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Improving Sinterability of Ceramics Using Hybrid Microwave Heating

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ABSTRACT

Microwave processing, as a new method for sintering ceramics, has key advantages such as increased heating rate, uniform heating and reduced cost compared to conventional methods. It is generally accepted that microwave sintering can improve the macroscopic mechanical performances of ceramics, however, the performances of microwave sintered ceramics on the microscopic scale are rarely investigated. In the

present study, the ceramics are sintered by hybrid microwave sintering (HMS), which combines the characteristics of microwave heating and conventional heating. To evaluate the homogeneous performance of the sintered ceramics, the behaviors of thermal residual stress distribution in the microwave sintered and conventionally sintered ceramics were investigated by X-ray diffraction technique. The thermal residual stress investigation shows microwaves can sinter an ceramics in entire volume while offering improved mechanical properties. Subsequently, the distribution behaviors of pore ratio and hardness in the ceramics were investigated respectively. The experiment results confirm that the sinterability of ceramics is homogenously improved by hybrid microwave sintering.

KEY WORDS: Microwave sintering, Ceramics, thermal residual stress, pore ratio, Hardness.

1. INTRODUCTION

Microwave heating is a process in which the materials couple with microwaves, absorb the electromagnetic energy volumetrically, and transform it into heat. This is different

from conventional methods such as electric heating or vapor heating, in which heat is transferred between objects by the mechanisms of conduction, radiation and convection. In conventional heating, the material's surface is first heated followed by the heat moving inward. This means that there is a temperature gradient from the surface to the inside. However, microwave heating generates heat within the material first and then heats the entire volume (Yadoji et al., 2003). This heating mechanism is advantageous to rapid heating rates, uniform heating, selective energy absorption, high efficiency and reduced costs (Yadoji et al., 2003; NMAB, 1994; David et al., 2000). In recent years, microwave heating has been well employed in the sintering and joining of ceramics. It has been demonstrated that microwave sintering has the potential of enhanced densification and suppressed grain growth due to a fast heating rate and apparent low-temperature firing (Tsay et al., 2004; Clark et al., 1997). In the previous studies (Gupta and Wong, 2005; Mizuno et al., 2004; Travitzky et al., 2000), researchers have evaluated the advantages of the performance of microwave sintered ceramics just on a macroscopic scale, focusing on tensile strength, elastic modulus, toughness and so on, and found overall mechanical performance is improved by microwave sintering. However, the performances of microwave sintered ceramics on a microscopic scale are rarely investigated. In addition, the sinterability of ceramics is generally evaluated by

measuring the relative densification. It should be noted that densification is difficult to estimate at a local scale, which leads to difficulties in characterizing the homogenous sinterability of microwave sintered ceramics (Boch and Lequeux, 1997).

In the present study, Al_2O_3 ceramics are sintered by hybrid microwave heating and conventional heating method respectively. The behaviors of thermal residual stress and the pore ratios were investigated, and utilized to characterize hybrid microwave sintered specimens and conventionally sintered specimens. The characteristics of two-directional hybrid microwave sintering were also confirmed by using thermal residual stress and the pore ratio distribution. Otherwise, Vickers Hardness (HV) distribution was also investigated. The advantages of the performance of hybrid microwave sintered ceramics are evaluated on the microscopic scale, and the experimental results confirm that the sinterability of ceramics is improved by hybrid microwave sintering.

2. EXPERIMENT

2.1 Sample preparation

High-purity Al_2O_3 (purity > 99.5%) powder was used as a raw material. The

MgO-Al₂O₃-SiO₂ system sintering additives, which consist of 21.5 wt.% MgO, 61 wt.% SiO₂, and 17.5 wt.% Al₂O₃, were employed to control the microstructure and decrease the sintering temperature (Singh, 1981; Nakajima and Messing, 1998). The average size of the powders is about 1 μ m. Al₂O₃ powder and sintering additives were mixed with organic binder, and consolidated by uniaxial pressing into disks (35 mm diameter x 15 mm thickness) at 130 MPa. The green compacts had a density of approximately 60%.

