Densification of Al₂O₃ powder using spark plasma sintering

S.W. Wang,^{a)} L.D. Chen, and T. Hirai

Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

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 Al_2O_3 powders with four different particle sizes were densified using a spark plasma sintering (SPS) apparatus under three different sintering conditions: holding time, heating rate, and mechanical pressure. The Al_2O_3 powder compact sintered at a higher heating rate produced a sample with a higher density and a fine-grained microstructure, while abnormal grain growth and a lower density resulted when a lower heating rate was applied, though the sintering temperature and holding time were the same in both cases. This revealed that rapid sintering by SPS was effective for promoting the densification of the powder. However, the powder with a coarse particle size was hard to sinter at a higher heating rate. Microstructural observation revealed that the edge part was denser than the inside of the sample when the holding time was short. Increasing the holding time made it possible for the inside to be sintered almost as dense as the edge part. Mechanical pressure was found to enhance densification of the Al_2O_3 powder. On the basis of these results, the SPS process is discussed.

I. INTRODUCTION

Plasma activated sintering (PAS) and spark plasma sintering (SPS) apparatuses were developed in 1988 and 1990, respectively.¹ Since then, a variety of materials such as metallic materials,^{2,3} structural ceramics,^{4,5} oxide superconductors,^{6,7} ceramic composites,^{8,9} polymers,¹⁰ thermoelectric materials,¹¹ and functionally graded materials (FGMs)^{12,13} have been prepared by SPS and PAS. SPS and PAS apparatuses are somewhat like the conventional hot-press. However, a pulse electric current and/or a direct current are applied directly to the graphite mold in SPS and PAS. Thus, the graphite mold and punches act as heating elements, which is different from the case of the hot-press. In SPS, a pulse electric current is employed for heating, while generally in PAS a pulse electric current is first applied for a short period and then a direct current is used. Details of the PAS and SPS apparatuses can be found elsewhere.^{14,15}

Recently, there has been growing interest in clarifying the sintering process of SPS and PAS, focusing on whether plasma is generated or not by the pulse electric current. According to Ishiyama,¹⁴ PAS is a technique to sinter metallic powder, possibly resulting in the generation of plasma among the metallic particles when pulse voltage is applied, which would purify and activate the particles to be sintered. Tokita¹⁵ observed neck formation among some bronze alloy grains after the SPS process and suggested that the neck formation was attributed to the effect of spark plasma caused by the pulse electric current. Furthermore, in sintering of non-metallic materials, plasma generation by pulse electric current was also suggested in both PAS¹⁶ and SPS.¹⁷ Risbud et al.¹⁶ observed clean grain boundaries in the PAS-sintered aluminum nitride (AlN) ceramics from high-purity AlN powder and suggested that plasma might be generated among the AlN particles and be effective for the removal of impurities and/or oxide layers on the surface of AlN particles. Omori¹⁷ reported several unique phenomena observed during the SPS process as follows: a lighteninglike discharge pattern on the surface of CeSiON₂ ceramics, an etched pattern on polypropylene fibers, and structural transformation from an insoluble poly(monomethylsilane) to its soluble isomer. Omori mentioned that these observed phenomena might imply the generation of plasma by the pulse electric current during the SPS process.

Kinemuchi *et al.*¹⁸ found that the chemical reaction between carbon and Si_3N_4 was promoted when the carbon-coated Si_3N_4 powder compact was sintered by SPS. However, such an effect was not observed when the powder compact was sandwiched between two insulating boron nitride (BN) pellets. They suggested that the promoted reaction was caused by electric conduction through the carbon layer on the surface of Si_3N_4 particles. Furthermore, Tomino *et al.*¹⁹ measured the electric current path in a graphite mold and in an Al₂O₃ powder compact sintered by the SPS process and reported that

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^{a)}Present address: Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, People's Republic of China.

the electric current went only through the mold and punches. Similarly, Sumi *et al.*²⁰ examined the temperature distribution within a graphite mold and Al_2O_3 powder compact during the PAS process. They found that the temperature of the mold was higher than that of the compact.

On the basis of the above findings, it can be seen that one's understanding of the SPS and PAS processes is still unclear, including whether plasma might be generated or not and in what way SPS and PAS are more advantageous than hot pressing. In our opinion, metallic and non-metallic materials should be considered individually when attempting to clarify the SPS and PAS processes. Previously, effects of PAS conditions on densification of copper powder were carried out.²¹ It was indicated that the powder was heated by Joule heat caused by the electric current passing through the powder compact and that the pulse electric current was effective for promoting densification of the copper powder. The purpose of the present study was to help clarify the SPS process concerning the sintering of nonmetallic powder, i.e., Al₂O₃ powder. Effects of SPS conditions, such as heating rate, holding time, mechanical pressure, and particle size of the starting powder, on the densification and microstructural development of Al_2O_3 powder compacts were investigated.

