

Sintering of Partially Stabilized Zirconia using a Domestic Microwave Oven

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Partially stabilized zirconia (PSZ) powders were fully densified by microwave heating using a domestic microwave oven. The pressed powder compacts of PSZ were sandwiched between two ZnO-MnO₂-Al₂O₃ (ZMA) ceramic plates acting as preheaters in the microwave oven and put in the oven. PSZ ceramics fabricated with the domestic microwave oven for 16 min exhibited a density of 5.94 g/cm³, which is approximately equal to the density of bodies sintered at 1350°C for 4 h or at 1400°C for 16 min by the conventional furnace method. The PSZ pellet pre-heated by the ZMA ceramics more easily absorbed the microwave energy and self-heated to a higher temperature. The microwave heating enhanced not only the densification but also the grain growth. From this viewpoint, it was judged that the atomic diffusion should be promoted by irradiation of the microwave.

Key words: partially stabilized zirconia, domestic microwave oven, microwave sintering

1. INTRODUCTION

Microwave heating is a self-heating process that occurs through the absorption of electromagnetic energy by a dielectric material. A heating rate and a thermal efficiency higher than those achieved by conventional methods are obvious characteristics of this process.¹ As a novel sintering method, microwave heating has been applied to a number of ceramics such as ZnO,² Al₂O₃,³ ZrO₂,⁴ PZT,⁵ oxide superconductor⁶ etc. The microwave energy (P) absorbed into a dielectric material with volume (V_s) is estimated as¹

$$P = \frac{1}{2} \epsilon_0 \epsilon'' \omega E^2 V_s \quad (1)$$

where ϵ_0 is the dielectric constant in a vacuum, ϵ'' is the dielectric loss, ω is the angular frequency of the irradiated microwave and E is the electrical field strength. In this equation, it can be seen that the heating of material with high ϵ'' is easy, while a high power microwave is necessary to heat material with a low ϵ'' .

The domestic microwave oven used for cooking is one of the available microwave heating instruments. Since its power density is low, it generally cannot heat ceramics to a high temperature. Domestic microwave ovens, however, are very cheap as well as convenient to use; therefore, if a dense ceramic could be obtained using one of these ovens, this new process could make a significant contribution to the economical fabrication of various ceramics with homogeneous, fine grain microstructures.

Baghurst *et al.*⁶ have reported that several inorganic oxides, including CuO, absorb microwave radiation very strongly, and in their study a YBa₂Cu₃O_{7-x} superconductor was prepared using a domestic microwave oven. Donor doped ZnO is also an exception and self-heats up to 500°C in a domestic microwave oven.⁷ Hayashi *et al.* have reported that the ZnO-MnO₂⁷ and ZnO-Fe₂O₃⁸ ceramics

self-heat up to 800°C using a microwave oven. It is known that the dielectric loss increases with increasing temperature. Thus, even in materials with a low absorbance of microwaves energy can absorb very effectively at elevated temperatures, resulting in self-heating up to an even higher temperature.

Given this relationship, we have proposed a new process for sintering of ceramics with a low absorbance of microwave radiation at a low temperature in a domestic microwave oven; using this method, we have obtained dense partially stabilized zirconia (PSZ) ceramics.^{9,10} The heating of PSZ, however, is not possible in a domestic microwave oven without a preheater. In this new process, the pressed PSZ powder compact is heated initially with an attached ZnO-MnO₂-Al₂O₃ ceramics preheater, resulting in an increase in the dielectric loss. As a consequence, the PSZ specimen pre-heated in the first step effectively absorbs the microwave energy and attains a higher temperature in a microwave oven with low microwave power density. Temperatures over 1200°C can be reached, and dense ceramics over 5.9 g/cm³ can be successfully prepared. On the other hand, the attained temperature was lower than 1300°C and this temperature is too low to prepare the sample with high density using the conventional furnace method.

In this paper, we will discuss the efficiency of the sintering of PSZ using a domestic microwave oven from comparison with the sintering using a conventional furnace method.

2. EXPERIMENTAL PROCEDURE

The material employed as a microwave heater was 72.5ZnO-27MnO₂-0.5Al₂O₃. This material is referred to as ZMA hereafter. ZMA was prepared by the following procedure. Zinc oxide, manganese dioxide, and alumina

powders (purity of 99.99%, High Purity Chemical Lab., Sakado, Japan) were mixed in iso-propanol and then dried. This powder was then pressed into a pellet (30 mm in diameter, 4 mm in thickness) in a steel die and sintered at 1300°C for 4 h in air.

