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Densification and grain growth in pulse electric current sintering of alumina

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Abstract

Pulse electric current sintering (PECS) method was used to sinter an ultrafine and high purity α-Al_2O_3 powder. The powder compact was either slowly heated (50 °C/min) or rapidly heated (300 °C/min) to temperatures ranging between 1000 and 1400 °C and then rapidly cooled down without holding. The densification and grain growth behaviors at different stages of the PECS process were investigated. At the earlier stages, fast heating greatly promoted the formation of necking between particles and enhanced both densification and grain growth; at the late stage, faster heating resulted in smaller grain sizes.
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Keywords: Al_2O_3; Densification; Grain growth; Pulse electric current sintering; Sintering

1. Introduction

Pulse electric current sintering (PECS) is a non-conventional sintering technique developed in Japan in the 1990s.[1,2]In a PECS process, a large pulsed electric current is applied to heat the graphite mould and the powder specimen which is subjected to a modest pressure inside the mould. The inventors of this technique postulated that the high pulsed electric power might generate spark or plasma in the space between the powder particles during heating, thereby calling the process spark plasma sintering (SPS).[1] This technique is also known under other names such as plasma-activated sintering (PAS),[3] or electric pulse assisted (EPA) consolidation,[4] or field-assisted sintering technique (FAST).[5,6] So far, the generation of spark or plasma during PECS has not been verified, and the mechanism involved in the process is still not clear.

PECS has recently attracted increasing interest due to its ability of rapidly heating the powder compact to high temperatures and consolidating it to high densities within very short time. It is known that for conventional sintering rapid heating is often desirable, because rapid heating usually enhances densification and suppresses grain growth so as to prepare a sintered material with high density and fine microstructure which are good for many properties. For the non-conventional PECS, the effects of heating rate on densification and grain growth have been reported to be different from that for the conventional sintering. For instance, Zhou et al.[7] found that faster heating rate resulted in larger grain size in liquid-phase sintering of SiC by PECS; and Shen et al.[8] reported that rapid heating led to the formation of large elongated grains and slow heating yielded fine equiaxed microstructure in liquid-phase sintering of Si_3N_4 by PECS. In the case of solid-state sintering by PECS, some conflicting experimental results have been reported. For example, in the PECS of alumina, Stanciu et al.[9] reported that faster heating rate resulted in smaller grain size, but Murayama and Shin[10] reported that faster heating rate led to greater grain growth. Recently, Shen et al.[11] reported that the grain growth in PECS of Al_2O_3 above a certain critical temperature could be orders of magnitude faster than that occurring in a conventionally hot-pressing process. The reason for the disparity in the above-mentioned results remains to be cleared up. In the present work, a series of PECS experiments on an ultrafine and high purity α-Al_2O_3 powder were conducted by either rapidly or slowly heating the powder to various temperatures, then rapidly cooling it down. The purpose was to investigate the densification and grain growth behaviors at different sintering stages through the entire PECS process and the effects of heating rate on densification and grain growth.

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2. Experimental

The starting powder was α-Al_2O_3 (TM-DAR, Taimei Chemical Co., Japan) with a specific surface area of 13.8 m^2/g and an average particle size of 0.15 μm. It had a purity of over 99.99% and only contained traces of impurities (Table 1). As shown in Fig. 1, the starting powder was well dispersed and had a rather narrow particle size distribution.

The PECS experiments were performed using an SPS apparatus (SPS-1050, Sumitomo Coal Mining Co., Japan). Eight grams of raw powder was loaded into a graphite die and punch unit whose outer and inner diameters were 50 and 20 mm, respectively. The unit was heated by applying pulsed dc current (pulses of 36 ms on/6 ms off) under a uniaxial mechanical pressure of 47 MPa in vacuum. The heating from room temperature to 600 °C was controlled by a preset heating program and completed within 3 min. From 600 °C, the heating continued at a heating rate of either 50 or 300 °C/min till reaching a certain maximum temperature (T_m). The heating rate was controlled by feedback of measured temperature by a microprocessor. The values of T_m chosen for experiment were 1000, 1050, 1100, 1150, 1200, 1300 and 1400 °C. The holding time at T_m was 0 min, that is to say, as soon as the temperature reached T_m the electric current was shut off and the unit rapidly cooled down. The cooling rate was about 300 °C/min from T_m down to 800 °C.

