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Fabrication of transparent $MgAl_2O_4$ spinel via spray freeze drying of microfluidized slurry

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A R T I C L E I N F O

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A B S T R A C T

Spherical granules were prepared from a monodispersed slurry by combining the microfluidization (MF) method and the spray freeze-drying (SFD) process. Starting with the prepared granules, transparent $MgAl_2O_4$ ceramics were fabricated through pressureless sintering followed by hot isostatic pressing. A comparison with a polydispersed slurry prepared by the ball-milling method showed successful fabrication of a mono-dispersed state by microfluidization method, and 80% visible in-line transmittance was obtained at a 600-nm wavelength from a process starting with a monodispersed slurry of low solid content. Microstructural analysis of the green bodies, the pre-sintered bodies, and the hot isostatic pressed bodies of the prepared $MgAl_2O_4$ ceramics revealed that the slurry dispersion should be controlled to a high level in order to suppress scattering sources such as pores and microcracks, which affect the in-line transmittance of visible light.

1. Introduction

Spinel $MgAl_2O_4$ is a solid solution of MgO and Al_2O_3. It does not have birefringence owing to its cubic crystal structure, and thus $MgAl_2O_4$ has intrinsic transparency if there are no scattering sources within. The refractive index of $MgAl_2O_4$ in the visible light range (400–800 nm wavelength) is approximately 1.72 and the corresponding theoretical light transmission is 86.9% [1,2]. In terms of its mechanical properties, the flexural strength and hardness are in the range of 150–300 MPa and 12–16 GPa, respectively, depending on the grain size and the processing route [2–6]. $MgAl_2O_4$ has a slightly longer cut-off wavelength in the mid-infrared (IR) range than its competitors, AlON and sapphire, and so it is considered the most appropriate material for protective domes of multimode seekers under high-velocity conditions [7].

Fabrication of transparent polycrystalline $MgAl_2O_4$ is a cutting-edge technology requiring delicate green-body compaction and a controlled sintering technique. For highly transparent $MgAl_2O_4$, the total volume porosity should be strictly controlled, and the number of nano pores 40–80 nm in size (one-tenth the visible wavelength range) should also be minimized according to the Mie scattering theory [8]. Thus, $MgAl_2O_4$ nanopowder is widely used as a raw material to achieve zero porosity and inhibit grain growth at lowering sintering temperatures [9–11].

Typically, many strong agglomerates are incorporated in the as-synthesized nanopowder. Sometimes the agglomerates are so hard that they cannot be broken, even when the nanopowder is compacted into a green body under very high pressure (e.g., hundreds of megapascals) [12]. When strong agglomerates made by conventional spray drying are used for the green-body shaping, crack-like grain boundaries can form after sintering at high temperatures [13]. Dericioglu et al. and Glide et al. reported that microcracks in sintered $MgAl_2O_4$ degrade the light transmittance largely because they act as scattering paths of the incident light [14,15]. Therefore, in order to avoid the development of such microcracks, it might be necessary to remove the strong agglomerates in the starting nanopowder.

Spray freeze drying (SFD), also known as freeze granulation (FG), is a recently developed method for making soft and agglomerate-free granules of nanopowder [12,16]. Once a well-dispersed slurry of ceramic nanopowder is prepared by an effective disintegrating process, it is directly sprayed into liquid nitrogen to inhibit the strong agglomeration of individual nanoparticles. Moritz et al. [16] reported that SFD granules are at least 10 times softer than thermal spray-dried granules. Binner et al. [12] reported that SFD granules are soft enough to be broken completely under pressure and that no trace of the granule shape (i.e., microcracks) remains in the green body. Therefore, the SFD technique is considered a desirable process for manufacturing transparent ceramics without microcracks. SFD has been used to fabricate

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transparent ceramics such as Al_2O_3, Nd:YAG, and Co^{2+}:$MgAl_2O_4$ [17–19]. However, detailed process parameters to optimize the transparency of $MgAl_2O_4$ ceramics have not yet been reported.

We previously reported that the microfluidization method is a highly effective technique for disintegrating agglomerates of nanopowders into individual particles in a slurry [20]. Therefore, combining SFD with microfluidization would inhibit the formation of microcracks when the granules are pressed into a green body under a certain pressure.

In this study, the SFD method was combined with the microfluidization technique to fabricate a transparent $MgAl_2O_4$ spinel ceramic. The microstructural characteristics of the green bodies, the sintered bodies, and the resulting transparent bodies were analyzed. The in-line transmittance of $MgAl_2O_4$ subjected to hot isostatic pressing (HIP) is then discussed in view of the microstructural differences resulting from the different processing parameters.

2. Experimental procedure

A commercial $MgAl_2O_4$ nanopowder (S30CR, Baikowski, France) was used as the starting material. The primary particle size was reported to be 55 nm via direct observation [21]. The nanopowder was mixed with deionized water (18.5 MΩ), and 4 wt% of ammonium polyacrylic acid (NH_4PAA, R.T. Vanderbilt, Norwalk, CT, USA) was used as a dispersant. The solid loading of $MgAl_2O_4$ in the slurry was set as 10 and 20 vol% to check the effect of solid loading on the microstructure and the in-line transmittance. The slurry was ball milled in a Nalgene bottle with high-purity alumina balls at 80 rpm for 12 h. It was then passed through a narrow channel with a diameter of 75 μm in the microfluidizer (NLM-100, Ilshin Autoclave, Korea) five times under a pressure of 100 MPa.

