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Microwave sintering of transparent alumina

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Abstract

Transparent alumina samples have been successfully prepared by microwave sintering processing. In comparison to the conventional sintering processing, microwave sintering to transparent alumina can be achieved at lower sintering temperature and shorter sintering time. It was also found that the microwave heating could substantially increase the conversion rate of polycrystalline alumina to single crystalline sapphire, to improve the transparency and other properties of the transparent alumina samples.

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Keywords: Microwave sintering; Alumina; Transparency

1. Introduction

Transparent alumina (Al_2O_3) ceramics can be prepared either in single crystal (sapphire) or polycrystalline forms. Sapphire is used as highly transparent material for many industrial and military applications, such as optical windows for lasers, spectrometers, armor parts, and IR-domes for infrared missile guidance system. Polycrystalline transparent alumina has been available for optical applications since the early 1960s when Coble [1] invented translucent alumina, which has become a key element in high-pressure sodium vapor lamps and other optical instruments manufactured all over the world. Compared to sapphire, the cost to manufacture polycrystalline transparent alumina is much lower, and it is easier to produce in large size products.

Polycrystalline transparent alumina is made via powder processing using high purity and fine particle size alumina powder with the addition of small amount MgO, and sintering to pore-free state. The sintering is the key to obtain high transparency material. In the conventional sintering processes, extremely high sintering temperatures (up to 1900 °C) and long soaking times (several hours) under high vacuum or pure hydrogen atmosphere are applied in the fabrication of transparent alumina products to achieve the highest density and minimum porosity.

Microwave sintering is a novel technique for ceramic materials processing which differs fundamentally from the conventional processes. In the microwave processing, the samples positioned in microwave field absorb microwave energy and convert it into heat directly providing volumetric heating. As a result, microwave process offers several advantages, such as more rapid and uniform heating, shorter processing time, finer microstructure, enhanced energy efficiency, and improved materials properties and product per-

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formances. Enhanced densification behaviors were also observed in microwave process due to a reduction in the activation energy for sintering, which leads to lower sintering temperature and shorter sintering time as compared to the conventional sintering process [2,3].

The first attempt to prepare transparent ceramic samples by microwave sintering processing was conducted by Fang et al. [4] in our laboratory in 1995–1996. Recently, some highly transparent alumina, aluminum oxynitride (ALON) and aluminum magnisa spinel, and translucent aluminum nitride (AlN) samples were also successfully fabricated by microwave sintering processing [5]. This letter describes the developments on transparent alumina ceramics using microwave method.

2. Experimental

High purity (99.99%) commercial alumina powders (Baikalox CR10, Baikoski International, North Carolina) with primary particle size of 0.15 μm were used as starting materials in this study. The starting powder was blended in acetone with 0.05 wt.% of MgO (in form of $\text{Mg}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$) and organic binder (Acrycoid) using alumina mortar. Green samples were prepared by dry pressing uniaxially into

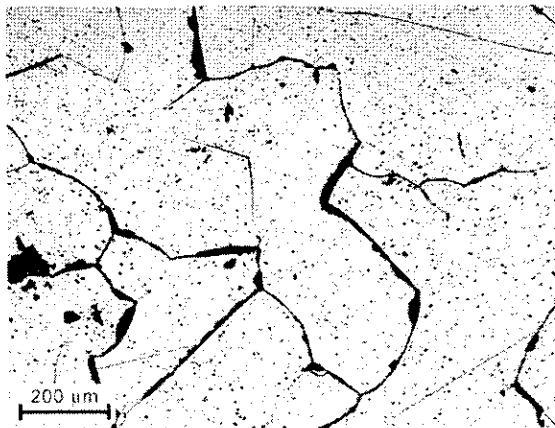


Fig. 1. Microstructure of the Al_2O_3 sample with no MgO addition shows an extreme grain growth and some cracks along the boundary. The sample was microwave sintered at 1850 $^\circ\text{C}$ for 5 min with a heating rate of 500–600 $^\circ\text{C}/\text{min}$.

