Electromagnetic-wave sintering of alumina ceramics from nano-sized particles: possible material for high-pressure cell for millimeter-wave electron spin resonance

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Abstract. Electromagnetic-wave sintering of alumina ceramics using 28 GHz gyrotron has been performed aiming for a high fracture toughness value in order for use as pistons for pressure cells of high-frequency electron spin resonance (ESR) measurements. We have tried to improve the fracture toughness by using nano-sized alumina powder (140 nm in average particle size) having smaller particle size than our previous work (400 nm in average particle size). Rapid densification was observed around the sintering temperature of 1200 °C. We obtained the relative density over 99 % above 1400 °C. It was found that alumina ceramics made in this work at sintering temperatures have smaller grain size and higher density simultaneously as compared to the previous work. These results suggest that alumina ceramics made from powder of smaller particle size sintered by electromagnetic-wave sintering possibly have high fracture toughness which can be used as materials for the pressure cell for ESR.

1. Introduction
Pressure is one of important parameters in measuring physical properties. Electron spin resonance (ESR) is one of the most reliable methods to detect electron spins and obtain information about magnetic properties of materials from the microscopic point of view. Recently, Ohita and co-workers developed high-pressure, high-field and multifrequency electron spin resonance system in the millimeter wave (MMW) / sub-millimeter wave (SMMW) region by using a clamped-type piston-cylinder pressure cell [1]. In order for high-sensitive ESR measurements, the ceramic material for the piston of the pressure cell is required to have two properties simultaneously: 1) Less attenuation of electromagnetic waves and 2) hardness and toughness value withstanding the high pressure. They examined several commercially available products of ceramics and found that zirconia-based ceramics have high fracture toughness and rather low electromagnetic wave transmittance which decreases significantly with increasing proportion of zirconia, and that alumina has relatively low fracture toughness and high electromagnetic wave transmittance [1].

In the conventional sintering method of ceramics which is heating from outside of the sample with an electric furnace or even fire etc., the temperature inside the sample changes by thermal conduction from the outside. Since this method requires thermal equilibrium condition (or close) inside the sample, it takes several hours to several tens of hours to complete sintering. On the other hand, electromagnetic-
wave sintering is an internal heating method based on absorption of the electromagnetic wave by the sample, which makes possible to heat uniformly the sample and in a shorter sintering time.

The continuous MMW/SMMW with an order of ten kilowatts can be produced only by the gyrotron at present. Progress in the high-frequency and high-power radiation source technology stimulates the electromagnetic wave sintering technology. We have been studying MMW/SMMW sintering of ceramics such as alumina, zirconia, silica xerogel and so on by using gyrotrons [2,3]. In our previous work on MMW sintering of alumina [2], the sintered alumina had higher density than those of conventional method with any sintering temperature. In addition, microstructure evaluation demonstrated that grain growth of MMW annealed alumina was faster than in conventional annealing. It indicates that the applied MMW enhances mass transport and solid-state reaction rates during sintering. Such empirical observations of microwave enhancements have been broadly known as microwave (or non-thermal) effect. Therefore, electromagnetic-wave sintering has a potential to make materials with unprecedented physical properties or functions.

It is known that a grain growth in the sintering process causes decreasing of fracture toughness value [4]. Since the average grain size of the MMW sintered alumina was smaller than that of conventional alumina at high density region [2], one can expect to make the MMW sintered alumina with an improved fracture toughness property which can be used for pressure cell for ESR measurements.

We have been sintered alumina ceramics by electromagnetic wave sintering using 28 GHz gyrotron. In this paper, we report the results with newly adopted nano-sized alumina particles as a starting material which is smaller than what is used in our previous work [2] in order to prevent grain growth. After the experimental backgrounds and sintering procedures in the following sections 2 and 3 respectively, we will describe the properties of sintered alumina including analyses of scanning electron microscope (SEM) images in section 4. We will also discuss on a comparison with our previous work.