2.2 Hybrid microwave sintering and conventional sintering

Compacts formed above were sintered by microwave and conventional processing respectively. The 2.45 GHz microwave sintering system, which consists of a rectangular multimode cavity, a continually adjustable power supply (0.5 – 2.7 kW) and an insulation system, was used for microwave sintering experiment. Due to its low dielectric loss factor at room temperature and lengthy heating time, Al₂O₃ is difficult to heat via microwave radiation (Peelamedu et al., 1999; Zhao et al., 2000). However, Al₂O₃ begins to absorb microwave energy intensely after arriving the coupling temperature about 700°C. Therefore, SiC is used as a susceptor in the microwave furnace to raise the temperature of Al₂O₃ to microwave coupling temperature because of

its high dielectric loss factor and excellent refractory properties (Peelamedu et al., 1999; Zhao et al., 2000). The microwave sintering technique using susceptors is termed “hybrid microwave sintering” (Zhao et al., 2000). To enhance the sintering efficiency, a special hybrid heating system was used. SiC plates with thicknesses of 6 mm were set around the Al_2O_3 sample to initially heat it at a relative lower temperature. The temperature of specimens was measured by a far infrared fiber optic pyrometer with a range of 550-2000°C. The arrangement of the sample, the SiC susceptors and the thermal insulations are shown in Fig.1. In the conventional sintering experiment, the electric heating furnace was used, and a heating rate of 5°C/min and a holding time of 4 h at 1480°C were employed in this work.

2.3 Thermal residual stresses measurement

The thermal residual stresses in the specimens caused by the sintering were measured by X-ray diffraction (XRD) (Suzuki and Tanaka, 1999). The most important conditions for X-ray stress measurement are summarized in table 1 (Suzuki et al., 1989).

Residual stress is obtained from a gradient of a straight-line obtained from $\sin^2\psi$ diagram. The $\sin^2\psi$ diagram is drawn by measurement of the Bragg angle at 2θ every

tilt angle ψ . In plane stress state, the stress σ can be expressed as

$$\sigma = K \cdot M \quad [\text{MPa}] \quad (1)$$

$$K = -\frac{E}{2(1+\nu)} \cdot \cot \theta_0 \cdot \frac{\pi}{180} \quad [\text{MPa/deg}] \quad (2)$$

$$M = \frac{\partial(2\theta)}{\partial(\sin^2 \psi)} \quad [\text{deg}] \quad (3)$$

where, M is the gradient of straight-line obtained from $\sin^2 \psi$ diagram, K is the stress constant, E is the X-ray Young's modulus, and ν is the X-ray Poisson's ratio. E and ν depend on the diffraction plane. θ_0 is the diffraction angle of the material with a free stress state.

Thermal residual stress distributions in the radius and depth directions were determined respectively, (Fig.2). In the case of thermal residual stress, the measurement point was selected every 5 mm from the center point (maximum 15 mm radially) and was selected every 2 mm from the center point (maximum 6 mm in the depth).

2.4 Pore ratio test

Pore ratio is an important parameter for evaluating the sinterability of ceramics. In the present study, to prove the homogenous sinterability in the specimens, distributions of the pore ratio in the specimens were investigated. For investigating the distribution behaviors of the pore ratios, Scanning Electron Microscope (SEM) photos in various regions were observed. SEM observation was carried out by using the HITACHI S-4500 FE-SEM equipment. SEM photos were then imported into AT-Image, a software which can perform binary image statistics for calculating the pore ratio. The measurement points of pore ratio are shown in Fig.2. The measurement point was selected every 7.5 mm from center point (maximum 15 mm radially) and was selected every 2 mm from center point (maximum 6 mm in the depth). Additionally, in every measurement region, 15 pieces of SEM photos were used for calculations, and the average value was employed as the test result.

2.5 Micro hardness test

Hardness distributions in radial direction and in depth direction were investigated by carrying out Vickers hardness test. The objective of this test is to reveal superior

mechanical properties of the microwave sintered specimens compared to the conventionally sintered specimens. The equipment used for this test was a micro hardness tester (Akashi HM-102). The measurement points of Vickers hardness were the same as those of pore ratio test shown in Fig.2. In every measurement region, the test was carried out 15 times, and the average value was employed as the test result.