PSZ powder (HSY-3W-SD, 3 mol% yttria, Daiichi Kigenso Kagaku Kogyo Co., Ltd., Osaka, Japan) for sintering was pressed into a pellet (20 mm in diameter, 3 mm in thickness) in a steel die. The green density of the compacted pellets was 3.2 g/cm³. As reported in Ref.10, the diameter of the pellet (>20 mm is preferred) is the important factor to obtain the dense PSZ ceramics.

Figure 1^{9,10} shows the assembly used to sinter the PSZ in the domestic microwave oven. The pressed compact of PSZ was sandwiched between ZMA ceramic pellets. Fibrous alumina-silica board (Kaowool 1600 Board, Isolite Insulating Products Co., Ltd., Osaka, Japan) was used for the thermal insulation. The employed microwave oven (KD540, Maruman Co., Ltd., Tokyo, Japan, 2.45 GHz in frequency, 500 W in power) was the simplest available type of oven for cooking, with two modes ("heating" and "defrosting") and a timer. The inside dimension of the oven was 250×250×180 mm³. The turntable (230 mm in diameter) was equipped to make the heating uniform. The assembly was put in the optimum position on the turntable so as to attain the highest temperature and then heated for 2-20 min using the "heating" mode. The temperature attained was estimated using a Pt-Pt(13%Rh) thermocouple. Since one thermocouple was broken by a serious discharge

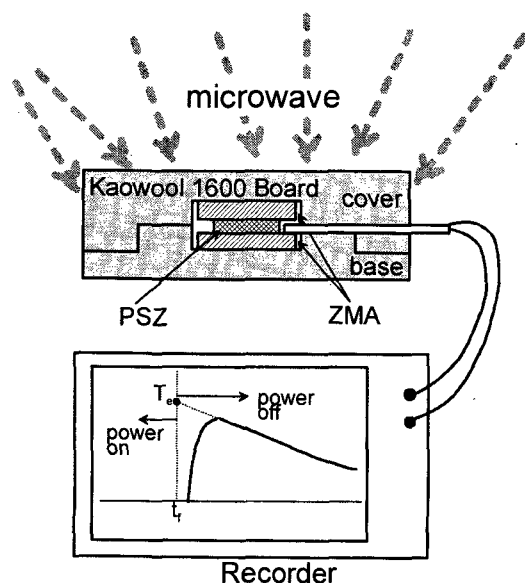


Fig.1 Diagram of the sintering fixture and the temperature estimation. Outer shell (cover and base) produced by Kaowool 1600 Board size: 100×60×40 mm³. The Pt-Pt(13%Rh) thermocouple was inserted quickly after turning off the power of the microwave oven and its thermoelectric motive force was recorded. An attained temperature (T_e) was estimated by extrapolating the cooling curve to the finish operation time of the microwave oven (t_f).^{9,10}

in the operating microwave oven, a thermocouple was quickly inserted through the hole of the assembly after turning off the power and its thermoelectric motive force was recorded. The attained temperature was estimated by extrapolating the cooling curve to the finish operation time of the microwave oven, as shown in Fig. 1. The mathematical formula for this curve fitting was described in Ref.9. The estimated temperature by this method agreed with the temperature measured by a thermal shrinkage type sensor (Ref-thermo, JFCC, Nagoya, Japan) within $\pm 10^\circ\text{C}$. All temperatures attained by microwave heating were estimated by this method using a thermocouple.

The PSZ pellets were sintered by the conventional furnace method at 1100-1500°C for 16 min and 4 h. For the short period sintering (16 min), the pellets were inserted into the furnace kept at sintering temperature for 16 min and then quenched to room temperature. The pellets sintered for 4 h were heated and cooled with the normal rate of 10°C/min.

The microstructure of the fracture surface was observed by SEM (Jeol 6300F).

3. RESULTS AND DISCUSSION

ZMA used as a microwave pre-heater is a porous material consisting of ZnO and ZnMn₂O₄ phases. The density of the used ZMA ceramics was 4.35 g/cm³. (The theoretical densities of ZnO and ZnMn₂O₄ are reported to be 5.68 g/cm³ and 5.18 g/cm³, respectively.) The addition of Al₂O₃ to ZMA increased electrical conductivity (thereby increasing the dielectric loss) and prohibited densification. The maximum temperature reached by the self-heating of ZMA in the microwave oven increased from 800°C to 1000°C with doping Al₂O₃.

As shown in Fig.2^{9,10}, the ZMA couple self-heated up to over 1000°C after 12 min in the microwave oven. When the PSZ pellet was sandwiched by the ZMA pellets, the temperature reached over 1200°C after 8 min of operation.