2. Experimental
In all sintering process in this study, we have used MMW heating system where a 28 GHz gyrotron is used as the radiation source as is used in our previous work [2].

The schematic diagram of a pressure cell device for ESR system is shown in figure 1. The top/bottom backups and pistons must be tough enough as well as having good transmittance of MMW. The sizes of the pieces are summarized in table 1. We have developed alumina ceramics for top and bottom backups sintered by the MMW heating system with 28 GHz gyrotron by using alumina powders AES - 11C (Sumitomo Chemical Co. Ltd., 99.8 %, 400 nm in average particle size, and 7-8 m²/g of specific surface area). Since a relatively strong force is applied to the piston, higher strength and toughness is required for the material of pistons. In order to obtain a higher toughness, we used in this study smaller alumina powder TM-DAR (Taihei Chemical Co., Ltd., 99.95%, 140 nm in average particle size, and 13.3 m²/g of specific surface area). Further, the size of the sintered sample needs to be 6 x 20 mm in order to carve it into a shape of the top piston with the length of 10 mm. Making such a long shape sample is a challenging for us, because it may become difficult to pull out air and water from the long-rod shaped sample in the procedure of making green sample which is described later.

Figure 1. The schematic diagram of a pressure cell device for ESR system [1].
The fracture surfaces of the obtained sample were observed using a field-emission scanning electron microscope (SEM for short, S-2600H, Hitachi).

3. Procedure of sintering
We basically followed the previously reported procedure to make the green sample [5]. First, 200 g of alumina powder (TM-DAR), 50.0 g of distilled water, 0.06 g of magnesium oxide as an additive and 2.0 g of dispersant Aron A 6114 (ammonium carboxylate) were charged into a stirring vessel with 150 g of alumina ball for stirring and stirred for 18 hours with a dedicated machine. Next, the resulting muddy was degassed by using a vacuum pump in order to remove the air mixed in stirring. Then the muddy was poured into a silicon mold placed on the porous resin connected to a rotary pump. The air and the moisture were taken out from the muddy through the pores of the resin by pumping, then we obtained green samples. Note that for such a long-rod shape sample about 20 mm, viscosity of the muddy should be optimized before the degassing procedure to obtain good shape of the green sample. Otherwise we may obtain a sample with a hole inside the rod after the pumping, because the surface of the muddy is first dried during the pumping procedure. In our case, we solved it by increasing water to reduce the viscosity and by using a stronger pump.

The obtained compact is dried at 120 °C in a drier for 2 hours to remove water sufficiently, then presintered at 600 °C for 2 hours in an electric furnace to remove water and dispersant completely.

The green sample after the pre-sintering was covered by a thermal insulator Denka Arsen Board (BD-1700 LNH, Denki Kagaku Kogyo Co., Ltd.) during the sintering procedure. It is composed of 100% alumina with the maximum operating temperature 1700 °C and with a low absorption of electromagnetic waves. The thermocouple, heat insulating material, and sample were placed as shown in figure 2.

Figure 3 shows a sintering curve used in the electromagnetic wave sintering procedure for this study. Each sample was heated from the room temperature to the sintering temperature at the heating rate of 45 °C/min. After the holding time of 20 min, the irradiation of the electromagnetic wave was stopped and cooled naturally. The sintering temperature was changed from 1000 °C to 1500 °C by 100°C.

Table 1. The size of the pressure

|                | Height (mm) | Diameter (mm) |
|----------------|-------------|---------------|
| top backup     | 6           | 12            |
| bottom backup  | 6           | 12            |
| top piston     | 10          | 5             |
| back piston    | 8           | 5             |

The placement of the sample, the thermocouple and the thermal insulator.

The typical sintering curve showing time change of the temperature.
4. Experimental results and discussions
The density of the sintered sample obtained by electromagnetic wave sintering was calculated by the Archimedes method. We took data of the relative density by averaging over at least three samples. The obtained relative density as a function of the sintering temperature is shown in figure 4.