3. RESULTS AND DISCUSSION

3.1 Generation of thermal residual stress

Thermal residual stresses caused in the sintering processing are generally caused by the non-uniform temperature distribution in the material or the different expansion/contraction mismatch between the constituent phases. In this work, the thermal residual stress caused by the non-uniform temperature distribution in the cooling process is averted because the cooling speed was strictly controlled. To investigate whether the thermal stress is caused by the different contraction mismatch between the constituent phases in the cooling process, SEM observation and Energy Dispersive X-Ray (EDX) analysis were carried out to observe the constituent phases in

the sample after sintering. As shown in the SEM micrograph (Fig.3), the sintered ceramics sample consists of three phases. The elements of every phase can be confirmed via line scanning of EDX. Line scanning of EDX is useful for investigating the change in elements along a line of traverse on the specimen surface. Each pixel along the line is analyzed and contains its own spectrum of data for selected elements. The result of line scanning of EDX is given in Fig.3. It shows that the three phases are Al_2O_3 phase, $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ (MAS) system glass phase and pore respectively. Moreover, it has been indicated in a previous study (Akira and Gary, 1998) that spinel (MgAl_2O_4) and mullite ($\text{Al}_6\text{Si}_2\text{O}_{11}$) are crystallized in a part of glass phase after the heat treatment at 1480°C . Thus, the glass phase observed in the SEM micrograph may include MAS system glass, spinel (MgAl_2O_4) and mullite ($\text{Al}_6\text{Si}_2\text{O}_{11}$). It has been proved that the thermal residual stress is generated during the cooling process due to the difference of thermal expansion coefficient of each constituent phase. From table 2 (Svancarek et al., 2006; Chen and Liu, 2007; Touloukian, 1977; JSTP, 1990), it is observed that the thermal expansion coefficient of Al_2O_3 phase is more than that of other phases. During the cooling process of sintering, all phases begin to contract but the contraction speed of the Al_2O_3 phase is the highest. Therefore Al_2O_3 phase obtains the tensile forces from others constituent phases for restraining the contraction and the thermal residual stress

in the Al_2O_3 phase is tensile stress.

Pore ratio is an important parameter that is used for evaluating the sinterability of ceramics. It is also a factor that should be considered when evaluating the residual stress states for the composite materials including the pore, because the pore induces the stress relaxations in the constituent phases. In Fig.4A, the Al_2O_3 phase is surrounded by the glass phase entirely, and the tensile thermal residual stress occurs in the Al_2O_3 phase during the cooling process. However, in the case of Fig.4B, the Al_2O_3 phase is not surrounded by the glass phase entirely, a part of the residual stress in the Al_2O_3 phase is relaxed by the pore, and the value of residual stress in the Al_2O_3 phase is lower than that in the case shown in Fig.4A. Therefore it is considered that an inverse ratio relationship exists between thermal residual stress and pore ratio. In other words, the thermal residual stress value of the zone with a large pore ratio should be small. According to the relationship between the thermal residual stress and the pore ratio, it may be possible to evaluate the sinterability of ceramics from its distribution of thermal residual stress. To confirm this deduction, thermal residual stress measurement and pore ratio measurement were carried out and the relationships between them are discussed.

3.2 Thermal residual stress distributions

In this study, thermal residual stresses in the samples after sintering are measured by X-ray. Fig.5 shows that the distribution behaviors of the thermal residual stress in the samples that sintered by the two methods are different. In the sample sintered by the conventional method, stress gradients are observed in the radius and the depth directions of the sample: in the radius direction, the residual stress values in the depth of 0 mm are almost the same, but from depth of 2 mm, the thermal residual stress value of the outer part are greater than those of the inside. In the depth direction, the residual stress values in the radius of 15 mm are similar, and the stress value decreases with approaching the center point. However, the thermal residual stress gradient is not observed in both the depth and the radius directions of the microwave sintered sample. In other words, in the microwave sintered sample, thermal residual stress value of every part is almost the same. Furthermore, the thermal residual stress values of the microwave sintered sample are roughly the same as those of the stress values measured on the surface of the conventionally sintered sample.

The different thermal residual stress distribution behaviors in the two kind samples are caused by the different heating mechanisms of conventional heating and hybrid microwave heating. In the case of conventional heating, the sample is heated through

three ways of conduction, radiation and convection, so the surface of sample heats firstly and then the heat moves inward. Thus, a temperature gradient exists between the surface and the inside of the sample, which induces sintering of the outer part first.” Therefore the pore ratio of the outer side is less than those of the inside. It has been discussed above that the pore causes stress relaxation in the constituent phases, and the thermal residual stress values of the outer part is greater than those of the inside. In the case of hybrid microwave sintering, microwave heating generates heat within sample first and then heats the entire volume. Moreover, the hybrid microwave sintering realized in the present study was 2-directional as microwave assisted the sintering from inside-outside direction while SiC susceptor assisted the sintering from outside-inside direction, as shown in Fig.6. Therefore the sample heat uniformly and the temperature of every part is almost the same. Thus, pore distribution in a microwave sintered sample is roughly uniform, and the thermal residual stresses value of every part is almost the same. Furthermore, it is considered that the thermal residual stress value of the microwave sintered sample is roughly the same as those of outer part of conventionally sintered sample because of the same pore ratio.

