

## Densification of $\text{Al}_2\text{O}_3$ powder using spark plasma sintering

Ciofu Florin, Nioata Alin

SC ROMINEX SA Timisoara-filiala Tg-Jiu, Universitatea "Constantin Brâncusi"-Tg-Jiu

**Keywords:** plasma, powders, sintering, graphite mold, vacuum chamber

**Abstract:**  $\text{Al}_2\text{O}_3$  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  $\text{Al}_2\text{O}_3$  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.

### 1. Introduction

Plasma activated sintering (PAS) and spark plasma sintering (SPS) apparatuses were developed in 1988 and 1990, respectively. Since then, a variety of materials such as metallic materials, structural ceramics, oxide superconductors, ceramic composites, polymers, thermoelectric materials, and functionally graded materials (FGMs) 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. 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. 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.

The purpose of the present study was to help clarify the SPS process concerning the sintering of nonmetallic powder, i.e.,  $\text{Al}_2\text{O}_3$  powder. Effects of SPS conditions, such as heating rate, holding time, mechanical pressure, and particle size of the starting powder, on the densification and microstructure of  $\text{Al}_2\text{O}_3$  powder compacts were investigated.

### 2. Experimental procedure

Four kinds of  $\alpha\text{-Al}_2\text{O}_3$  particles (in purity >99%) with different particle sizes were used. One was from Sumitomo Chemicals (Tokyo, Japan), with an average particle size of 3.33  $\mu\text{m}$ . Three others were the products of Showa Denko (Tokyo, Japan), the average particle sizes (D-50) being 21.40, 3.46, and 0.4  $\mu\text{m}$ , respectively.

The powder with the particle size of 3.46  $\mu\text{m}$ , which was the one being 0.37%  $\text{SiO}_2$ , 0.03%  $\text{T-Na}_2\text{O}$ , and 0.02%  $\text{Fe}_2\text{O}_3$ . The others contain the same impurities at almost the same level.

Figure 1 shows the main components of the SPS apparatuses (SPS-1050, Sumitomo Coal Mining Co. Ltd., Japan). A 6-g amount of  $\text{Al}_2\text{O}_3$  powder was poured into the graphite mold (inner diameter 20 mm, outer diameter 40 mm) and 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.

### 3. 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  $200^\circ C/min$  and sintered at  $1550^\circ C$  for 0 to 30 min (noted as  $200^\circ C/min - 1550^\circ C - 30 MPa$ , hereafter). It can be seen that smaller the particle sizes of the starting powder, the higher the relative density under the same SPS conditions.

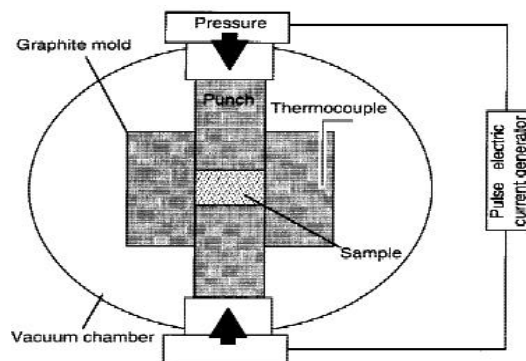


Figure 1: Main components of the spark plasma sintering apparatus.

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. It is therefore seen that the powder with a finer particle size was easily sintered to a higher density in the present case.

Application of a higher heating rate did not work effectively on the powder with a coarse particle size ( $21.4\mu m$ ), 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:  $3.46\mu m$ ) 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.

