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In-situ Fabrication of Transparent Magnesium Aluminate Spinel by Spark Plasma Sintering

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ABSTRACT

In this research, transparent polycrystalline spinel ceramic was fabricated without any sintering aids and by performing spark plasma sintering method on a mixture of Al_2O_3 and MgO powders for only 10 min soak at 1250°C. Densification, microstructure and optical transparency of spinel were examined. The result indicate that spinel exhibits an in-line transmission of 55% for an IR-wavelength of 4.7µm and high hardness value of 2040 HV.

1. INTRODUCTION

Transparent polycrystalline ceramics such as Al_2O_3 [1-4], Y_2O_3 [5-7], MgO [8, 9], $Y_3Al_5O_{12}$ (YAG) [10-13] and $MgAl_2O_4$ [14-16] have recently acquired a high degree of research interest for various optical applications due to their reduced cost, and improved mechanical and optical properties. Spinel has a distinct transmission advantage over the other mentioned polycrystalline ceramics in the range of 4.5–5.5 µm, a region of particular importance for seeker and electro-optic imaging systems [17]. Given its excellent transmittance in the visible and IR-wavelength ranges, owing to its symmetric cubic crystal structure, spinel is very attractive material to manufacture high performance optical components such as lenses, IR windows, and domes. Spinel is also very promising for applications as windows or windshields for military vehicles such as large and bulletproof windows, due to its mechanical and ballistic properties [18].

It is difficult to fabricate transparent spinel directly from high purity precursor powders by using the conventional pressureless sintering techniques [19]. Therefore, it is necessary to use HP, HIP, or SPS. Very recently, SPS has been proved to be an alternative technique for fabrication of fine-grained transparent spinel [20]. Spark Plasma Sintering is a newly developed rapid-sintering technique for obtaining fully dense and fine-grained ceramics at a short sintering time owing to its high heating rate. Densification of polycrystalline ceramics to optical transparency in the visible range is yet a challenge and necessitates prolong sintering at very high temperatures under high vacuum conditions [10]. Frage et al. [21] reported SPS method to fabricate commercial $MgAl_2O_4$ powder. They studied the effect of LiF addition on optical properties of spinel [21]. Morita et al. have reported the result of transparent spinel fabrication by SPS to fabricate spinel using commercial $MgAl_2O_4$ powder at 1300°C for a 20min soak. It was found that the obtained spinel exhibited an in-line transmission of 47% for a visible-wavelength of 0.55µm and a fracture strength of ~500 MPa [16]. Wang et al. studied the influence of pressure profile on the optical properties of SPS-ed spinel specimens using commercial $MgAl_2O_4$ powder. They found that at low pre-load pressure, 5MPa, high in-line transmittance of 55% at 550nm can be achieved [22].

However, lack of information necessitates a study of continues process on the synthesis and sintering of spinel prepared by SPS method. In the present work, the conditions for a continuous process (simultaneous synthesis and densification) of transparent spinel fabrication using the SPS and commercially available oxide powders (Al_2O_3 and MgO) are described. Spinel formation, microstructure, Vickers hardness and optical

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property of spinel transparent ceramic fabricated by SPS were studied.

2. MATERIALS AND METHODS

2.1. Sample preparation In this study high-purity nano-Al_2O_3 (99.9%, average particle size≈50nm, US Research Nanomaterials, Inc.) and nano-MgO (99.9%, average particle size≈20nm, US Research Nanomaterials, Inc.) powders were used as starting materials to prepare the magnesium aluminate ($MgAl_2O_4$) spinel. To improve the phase homogeneity, these powders were milled with alumina balls by using ethanol as dispersing agent. Subsequently, the slurry was dried and then the dried powders were placed in a graphite die and set in spark plasma sintering system (SPS-20 T-10, Easy Fashion metal products trade Co., China). The temperature was measured by an optical pyrometer adjusted on top of the lower punch surface. A low pressure of 20MPa was applied during the heating up procedure and was increased gradually to 90MPa after reaching the final sintering temperature (1250°C) and then 10 min soaking time was applied.

2.2. Characterization Phase composition was determined by X-ray diffraction (XRD) of specimen using a Philips-PW3710 operating at 40 kV and 30 mA with Cu-Kα radiation (λ = 0.15406 nm). The density of the specimen was measured by the Archimedes method in distilled water. Vickers hardness (HV) was measured by a hardness tester (MVK-H21, Akashi., Japan) at a load of 100g with 10s dwell time at room temperature. The average hardness value was attained from at least 5 measurements for each sample. IR transmittance was evaluated by a Fourier-transform infrared spectrometer (FTIR) (Vector 33, Bruker Biospin Corp, USA) in the wavelength range of 2.5-25µm. The microstructure observation of the sintered specimen was determined by a field emission scanning electron microscope (FESEM, TESCAN Mira 3-XMU, Czech Republic) equipped with energy dispersive spectroscopy (EDS).

