NOTE

Rapid sintering of 3 mol % Y_2O_3 -doped ZrO_2 by a combined rapid furnace heating and shrinkage-controlled flash sintering protocol

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Flash sintering has attracted much attention as a useful sintering technique that is able to lower the sintering furnace temperature and shorten the sintering time. To further improve this original flash sintering technique, we have developed a technique to facilitate shrinkage at a constant shrinkage rate by controlling the power dissipation during a flash state, which is termed as shrinkage-controlled flash (SCF) sintering. Here, we combine this SCF sintering method with a rapid furnace heating process to shorten the entire sintering process time. Accordingly, we succeed in sintering 3 mol % Y_2O_3 -doped ZrO_2 (3YSZ) polycrystals with a high density of 6.05 g/cm³ and a uniform grain size of approximately 0.47 μm with a short sintering time of approximately 40 min. The obtained 3YSZ polycrystals are confirmed to exhibit a Vickers hardness and fracture toughness [by an indentation fracture method] of approximately 1295 HV and 5.3 MPa m^{1/2}, respectively.

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Ceramic polycrystals are mostly fabricated by a sintering process that requires a high temperature and long heat treatment time. For example, in the case of partially stabilized zirconia, which is known as a structural ceramic, a sintering process at approximately 1400–1500 °C for a few hours is required. The development of a method to shorten the sintering process with a lower furnace temperature, as well as to realize a near theoretical density with an appropriate grained structure, is important as a ceramic fabrication process. In this sense, the application of flash sintering is a potential candidate to realize this purpose.¹⁾ Flash sintering is able to accelerate the shrinkage rates using electric power injection, owing to a steep electric power spike occurring during a furnace heating process under electric fields. The usefulness of flash sintering has been demonstrated for a number of ceramics.^{2),3)} However, too rapid shrinkage rates, owing to excessive Joule heat during the original voltage-to-current flash sintering, often result in issues such as grain coarsening and microstructure heterogeneity.^{4)–6)} To improve the original flash sintering process, we applied a concept of rate-controlled sintering technique to flash sintering, which is termed as shrinkage-controlled flash (SCF) sintering.^{7),8)} SCF precedes the sintering to keep the shrinkage rate constant by controlling power dissipation during the flash state. Although the sintering time increases compared with that using the original flash sintering method, we have succeeded in using SCF

sintering to obtain a fully stabilized zirconia (8 mol % Y_2O_3 -doped ZrO_2) polycrystal with a near theoretical density by using a furnace temperature of approximately 670 °C.⁸⁾ An issue to overcome for the further improvement of the present SCF sintering method is to shorten the sintering process time. Hence, in this study, we report on a method of combining SCF sintering with rapid furnace heating to obtain sintered compacts with a sintering time of approximately 40 min, whose density is close to the theoretical density.

Commercially available 3 mol % Y_2O_3 -doped ZrO_2 (3YSZ; TZ-3Y, Tosoh Corp., Japan) was used as a raw powder. Green compacts with a size of 3.5 × 3.5 × 15 mm³ were prepared by a conventional compacting procedure involving uniaxial pressing at 75 MPa and cold isostatic pressing at 100 MPa. Platinum sheets were used as electrode materials and were adhered with Pt paste on both longitudinal faces of the compact. A high-temperature dilatometer (Thermo plus EVO2 TMA8301, Rigaku, Japan), which was modified to apply an electric field, was used for sintering in a controlled electric field. The details of the experimental procedure are described in Ref. 9.

Green compacts were heated at a rapid heating rate of 50 °C/min under alternating current fields at 100 V/cm and 1000 Hz (Asterion AST-751, AMETEK Programmable Power.com). In this heating regime, a power supply was operated in a voltage control mode set at 50 mA as the initial current limit value. When the current reached the limit value of 50 mA, the furnace temperature was maintained, and the power supply was switched to a current

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control mode. Then, the constant shrinkage control process (SCF regime) was started by changing the current limit value from an initial value of 50 mA to a maximum value of 800 mA, where the shrinkage rate was maintained at 200 $\mu\text{m}/\text{min}$. When the current reached 800 mA, soaking was conducted for 5 min (soaking regime). Subsequently, the power supply and furnace were switched off. During the SCF regime, the shrinkage rate was checked at approximately 3 s intervals, and the current limit of the power supply was increased manually at intervals of approximately 30–60 s.⁸⁾

The microstructures of the sintered compacts were investigated using scanning electron microscopy (SEM; S-3000H, Hitachi High Technologies, Japan) using thermally etched sections at 1250 °C for 1 h after mechanically grinding and polishing the sintered compacts. Grain sizes were estimated around the body center and an area near the sides of the sintered compacts using a simple linear intercept method with a factor of 1.57. The density of the sintered compacts was measured using the conventional Archimedes method. For comparison, the density and the grains size of a 3YSZ polycrystal thermally sintered at 1400 °C for 3 h was benchmarked, in which the density is 6.06 g/cm³ and the grain size is 0.37 μm , respectively.