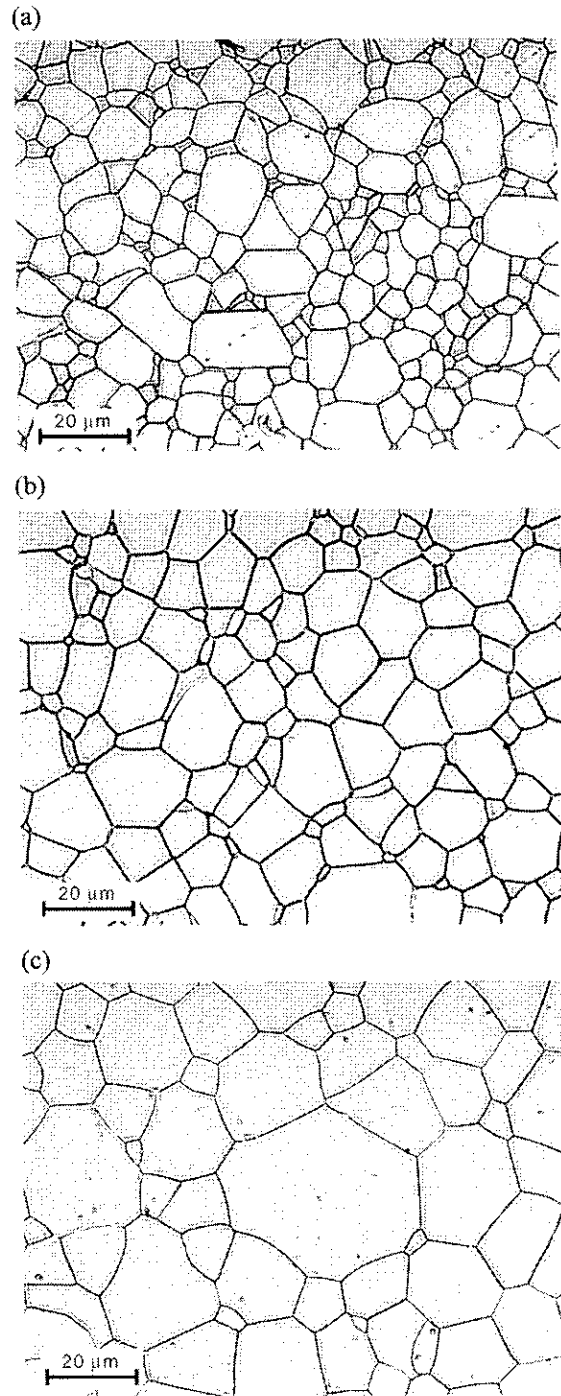


Fig. 2. Microstructures of the Al_2O_3 samples with 0.05 wt.% MgO addition show very neat boundary structure and relatively uniform grain growth. The sample was microwave sintered at 1750 $^\circ\text{C}$ with a heating rate of 100 $^\circ\text{C}/\text{min}$ for (a) 15, (b) 30, and (c) 45 min.

pellets followed by cold isostatic press at a pressure of 280 MPa. The green densities of the compacts were around 52–54%. The compacted pellets were preheated at 1100 °C for 2 h in a resistance furnace to burn out the binder.

The microwave sintering was carried out using a TE₁₀₃ single mode microwave applicator coupled with a 1.5-kW microwave generator operating at 2.45 GHz for small samples (less than 12.7 mm diameter), and a multimode microwave applicator with a 6-kW microwave power source for large samples (up to 25.4 mm diameter). Ultrahigh purity hydrogen under room pressure was used as sintering atmosphere for all samples.

The densities of sintered Al₂O₃ samples were measured by the Archimedes' method. Microstructures were studied with an Olympus BX60M optical microscope (Olympus Optical, Tokyo, Japan) and the transmittances were measured using CARY 2300 (Varian, Texas) spectrophotometer.