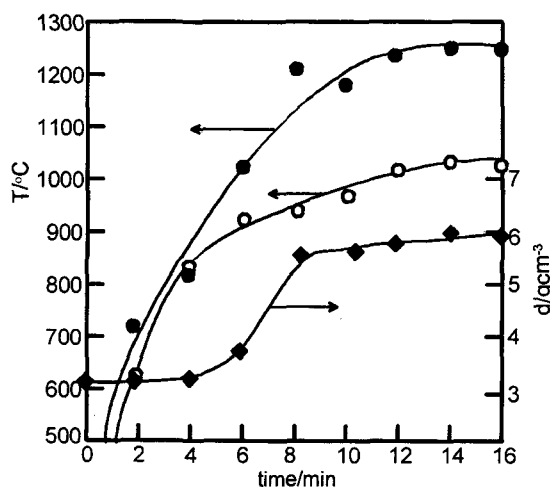


Fig.2 Achieved temperature for only ZMA couple (○), for ZMA-PSZ-ZMA assembly (●) and the resulting density of PSZ (◆) over the operating time of the microwave oven.

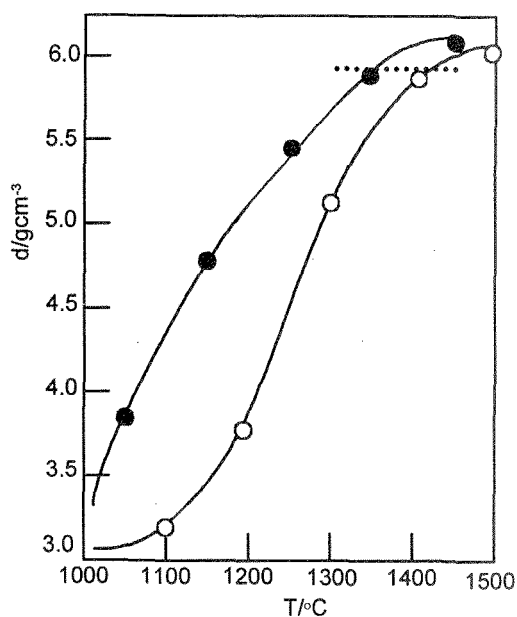


Fig.3 Density of PSZ sintered by the conventional furnace method for 4 h (●) and 16 min (○). The dotted line indicates the density sintered by the domestic microwave oven.

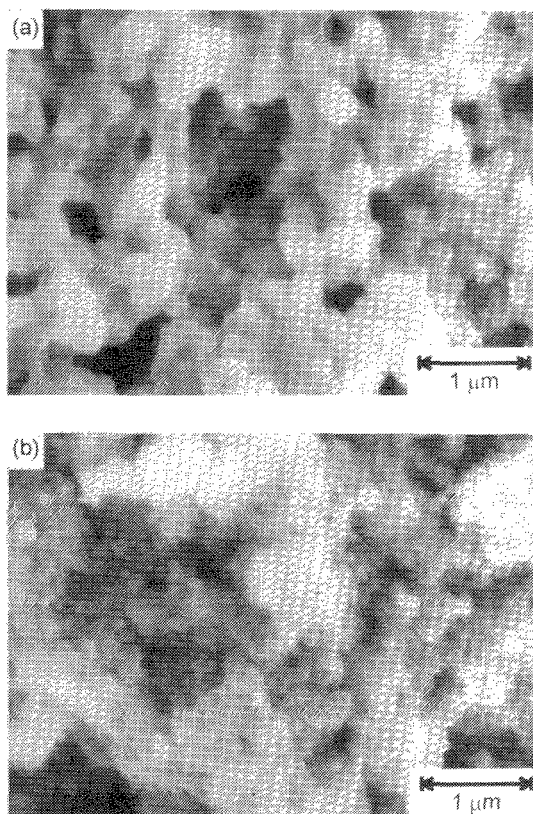


Fig.4 Microstructures of the fracture surface for the specimens (a) fabricated by a domestic microwave oven for 16 min, (b) heated by furnace at 1250°C for 16 min.

The densification of the PSZ pellets started after 4 min, and the highest density attained was 5.94 g/cm³ after heating for 14-16 min. The density of the fully densified PSZ was 6.05 g/cm³.¹¹ The sintered PSZ bodies consisted of a tetragonal phase.

The authors consider that the densification of PSZ in this study proceeded as follows. The ZMA pellet self-heated through the irradiation of microwaves (1000°C) and acted as a preheater for the PSZ pellet. The oxygen ionic conductance in the PSZ pellet increased at a higher temperature, and the dielectric loss then increased. In this manner, a more effective absorption of microwave energy into the PSZ pellet occurred, and the PSZ pellet was then sintered with self-heating up to higher temperature (1250°C).

