Constant shrinkage rate control during a flash event for 8 mol % Y2O3-doped ZrO2 polycrystals

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NOTE

The shrinkage rate during a flash event is controlled at a constant value by current ramping for 8 mol % Y2O3– ZrO2 green compact with a rectangular shape. The green compact is heated at a constant heating rate of 5°C/min until the occurrence of a flash event under a constant alternative current (AC) field of 50 Vrms/cm and 1000 Hz at a limit current of 100 mA rms. After the flash event, current ramping is started to keep the shrinkage rate at a constant value of 120 µm/min. Current ramping is conducted by controlling the limit current using a programmable power supply operating in a current control mode. When the limit current reaches 1200 mA rms, the sintering condition is kept as it is for 5 min, and the sintering process is completed. 8 mol % Y2O3–ZrO2 sintered polycrystal with a relative density of approximately 99 % and a grain size of about 2.5 µm can be obtained at a furnace temperature of 870 °C for a current ramping and soaking regime of approximately 30 min.

Key-words : Flash sintering, Sintering, Zirconia, Rate control sintering

Flash sintering, which is classified as a field assisted sintering technology, is now attracting attention as a pressure-less sintering technique to decrease the furnace temperature and shorten the sintering time by using electric fields.1,2) When ceramic green compacts are heated under application of an electric field, an electric current spike occurs at the threshold furnace temperature. The phenomenon of the current spike is called a flash event that characterizes the flash sintering. Shrinkage of the green compact is observed immediately with the occurrence of the flash event. With flash sintering, densified compacts can be obtained at lower furnace temperatures and with shorter sintering times compared with those required using a conventional thermal sintering process. After the first report by Raj’s research group,3) the effectiveness of flash sintering has been confirmed for various kinds of ceramics.1,2,4) The huge mass diffusion during flash sintering mostly results from the electric power input, i.e., Joule heat,5,6) although other particular phenomena related to electric fields have also been identified.7–9) An excessive power input at the flash event often induces effects such as melting of the electrodes and materials and cracking in the sintered body.10) Therefore, flash sintering is technically performed by setting an upper limit of the input electrical power to avoid thermal runaway at the flash event. In recent years, a technique of flash sintering while controlling the electric power has been reported to suppress the power spike at the flash event.11–15) The power control is conducted by ramping current during flash sintering, and so it is generally called “current ramping”. For example, a current-ramping technique after the occurrence of a flash event has been reported by monitoring the current-ramping functions, such as stepwise, square-root, proportional and so on, against sintering time.15) To use these techniques, the peak of the power input can be decreased or avoided completely. However, the previously reported techniques are performed from the viewpoint of current ramping under a flash event and not from the viewpoint of controlling the shrinkage behavior. It is important from the viewpoint of the sintering technique to control the current value so that the intended shrinkage behavior can be realized. Regarding a control technique for the shrinkage behavior, a rate-control technique has been proposed in the case of conventional thermal sintering, which means no electric fields, by several workers.16–23) The rate-control technique proceeds at a constant shrinkage rate during the heating process by controlling the heating rate of the furnace temperature. These studies suggest that the shrinkage is often enhanced and the grain size is decreased effectively compared with those obtained by conventional thermal sintering.

Thus, in this study, this concept performed for conventional thermal sintering is applied to flash sintering as a first trial. For this purpose, the shrinkage rate is kept at a constant value against the sintering time by ramping the electric current during a flash event.

Commercially available 8 mol % Y2O3-doped ZrO2 (8YSZ; TZ-8Y, Tosoh Corp., Japan) was used as a raw powder which had a specific surface area and average
particle size of 13.4 m²/g and 22 nm, respectively, as determined by the manufacturer’s report. Green compacts with a cross-section of 3.5 × 3.5 mm² and a length of 15 mm were prepared by uniaxial pressing at 75 MPa followed by cold isostatic pressing at 100 MPa. Flash sintering was conducted using a high-temperature dilatometer (EVO2 TMA8301, Rigaku, Japan) modified to apply an electric field to the rectangular green compact along the longitudinal direction after thin Pt sheets were fixed by Pt paste on both faces in the longitudinal direction as electrodes. In this study, the electric current after the occurrence of a flash event was ramped to keep the linear shrinkage rate at a constant value against sintering time, as schematically shown in Fig. 1. Prepared green compacts were heated at a constant heating rate of 5 °C/min under alternative current (AC) fields of 50 Vrms/cm with 1000 Hz using a programmable power supply (Asterion AST-751, AMETEK.com). In this regime, the power supply was operated in a voltage control mode with an initial limit current of 100 mArms. When a flash event occurred at the threshold furnace temperature, the electric current spiked at this limit current of 100 mArms. Then, the furnace temperature was kept at the flash temperature, and the power supply was switched from a voltage control mode to a current control mode. Current ramping was started by increasing the limit current in a stepwise manner at 3-s intervals, as schematically shown in the inset of Fig. 1. The adjustment of the current limit value for power adjustment was performed with respect to the difference between the actual shrinkage rate and the assumed shrinkage rate. When the electric current reached at a final value of 1200 mA rms, the furnace temperature and electric field condition were kept as they were for 5 min. Then, the furnace and the power supply were switched off and the sintered compacts were furnace-cooled to room temperature. Hereafter, the flash sintering used in this study will be described as shrinkage-controlled flash (SCF). The linear shrinkage rate was temporally targeted at 120 μm/min, assuming that densification could be completed in approximately 30 min after the appearance of the flash event. For comparison, conventional flash sintering was also conducted at the same AC electric field of 50 Vrms/cm with 1000 Hz and a limit current of 1200 mA rms. The microstructures of the sintered compacts were observed by a scanning electron microscope (Hitachi High-Tech Corp. S-3000). Scanning electron microscopy (SEM) observation was performed with polished surfaces for the SCF compacts after thermal-etching at 1250 °C for 1 h and with fractured surfaces for conventional flash sintered compacts. Figures 2(a) and 2(b) show a linear shrinkage behavior and electric power dissipation as a function of time for conventional flash and SCF. The inset photograph is the entire view of the SCF compact.
realize the assumed shrinkage rate. The obtained shrinkage rate was confirmed to be approximately 120 μm/min, which was similar to the assumed rate. The power dissipation behaviors were found to be vastly different between conventional flash and SCF, as shown in Fig. 2(b). The power dissipation exhibited a spike at the occurrence of a flash event, as indicated by the arrow, which is a common phenomenon observed in conventional flash sintering. After the spike, the power dissipation decreased and showed a constant value of approximately 40 W. In contrast, such a spike of the power dissipation was not observed in SCF sintering. The power dissipation during SCF exhibited a characteristic behavior like an inverted S-shaped curve, which is different from the previous reports using a current-ramping technique during a flash state.\(^{11-15}\) The power dissipation was constant at approximately 40 W during the soaking regime, which is a similar value as that observed with conventional flash sintering. The actual temperature of the compacts during power dissipation was higher than that of the furnace temperature owing to Joule heating resulting from the input power. According to the report by Raj et al.,\(^{5}\) the actual temperature of the compacts was estimated as approximately 1400 °C at the soaking regime, which is around the sintering temperature generally used for thermal sintering of 8YSZ.