Bulk density was determined by Archimedes' principle, and the relative density was calculated using the theoretical density value of alumina (3.987 g/cm^3).

Table 1
Impurities in the starting α-Al_2O_3 powder

Element	Si	Fe	Na	K	Ca	Mg
Content (ppm)	4	4	2	1	1	1

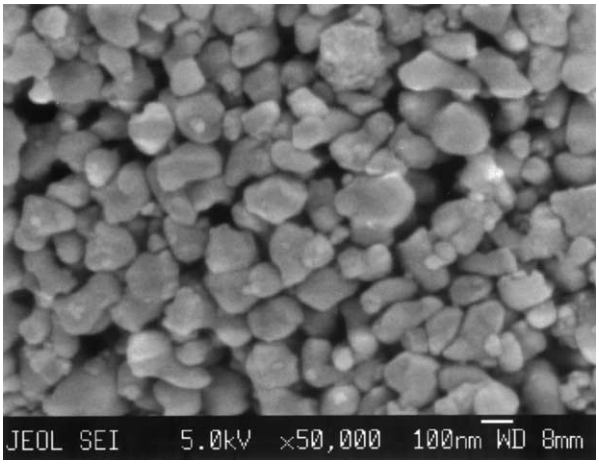

Fig. 1. SEM micrograph of the starting α-Al_2O_3 powder.

Microstructures of fracture surfaces of sintered specimens were observed with a high resolution scanning electron microscope (SEM) (JSM-6360F, JEOL, Japan) equipped with a field emission gun. Grain size analysis was performed on the digitized SEM photographs using image analysis software (Scion Image, Scion Corporation, USA).

3. Results

Table 2 summarizes the relative densities and average grain sizes of the Al_2O_3 ceramics sintered by PECS at various temperatures (T_m) and with different heating rates. Figs. 2–6 show SEM micrographs of fracture surfaces of those ceramics. These data reveal how densification and grain growth behaviors evolved in response to sintering temperature and heating rate. The detailed explanations are given below.

Heated to 1000 °C, both the slow-heated and the fast-heated specimens underwent little densification and no grain growth (Hereafter slow-heated and fast-heated specimens refer to the specimens heated at heating rates of 50 and 300 °C/min, respectively.), and the fast-heated specimen had a higher density than the slow-heated specimen (63.5% vs 61.2%). SEM micrographs (Fig. 2) reveal that their microstructures were quite different. In the fast-heated specimen necking between neighboring particles extensively occurred, but necking could hardly be observed in the microstructure of the slow-heated counterpart.

With T_m increasing to 1050 °C, the densities of the slow-heated and the fast-heated specimens increased to 61.7 and 66.5%, respectively. Obviously, the difference in density between the slow-heated and the fast-heated specimens increased. The average grain sizes of both

Table 2
Sintering conditions, relative densities and average grain sizes for the PECSed Al_2O_3 ceramics[a]

T_m (°C)	H.R. (°C/min)	R.D. (%)	G.S. (μm)
1000	50	61.2	0.15
1000	300	63.5	0.15
1050	50	61.7	0.15
1050	300	66.5	0.15
1100	50	68.6	0.15
1100	300	80.4	0.18
1150	50	76.6	0.17
1150	300	91.3	0.31
1200	50	98.7	0.58
1200	300	96.3	0.46
1300	50	99.6	3.17
1300	300	99.3	1.98
1400	50	99.4	7.65
1400	300	99.3	2.37

[a] T_m = maximum temperature; H.R. = heating rate; R.D. = relative density; G.S. = average grain size.