3.3 Results of pore ratio measurement

The pore ratio distributions in the two kind samples are investigated from the SEM micrographs, and the results are shown in Fig.7. Fig.7 shows that the distribution behaviors of the pore ratio in the samples that sintered by the two methods are different. In the sample sintered by the conventional method, pore ratio gradients are observed in the radius and the depth directions of the sample: in the radius direction, the pore ratio values in the depth of 0 mm are almost the same, but from depth of 2 mm, the thermal residual stress value of the outer part are smaller than those of the inside; in the depth direction, the pore ratio values in the radius of 15 mm are almost the same, and the pore ratio value increases with approaching the center point. However, the pore ratio gradient is not observed in both the depth and the radius directions of the microwave sintered sample. In other words, in the microwave sintered sample, pore ratio value of every part is almost the same. Furthermore, the pore ratio values of the microwave sintered sample are roughly the same as those of the values measured on the surface of the conventionally sintered sample.

The different pore ratio distribution behaviors in the two kind samples are also caused by the different heating mechanisms of conventional heating and hybrid microwave heating that has been discussed in the last section. The result of pore ratio distribution

behaviors corresponded with the result of thermal residual stress distribution behaviors. According to the results, the relationship between thermal residual stress and pore ratio was confirmed and it is possible to evaluate the sinterability of ceramics from thermal residual stress distribution. From the behaviors of thermal residual stress distribution and pore ratio distribution, it was confirmed that sinterability of the outside is better than those of the inside in conventionally sintered sample, but the sinterability of every part is almost the same in microwave sintered sample.

3.4 Results of micro hardness test

HV hardness distributions are shown in Fig.8. As shown in this figure, HV hardness values of every part whether in the conventionally sintered sample or in the microwave sintered sample are almost the same. Moreover, the HV hardness value of microwave sintered sample is about twice as big as that of the conventionally sintered sample. The reason is that the fine grained microstructure is attained by microwave sintering (Tsay et al., 2004). These results revealed superior mechanical properties of microwave sintered sample compared to conventionally sintered samples.

4. CONCLUSIONS

The following conclusions can be made from the present study:

- A) The correlation between the thermal residual stress and the pore ratio in the composite ceramic material is confirmed, and it is possible to evaluate the sinterability of ceramics from thermal residual stress measurement.
- B) The uniform heating property of two-directional hybrid microwave sintering is confirmed by the thermal residual stress and the pore ratio investigations on microscopic scale.
- C) The results of the thermal residual stress and the pore ratio investigations confirmed that sinterability of the ceramics is improved by hybrid microwave heating, and Vickers hardness test on microwave sintered specimen revealed superior mechanical properties compared to conventionally sintered specimen.

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References

- Akira, N., Gary, L., 1998. Liquid-Phase Sintering of Alumina Coated with Magnesium Aluminosilicate Glass. *J. Am. Ceram. Soc.* 81 (5), 1163-1172.
- Boch, P., Lequeux, N., 1997. Do microwaves increase the sinterability of ceramics?. *Solid State Ionics*. 101-103, 1229-1233.
- Chen, G.H., Liu, X.Y., 2007. Thermophysical properties of AlN/MAS glass-ceramic composites (in Chinese). *J. Cent. South Univ. (Science and Technology)*. Vol.38 No.6, 1078-1082.
- Clark, D., Sutton, W., Lewis, D., 1997. Microwaves: theory and application in materials processing IV. *Amer. Ceramic Soc.*, pp.61-96.
- David, E., Diane, C.F., Jon, K.W., 2000. Processing materials with microwave energy. *Materials Science and Engineering*. A287, 153-158.
- Gupta, M., Wong, W.L.E., 2005. Enhancing overall mechanical performance of metallic materials using two-directional microwave assisted rapid sintering. *Scripta Materialia*. 52, 479-483.
- JSTP (Japan Society of Thermophysical Properties), 1990. Thermophysical

Properties Handbook (in Japanese). Yokendo Co., Ltd, p.257.

