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INFLUENCE OF THE LIQUID-PHASE COMPONENT ON A MICROWAVE SINTERING PROCESS

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Sintering of barium titanate by microwave heating with barium borate as a liquid-phase forming material was examined as a means of saving energy. A liquid phase was generated faster and over a wider temperature range by intermittent heating at constant power than by constant heating with variable power. When sufficient amount of the liquid-phase forming material were present, the samples were densified at temperatures below those at which the liquid-phase is normally formed. A sample containing 10 mol% of the liquid-phase forming material was densified efficiently. When too much liquid-phase forming material was present, densification of the sample was obstructed.

Keywords: *barium borate, barium titanate, dielectric substance, liquid-phase sintering, microwave sintering*

Introduction

To protect the Earth's environment, manufacturing industries in the 21st century will have to reduce their consumption of energy. The sintering processes that are used to produce ceramic products involves high temperatures and consumes large quantities of energy. Sintering is normally performed by placing ceramic products in the uniformly heated environment of a gas or electric furnace. This method permits uniform control of the temperature over a relatively large volume, and is therefore suitable for mass production. However, a considerable portion of the energy that is used in the process is consumed in maintaining the temperature of the surrounding furnace material or container, rather than being used directly in product manufacture. If energy could be used more efficiently in the manufacturing of products by improving the sintering process, less energy would be consumed in the manufacture of ceramic products, resulting in an overall saving of energy. The microwave sintering process has attracted attention since the 1990s [1, 2] as a sintering process that uses energy more efficiently. The advantages of microwave sintering are as follows: 1) selective heating is possible, 2) uniform heating can be achieved, and 3) the temperature can be raised or lowered rapidly. By employing these advantages efficiently, the technique can be applied in various small-scale production processes.

Barium titanate is widely used as a material for multilayer ceramics and thick-film capacitors because of its high dielectric constant [3, 4]. Because barium titanate is used in large quantities as a material in electronic devices, considerable energy savings could be achieved if barium titanate could be sintered at a reduced temperature. It is reported that for LTCC application, barium titanate is sintering at 1000°C for 24 h with the incorporation of silicate glass system [5]. In addition, there is a report saying that a sintered body of relative density around 90% was achived by 900°C for 8 h by adding boron oxide or lead borate to a barium titanate [6]. Our aim in this research was to develop a low-temperature sintering method that combines the microwave sintering method, which is expected to give an energy-saving effect, with the liquid-phase sintering method currently used as a low-temperature sintering method [7–11]. The liquid-phase component used was barium borate, which forms a liquid phase was melting at 924°C when mixed with barium titanate [12]: no other chemical components are formed. We conducted experiments by varying the amount of barium borate and modifying its method of addition. Also, we examined the effects of combining microwave sintering and liquid-phase sintering and we compared the resulting samples with samples produced by conventional heating in an electric furnace.

Experimental

Barium titanate (BT-01, Sakai Chemical Industry Co., Japan) was used as a raw material. Barium borate, used as the liquid-phase material, was pre-

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pared in situ from barium carbonate (99.9%, Wako Pure Chemical Industries Co., Japan) and boric acid [99.5% (minimum), Kanto Kagaku, Japan]. The amount of liquid-phase material added was varied between 1.5 and 20 mol%. The liquid-phase forming material was added by mixing barium carbonate and boric acid with barium titanate.

Green pellets with a diameter of 18 mm were formed by using a uniaxial pressure of 17 MPa and a cold isostatic pressure of 98 MPa. A magnetron multimode microwave furnace (MW-Master, Mino Ceramic Co. Ltd., Mizunami Japan) operating at 2.45 GHz was used for the sintering experiments. The sample was placed in a thermally insulated box, the inner surface of which was coated with SiC to act as a susceptor. The microwaves were generated by a magnetron with a 1.5 kW maximum rating at 2.45 GHz. In the power-control method, the temperature was controlled by adjusting the voltage and current to induce a variable load on the magnetron. In the time-control method, the temperature was controlled by adjusting the oscillation time of the magnetron, which was operated under a maximum load. The sample temperature was measured by using an optical radiation thermometer. The density of the sintered samples was measured by the Archimedes method. The microstructures of polished and thermally etched surfaces were examined by scanning electron microscopy (SEM, JSM-5600N, JEOL Ltd., Japan).