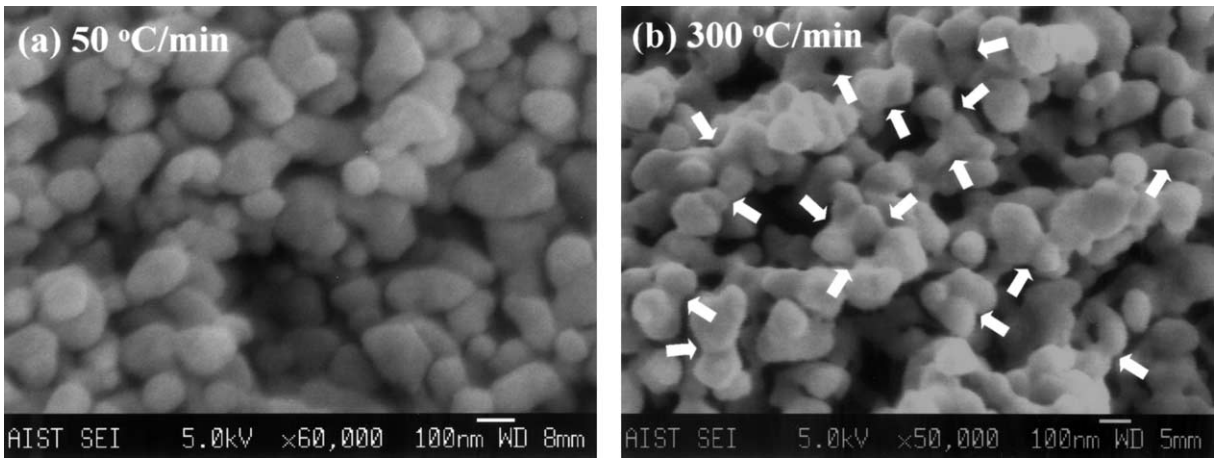

Fig. 2. SEM micrographs of the fracture surfaces of the Al_2O_3 ceramics heated to 1000 °C: (a) the heating rate was 50 °C/min and (b) the heating rate was 300 °C/min.

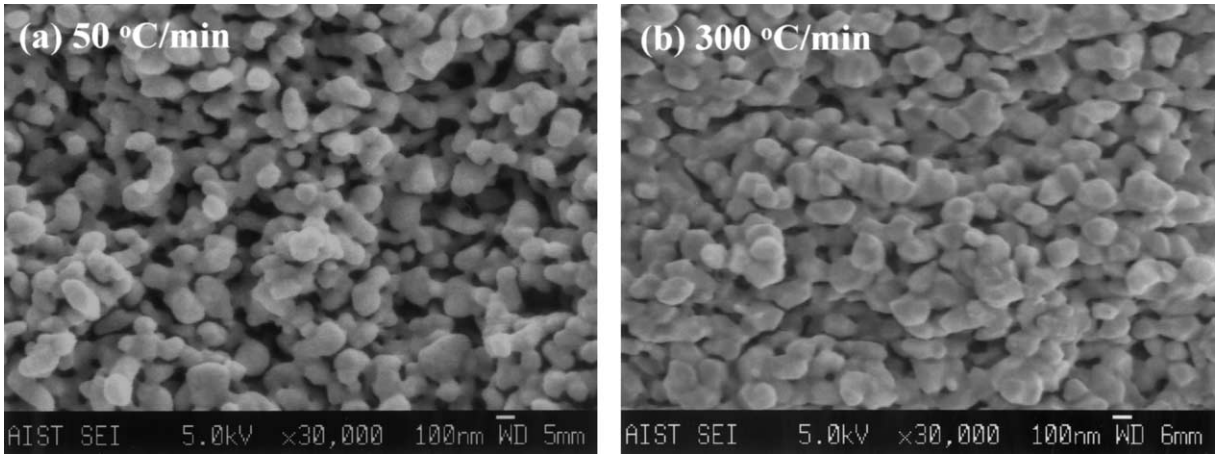

Fig. 3. SEM micrographs of the fracture surfaces of the Al_2O_3 ceramics heated to 1100 °C: (a) the heating rate was 50 °C/min and (b) the heating rate was 300 °C/min.