- Mizuno, M., Obata, S., Takayama, S., Ito, S., Kato, N., Hirai, T., Sato, M., 2004. Sintering of alumina by 2.45 GHz microwave heating. Journal of the European Ceramic Society. 24, 387-391.
- Nakajima, A., Messing, G.L., 1998. Liquid-phase sintering of alumina coated with magnesium aluminosilicate glass. J. Am. Ceram. Soc. 81(5), 1163-1172
- NMAB (National Materials Advisory Board), 1994. Microwave processing of materials. National Academy, pp. 1-8.
- Peelamedu, D.R., David, B., Levi, S., 1999. Use of partially oxidized SiC particle bed for microwave sintering of low loss ceramics. Materials Science and Engineering. A266, 211-220.
- Singh, V.K., 1981. Densification of alumina and silica in the presence of a liquid phase. J. Am. Ceram. Soc. 64(10), C133-C136.
- Suzuki, K., Tanaka, K., 1999. X-Ray Analysis of Residual Stresses in Ceramics (in Japanese). J. Soc. Mat. Sci. Japan. Vol.48 No.10, pp.1147-1154.
- Suzuki, K., Tanaka, K., Mine, N., Yamamoto, Y., 1989. Strengthening of Ceramics with Quenching Residual Stress (in Japanese). J. Soc. Mat. Sci. Japan. Vol.39 No.441, pp.590-595.

- Svancarek, P., Galusek, D., Loughran, F., 2006. Microstructure-stress relationships in liquid-phase sintered alumina modified by the addition of 5 wt.% of calcia-silica additives. *Acta Materialia*. 54, 4853-4863.
- Touloukian, Y.S., 1977. THERMOPHYSICAL PROPERTIES OF MATTER VOLUME 13: Thermal Expansion- Nonmetallic Solids. IFI/PLENUM, p.479.
- Travitzky, N.A., Goldstein, A., Avsian, O., Singurindi, A., 2000. Microwave sintering and mechanical properties of Y-TZP/20 wt.% Al_2O_3 composites. *Materials Science and Engineering*. A286, 225-229.
- Tsay, C.Y., Liu, K.S. Lin, I.N., 2004. Microwave sintering of $(\text{Bi}_{0.75}\text{Ca}_{1.2}\text{Y}_{1.05})(\text{V}_{0.6}\text{Fe}_{4.4})\text{O}_{12}$ microwave magnetic materials. *Journal of the European Ceramic Society*. 24, 1057-1061
- Yadoji, P., R. Peelamedu, R., Agrawal, D., Roy, R., 2003. Microwave sintering of Ni-Zn ferrites: comparison with conventional sintering. *Materials Science and Engineering B98*, 269-278.
- Zhao, C., Vleugels, J., Groffils, C., Luypaert, P.J., 2000. Hybrid Sintering With a Tubular Susceptor in a Cylindrical Single-Mode Microwave Furnace. *Acta mater*. 48, 3795-3801.

Fig.1 Hybrid microwave heating system

Fig.2 Measurement points

Fig.3 Line scanning of EDX

Fig.4 Stress relaxation

(A) Sample sintered by conventional method (B) Sample sintered by microwave

Fig. 5 Thermal residual stress distributions in the samples

Fig.6 Schematic diagram showing the concept of two-directional sintering

(A) Sample sintered by conventional method   (B) Sample sintered by microwave

Fig.7 Pore ratio distributions in the samples

(A) Sample sintered by conventional method   (B) Sample sintered by microwave

Fig.8 HV hardness distributions

Table 1. Conditions for X-ray stress measurement

Characteristic X-ray	Fe-K α
Diffraction plane	2 1 10
Filter	Mn foil
Tube voltage	30 kV
Tube current	10 mA
Stress constant	-458 MPa/deg.

Table 2. Thermal expansion coefficients of the constituent phases

Constituent phases		Thermal expansion coefficient ($\times 10^{-6}/^{\circ}\text{C}$)
Al ₂ O ₃ phase		8.93
Glass phase	MAS glass	3.5
	Spinel (MgAl ₂ O ₄)	7.5
	Mullite (Al ₆ Si ₂ O ₁₁)	4.8
Pore		0