3. RESULT AND DISCUSSION

XRD pattern for the sample containing 50 mol% Al_2O_3 and 50 mol% MgO densified by reactive spark plasma sintering at 1250°C as a representative together with the standard pattern of the synthetic stoichiometric $MgAl_2O_4$ is given in Fig. 1. It can be noticed that spark plasma sintering at 1250°C did result in the synthesis of single-phase $MgAl_2O_4$. A uniform phase composition of $MgAl_2O_4$ spinel ($MgAl_2O_4$, reference code: 01-077-1203) was formed and there was not unreacted MgO and Al_2O_3 phases remaining in the sample, which means that the reaction of Al_2O_3 and MgO was occurred completely during the sintering process.

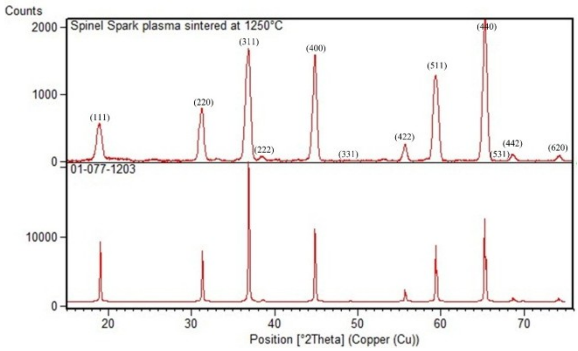

Figure 1. X-ray diffraction pattern of the standard synthetic and SPS-ed sample at 1250°C.

The densification of spinel at 1250°C during the SPS process was evaluated based on the displacement of punch rods caused by shrinkage of the specimen. The profile of the main process parameters (temperature, time, and displacement of the upper punch), used during the SPS sintering, is given in Fig. 2. Negative and positive displacements that indicate contraction and expansion of the sample are plotted along the positive and negative y-axis of the graph, respectively. According to the data of SPS graph, after about 35min, the sintering began at 850°C, when the material was still composed of two phases (MgO and Al_2O_3).

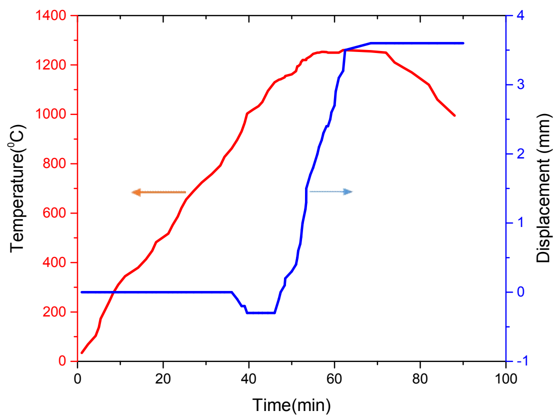

Figure 2. Displacement of the spinel as a function of sintering time.

A significant expansion of the sample occurred at 850°C, which corresponds to the beginning of the reaction between MgO and Al_2O_3. The complete transformation from the precursor phases to $MgAl_2O_4$ was observed at 1250°C for 10 min at 90MPa. The volume increase is due to the difference between the unit cell volumes of starting materials and $MgAl_2O_4$. During the formation of the spinel, 5-7% volume expansion has been reported. Bailey et al. attempted to fabricate dense spinel specimens by a one-step process from MgO and Al_2O_3 as starting materials. A mixture of

1:1 molar ratio of magnesia and alumina was compacted and heat treated in the 900°C–1300°C temperature range. After 3 h holding at 1300°C, only 89% of the starting oxides were transformed into the spinel phase [23], while the SPS treatment allows achieving full transformation at 1250°C for 10 min soaking time.

The real density value of the spark plasma sintered $MgAl_2O_4$ which was measured by the Archimedes method, was 3.55g/cm^3 and the relative density was 94.3%. The density value has a tendency to approach to the theoretical density (ρ_{theo}= 3.58 g/cm^3). The hardness value of the consolidated sample attained after the SPS cycle was nearly 2040HV. This hardness result is comparable with the sample that was spark plasma sintered at 1250°C at 250 MPa (1640 HV) for 2min as reported by Sokol et al., [24].

SEM/EDS analysis of the fracture surface of the spinel sample which was spark plasma sintered at 1250°C for 10 min is presented in Fig. 3. As can be seen from the graph, the spark plasma sintered spinel ceramic present homogeneous microstructure in term of phase distribution. The fracture mode appears to be intergranular fracture, which indicates a high strength of the intergrain links.