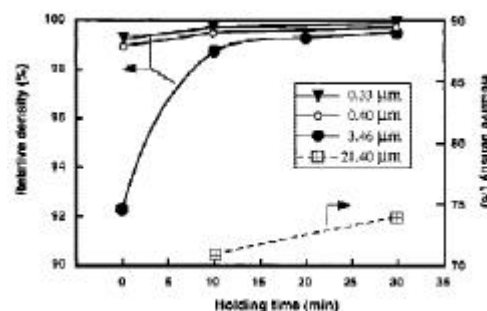
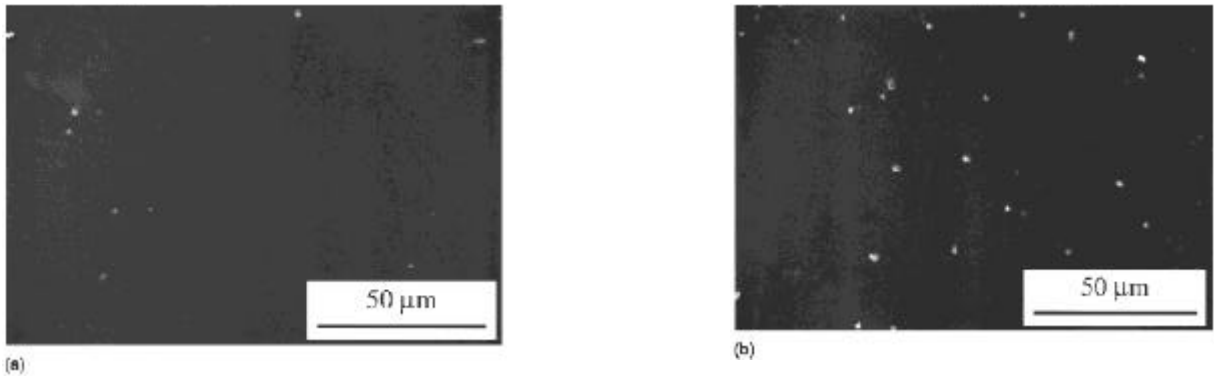


Figure 2: Effects of particles size and holding time on relative densities of  $Al_2O_3$  samples (sintering condition:  $200^\circ C/min - 1550^\circ C - 30 MPa$ ).

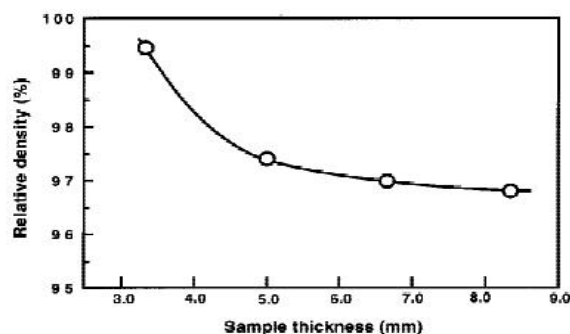
For the sample with a relative density of 98.7% TD, microstructure observation was carried out a polished cross section parallel to the direction of mechanical pressure (Fig.3.). The edge part was revealed to be fully dense while the inside was not; namely, there were more pores toward the inside on 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 well densified microstructure than that with a holding time of 10 min mentioned in Fig.3.



**Figure 3: Microstructures at the (a) edge and (b) inside of the  $Al_2O_3$  sample on the polished cross section parallel to the direction of pressure (starting powder:  $3.46 \mu m$ ; sintering condition:  $200^\circ C/min - 1550^\circ C \times 10min - 30MPa$ ).**

As for the microstructure inhomogeneity in the sample sintered with a holding time of 10 min (Fig.3), such case was also observed in  $Al_2O_3$  sintered bodies prepared by PAS from the starting powder. 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  $Al_2O_3$  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. To further confirm the relationship between the differential densification and thermal gradient, sintering of several  $Al_2O_3$  samples with different thickness (by changing sample weight) was carried out. Figure 4 shows the effect of the sample size on relative densities of  $Al_2O_3$  samples.

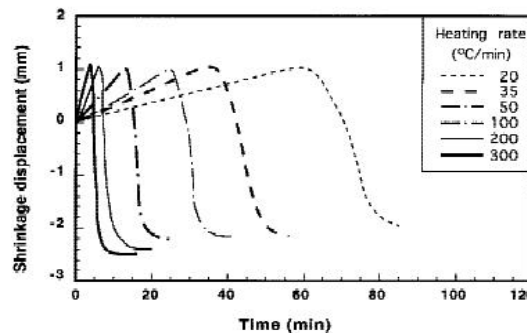


**Figure 4: Effect of the sample size on relative densities of the  $Al_2O_3$  samples (starting powder:  $3.46 \mu m$ ; sintering condition:  $200^\circ C/min - 1550^\circ C \times 20MPa$ ).**

The starting powder had a particle size of  $3.46 \mu m$  and was sintered at  $200^\circ C/min - 1550^\circ C \times 10 min - 20MPa$ . 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

