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Direct Evidence of Temperature Variation Within Ceramic Powder Compact During Pulse Electric Current Sintering

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Pulse electric current sintering (PECS) is a powerful technique for the preparation of nanoceramics. However, the temperature distribution within the ceramic powder compact during PECS is not uniform. In the present study, aluminum hydroxide powder is used as an *in situ* temperature indicator to determine the temperature uniformity. The phase evolution within the powder compact is taken to estimate its temperature distribution. The temperature is highest near the top surface of the compact; it then reduces with increasing distance away from the top surface of the compact. The temperature variation can be significantly reduced by inserting a carbon paper in between graphite punches and graphite mold and also by reducing the heating rate.

I. Introduction

Pulse electric current sintering (PECS, also known as spark plasma sintering, SPS) is a potential technique for densifying ceramic materials. Dense alumina has been prepared by applying this technique at 1150°C for 10 min[1] or at 1250°C for 3 min.[2] The technique is also capable of producing ceramic matrix composites. It has been used to prepare dense Al_2O_3/3 vol% ZrO_2[3] and Al_2O_3/SiC nanocomposites[4] at 1450°C within 5 min. Although the densification rate during PECS is very fast, the ability to use PECS for tailoring the microstructure of ceramics is very much questionable. The coarsening rate during PECS has been reported to be extremely fast.[5] Shen *et al.* had noticed that the length of silicon nitride grains increases to five times its original length within the first minute at the peak sintering temperature; the coarsening then slows down in the next 10 min.

Regarding concerns of microstructural control, previous studies all recognized the importance of processing parameters during PECS. Systematic studies had been conducted[2,6]; the peak temperature, pressure, and heating rate are suggested to be the key parameters. Raising the peak temperature during PECS typically gives rise to a larger final grain size. The increase of pressure can shorten the time needed to reach full density. If the dwell time at the peak temperature is not reduced accordingly, it would typically result in a larger grain size. The role of the heating rate in the coarsening behavior of grains remains unclear. The increase of heating rate has been reported to result in finer grain sizes[2,3,6–8]; however, a fast heating rate has also been documented as the key to enhancing grain growth.[5] A recent study suggested that the coarsening behavior during PECS is more complicated than expected.[9] Zhou *et al.* indicated that a higher heating rate induces a declining grain coarsening rate throughout the sintering process.

More importantly, several previous studies indicated that the microstructure of the specimens prepared by PECS is not uniform.[6–8] Although the microstructure uniformity could be improved by increasing the holding time at the peak temperature,[6,7] the trade-off would be the loss of ability of the technique to produce nanostructures. The microstructural heterogeneity has been related to differential sintering induced during PECS.[8] The differential sintering is highly suspect because of the nonuniform temperature distribution within the powder compact. Nevertheless, direct evidence on temperature variation within the powder compact is still not yet available. The microstructure uniformity is one of the most important criteria to evaluate the potential of the PECS technique, and therefore, determination of the detailed mechanism for the microstructural inhomogeneity is essential.

In the present study, an *in situ* temperature indicator is used to investigate the temperature distribution within the powder compact. Aluminum hydroxide, which undergoes a series of temperature-dependent phase transformations, is introduced into the ceramic compact and treated as a temperature indicator; the temperature distribution within the compact during PECS can thus be estimated.

II. Experimental Procedure

Aluminum hydroxide powder (Zhengzhou Aluminum Co., Zheng Zhou, China) with a particle size ranging from 50 to 100 μm was used in the present study. The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) on the powder were carried out from room temperature to 1200°C using a thermal analyzer (STA 449C, Netzsch Co., Selb, Germany). The heating rate was 10°C/min. Powder compacts with a diameter of 25.4 mm were formed by uniaxial pressing at 30 MPa. A box furnace was used for the heat treatment of the powder compacts. According to the resulting TGA/DTA curves, the following temperatures: 580°, 800°, 900°, and 1200°C were chosen to heat treat the powder compacts. The heating rate was 3°C/min, and the dwell time was 0.5 h. The phases in the heat-treated and PECS specimens were analyzed using X-ray diffractometry (XRD, PW1830, Philips Co., Eindhoven, the Netherlands). The X ray first passed a slot that guided the X ray toward the central area of the specimen. The detected area covered most of the specimen surface, about 10 mm × 10 mm and 15 mm × 10 mm for a high and a low angle, respectively.