Both the ball-milled and the microfluidized slurries were directly sprayed by a hand-sprayer into a Dewar flask filled with liquid nitrogen. The frozen granules were recovered and dried in a freeze-dryer (TFD series, Ilshin Lab Co., Korea) for 48 h. The recovered granules were uniaxially pressed into button shapes, followed by cold isostatic pressing (CIP) under 200 MPa for 5 min. The green bodies were sintered under air atmosphere at 1400–1600 °C for 2 h to analyze the sintering behavior and to remove open pores prior to HIP. The selected pre-sintered bodies were subjected to HIP in a graphite-structured heating system under a 180 MPa Ar atmosphere at 1450 °C for 5 h to obtain transparent $MgAl_2O_4$.

The shapes of the freeze-dried granules, the fracture surfaces of the green compacts, and the polished surfaces of the sintered specimens were observed by a scanning electron microscope (SEM; JSM-5800, JEOL, Tokyo, Japan). The pore-size distributions of the green compacts were measured by a mercury porosimeter (Autopore IV 9510, Micromeritics, GA, USA) to check the homogeneity of the green body. The densities of the green and sintered bodies were evaluated by Archimedes' principle (ASTM 792), assuming that the theoretical density of $MgAl_2O_4$ is 3.578 g/cm^3. For the green compacts, heating at 800 °C for 2 h in air was performed before the porosity and density measurements. The in-line transmittance of polished 1-mm-thick samples was measured by ultraviolet–visible (UV–vis) spectrometer (Cary 5000 spectrometer; Varian Inc., Palo Alto, CA).

3. Results and discussion

Fig. 1 shows the particle-size distribution of as-received raw powder, the ball-milled slurry (denoted as BM20), and the microfluidized slurries (denoted as MF10 and MF20). In the case of as-received powder, agglomerates exceeding 1 μm in size were dominant. In the case of BM20, both the size and the number of agglomerates were reduced from the initial state, but a large number of agglomerates remained in comparison to the primary particle size. On the other hand, the microfluidized slurries, MF10 and MF20, showed narrow unimodal size distribution, regardless of the volumetric content. In the particle-size distribution diagram, it was confirmed that the nanoparticle dispersion was acceptable: the median particle size (D_{50}) was 150 nm and the maximum cutoff size was only 230 nm. We reported similar results in our previous paper [20]. In this study, we again confirmed that the microfluidization method had a significant effect on the disintegration of nanoparticle agglomerates.

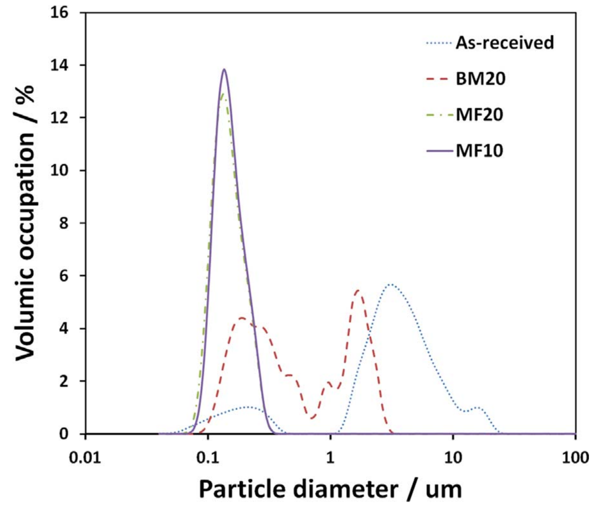

Fig. 1. Particle-size distribution of $MgAl_2O_4$ nanopowder after different disintegration conditions. (BM20: ball-milled 20 vol%, MF20: microfluidized 20 vol%, MF10: microfluidized 10 vol%.)

Fig. 2 shows SEM images of the shapes of the granules formed by SPD. The overall shape and size of the freeze-dried granules, seen in Fig. 2(a), was spherical, and the average size of the granules, averaging 100 different granules, was 48.3 ± 18.5 μm. Collapsed granules were observed in several places, which seems to be a result of the softness of the freeze-dried granules rather than a problem with the granulation process. Fig. 2(b) and (c) are typical representations of granules prepared from the 10 vol% and 20 vol% $MgAl_2O_4$ nanopowders, respectively. Both granules show a porous spherical shape, but the 10 vol% granules are more porous because of the low solid loading, which is consistent with the result of Binner et al. [12], who reported freeze granulation of ZrO_2 nanoparticles with different solid loading.

The fracture surfaces of the green compacts are shown in Fig. 3. As shown in Fig. 3(a), the fracture surface of the green compact fabricated from BM20 granules exhibits a stepped shape, indicating that the granule boundary was not completely crushed under high-pressure CIP conditions. It was difficult to find such remaining granule boundaries at the fracture surface of the green bodies from both MF20 and MF10 granules subjected to CIP. However, in Fig. 3(b), a few of regions with higher densities than those of the surrounding regions in the fracture surface of the MF20 green body were observed, which seemed to be agglomerates. In Fig. 3(c), MF10 not only had no granule boundaries but also showed a smooth fracture surface as compared to MF20.

Isobe et al. [22] experimentally proved that the agglomeration of Al_2O_3 nanoparticles inevitably occurs when the solids content in the slurry is increased, according to the separation distance between particles (SDP) theory [23]. The SDP theory indicates that there exists a threshold amount at which agglomeration begins to take place, which is strongly dependent on the particle size. For example, in the case of 43 nm particles, agglomeration starts when the content exceeds 15 vol%, whereas no agglomeration occurs even when the content of 570 nm particles reaches 50 vol%. Because it has been reported that the zeta potential value of $MgAl_2O_4$ almost coincides with that of Al_2O_3 throughout the pH range [22,24,25], it is reasonable to apply the same SDP theory used by Isobe et al. [22] to the current study. Therefore, when the SDP theory was applied to $MgAl_2O_4$ nanopowder particles 55 nm in size, 18 vol% was calculated as a threshold amount at which agglomeration starts in earnest.