3. Results and discussion

Some pure Al₂O₃ samples without any MgO addition were tried to sinter in microwave at very high heating rate (550–600 °C/min) to 1850 °C and dwelled at that temperature for only 5 min under pure H₂ atmosphere. The purpose of this work was to investigate that if a very high heating rate and short sintering time by microwave radiation can provide fully dense and fine-grained Al₂O₃ body in the absence of MgO. The density of the sample was 3.83 g/cm³, about 96.5% of T.D. It was found that

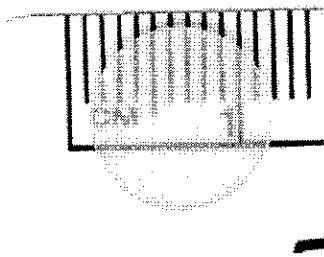


Fig. 3. Appearance of a highly transparent Al₂O₃ sample microwave sintered at 1750 °C for 45 min.

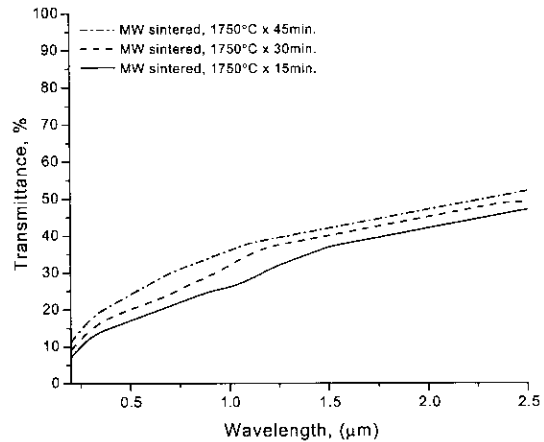


Fig. 4. The transmittance measurements of the microwave sintered Al₂O₃ samples.

the sintered body has enormous grain size (a few hundred microns), with lots of small pores trapped within the grains, as shown in Fig. 1. The samples were only partially translucent with some visible cracks. The first thing we learned from these results is that the sintering aid such as MgO is indispensable, and the second is that high grain growth can occur during microwave sintering.

The following work was carried out using 0.05 wt.% MgO (in form of Mg(NO₃)₂·5H₂O) as sintering aid for all of Al₂O₃ samples. Fig. 2 shows the microstructures of the samples microwave sintered at 1750 °C with different dwelling times. As shown below, these samples exhibited very neat grain boundary structure and uniform grain growth with no porosity. All samples had a same density of 3.97 g/cm³ (~100% of T.D.), but the average grain size increased from 20 to 40 μm while the sintering time increased from 15 to 45 min. A typical transparent Al₂O₃ sample that was microwave sintered at 1750 °C for 45 min is shown in Fig. 3. The transmittance measurements of the microwave sintered Al₂O₃ samples are shown in Fig. 4. The sample microwave sintered for longer time has a little higher transmittance. For comparison, the transmittance of single crystal Al₂O₃ (sapphire) is about 80% at all these wavelengths.

Compared to single crystals, sintered polycrystalline Al₂O₃ ceramic body possesses much more complicated microstructures that consist of grains, grain

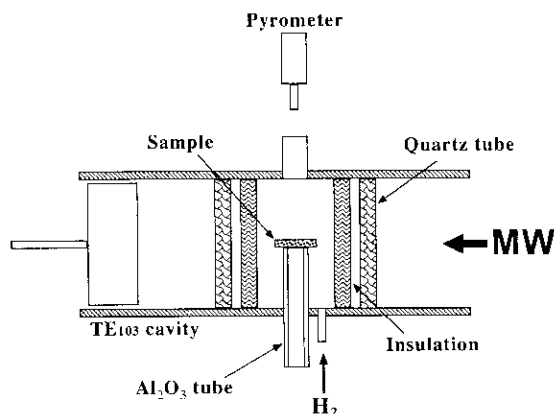


Fig. 5. Scheme of the microwave setup for solid-state conversion of polycrystalline Al_2O_3 sample to single crystal sapphire.