II. EXPERIMENTAL PROCEDURE

Four kinds of α -Al₂O₃ particles (in purity >99%) with different particle sizes were used. One was from Sumitomo Chemicals (Tokyo, Japan), with an average particle size of 0.33 µm. Three others were the products of Showa Denko (Tokyo, Japan), the average particle sizes (D-50) being 21.40, 3.46, and 0.4 µm, respectively. The powder with the particle size of 3.46 µm, which was the one being used in discussing the effect of SPS conditions on the sintering process, contains 0.37 wt% SiO₂, 0.03 wt% T-Na₂O, and 0.02 wt% Fe₂O₃. The others contains the same impurities at almost the same level.

Figure 1 shows the main components of the SPS apparatus (SPS-1050, Sumitomo Coal Mining Co. Ltd., Japan). A 6-g amount of Al_2O_3 powder was poured into the graphite mold (inner diameter 20 mm, outer diameter 40 mm) and then sintered at 1550 °C for 0 to 30 min. The heating rate varied from 20 to 300 °C/min. The applied mechanical pressure was in the range of 20 to 40 MPa. Temperatures of the samples during sintering were measured by a sheathed 13% Rh/Pt–Pt thermocouple, which was inserted into the wall of the graphite mold, as illustrated in Fig. 1. A multipen recorder recorded temperatures and shrinkage displacements of the powder compacts.

Densities of the sintered samples were determined by the Archimedes method. The surfaces and cross sections of the sintered samples were ground and polished (some of them were thermally etched) for microstructural observation by scanning electron microscopy.

III. RESULTS AND DISCUSSION

A. Effect of particle size, holding time, and sample size

Figure 2 shows the effects of particle size and holding time on relative densities of Al_2O_3 samples. Under a pressure of 30 MPa, these samples were heated at a rate of 200 °C/min and sintered at 1550 °C for 0 to 30 min (noted as 200 °C/min–1550 °C–30 MPa, hereafter). It can be seen that the smaller the particle sizes of the starting powder, the higher the relative density under the same SPS conditions. Evidently, the particle size of the starting powder played an important role in the SPS process, as in conventional sintering process.



FIG. 1. Main components of the spark plasma sintering apparatus.



FIG. 2. Effects of particle size and holding time on relative densities of Al₂O₃ samples (sintering condition: 200 °C/min–1550 °C–30 MPa).

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It is well known that the driving force of densification is greater for a powder with a finer particle size than for the one with a coarser particle size.²² It is therefore seen that the powder with a finer particle size was easily sintered to a higher density in the present case. Additionally, in SPS, the powder was brought directly to the hightemperature regime by application of a higher heating rate and then densification of the powder was further promoted, as suggested by Harmer and Brook,²³ that rapid sintering may maximize densification with minimum microstructural coarsening. Application of a higher heating rate did not work effectively on the powder with a coarse particle size (21.4 μ m), because its driving force was lower. The above results implied that selecting a powder with a fine particle size and sintering it at a high heating rate facilitate producing a fine-grained, fully densified material.

Relative densities of these samples increased with lengthening the holding time, as revealed in Fig. 2. Relative densities of the samples (starting powder: $3.46 \,\mu\text{m}$) increased from 92% to 98.7% and 99.4% theoretical density (TD) when the holding time was increased from 0 to 10 and 30 min. For the sample with a relative density of 98.7% TD, microstructure observation was carried out on a polished cross section parallel to the direction of mechanical pressure (Fig. 3). The edge part was revealed to be fully dense while the inside was not; namely, there were more pores toward the inside on the cross section of the sample. With increase of the holding time to 30 min, this sample was sintered to a relative density of 99.4% TD and possessed a more welldensified microstructure than that with a holding time of 10 min mentioned in Fig. 3.