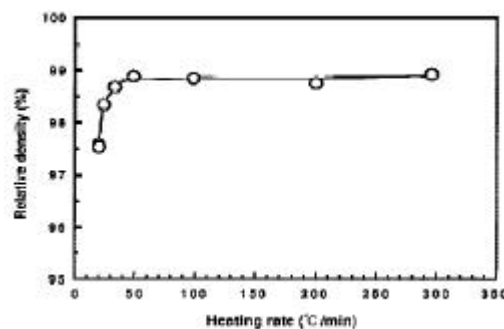
dense when the sample was sintered for a short holding time (e.g., 10 min). So, under the same sintering conditions, an increase in the sample thickness resulted in an increase of undensified volume and therefore a decrease of average relative densities of the sintered  $\text{Al}_2\text{O}_3$  samples.

**B. Effect of heating rate** - Figure 5 displays the effect of heating rate on shrinkage displacement of  $\text{Al}_2\text{O}_3$  powder compacts, and Fig. 6 shows the relative densities of  $\text{Al}_2\text{O}_3$  samples sintered at different heating rates. The starting powder ( $3.46 \mu\text{m}$ ) was sintered at  $1550^\circ\text{C} \times 10 \text{ min} - 30 \text{ MPa}$ . When the heating rates were higher than  $50^\circ\text{C}/\text{min}$ , the shrinkage of these samples stopped before the holding time was over.



**Figura 5: Effect of heating rate on shrinkage displacement of  $\text{Al}_2\text{O}_3$  powder compacts (starting powder,  $3.46 \mu\text{m}$ ; sintering condition:  $1550^\circ\text{C} \times 10 \text{ min} - 30 \text{ MPa}$ )**

As can be seen in Fig. 6 the densities of these samples reached about 99% TD. However, when the heating rates were lower than  $50^\circ\text{C}/\text{min}$ , the samples had not shrunk sufficiently by the end of the sintering schedule. For example, the sample sintered at a heating rate of  $20^\circ\text{C}/\text{min}$  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  $\text{Al}_2\text{O}_3$  powder by SPS.

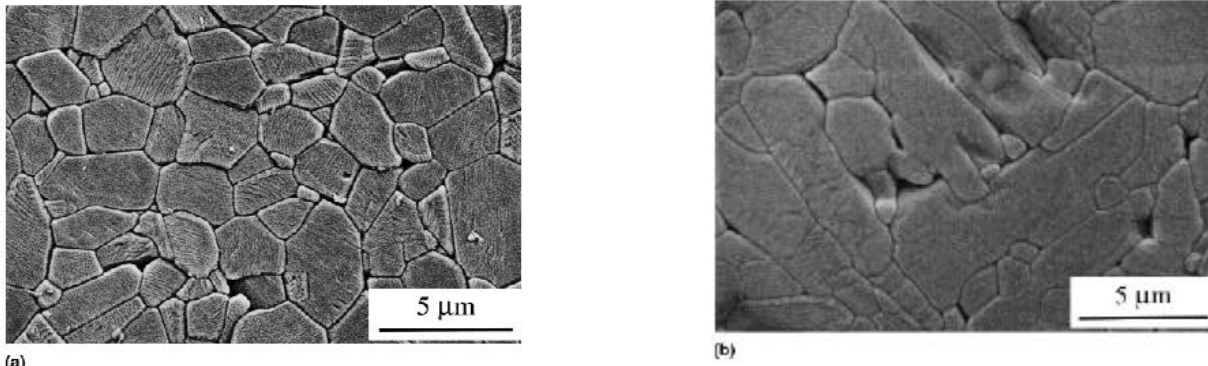


**Figure 6: Relative densities of the  $\text{Al}_2\text{O}_3$  samples sintered at different heating rates. (The sintering condition is that shown in fig. 5).**

Figures 7(a) and 7(b) show microstructures of the upper surfaces of  $\text{Al}_2\text{O}_3$  samples sintered at a heating rate of 200 and  $20^\circ\text{C}/\text{min}$ , respectively. The heating rate of  $200^\circ\text{C}/\text{min}$  resulted in a homogeneous microstructure and an average grain size of about  $3 \mu\text{m}$  in the obtained  $\text{Al}_2\text{O}_3$  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. Therefore, the powder was nearly fully densified and the size of the starting powder

(3.46 $\mu\text{m}$ ) was retained in the final microstructure. Similar retention of the size of the starting powder was also reported in the final microstructures of  $\text{Al}_2\text{O}_3$ ,  $\text{Si}_3\text{N}_4$  and  $\text{AlN}$  sintered by SPS and PAS.