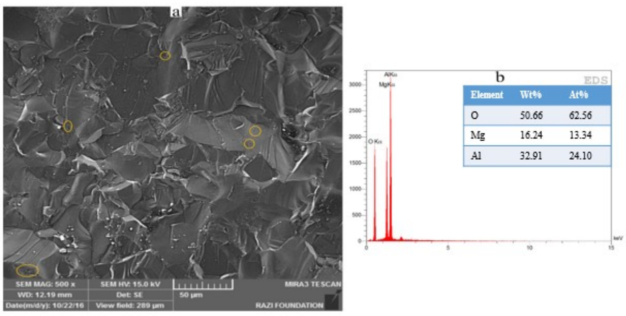

Figure 3. SEM image of the fracture surface (a), (b) EDS spectra of the spinel sample sintered at 1250°C. Notice some residual pores (pointed at by circles in the image).

Some occasional pores (pointed at by circles) were distinguishable in the sample. The pore size and the porosity are the main factors affecting the light transmitting properties of the samples. Therefore, eliminating the pores from the microstructure is important. The higher pressure is an effective way to decrease the porosity during the sintering process. To further confirm the presence of spinel phase, EDS analysis was investigated. Figure 3(b) shows EDS spectra of the sample. EDS analysis indicated the existence of O, Al and Mg elements in the microstructure. The atomic ratio of Mg, Al and O elements is about 13:24:63, which is close to the stoichiometric atomic ratio of $MgAl_2O_4$. This result is consistent with the XRD analysis.

In the second part of the study, the optical property of the sample was also investigated. By heating-rate-controlled SPS processing, spinel with a high transmittance was fabricated from a mixture of Al_2O_3 and MgO powders without any sintering aids. A circular disk 4 mm in diameter and 2 mm thick was prepared. Visible transparency of the sample is given in Fig. 4. As it can be seen, the spinel exhibits good transparency. The sample is above the printed text and the text placed 10 mm below the sample, is clearly visible through the plate.

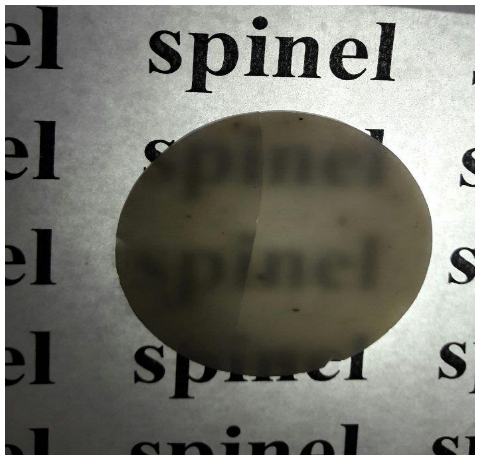

Figure 4. Picture of the thin, 40 mm diameter, transparent disc consolidated by SPS.

A critical parameter of transparent ceramics is their light transmission characteristics. Fig. 5. shows the in-line transmittance (T_{in}) of the sintered spinel as a function of wavelength. The in-line transmittance (T_{in}) at 4.7 µm, approximately reached 55%. Spinel, $MgAl_2O_4$, shows a good optical transmittance in the wavelength range of 3-5 µm. According to the result, this transparent ceramic can be used as an optical mid -IR-window.

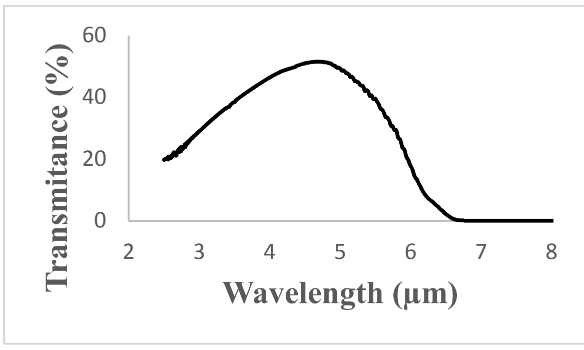

Figure 5. Optical transmission of a spinel sample as a function of the incident light wavelength.

The light transmission of polycrystalline ceramic medium is sensitive to different microstructural factors including grain size, grain boundary, second phase precipitates, impurities, residual pores, defects and so on, because these factors act as sources of light scattering and absorption losses. This indicates that special carefulness is required for processing the transparent ceramics. In the present study, a high-purity powder without any sintering aids was used, so the second phase and impurities can be excluded when calculating the light absorption. Thus, grain size, residual pores and defects are the main factors to be considered [16]. However, 99.2% of the theoretical density was achieved by spark plasma sintering, where some residual pores in the sample prevented transparency (Fig. 3).

4. CONCLUSION

In summary, the present study successfully showed that a high transmittance for pure spinel ceramic from a mixture of Al_2O_3 and MgO powders can be obtained by spark plasma sintering, without sintering aids. A significant expansion of the spinel was occurred, which corresponds to the beginning of the reaction between MgO and Al_2O_3. The optical property of transparent polycrystalline $MgAl_2O_4$ ceramic is discussed. Transparent polycrystalline $MgAl_2O_4$ spinel with an in-line transmission of 55% for an IR-wavelength of 4.7µm, was fabricated by spark plasma sintering.

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