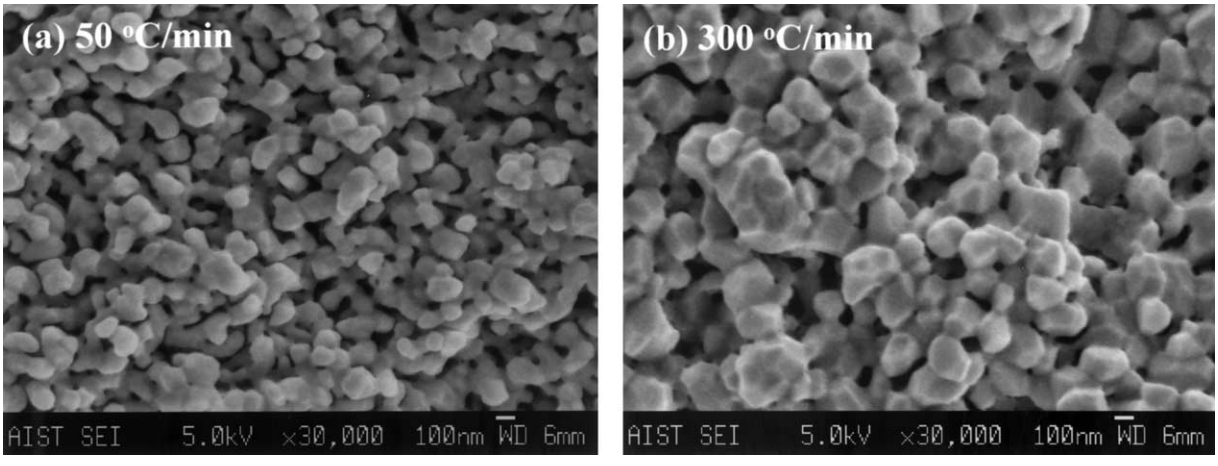

Fig. 4. SEM micrographs of the fracture surfaces of the Al_2O_3 ceramics heated to 1150 °C: (a) the heating rate was 50 °C/min and (b) the heating rate was 300 °C/min.

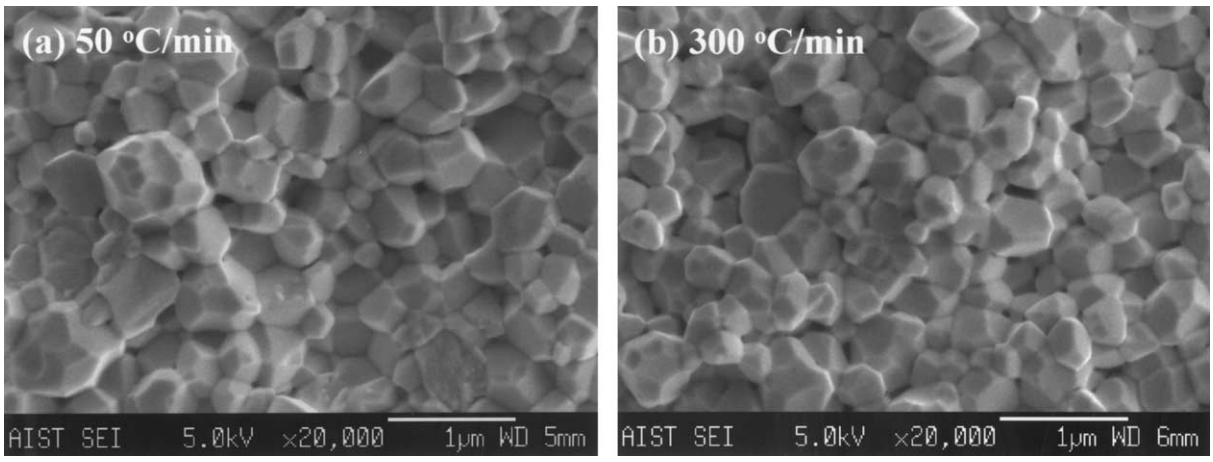

Fig. 5. SEM micrographs of the fracture surfaces of the Al_2O_3 ceramics heated to 1200 °C: (a) the heating rate was 50 °C/min and (b) the heating rate was 300 °C/min.