The density of PSZ sintered by the conventional furnace method for 16 min and 4 h is shown in Fig.3. Heating at 1350°C for 4 h or at 1400°C for 16 min was required to get the density as high as 5.94 g/cm³ by conventional furnace heating. The density of PSZ sintered at 1250°C for 16 min which is compatible to the microwave heating condition was estimated to be 4.7 g/cm³. From these results, it is judged that use of the microwave oven enhances the densification of the PSZ. It is known that densification by the normal microwave heating with a high power density occurs at a lower temperature than that by the conventional heating method.¹ A similar phenomenon occurs in this process using a domestic microwave oven.

The microstructures of the fracture surfaces for the specimens obtained by microwave heating for 20 min, and the specimen fabricated by conventional furnace heating at 1250°C for 20 min with rapid heating and quenching process are shown in Fig.4 (a) and (b), respectively.⁹ The microstructure was homogeneous, and no cracks were observed in these specimens. Though both specimens shown in (a) and (b) were prepared with the similar heating processes, the grain size of the samples shown in (b) obtained by the conventional method was smaller than those obtained by using the microwave oven. The grain size shown in (a) was estimated to be 0.2 μm and that shown in (b) was estimated to be <0.1 μm.⁹ From this result, it is suggested that the microwave oven process enhances not only the densification but also the grain growth.

Several models have been proposed to explain the densification at low temperature by the microwave method.¹² Among them, the model of the activation of the surface by the microwave irradiation is most accepted. Janney et al. measured the depth profile of ¹⁸O into the sapphire and reported that the oxygen diffusion was promoted by the microwave irradiation.¹³ But, since the remarkable grain growth did not occur generally during the microwave heating, it is considered that the promotion of the diffusion is an assisting factor to densify the ceramic at the low temperature. In the present case, the remarkable grain growth was observed. As mentioned above, the densification and the grain growth in the microwave oven occurred at lower temperature (>100°C) than that required for the conventional sintering. Though the estimation for

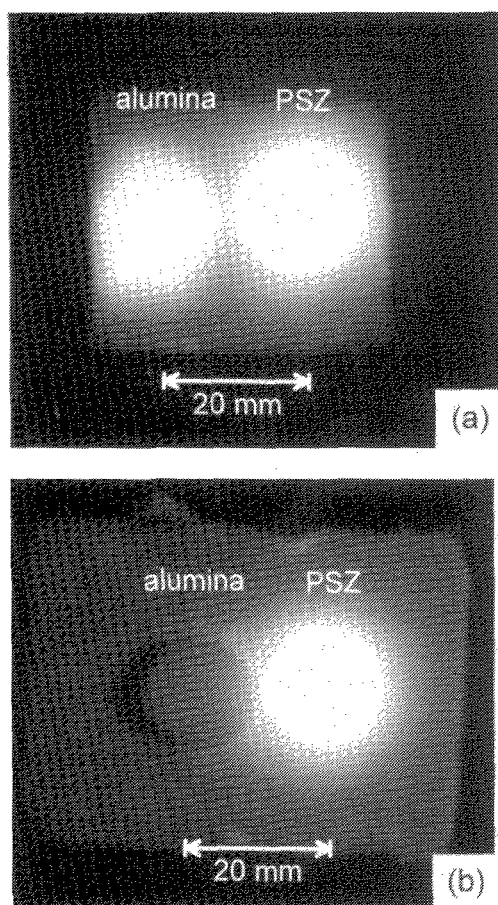


Fig.5 PSZ and alumina pellets heated by a furnace at 1200°C (a), quickly moved into the microwave oven and 10 min operating (b).

attained temperature contains any error, it can not exceed over 50°C. From these viewpoints, it is judged that the promotion of the atomic diffusion plays an important role to densify PSZ ceramics in the microwave oven at the lower temperature.

The most important point in this microwave heating is that the self-heating by the absorption of the microwave caused in the domestic microwave oven and its sintering behavior were almost the same as those done in the microwave heating system for ceramics. It is clear from the temperature measurement shown in Fig.2 that the self-heating of the PSZ by the microwave irradiation occurred. The self-heating of the PSZ up to a high temperature was also visually confirmed as follows. The PSZ and alumina pellets were pre-heated by a furnace at 1200°C and quickly moved into the microwave oven. At this stage, both the PSZ and alumina pellets showed a red heat color, as shown in Fig.5(a). The red heat of the PSZ pellet continued, but that of the alumina pellet disappeared after the microwave oven operated for 10 min, as shown in Fig.5(b).

By using this domestic microwave oven process, we were able to obtain dense ZnO, ZnO varistor, TiO₂,

semiconducting BaTiO₃ and PZT ceramics, but alumina could not be densified.

4. ACKNOWLEDGEMENT

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