Vickers hardness and fracture toughness (K_{IC}) were measured using a Vickers indenter (Via-S, Matsuzawa Co., Ltd.). K_{IC} was estimated by the indentation fracture (IF) method using the crack length generated from the edges of the Vickers indentation.^{10,11)} Vickers tests were conducted on the mirrored surfaces of the sintered compacts at 5 kgf maintained for 15 s, which were performed at 20 points.

Figure 1(a) shows a comparison of the shrinkage behaviors between flash and SCF sintering as a function of elapsed time from the onset of furnace heating. The furnace temperature was raised at a very high rate of 50 °C/min up to T_{S} , as indicated by the arrow in the plot, where T_{S} is the temperature at which the current reached the initial current limit value of 50 mA. After T_{S} , a shrinkage control process was started for SCF sintering. As for flash sintering, specimen current hits at the maximum value of 800 mA just after T_{S} , and after that, soaking process was conducted. First, it was noted that both sintering processes presented in the plot were completed in approximately 40 min, in which the furnace heating regime is included. In the case of flash sintering (blue curve), the shrinkage occurred steeply up to approximately 20 % at T_{S} , which is typical of flash sintering. However, the shrinkage did not increase further during the soaking regime, as indicated by the dotted line. In contrast, SCF sintering enabled us to obtain a final shrinkage of approximately 22 %, as presented by the red curve. The actual density of the SCF compact was approximately 6.05 g/cm³, which was similar to the density of the thermally sintered compact of 6.06 g/cm³ at 1400 °C for 3 h. The shrinkage rate during the SCF regime was well controlled to be constant at approximately 200 $\mu\text{m}/\text{min}$. As presented in Fig. 1(b), shrinkage with thermal sintering did not occur before T_{S} as indicated by the arrow. A shrinkage of approximately 22 % obtained by SCF sintering could be

Fig. 1. Linear shrinkage behaviors during (a) flash sintering (blue curve) and SCF sintering (red curve), and (b) thermal sintering, and (c) volumetric power dissipation behaviors during flash sintering (blue curve) and SCF sintering (red curve) as a function of elapsed time from the onset of furnace heating. In (a), T_{S} indicates the onset of a flash event for flash sintering and of the shrinkage control process for SCF sintering. The arrows of A and B indicate the sintering time used for the SEM images shown in Figs. 2(d) and 2(e). Actual densities measured by the Archimedes method are 5.38 g/cm³ for the flash sintered and 6.05 g/cm³ for SCF sintered compacts. The temperatures shown beside the respective power dissipation curves in (c) are compact temperatures estimated using a blackbody radiation model expressed by Eq. (1).

gained from a green compact state in only approximately 22 min.

A characteristic feature during the SCF regime was observed from the power dissipation behavior, as presented in Fig. 1(c). In flash sintering, a spike of power dissipation was clearly observed, which is typical in original voltage-to-current flash sintering.¹⁾ The power dissipation curve decreased largely after the spike to show a near constant value, which corresponded to the soaking regime under a current control mode of the power supply. In contrast, power dissipation exhibited a rotated S-like curve, which appeared to keep the shrinkage rate constant during the SCF regime.^{7,8)} There was no power spike, which is a common feature in flash sintering.^{1–3)} Because electric power was injected during both sintering processes, the actual specimen temperature was higher than the furnace temperature of T_{S} . The specimen temperature can be estimated from a heat balance between the input Joule heat and blackbody radiation using the following equation,^{1),12)}

Fig. 2. (a) Photograph of the whole view of the SCF sintered compact. (b) and (c) SEM images of thermally etched sections of the SCF sintered compact at a body center and near a side areas. (d) and (e) SEM images of thermally etched sections of the flash sintered compact with sintering times of A and B as indicated in Fig. 1(a).