The inset photo in Fig. 2(b) shows the entire view of a sintered 8YSZ polycrystal obtained by SCF. The actual density measured by the Archimedes method was 5.91 g/cm\(^3\), which is similar to the theoretical density of 8 mol% Y\(_2\)O\(_3\)-ZrO\(_2\) of 5.971 g/cm\(^3\).\(^{25}\) It is noted that this density was obtained without any mechanical machining after SCF, which is different from the cases using green compacts with a dog-bone shape. The density was obtained only by removing the Pt sheets used as electrodes by hand after SCF.

**Figure 3** show SEM micrographs taken from the conventional flash and SCF compacts. Many voids surrounded by grains were seen in the conventional flash compact, which exhibited a lower density, as shown in Fig. 2(a). In contrast, such voids disappeared in the SCF compact. Although some residual pores could be seen at the grain boundaries and also grain interior, it was confirmed with this microstructure that the SCF compact had a high relative density of approximately 99%. Comparing the grain sizes of the respective compacts, the SCF compact exhibited a smaller grain size of approximately 2.5 μm.

A rate-control technique for thermal sintering was first reported by Palmour et al., where the shrinkage rate was controlled at a constant value by ramping the heating rate of the furnace.\(^{18}\) The shrinkage during thermal sintering starts gradually as the furnace temperature is increased. With the progress of sintering, the shrinkage rate is accelerated in the middle stage of sintering, and then slows down to a very sluggish rate in the final stage of sintering. To enable this shrinkage rate to be at a targeted constant value, the heating rate of the furnace temperature needs to be successively controlled to be higher, lower and higher by changing electric power of the furnace heater. The behavior of the furnace power is similar to that of the power dissipation observed during SCF, which exhibits an inverted S-curve shape against sintering time, as shown in Fig. 2(b). Campos et al. pointed out the difficulty of rate control in the final stage of the sintering process.\(^{14}\) In the final sintering stage, the shrinkage rate is greatly reduced so that the heating rate of the furnace must be increased substantially to maintain the targeted rate. The heating rate of the furnace temperature eventually cannot maintain the determined constant shrinkage rate. This arises from the large heat capacity of commonly used furnaces. In contrast, SCF can control the temperature of the compact directly by changing the input power. This means the response of the heating temperature against time is very high in the case of SCF. In this sense, SCF is considered compatible with the concept of a rate-control method.

Meanwhile, the power dissipation behavior, as shown in Fig. 2(b), increases substantially in the regime of the final sintering stage. In general, grain growth becomes remarkable in this regime. Thus, it can be considered that the power dissipation in the final regime plays an important role for controlling the grain sizes in SCF. As shown in Fig. 3(b), some residual pores are included in the grain interior. This means that the sintering condition, i.e., setting of a final limit current value, used in this study is slightly different from the most suitable value for obtain-
ing a fully densified compact. This is possibly a key to optimize the power dissipation behavior in the regime of the final sintering stage.

In this study, the shrinkage rate against sintering time after the occurrence of flash event could be controlled at a constant value of 120 μm/min by current ramping in a range between 100 and 1200 mA with an AC field of 50 Vrms/cm and 1000 Hz. 8YSZ polycrystal with an actual density of 5.91 g/cm³ and a grain size of about 2.5 μm could be obtained at a furnace temperature of 870 °C for a ramping and soaking process of approximately 30 min by SCF. SCF can be considered a useful flash sintering technique.

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