boundaries, second phases and pores, which greatly influence their optical properties. The transmissivity (I/I_0) is depended not only on the crystal characteristics of the material, but on the grain size and boundary structure

$$I/I_0 = (1 - R)^2 \exp(-\mu x). \quad (1)$$

where I is the intensity of transmitted light, I_0 is the intensity of incident light, R is the reflectivity, μ is the absorption coefficient, and x is the thickness of a sample body. The absorption coefficient, μ , can be given as

$$\mu = \alpha + S_{\text{im}} + S_{\text{op}}. \quad (2)$$

Where α is the absorption term characteristic of electron transition, S_{im} is the scattering terms due to structural inhomogeneities such as pores and second phase, S_{op} is the scattering terms due to optical anisotropy. Since Al_2O_3 has a hexagonal rather than cubic crystal structure, and the light gets scattered at interfaces such as grain boundaries where refractive indices are discontinuous, and as a consequence, transmitted light becomes diffuse. In this case, S_{op} is always an issue there. To increase the transmissivity of a sintered polycrystalline Al_2O_3 body, it is most important to reduce S_{im} . That is to reduce porosity and the grain boundary area as much as possible by optimizing the sintering process. Final, the best approach to improve the transparency is to remove boundaries to eliminate

the S_{im} and S_{op} in Eq. (2), that means to convert the polycrystalline to single crystal structure.

In 1995, Scott et al. [6] patented their processing of the solid state thermal conversion of polycrystalline alumina to sapphire material. In their process, the sintered alumina tube, usually it was transparent body, with lower MgO content (300–400 wppm) was reheated at 1700 °C in high purity hydrogen atmosphere for 300 h, or at 1880 °C for 3–9 h. They claimed that the original polycrystalline alumina was converted to single crystal sapphire by this process. This was achieved by gradually evaporating MgO

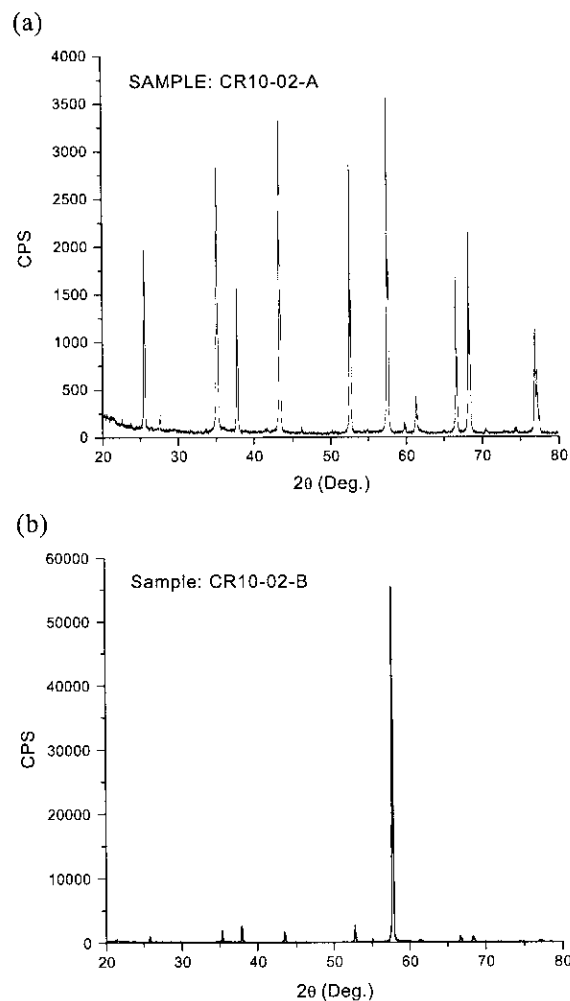


Fig. 6. The X-ray diffraction patterns of the as-sintered (a) and microwave post-sintered (b) Al_2O_3 samples.

from the grain boundaries, and thereby eliminating the grain boundaries themselves resulting into a single crystal.