As for the microstructure inhomogeneity in the sample sintered with a holding time of 10 min (Fig. 3), such case was also observed in Al₂O₃ sintered bodies prepared by PAS from the same starting powder.²⁴ In the PAS process, a direct current of 1300 A was used for Joule heating after a 30-s pulse electric current (800 A) was applied. Similar microstructures of the Al₂O₃ sintered bodies were obtained in both processes, indicating that the two processes were similar. Microstructure inhomogeneity may imply the occurrence of differential densification at the edge of and inside of the sample. Assuming the electric current went only through the mold and punches in sintering Al₂O₃ powder by SPS, as per the result of Tomino *et al.*,¹⁹ it is suggested that the present Al_2O_3 powder was sintered by the heat transferred from the graphite mold and punches. Subsequently, differential densification process occurred due to the thermal gradient in the samples during the SPS process, similar to the case of pressureless sintering.²⁵

To further confirm the relationship between the differential densification and thermal gradient, sintering of several Al_2O_3 samples with different thickness (by



(a)



(b)

FIG. 3. Microstructures at the (a) edge and (b) inside of the Al₂O₃ sample on the polished cross section parallel to the direction of pressure (starting powder: 3.46 μ m; sintering condition: 200 °C/min–1550 °C × 10 min–30 MPa).



FIG. 4. Effect of the sample size on relative densities of the Al_2O_3 samples (starting powder: 3.46 μ m; sintering condition: 200 °C/min–1550 °C \times 10 min–20 MPa).

changing sample weight) was carried out. Figure 4 shows the effect of the sample size on relative densities of Al_2O_3 samples. The starting powder had a particle size of 3.46 µm and was sintered at 200 °C/min–1550 °C × 10 min–20 MPa. The smaller samples have higher densities. On assumption of the Al_2O_3 powder being sintered by the heat from the graphite mold and punches, only the edge part could be sintered to nearly full density and the inside could still remain less dense when the sample was sintered for a short holding time (e.g., 10 min). So, under the same sintering conditions, an increase in the sample thickness resulted in an increase of undensified volume and therefore a decrease of average relative densities of the sintered Al_2O_3 samples.

B. Effect of heating rate

Figure 5 displays the effect of heating rate on shrinkage displacement of Al₂O₃ powder compacts, and Fig. 6 shows the relative densities of Al₂O₃ samples sintered at different heating rates. The starting powder $(3.46 \ \mu m)$ was sintered at 1550 °C \times 10 min–30 MPa. When the heating rates were higher than 50 °C/min, the shrinkage of these samples stopped before the holding time was over. As can be seen in Fig. 6, the densities of these samples reached about 99% TD. However, when the heating rates were lower than 50 °C/min, the samples had not shrunk sufficiently by the end of the sintering schedule. For example, the sample sintered at a heating rate of 20 °C/min kept shrinking till the end of the schedule. Consequently the relative density of this sample was only 97.6% TD. It is thus clear that the heating rate is an important factor in densification of Al₂O₃ powder by SPS.

Figures 7(a) and 7(b) show microstructures of the upper surfaces of Al_2O_3 samples sintered at a heating rate of 200 and 20 °C/min, respectively. The heating rate of



FIG. 5. Effect of heating rate on shrinkage displaement of Al_2O_3 powder compacts (starting powder, 3.46 μ m; sintering condition: 1550 °C × 10 min–30 MPa).



FIG. 6. Relative densities of the Al_2O_3 samples sintered at different heating rates. (The sintering condition is that shown in Fig. 5.)





(b)

FIG. 7. Microstructures of the upper surfaces of Al_2O_3 samples sintered at a heating rate of (a) 200 °C/min and (b) 20 °C/min (starting powder: 3.46 μ m; sintering condition: 1550 °C \times 10 min–30 MPa).

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200 °C/min resulted in a homogeneous microstructure and an average grain size of about 3 μm in the obtained Al_2O_3 sample; i.e., the particle size of the starting powder was retained in the final product [Fig. 7(a)]. Rapid sintering of SPS (by means of a higher heating rate) made it possible for the sample to skip over the low-temperature regime where the nondensifying mechanism (surface diffusion) is active and to proceed directly to the elevated temperature regime where densifying mechanisms (grain boundary and volume diffusion) are predominant.²³ Therefore, the powder was nearly fully densified and the size of the starting powder (3.46 µm) was retained in the final microstructure. Similar retention of the size of the starting powder was also reported in the final microstructures of Al_2O_3 ,⁴ $Si_3N_4^{5}$ and AlN^{16} sintered by SPS and PAS. However, abnormal grain growth was found in the sample sintered at a heating rate of 20 °C/min [Fig. 7(b)] though the starting powder was the same powder $(3.46 \ \mu m)$. The appearance of abnormal grain growth in commercial alumina is strongly correlated with the presence of impurities, especially when SiO2 presented with other oxides.^{26,27} It is evident that the powder $(3.46 \ \mu m)$ containing impurities (SiO₂, Na₂O, and Fe_2O_3) meets the prerequisite for abnormal grain growth. Abnormal grains appeared only when the powder was sintered for long sintering time (due to a lower heating rate, 20 °C/min). Subsequently, the grain growth decreased the driving force for densification and resulted in a sample with poor density (Fig. 6). In the case of conventional sintering methods such as pressureless sintering or hot pressing, abnormal grain growth easily occurs in Al₂O₃ ceramics and secondary phases (e.g., MgO) are often added to inhibit surface diffusion and to promote densification when Al₂O₃ powder is sintered.28