$$T = \left(T_f^4 + \frac{W}{A\epsilon\sigma} \right)^{\frac{1}{4}}, \quad (1)$$

where T is the specimen temperature, T_f is the furnace temperature, W is the electric power dissipation, A is the total surface area of the specimen, σ is the blackbody radiation constant and ϵ is the emissivity of heat radiation. In this study, 0.9 was used for ϵ .¹²⁾ Using Eq. (1), the estimated specimen temperatures during the soaking regimes are indicated with the respective power dissipation curves. The specimen temperatures during both sintering processes were not largely different, which were near the sintering temperature used for thermal sintering at 1400 °C benchmarked in this study. From these temperatures, we can understand that SCF realized shrinkage up to near the theoretical density in a very short time even at a similar furnace temperature compared with that by thermal sintering.

Figure 2(a) shows a photograph of the entire SCF compact. Although small areas with a pale black color were seen near the areas beside the electrodes,¹³⁾ shrinkages uniformly occurred. The mentioned density was obtained from this sintered compact as a bulk style without any mechanical machining after SCF sintering. SEM images show thermally etched sections at (b) the body center and (c) a near side area of the SCF sintered compact. Grain sizes at the respective areas were similar, with values of approximately 0.47 μm. In the case of flash sintering, the grain size became larger inside the sintered compact because Joule heat injected during the flash event tended to be trapped inside the sintered compact owing to the too rapid power peak.⁴⁾ As can be seen in Figs. 2(b) and 2(c),

the difference in grain sizes could be made to be uniform to a negligible degree by a proper control of the power dissipation behavior during the flash state in SCF sintering.

As mentioned before, further shrinkage did not occur during the soaking regime in flash sintering, as shown in Fig. 1(a). Figures 2(d) and 2(e) shows thermally etched sections of the flash sintered compact at the states indicated by the arrows in Fig. 1(a). It can be clearly understood that the grain and pore coarsening suppressed further shrinkage during the soaking regime in the case of flash sintering.¹⁴⁾ SCF sintering avoided this detrimental phenomenon that occurred in flash sintering.

Figure 3 presents the Vickers hardness and fracture toughness of the SCF and the thermally sintered compacts, which were estimated by the IF method using a Vickers tester.^{10),11)} As can be seen from the plot, both the hardness and fracture toughness obtained from the SCF compact were almost the same as those of the thermally sintered compact.¹⁵⁾

As presented, this study realizes rapid sintering up to near theoretical density with smaller grain sizes in approximately 40 min even in pressure-less sintering. In addition, the SCF sintered compact exhibits similar mechanical properties to those of the thermally sintered compact despite the very short sintering time. A modified flash sintering technique to avoid the occurrence of a steep power dissipation peak has been reported so far, which controls the power dissipation behaviors from the viewpoint of a transient specimen current during or before a flash event.^{16)–19)} In contrast, SCF sintering controls specimen current from a viewpoint of shrinkage rate, which is the rate-controlled method used in the past for thermal

Fig. 3. (a) Vickers hardness and (b) K_{IC} of the thermally sintered (black) at 1400 °C for 3 h, and SCF sintered (red) compacts. K_{IC} was measured by an IF method. The black and red dots show the median values.

sintering. In the rate-controlled method, the heating rate of the furnace is important to keep the shrinkage rate constant.^{20)–23)} Thus, it becomes difficult to adjust the furnace heating rate in the final sintering stage,¹⁹⁾ in which the sintering rate is significantly reduced. This arises from poor feedback of the furnace heating rate to maintain a constant shrinkage rate. In contrast, SCF sintering has the advantage of controlling the sintering rate by self-heating with electric power.⁸⁾ This is a useful attribute of SCF. Meanwhile, shrinkage does not occur up to T_S in thermal sintering [black line in Fig. 1(b)] because of the rapid furnace heating. This means that the amount of shrinkage by SCF sintering is almost the same as that from a green compact state. The completion of shrinkage in SCF sintering needs no initial shrinkage at the onset of the SCF regime. Further shortening of the entire sintering time would be achieved by shortening the time up to T_S and increasing the shrinkage rate during the SCF regime. With regards to this issue, additional techniques will be published in the near future.

In this study, we are able to sinter uniformly grained and highly densified 3YSZ polycrystals with similar mechanical properties to thermally sintered polycrystals obtained with a whole sintering process time of approximately 40 min by combining rapid furnace heating and SCF. It can be considered that optimizing furnace heating and SCF process can possibly shorten the developed sintering process further.

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