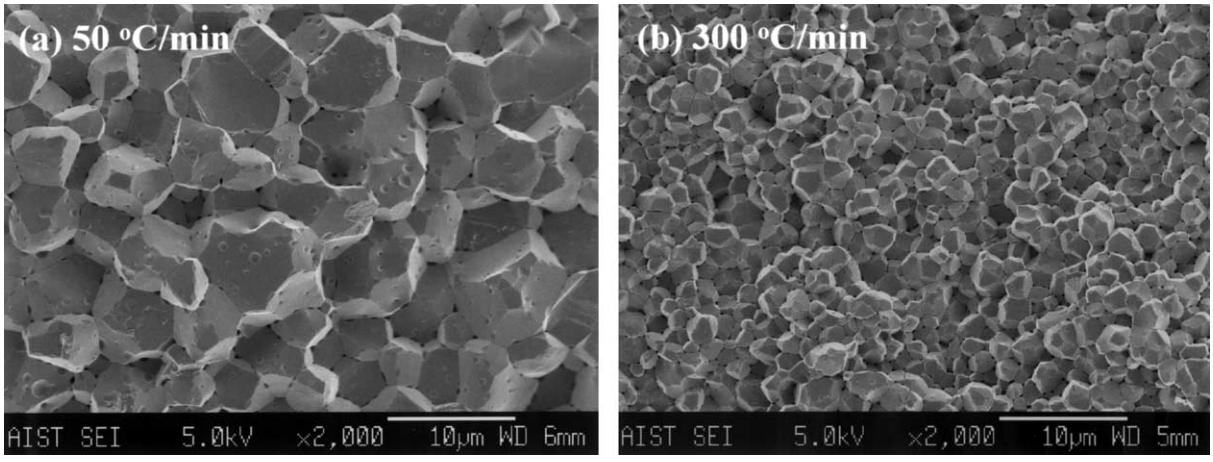

Fig. 6. SEM micrographs of the fracture surfaces of the Al_2O_3 ceramics heated to 1400 °C: (a) the heating rate was 50 °C/min and (b) the heating rate was 300 °C/min.

specimens were still same as the particle size of the starting powder.

When T_m was 1100 °C, for the slow-heated specimen, density increased to 68.6%, necking between particles extensively formed (Fig. 3(a)), yet there was no detectable grain growth; for the fast-heated specimen, density increased to 80.4%, necking between particles grew further (Fig. 3(b)), and its average grain size was 0.18 μm which was a little bigger than that of the starting powder.

With T_m improving to 1150 °C, for the slow-heated specimen, density increased to 76.6%, grain coarsening started to take place, and its average grain size was 0.17 μm; for the fast-heated specimen, density already reached 91.3% and its average grain size was 0.31 μm. Fig. 4 reveals that the grain sizes and morphologies were quite different between the slow-heated and fast-heated specimens.

The above-mentioned results show that the faster heating rate led to higher density and larger grain size when T_m was 1150 °C and below. However, such a correlation between heating rate and density and grain size reversed when T_m was 1200 °C and above.

When T_m was 1200 °C, the microstructures of the two sintered specimens became quite dense and the grains had developed faceted morphologies (Fig. 5). For the slow-heated and the fast-heated specimens, the densities were 98.7 and 96.3% and the average grain sizes were 0.58 and 0.46 μm, respectively. That is to say, the slow-heated specimen had higher density and larger grain size than the fast-heated specimen.

Heated to higher T_m, the difference in grain size between the slow-heated and the fast-heated specimens further increased, which can be clearly seen by comparing Fig. 5 with Fig. 6. The ratios of the average grain size of the slow-heated specimen to that of the fast-heated specimens were 1.3, 1.6 and 3.2 when the maximum heating temperatures were 1200, 1300 and 1400 °C, respectively.

4. Discussion

Densification and grain growth are two competing processes during sintering. In preparing high performance ceramics, it is often desirable to achieve full densification with minimal grain coarsening. For the sintering of α-Al_2O_3, Harmer and Brook[12] firstly found that samples with higher density and finer grain microstructure could be produced by faster firing. Now it is well recognized that fast heating is an effective way of enhancing densification while simultaneously limiting grain growth during conventional sintering of Al_2O_3. The effectiveness has been generally understood in terms of the difference in the activation enthalpies for densification and grain growth. During fast heating, a powder compact quickly passes through a low-temperature regime where grain growth mechanisms dominate, and proceeds to a high-temperature regime where densification mechanisms prevail.[12]

In this study, faster heating rate did not always lead to higher density and smaller grain size during PECS of Al_2O_3. The effects of heating rate on densification and grain growth varied with sintering temperatures (i.e., T_m). By plotting the relative densities and average grain sizes against T_m (Fig. 7), we found that the whole PECS process might be divided into three stages according to the different effects of heating rate on densification and grain growth. It should be aware that this way of dividing is rather arbitrary and the boundaries between stages are actually not clear and difficult to define, however, such a treatment helps lead to a meaningful analysis and it may yield an instructive insight into the PECS mechanism.