The relative density at the sintering temperature of 600 °C was obtained from the pre-sintered green sample. A rapid densification around the sintering temperature of 1200 °C was observed. The relative density increased to above 98 % at a sintering temperature of 1300 °C and even higher relative densities (over 99 %) were obtained for sintering temperatures of 1400 °C and 1500 °C.

![Figure 4](image)

**Figure 4.** Relative density of sintered alumina sample as a function of the sintering temperature. The line is drawn for guide for eyes.

The sintered alumina ceramics for sintering temperatures above 1300 °C are expected to have high fracture toughness values. In order to examine the grain size, we observed SEM images. The sample for each sintering temperature was selected to have the relative density being closest to the averaged value for the sintering temperature. The captured SEM images are shown in figures 5, 6, and 7 for the sintering temperatures of 1300 °C, 1400 °C and 1500 °C, respectively. It is found that the grain size grows with increasing temperature.

Next, the particle size was measured using "image analysis method". The sintering temperature dependence of the average particle size is shown in figure 8. It is suggested that the grain growth proceeds rapidly around the sintering temperature of 1500 °C. The particle size at 1500 °C became more than twice as large as that at 1400 °C. Considering the relative densities of sintered alumina ceramics at sintering temperatures of 1400 °C and 1500 °C is little different, we can expect that the alumina sintered at 1400 °C possibly has higher fracture toughness value. The toughness value for 1300 °C is possibly also high, though the relative density is slightly smaller (by approximately 1 %) than that for 1400 °C. The measurements of the toughness value must be of interest, which is a future plan.
Figure 5. SEM image for the sintering temperature 1300 °C.

Figure 6. SEM image for the sintering temperature 1400 °C.

Figure 7. SEM image for the sintering temperature 1500 °C.
Figure 8. Average particle size as a function of the sintering temperature. The line is drawn for guide for eyes.

The grain size is plotted as a function of the relative density in figure 9, where the data for ceramics made from AES-11C by using the same heating system with 28 GHz gyrotron are also shown for comparison. In this graph, a high fracture toughness value is expected when the data comes to the lower right region. The data for TM-DAR at sintering temperatures of 1300 °C and 1400 °C are in the lower right of the graph than the data for AES-11C. Therefore, we can expect that the alumina ceramics made from TM-DAR for the sintering temperatures of 1300 °C and 1400 °C have higher fracture toughness values than those from AES-11C for any sintering temperatures.

Figure 9. The average particle diameter as a function of the relative density of sintered alumina ceramics made from AES-11C (data from ref. [2], shown as black solid circle) and TM-DAR (this work). The data from TM-DAR is shown as A, B and C for the sintering temperature of 1300, 1400 and 1500 °C, respectively.
5. Summary

We have sintered alumina ceramics by electromagnetic-wave sintering with 28 GHz gyrotron aiming for a high fracture toughness value in order for use as pistons for pressure cells of high-frequency ESR measurements. We have tried to improve the fracture toughness by using nano-sized alumina powder (TM-DAR, 140 nm in average particle size) having smaller particle size than our previous work (AES-11C, 400 nm in average particle size).

We have sintered alumina at sintering temperatures between 1000 °C and 1500 °C. Rapid densification was observed around the sintering temperature of 1200 °C. We obtained the relative density over 98 % at the sintering temperature above 1300 °C and over 99 % above 1400 °C. The grain size of the sintered alumina increased as the sintering temperature was increased. Nevertheless, as compared to the results for AES-11C, it was found that alumina ceramics made from TM-DAR at sintering temperatures of 1300 and 1400 °C have smaller grain size and higher density simultaneously. These results suggest that alumina ceramics made from powder of smaller particle size (140 nm in average) sintered by electromagnetic-wave sintering possibly have high fracture toughness.

In the future, it is planned to pressurize with a pressure cell after shaping the sintered alumina. It is also planned to improve the fracture toughness value of ceramics by adding zirconia. It is expected that the electromagnetic-wave sintering has a potential to produce new physical properties and/or functions which are unattainable by conventional sintering methods.

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