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High-pressure spark plasma sintering (SPS) of transparent polycrystalline magnesium aluminate spinel (PMAS)

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Abstract

A high pressure SPS (spark plasma sintering) process was applied for consolidation of un-doped polycrystalline magnesium aluminate spinel. This approach allows fabricating a fully dense transparent ceramic with submicron grain size and high hardness values at a relatively low temperature (1200 °C). The light transmittance of the specimens increases with increasing applied pressure, while the hardness gradually decreases. The optimal combination of properties was achieved after sintering at 1200 °C at a heating rate of 5°/min, a holding time of 15 min and an applied pressure of 350–400 MPa. The specimens display the level of transmittance in the visible wavelengths and hardness values comparable with the best results reported in the literature for the two-stage fabrication process (pressureless sintering and hot isostatic pressing).

Keywords: SPS; Spinel; Optical transparency; High pressure; Grain size

1. Introduction

The fabrication of transparent polycrystalline magnesium aluminate spinel (PMAS) has been widely discussed in the literature.[1–17] Two-stage process (pressureless sintering and hot isostatic pressing) allows fabricating fully dense specimens in the absence of any additive.[1–4] The unique combination of properties (transparency of about 82.7% at 550 nm wavelength and hardness values equal to 15 GPa, measured under 10 kg testing load) was reported by Krell et al.[2] for specimens with grain size of about 0.3 μm.

Spark plasma sintering (SPS) has been also applied to fabricate transparent PMAS.[7–17] It has to be pointed out that in most of the studies only structural characteristics and optical properties are discussed. Morita et al.[7] reported that the specimens with relatively high bending strength (400 MPa) may be fabricated by SPS. However, the transmittance of the specimens was only about 55% in the visible wavelengths range. The combination of optical and mechanical properties has been discussed in our previous contributions.[9,10] Specimens consolidated in the presence of LiF display relatively high transmittance and exhibit relatively low mechanical properties that reflect the large average grain size of about 40–50 μm. Significant grain growth during sintering LiF-doped powder has been widely discussed in the literature.[9,10,12,13,18–22] The effect of the average grain size of dense PMAS on the functional properties (mechanical and optical) was discussed in Refs. 3, 10, 21. Doping with LiF affects in a different manner optical transmittance and mechanical properties. Maximal transparency (80%) was achieved for specimens with an average grain size of about 40 μm fabricated with the LiF additive. These specimens display a hardness value (HV2) of about 1450 kg/mm^2 and a bending strength of about 150 MPa. Un-doped specimens fabricated at 1300 °C at a heating rate of 2 °C/min have a transmittance of about 77% at 1000 nm and 68% at 500 nm and display relatively high mechanical properties (HV2 1600 kg/mm^2 and 300 MPa bending strength).

The applied pressure in the 63–95 MPa range affects neither the transparency nor the mechanical properties of the SPS-processed specimens. It is noteworthy that in the review of Rubat du Merac et al.[22] on the state of the art of fabrication of transparent PMAS and the correlation between processing parameters and properties, the applied pressure that was used

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in the mentioned SPS process did not exceed 100 MPa. The sintering temperature that provides a good combination of the mechanical properties and the transmittance was to be equal or higher than 1300 °C.

A positive effect of the applied pressure in the 200–500 MPa range on transmittance of SPS-processed pure alumina[23] and MgO-doped alumina[24] has been clearly observed. The high-pressure device used in Ref. 23 consisted of an outer and inner graphite die; the powders were pressed between two punches made of a carbon fiber composite or of tungsten carbide. In order to achieve a pressure up to 400 MPa in Ref. 24, a composed die, consisting of a larger external and smaller inner graphite dies, was used. Unfortunately, no specifications of the graphite that could withstand the pressure values were provided.

To the best of our knowledge, the effect of applying a relatively high pressure during SPS consolidation of PMAS has not been discussed in the literature.

We suggest that a high-pressure device (Fig. 1) made of silicon carbide instead of graphite and the possibility of decreasing the sintering temperature will allow reducing the level of carbon contamination and fabricating nano-structured fully dense transparent PMAS in the absence of LiF addition.

In the present work, the effect of the applied pressure up to 400 MPa on the sintering temperature, microstructure, transparency and hardness of the SPS-processed un-doped PMAS was investigated and discussed.