Results and discussion

Figure 1 shows the relationship between the sintering temperature and the density for samples containing 1.5 mol% of liquid-phase material. When the time-control method was used, samples were not densified at 925°C, but they were densified above 950°C. Because the temperature rise of the sample was extreme when the time-control method was used, it is thought that a steady liquid phase was not generated. When the power-control method was used, however, a high density of $5.4\cdot10^3$ kg m^{-3} was obtained, even at 925°C; samples were also densified at above 950°C. With time control, densification of the sample increased rapidly with increasing temperature, whereas with power control, densification increased more slowly with increasing temperature. These results suggest that the power-control method permits more-precise experiments to be performed. To avoid big temperature fluctuations, we performed our subsequent experiments by using the power-control method.

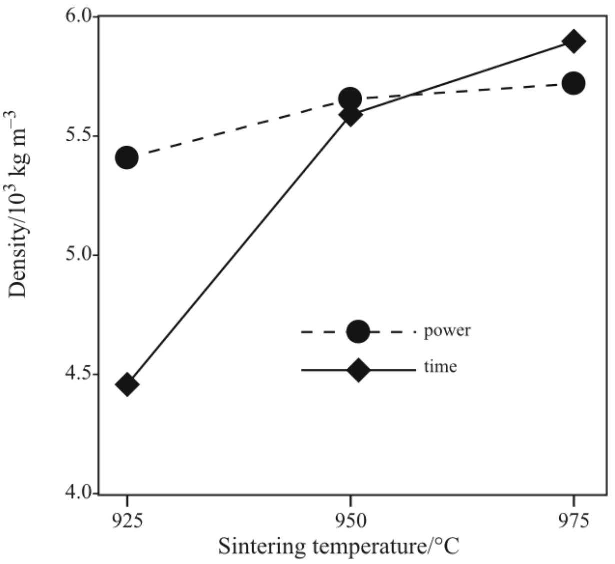

Fig. 1 Density of $BaTiO_3$ with liquid phase as a function of sintering temperature

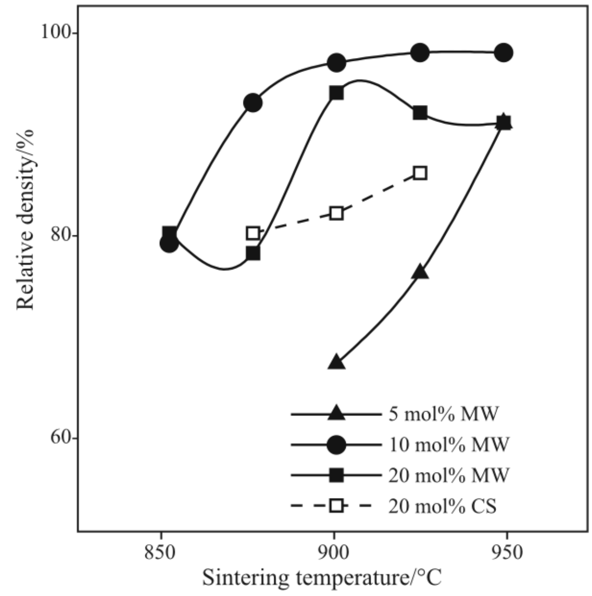

Fig. 2 Relative density of $BaTiO_3$ with liquid phase as a function of sintering temperature

Figure 2 shows the relationship between the amount of liquid-phase additive and the relative density of samples sintered at 850 to 950°C. The true density of the sample in each condition was calculated by summing the true density multiplied by the volume ratio of each raw material. The relative density was obtained by dividing experimental value by this calculated value. The sample was not densified at 900°C when 5 mol% of liquid-phase material was added. The density increased to 90% at 950°C, which is above the temperature necessary for the generation of a liquid phase. When the amount of liquid-phase material was 10 mol%, a relative density of 80% was achieved at 850°C. The density increased with increasing temperature, reaching 97% at 900°C: it then remained almost constant at up to 950°C. When 20% of liquid phase was used, the densification behavior

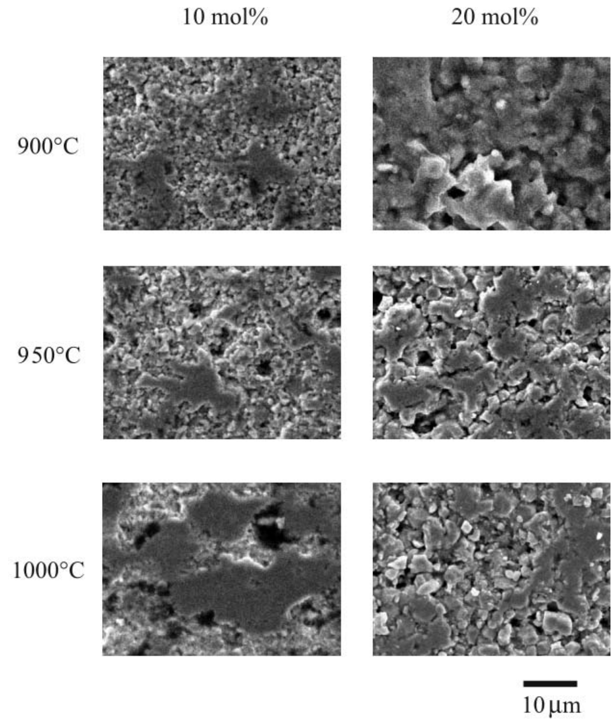

Fig. 3 SEM photographs of $BaTiO_3$–10/20 mol% BaB_2O_4 microwave-sintered sample