In this work, some microwave sintered transparent Al_2O_3 samples with 0.05 wt.% MgO doping were post-sintered in microwave field at 1850–1880 °C for 2 h under ultra high purity hydrogen atmosphere. The processing is schematically shown in Fig. 5. A 9.5-mm diameter Al_2O_3 disk (as-sintered transparent sample by microwave sintering at 1750 °C for 30 min) supported by a high purity Al_2O_3 tube was placed in a single mode microwave cavity to apply microwave post-sintering treatment. It was observed that there were some temperature differences between the center and periphery of the Al_2O_3 disk sample. For example, when the center area reached 1880 °C, the temperature around the peripheral was around 1850 °C. We think it was due to the cooling effect of the flowing H_2 on the peripheral area.

Fig. 6a and b showed the X-ray diffraction (XRD) patterns of the as-sintered Al_2O_3 sample and the microwave post-sintered sample, respectively. The as-sintered sample's XRD pattern exactly tallied with the standard Al_2O_3 (corundum) powder XRD pattern (Fig. 7a). The same sample subjected to microwave post-sintering at 1880 °C for 2 h. Its XRD patterns the {116} single crystalline plane as the dominant orientation, and there were still some small peaks corresponding to the polycrystalline structure (Fig. 7b).

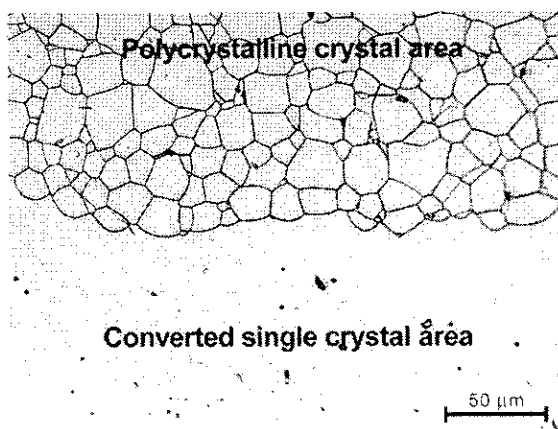


Fig. 7. The microstructure development of the Al_2O_3 sample microwave post-sintered at 1880 °C for 120 min.

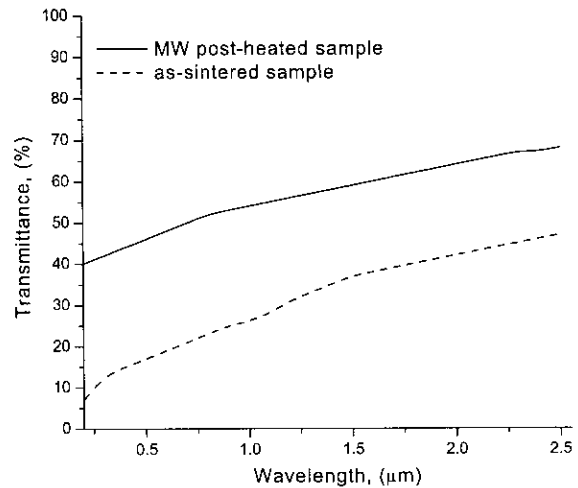


Fig. 8. The comparison of the transmittance of the as-sintered and post-sintered Al_2O_3 sample in microwave field.

Fig. 7 reveals the changes in the microstructures of the post-sintered Al_2O_3 sample that was microwave heated at 1880 °C (temperature in the center area of the disk sample) for 30 min. It clearly shows that the conversion of the polycrystalline structure to single crystal structure during the microwave post-sintering step has occurred. The microstructure picture showed that peripheral area of the sample remained in polycrystalline form with average grain size of 30–40 μm (the top area in Fig. 7); and the center part of the post-sintered sample converted into a single crystal structure with no grain boundaries (bottom area of the same picture). The transmittance of the microwave post-sintered sample is shown in Fig. 8. While comparing with Fig. 4, a 20% increase of the transmittance was achieved by microwave post-sintering treatment.

4. Conclusion

In the microwave field, the densification and grain growth of Al_2O_3 ceramic samples were enhanced to a great extent. The sample that was microwave sintered at 1750 °C for only 15 min showed full densification and good transparency. It was found that the microwave post-sintering treatment can provide a much faster processing method for the solid-state conversion of polycrystalline Al_2O_3 sample to single crystal state.

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