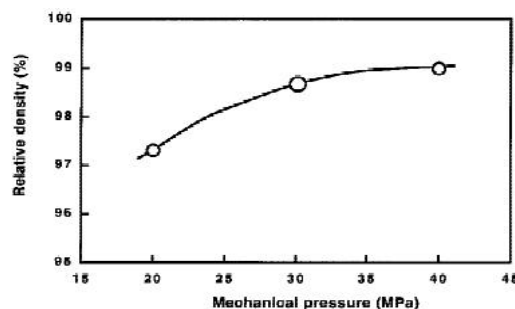
**Figure 7: Microstructures of the upper surfaces of the  $\text{Al}_2\text{O}_3$  samples sintered at a heating rate of (a) 200°C/min and 20°C/min (starting powder: 3.46 $\mu\text{m}$ ; sintering condition: 1550°C x 10min – 30MPa).**

However, abnormal grain growth was found in the sample at a heating rate of 20°C/min [Fig. 7(b)] though the starting powder was the same powder (3.46 $\mu\text{m}$ ). The appearance of abnormal grain growth in commercial alumina is strongly correlated with the presence of impurities, especially when  $\text{SiO}_2$  presented with other oxides. It is evident that the powder (3.46 $\mu\text{m}$ ) containing impurities ( $\text{SiO}_2$ ,  $\text{Na}_2\text{O}$ , and  $\text{Fe}_2\text{O}_3$ ) 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  $\text{Al}_2\text{O}_3$  ceramics and secondary phases (e.g.,  $\text{MgO}$ ) are often added to inhibit surface diffusion and to promote densification when  $\text{Al}_2\text{O}_3$  powder is sintered.

*C. Effect of mechanical pressure* - Figure 8 shows the effect of mechanical pressure on relative densities of  $\text{Al}_2\text{O}_3$  samples. The starting powder had a particle size of 3.46 $\mu\text{m}$ , and the sintering condition was 200°C/min-1550°Cx10min. The relative density of  $\text{Al}_2\text{O}_3$  samples increasing 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 sintering is helpful to remove pores from the powder compact and to provide additional driving force for densification. The advantage of applying mechanical pressure was also revealed in the present SPS process, the same as in the case of hot pressing.



**Figure 8: Effect of mechanical pressure on relative densities of  $\text{Al}_2\text{O}_3$  samples (starting powder: 3.46 $\mu\text{m}$ ; sintering condition: 200°C/min – 1550°C x 10min).**

In our previous report, the effect of PAS conditions on densification of copper powder was investigated. 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 ( $Q=I^2Rt$ ) 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 in influence on densification of the copper compact mainly by varying its temperature. However, the decreased in resistance of an  $Al_2O_3$  powder compact is considered to be slight since the resistance of  $Al_2O_3$  is very large.

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.

#### 4. Conclusions

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

- 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.  $21.4\mu m$ ) because its driving force for densification was low.

- 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

- Microstructure inhomogeneity, that is, the edge was denser than the inside of the sample, appeared in the sample sintered at  $1550^\circ C$  for a short holding time (10min). 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  $Al_2O_3$  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.

- 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.

#### 5. Bibliography.

- [1] Matsugi K., Hatayama T. – Jpn. Inst. Met. 59, 740 (1995).
- [2] Nishimura T., Mimoto M. – Sci. Lett. 14, 1046 (1995).
- [3] Omori M., Hirai T. – New Ceramics 7, 23 (1994)
- [4] Rishbud S., Shan H., Bow s. – Res. 10, 237 (1995)
- [5] Rishbud S., Shan C. – Mater. Lett. 20, 149 (1994)
- [6] Shan C., Rishbud S. – Mater. Sci. Eng. B 26, 55 (1994)
- [7] Wada M., Yamashita F. – Proc. Int. Magnetic Conf. (Magnetic Soc. of the Institute of Electrical and Electronics Engineers, 1990).