A graphite mold with a height of 60 mm, inner diameter of 20 mm, and an outer diameter of 50 mm was used as a container

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for the specimen. A 0.1 mm-thick carbon sheet was inserted into the small gap between the punches and mold unless otherwise stated. Approximately 4 g of aluminum hydroxide powder was then added into the graphite mold. An external load of 30 MPa was applied throughout the whole PECS process. Sintering was carried out in vacuum in an SPS furnace (Model SPS-1050, Sumitomo Coal Mining Co., Tokyo, Japan). A 12 ms-on and 2 ms-off pulse sequence was used. The temperature was measured by a K-type thermocouple inserted into a hole on the outer surface of the mold. A hole with a depth of 2 mm was located at the middle height of the outer surface. The peak temperature during PECS as detected by the thermocouple was 900°C. This peak temperature was chosen to limit the thermal radiation. The heating rates were either 260°C/min or 80°C/min. The current used to generate a heating rate of 260°C/min was almost four times that used to generate a heating rate of 80°C/min. The holding time at the peak temperature was 1 min. The final dimensions of the PECS specimens were 20 mm diameter and 9 mm height. For the phases at different depths in the specimens, successive XRD patterns were obtained by removing consecutive layers of materials, 0.3 mm- or 1.5 mm-thick, from the top and bottom surfaces.

III. Results and Discussion

The DTA/TGA shown in Fig. 1 suggest that the thermal decomposition mainly takes place below 550°C. A huge endothermic peak covers a large temperature range, from 580° to 1200°C, indicating that many phase changes take place within this temperature range. The phase analysis was therefore carried out on the specimens after heat treatment above 580°C.

Figure 2 shows the XRD patterns of the aluminum hydroxide powder and of the compacts after conventional heat treatment at various temperatures. The figure indicates that the aluminum hydroxide powder is mainly composed of γ-AlO(OH). After heating at 580°C for 0.5 h, χ-alumina and γ-alumina are formed. δ-alumina is then formed at 800°C in the presence of χ-alumina. κ-alumina is formed at 900°C on consumption of χ-alumina. When the powder compact is heated at 1200°C for 0.5 h, α-alumina is the only phase detected. Aluminum hydroxide thus follows the following transformation sequences as the powder compact is heated to elevated temperatures:

$$\begin{aligned}&\gamma\text{-AlO(OH)}\\&\overset{\sim 580^\circ\mathrm{C}}{\rightarrow}\chi\text{-Al}_2\mathrm{O}_3+\gamma\text{-Al}_2\mathrm{O}_3\\&\overset{\sim 800^\circ\mathrm{C}}{\rightarrow}\chi\text{-Al}_2\mathrm{O}_3+\delta\text{-Al}_2\mathrm{O}_3\\&\overset{\sim 900^\circ\mathrm{C}}{\rightarrow}\kappa\text{-Al}_2\mathrm{O}_3+\delta\text{-Al}_2\mathrm{O}_3\\&\overset{\sim 1200^\circ\mathrm{C}}{\rightarrow}\alpha\text{-Al}_2\mathrm{O}_3\end{aligned}\tag{1}$$

With the phase transformation sequences shown in Eq. (1), it is then possible to apply the phase analysis to estimate the temperature variation within the PECS powder compact.

Figure 3(a) shows the phases on the top surface and the bottom surface of the specimen after PECS at 900°C for 1 min at a heating rate of 260°C/min. Three test runs have been performed for each PECS condition. The typical results are shown in Fig. 3(a). For the specimens shown in the figure, no carbon paper was inserted into the gap between the punches and mold. The phases at depths of 0.3 and 1.5 mm under the top and bottom surfaces of the PECS powder compact are also shown. Apart from δ- and κ-alumina, α-alumina and graphite are also found on the top surface of the specimen. After removing a layer of 0.3 mm from the top surface, the intensity of α-alumina increases and no graphite is found. The phases at a depth of 1.5 mm under the top surface are δ- and κ-alumina, which are characteristic phases of the specimen heat treated at 900°C. Both χ- and δ-alumina are found on the bottom surface and within a 0.3 mm-thick layer from the bottom surface.

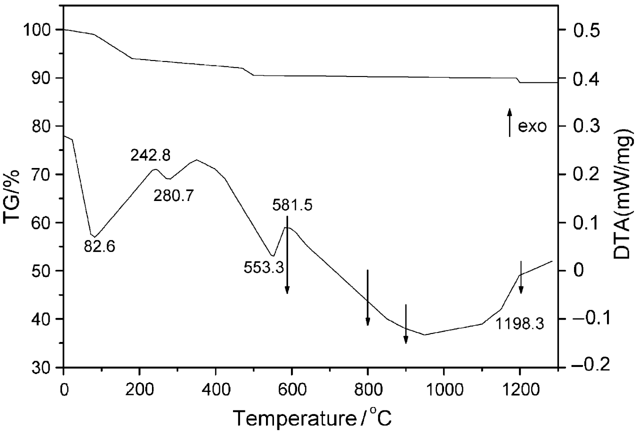

Fig. 1. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves of the aluminum hydroxide powder.