2. Experimental procedure

Commercial magnesium aluminate spinel $MgO{\cdot}Al_2O_3$ powder (S30CR Baikowski Chimie, La Blame de Silingy, France) with specific surface area of 30 m^2/g, impurities level of 10Fe, 10Na, 20Si and 5Ca ppm was used as a starting powder in this study.

The experiments were conducted in a SPS apparatus (FCT Systems GmbH, Rauenstein, Germany). The high-pressure device (Fig. 1) consisted of an outer graphite die (outer diameter 50 mm) and inner die made of silicon carbide. The silicon carbide die had 10 mm inner and 20 mm outer diameters. The powder was pressed between two punches of SiC. The SPS parameters varied as follows: sintering temperature from 1150 to 1300 °C, heating rate from 5 to 50 °C/min, holding time at the sintering temperature from 2 to 30 min and applied pressure from 150 to 400 MPa.

The density of the sintered specimens was determined by the Archimedes method. The samples were polished to an optical level for transmission measurements in the 400–1000 nm wavelengths range (Spectrophotometer V-1100D, MRC Israel). The thickness of the polished samples was 1.5 mm. Hardness measurements were performed under 2000 g load using a Buehler, Micromet 2010 apparatus. The Young modulus was determined by the "pulse echo" method.

The microstructural examination was conducted using a High Resolution Scanning Electron Microscope (JEOL, JEM-7400 HRSEM). The grain size was estimated using the Thixomet software[25,26] for image analysis. The polished specimens were thermally etched at 1350 °C for 1–2 min under ambient atmosphere.

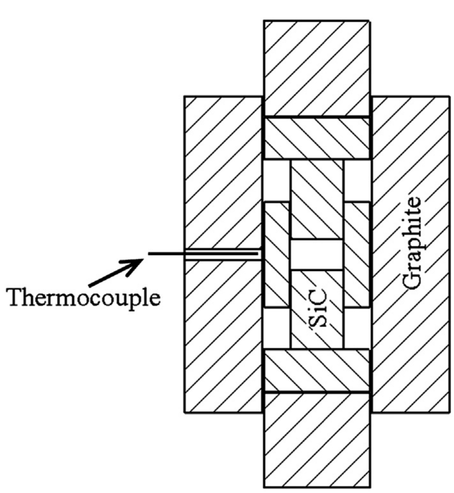

Fig. 1. The high-pressure device consisting of an outer graphite die and inner die made of silicon carbide.

3. Results and discussion

The effect of heating rate on transparency and hardness was investigated using specimens processed at 1200 °C under a pressure of 150 MPa and holding time of 15 min (Fig. 2). Increasing the heating rate from 5 to 50°/min gradually decreased both the hardness and the transparency of the ceramic. Although the sample fabricated under the above mentioned conditions at a heating rate of 5°/min displays a very high value of hardness (HV2 1750 kg/mm^2), the transmittance level was relatively low. The latter reflects the presence of residual porosity that is below the detectability of the Archimedes method, but affects significantly the transparency. This level of porosity has practically no effect on the hardness of the specimen.

According to the experimental results for the samples sintered at 1200 °C under 250 MPa pressure, the increasing holding time leads to an improved level of the transmittance and slightly decreased hardness values (Fig. 3). Optimal combination of these properties was obtained for a holding time of about 15 min.

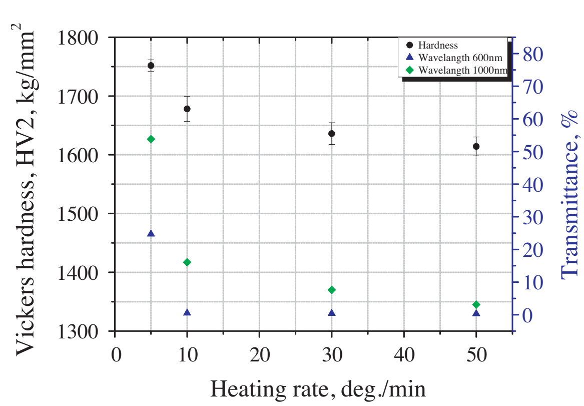

Fig. 2. The effect of heating rate on the hardness and the transmittance of the samples processed at 1200 °C under 150 MPa and 15 min holding time.