In a word, the SPS process makes rapid sintering possible by application of a high heating rate, and it also produces a sample with a low relative density and abnormal grains (as in samples made by a conventional method) when a lower heating rate is employed.

C. Effect of mechanical pressure

Figure 8 shows the effect of mechanical pressure on relative densities of Al_2O_3 samples. The starting powder had a particle size of 3.46 μ m, and the sintering condition was 200 °C/min–1550 °C × 10 min. The relative density of Al_2O_3 samples increased with increasing mechanical pressure. Generally speaking, pressureless sintering depends on the capillary pressures resulting from surface energy to provide the driving force for densification. Application of mechanical pressure during sintering is helpful to remove pores from the powder compact and to provide additional driving force for densification. The



FIG. 8. Effect of mechanical pressure on relative densities of Al_2O_3 samples (starting powder: 3.46 μ m; sintering condition: 200 °C/min–1550 °C × 10 min).

advantage of applying mechanical pressure was also revealed in the present SPS process, the same as in the case of hot pressing.²²

In our previous report, the effect of PAS conditions on densification of copper powder was investigated.²¹ It was found that a higher mechanical pressure resulted in a lower rate of temperature increase and a lower densification rate of a copper powder compact, which is contrary to the present case. In the sintering of the copper powder compact by PAS, the compact was mainly heated by the Joule heat caused by the electric current passing through the compact. The Joule heat $(Q = I^2 Rt)$ is proportional to the resistance (R) of the compact under a constant electric current. However, the resistance of the compact decreased when a higher mechanical pressure was applied. Therefore, mechanical pressure exerted influence on densification of the copper compact mainly by varying its temperature. However, the decrease in resistance of an Al₂O₃ powder compact is considered to be slight since the resistance of Al₂O₃ is very large. Moreover, it has been reported that the electric current passing through an Al₂O₃ powder compact in SPS was only 100 μ A when the temperature increased to 1000 °C²⁹ (while, generally, the current passing through the graphite mold is more than 1000 A). Therefore, mechanical pressure would not influence the temperature in sintering of Al_2O_3 powder but simply contribute to the removal of pores in the powder compact and to augmentation of driving force for densification.

In any case, heat transfer is effective because the graphite mold and punches are heating elements in SPS unlike in hot pressure. The Al_2O_3 powder in the graphite mold could be sintered by rapid sintering when a high heating rate was applied in SPS. To avoid microstructure inhomogeneity, the conditions of the sintering process of SPS should be optimized.



IV. CONCLUSIONS

From the experimental results mentioned above, some conclusions are drawn as follows:

(1) SPS was effective in the preparation of finegrained, nearly fully dense Al_2O_3 ceramics from the powder with a smaller particle size by employing a high heating rate. However, rapid sintering of SPS by a high heating rate did not work so well when the particle size of the starting powder was too large (e.g., 21.4 µm) because its driving force for densification was low.

(2) Abnormal grain growth was found in an Al_2O_3 sample when a slower heating rate was applied during the SPS process, prohibiting further densification of the sample, similar to the case of pressureless sintering or hot pressing.

(3) Microstructure inhomogeneity, that is, the edge was denser than the inside of the sample, appeared in the sample sintered at 1550 °C for a short holding time (10 min). When the holding time was 30 min, the inside could be sintered almost as dense as the edge of the sample. This result suggested that Al_2O_2 powder was heated by the heat from the graphite mold and punches. It also implied that optimization of the SPS process with regard to the starting powder, sample size, heating rate, holding time, and mechanical pressure is necessary for preparation of Al_2O_3 or other nonmetallic materials with a homogeneous microstructure.

(4) Rapid sintering was ascribed to the efficient heat transfer, because the graphite mold and punches were the heating elements, and to application of a high heating rate in SPS.

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