The phase analysis reveals that the temperature on the top surface is around 100°C higher than 900°C. The temperature of the PECS specimen just under the top surface is slightly higher than that on the top surface. A small amount of γ-alumina is found at the location 1.5 mm above the bottom surface, indicating that the temperature at the place is slightly lower than 800°C. The temperature variation in terms of thickness in the surface region (i.e., 0–1.5 mm from the top and bottom surfaces) is larger than that in the central region (i.e., 1.5–7.5 mm from the top surface).

The carbon paper separator was used in the PECS specimen shown in Fig. 3(b). The specimen was also heated by PECS at 900°C for 1 min at a heating rate of 260°C/min. The carbon paper had not adhered strongly to the specimen after PECS and could be removed from the specimen surface by light brushing. χ-, δ-, and κ-alumina are found across the entire cross section of the specimen, except that the intensity of κ-alumina is the highest on the top surface and lowest at a location 1 mm above the bottom surface. It indicates that a temperature variation still existed near the top and bottom surfaces. The temperature variation is smaller in the central region.

Comparing Figs. 3(a) and (b), it can be observed that the presence of a carbon paper separator reduces the temperature variation during the PECS process. Zavaliangos *et al.*[10] had suggested that the presence of a carbon paper separator could improve temperature uniformity. The present study reinforces this argument.

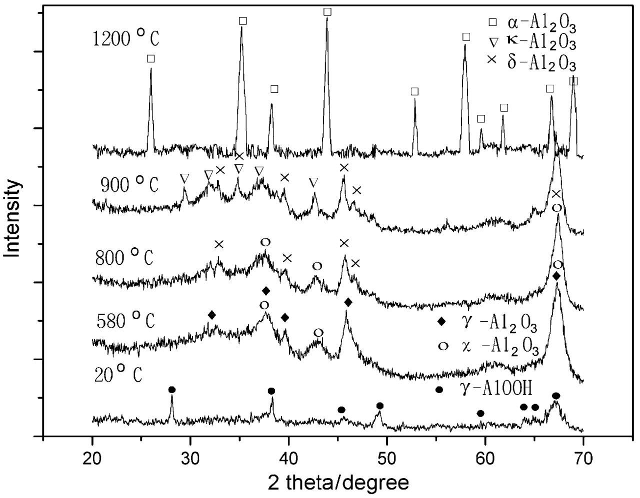

Fig. 2. X-ray diffractometry patterns for the aluminum hydroxide powder compacts after conventional heat treatment at various temperatures.

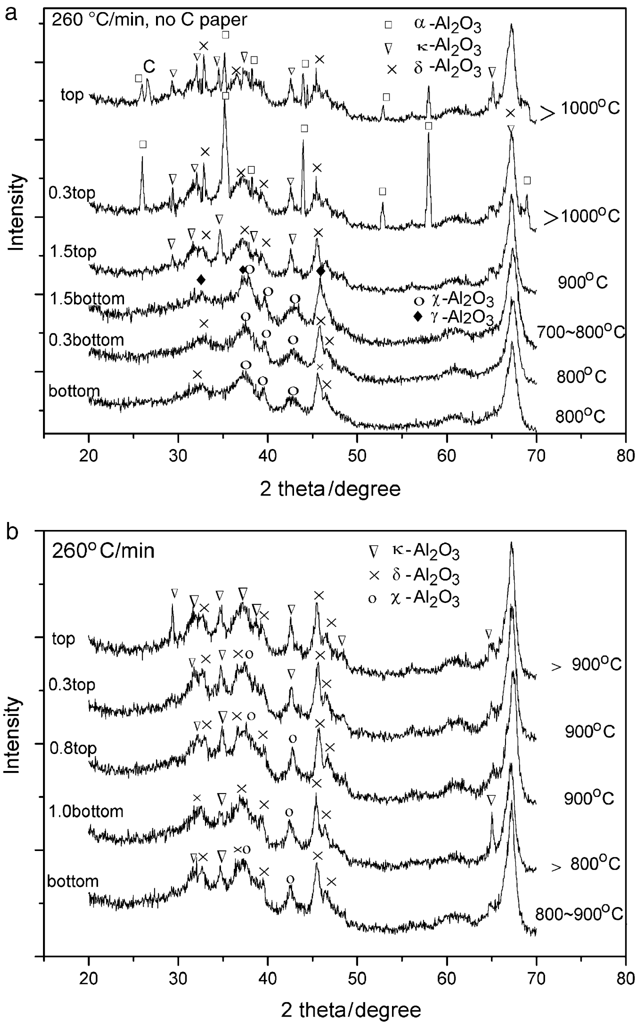

Fig. 3. X-ray diffractometry (XRD) patterns for the aluminum hydroxide powder compacts after pulse electric current sintering (PECS) at 900°C for 1 min at a heating rate of 260°C/min. The phases at a certain distance from the top and bottom surfaces are also shown. The estimated temperature for the XRD pattern is shown on the right-hand side of each pattern. The symbol 0.3 top indicates that it is 0.3 mm from the top surface. The thickness of the specimen is 9 mm. No carbon paper separator is used in (a).