was different: after decreasing tendency in relative density between 850 and 875°C, the densification of the sample advanced at up to 900°C, as in the case of the sample containing 10 mol% of liquid-phase. However, the density decreased when the sintering temperature exceeded 900°C. When we used a conventional electric furnace, a sample containing 20 mol% of BaB_2O_4 was not densified at 950°C. Figure 3 shows SEM photographs of the fracture surfaces of samples. When the amount of liquid phase was 10 mol%, the particle size was about 1 µm, whereas the grain size was about 2 µm in cases where the amount of liquid-phase was 20 mol%. A glasslike material can be seen in all the photographs. These results show that a liquid phase was generated at each of the sintering temperature.

Figure 4 shows the changes in the electric power consumed by the microwave furnace for samples of various compositions. The heating rate was 0.5°C s^{-1} and the sintering temperature was 900°C for 600 s. The least energy was consumed for the sample containing 5 mol% of liquid phase. Samples containing 10 or 20 mol% liquid-phase showed almost equal power consumptions. However, electric power was consumed more efficiently at low temperatures by the sample containing 20 mol% liquid-phase. Because the liquid-phase absorbs the microwave easily, it is thought that the generation of the liquid-phase became early.

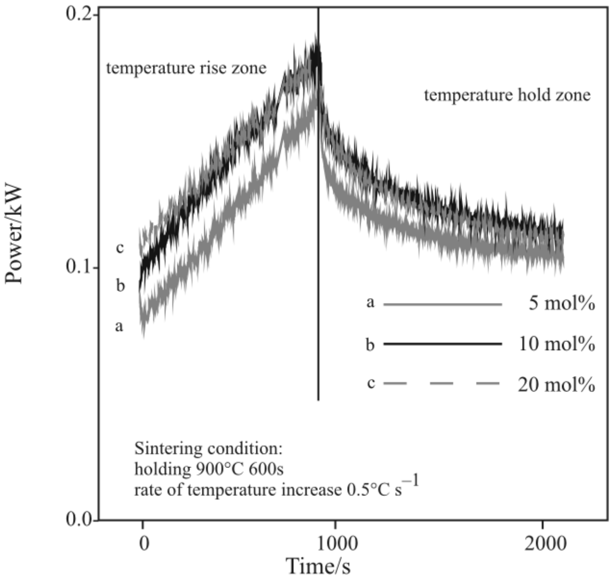

Fig. 4 Change in consumed power in the furnace with time

Let us consider the process for generating the liquid phase on the basis of the results that we obtained by using the microwave furnace. It is known that barium borate forms a liquid phase at 924°C when mixed with barium titanate. When we used the conventional furnace, none of the samples was densified at 900°C, but the samples containing 10 or 20 mol% barium borate were densified at this temperature when the microwave furnace was used. When large amounts of liquid-phase material were present, large amounts of energy were consumed in the furnace. This shows that the liquid-phase component itself absorbs large amounts of energy. Because the liquid-phase component absorbs microwave energy, the sample is self-heating. Therefore, it is likely that the temperature of the liquid phase rises above the measured temperature, because the measured temperature records the temperature of the composite as a whole. This hypothesis is confirmed by the examination of the SEM photographs where the liquid phase was observed at any temperature. Therefore, we believe that the samples underwent densification at a temperature below the normal liquid-phase generation temperature.

The density of 20 mol% of liquid phase containing sample decreased at sintering temperatures exceeding 900°C. We believe that the presence of lots of pores in the microstructure a result of effusion of the too much generated liquid phase to the outside of the sample. In other words, the liquid-phase forming component played a role even at 900°C. However, it flowed out from the sample easily and did not assist in the liquid phase sintering so the viscosity was lowered at temperatures higher than 900°C.

Conclusions

We obtained the following results when ceramics were sintered by liquid-phase microwave sintering.

- The sample was densified at a temperature below the temperature where the liquid phase is normally generated when a sufficient amount of the liquid-phase material was present.
- The sample containing 10 mol% of liquid-phase material was efficiently densified.
- When too much liquid-phase material was present, densification of the sample was obstructed.

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