with different solid loadings (used 0.7 wt% Ib600 and 0.1 wt% Ib104). Results showed the $MgAl_2O_4$ powders to be dispersed homogeneously through the interspaces, and the green body became denser at greater solid loading.

Fig. 3 shows the effect of solid loadings on properties of the $MgAl_2O_4$ bodies by using 0.7 wt% Ib600 and 0.1 wt% Ib104. The bending strength of green bodies is shown in Fig. 3(a). Higher solid loading of the $MgAl_2O_4$ slurries resulted in stronger green bodies. The highest bending strength of the green bodies, those prepared from slurry with 50 vol% solid loading and 0.7 wt% Ib600 and 0.1 wt % Ib104 was found to reach 2.62 MPa. As shown in Fig. 3(b), less porous, denser $MgAl_2O_4$ green bodies were be obtained by increasing the solid loading, which is consistent with the microstructure in Fig. 2. Fig. 3(c) demonstrates that in both the drying and pre-sintering processes, a smaller shrinkage ratio of the green bodies could be produced in slurries with higher solid loading. All of these were beneficial for the manufacturing of large size ceramic parts.

Fig. 4 (inset) shows the photographs of transparent $MgAl_2O_4$ ceramics samples with different solid loadings (used 0.7 wt% Ib600 and 0.1 wt% Ib104). The ceramic fabricated from slurry with 43 vol% solid loading was translucent. As the solid loadings increased, the optical quality of the ceramics increased as well. Fig. 4 shows the in-line transmittance of the $MgAl_2O_4$ transparent ceramics (1 mm thick). Likewise, the in-line transmittance of the spinel ceramics increased as the solid loadings of the slurries increased. The highest transmittance was 86.9% at 1100 nm when the solid loading was 50 vol%. This higher relative density (99.5%) and smaller defect size were the main reasons for the highest transmittance. The density results of the as-sintered ceramics were shown in Table 1. It can be found that with increasing the solid loadings, the measured density of the pre-sintered ceramics increased. However, after HIP treatment, all the ceramics were almost fully densified. There is no difference can be found from the density measurement results. The fracture surfaces of the $MgAl_2O_4$ ceramics prepared from slurry with the solid loadings from 43 vol% to 50 vol% are shown in Fig. 5. All the slurries were prepared by using 0.7 wt% Ib600 and 0.1 wt%

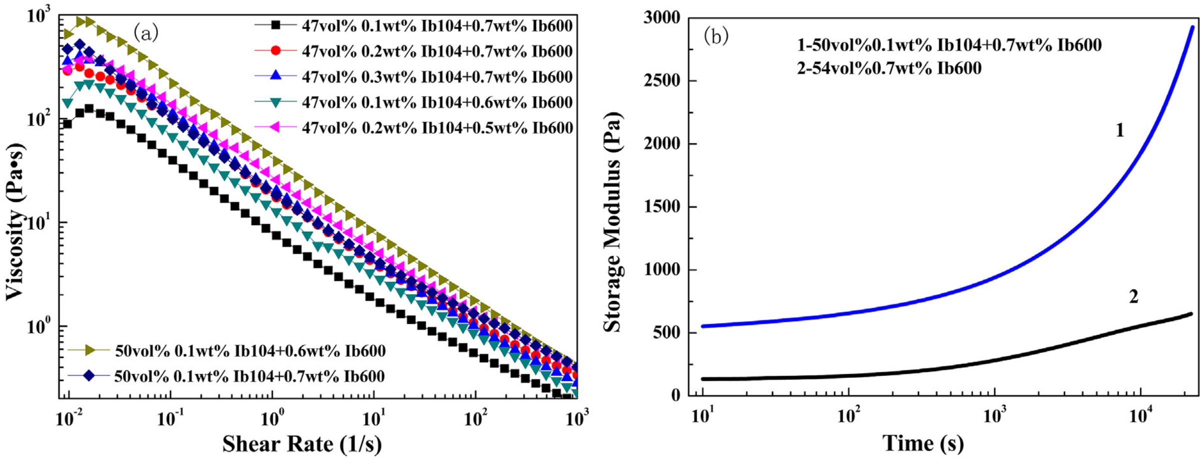

Fig. 1. (a) Viscosity of slurries with different concentrations of PIBM (Ib600 and Ib104). (b) Storage modulus (G') of slurries at room temperature.