Figure 4 shows the XRD patterns of the top and bottom surfaces prepared by the PECS at a heating rate of 80°C/min. The carbon paper separator was used for the specimen. Along with δ- and κ-alumina, χ-alumina is also detected, indicating that the temperature on the top surface is between 800° and 900°C. There is no χ-alumina found on the bottom surface, suggesting that the temperature at the bottom surface is around 800°C. Therefore, the temperature variation across the specimen still existed. It is also worth noticing that the temperature of the ceramic powder compact is lower than that of the graphite mold when a slow heating rate is applied. It demonstrates that Joule heating contributes to the temperature increase of the electric-conducting mold. The heat is dissipated with the increase of distance from the mold surface. The heat generated either by spark plasma or electric discharge within the nonconducting ceramic particles is relatively small if not negligible. As most Joule heating is generated from the punches,[10] the temperature near the punches is the highest. The carbon paper is less rigid compared with graphite punches, and therefore, the carbon paper can provide a good contact between the punches and the powder compact. The carbon paper is a good thermal conductor; the temperature variation can be reduced through heat conduction along the carbon paper.

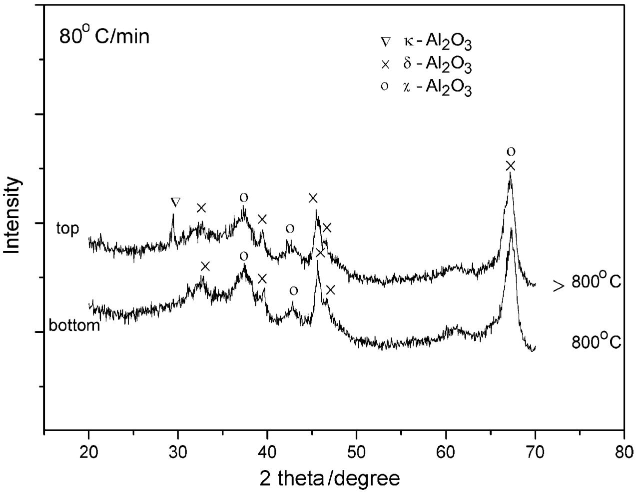

Fig. 4. X-ray diffractometry patterns for the aluminum hydroxide powder compacts after pulse electric current sintering at 900°C for 1 min at a heating rate of 80°C/min. A carbon paper separator is used.

The present study demonstrates that a reduction of temperature variation within the nonconducting ceramic compact is possible. The most effective method is to introduce a soft electrical conducting element, such as a carbon paper, to fill in the gap between the punches and the mold. However, the use of carbon paper is time consuming and might limit the industrialization potential of the PECS technique.

The area analyzed by the XRD technique is relatively large, covering most of the specimen surface. The temperature determined by the phase analysis can thus be treated as the average value at a certain depth from the top surface. Furthermore, the technique can only deliver information along the *Z*-direction of the specimen but not in the *X*–*Y* direction.

The phase transformation is a function of the surrounding temperature as well as a function of the heating rate. In the present study, the phase transformation of aluminum hydroxide is first determined by heating the specimens to various temperatures at a heating rate of 3 C/min in a box furnace. No phase variation is noticed within the specimens. The phase transition sequence as a function of temperature is therefore established. It allows us to use the resulting phases as a temperature indicator to estimate the temperature variation within the PECS specimens. A higher heating rate was used during the PECS process. The precise temperature is thus difficult to determine by using the methodology proposed in the present study. Nevertheless, the present methodology can provide an estimation of the temperature difference at different depths. Furthermore, by using the present methodology, it is possible to estimate each processing parameter, such as peak temperature, pressure, and heating rate, on the temperature uniformity within the powder compact during PECS. The methodology can thus be used to improve the application potential of the PECS technique.

IV. Conclusions

In the present study, a methodology is developed to estimate the temperature uniformity within a ceramic powder compact during PECS. A temperature variation is present within the alumina powder compact during PECS. The temperature is the highest near the top surface. The use of a carbon paper separator is an effective method of improving temperature uniformity. The decrease of heating rate can also contribute to the reduction of temperature variation within the powder compact.

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