During the early stage of the PECS process (stage I in Fig. 7), both the fast heating and the slow heating resulted in limited densification and no grain growth. But, the fast-heated specimen had higher densities than the slow-heated specimen, and the faster heating led to much more extensive formation of necking between particles. It implies that the combination of fast heating and low sintering temperature may be an effective way of preparing a strong porous Al_2O_3 material by the PECS method. During stage II, densification proceeded to higher degrees and grain growth started to occur. The fast-heated specimen always had higher density and larger grain size than the slow-heated specimen. Taking into account the much less time spent on heating the specimen while using a 300 °C/min heating rate than

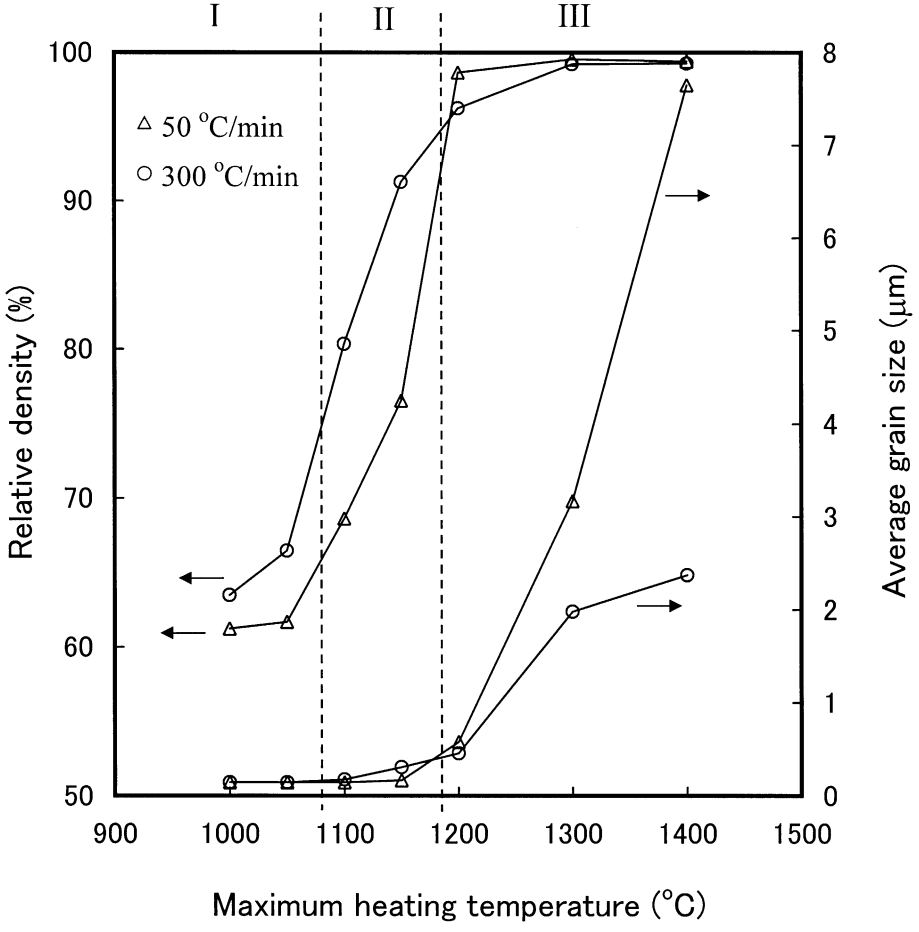

Fig. 7. Relative density and average grain size as functions of maximum heating temperature (T_m).

while using a 50 °C/min heating rate, the densification and grain growth rates in the fast- heated PECS process were much greater than those in the slow-heated PECS. During the late stage (stage III), the slowing heating started to yield higher density than the fast heating, and finally both the slow heating and the fast heating led to a near full-density; and the fast-heating specimen had smaller grain size than the slow-heated counterpart. That is to say, after the PECS process entered into the late stage, the fast-heating started to show its effect on suppressing grain growth, and such a grain-growth-limiting effect of fast heating became more obvious at higher T_m.

This study showed that the densification and grain growth behaviors during PECS of Al_2O_3 were much more complicated than those usually observed in conventional sintering. And, the effects of heating rate on densification and grain growth varied at different stages through the PECS process. The cause for these phenomena is not clear. A possible approach which may lead to a reasonable explanation is to examine whether the mass transfer mechanisms in PECS are affected or contributed by some external factors such as electric field effect.[5,11] This will be the topic of the continuing study.

5. Summary

An ultrafine and high purity α-Al_2O_3 powder was sintered by the PECS method by heating to various maximum temperatures ranging between 1000 and 1400 °C at two heating rates (50 and 300 °C/min). It was found that the effects of heating rate on densification and grain growth could vary at different stages of sintering through the PECS process. At the early stage, fast heating greatly promoted the formation of necking between particles and resulted in higher densities than slow heating; at the intermediate stage, fast heating enhanced both densification and grain growth; at the final stage, fast heating resulted in smaller grain sizes than slow heating.

Acknowledgements

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