Technique to control specimen electric current during a flash state with alternating current electric fields

Yudai YAMASHITA¹, Tsuyoshi KURACHI¹, Tomoharu TOKUNAGA¹, Hidehiro YOSHIDA² and Takahisa YAMAMOTO¹,†

¹Department of Materials Design Innovation Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464–8603, Japan
²The University of Tokyo, Department of Materials Science and Engineering, 7–3–1 Hongo, Bunkyo-ku, Tokyo 113–8656, Japan

A simple technique to control the specimen electric current during flash sintering was developed using AC electric fields in 3 mol% Y₂O₃-doped ZrO₂. Flash sintering is characterized by the occurrence of a flash event, i.e., a spike in the specimen electric current, which makes it difficult to control the specimen electric current at/after the flash event for AC electric fields. However, AC electric fields are very attractive from the viewpoint of a suppression of the severe reduction arising from the unidirectional ionic flow during the flash event, which is a fatal phenomenon with DC electric fields. In this study, we develop a simple technique to control the AC electric fields at/after the flash event by limiting the AC electric fields under certain values. As a result, the flash state after the flash event is successfully maintained. Further, it is found that 3 mol% Y₂O₃-doped ZrO₂ compacts prepared by DC- and AC-flash sintering emit blue fluorescence (FL) under 254 nm ultraviolet light. The blue FL is not obtained in the compacts prepared by conventionally-sintering. The application of electric fields is confirmed to result in the blue florescent properties of 3 mol% Y₂O₃-doped ZrO₂ compacts.

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When ceramic green compacts are heated under electric fields, a spike in the specimen electric current occurs and the shrinkage process completes immediately.¹) This sintering technique is called flash sintering, which is categorized as a field-assisted sintering technique. The flash sintering is characterized by the flash event showing the current spike. Flash sintering has been confirmed for various oxide ceramics;²) dense yttria stabilized zirconia (YSZ) polycrystals can be obtained at a furnace temperature below 1000°C for a few seconds.³) Yttria, which is difficult to sinter, can be fully densified at lower than 1300°C within a very short sintering time.⁴) The rapid shrinkage by flash sintering mostly results from Joule heating, owing to the current spike, although the origin of the current spike is still under discussion.⁵⁻⁶) DC electric fields are often used as power sources for flash sintering because the current control by a conventional power supply is easy at/after the occurrence of the current spike. However, a DC field induces a unidirectional flow of ions, such as oxygen anions, which leads to a severe reduction near the negative electrode.⁷) In particular, the severe reduction is observed in YSZ after a flash event for a long duration.⁸) An AC electric field, that is, an electric field with alternating polarity, is therefore much more desirable for flash sintering. As for AC electric fields, some studies have been reported,⁹⁻¹¹) however, duration time of flash events are limited. One reason for this seems to be the difficulty of automatically controlling an AC electric field at/after a flash event. Over the very short time of a flash event, the specimen current spikes up, and the peak in the AC field is barely controlled at the desired value.

In the present study, we employed to control AC electric fields for flash sintering and demonstrated that AC-flash sintering was effective to produce YSZ compacts. In addition, we observed that the flash sintered 3 mol% Y₂O₃-doped ZrO₂ (3YSZ) compacts emitted blue-light fluorescence (FL) under ultraviolet (UV) light.

3 mol% Y₂O₃-stabilized tetragonal ZrO₂ powder (3YSZ) (TZ-3Y, Tosoh Corp., Japan) was used as a starting material. The surface area and the average particle size of the raw powder, as determined by the manufacturer, were 15.4 m²/g and 27 mm, respectively. Green compacts with dimensions of 3.5 × 3.5 mm² in cross section and 15 mm in length were prepared by uniaxial pressing at 75 MPa followed by cold-isostatic pressing at 100 MPa. Thin Pt sheets were fixed with Pt paste on both sides in the longitudinal direction as electrodes, as shown in Fig. 1. Flash sintering was performed in air using a modified high-temperature dilatometer (EVO2 TMA8301, Rigaku, Japan), which enabled the application of electric fields to the green compact. The green compact was set in the
dilatometer, and heated at a constant heating rate of 300 °C/h under the application of constant DC and AC electric fields with a stabilized power supply (POPF 300-4; Matsusada Precision, Inc., Japan). The initial electric field and the limit current at the occurrence of a flash event were 100 V/cm and 1000 mA for a DC field, and 100 V/cm as an effective value, 100 Hz and 1000 mA for an AC field, respectively. Once the flash event occurred under a DC field, the power supply could be automatically switched from a voltage-control mode to a current-control mode. The current could be kept at 1000 mA at/after the flash event. In contrast, it was hard to control the spike of the AC current to be 1000 mA at the flash event automatically by keeping a sine wave form. Therefore, we controlled the current by cutting off a portion of the sine wave form over 1000 mA using the safety mode for overloading that was contained in the present power supply. Using this technique, the sine wave form was distorted to resemble a trapezoid form; however, an electric field with alternating polarity could be obtained, which was largely different from that of the DC field.

Figure 2 shows the densification behaviors during DC- and AC-flash sintering as a function of elapsed time. As seen in the plots, the onset of the flash event was confirmed at about 820°C for both the DC and AC fields. This indicated that the amount of input electric power by the DC and AC fields were similar, as targeted by the experimental setting of the power supply. The obtained relative density was slightly higher in AC-flash sintering than in DC-flash sintering. This was because that Pt sheet used for the positive electrode melted at the flash event in the case of DC-flash sintering, even when using the same input electric power. The inset photograph shows a melted positive electrode after a flash event by a DC field. A DC field enforces the unidirectional ionic flow of oxygen ions, which leads to the formation of excess oxygen vacancies at/near the negative electrode as reported in previous studies. The excess oxygen vacancies generate conducting electrons, which results in a decrease of resistivity. Therefore, a higher electric field is located at/near the positive electrode and the electrode at the positive side melts, as shown in the inset of Fig. 2. This phenomenon arising from DC fields limits the maximum input electric power compared with that achieved by AC fields. In contrast, the flash state after the occurrence of the flash event can be maintained for 3 h in the case of AC fields without melting the Pt electrode. This fact means that the alternating electric fields would effectively suppress the formation of excess oxygen vacancies.

Meanwhile, we observed that the flashed compacts emitted blue FL under excitation by UV light with a wavelength of 254 nm, as shown in Fig. 3. Photographs of the conventionally sintered, DC- and AC-flash sintered compacts under room light and UV light with a wavelength of 254 nm are shown in Figs. 3(a) and 3(b), respectively. As shown in Fig. 3(b), the flash sintered compacts clearly emitted blue FL, while the conventionally-sintered compact did not. The FL becomes clearer in the AC-flashed compacts. Furthermore, the intensity of the blue FL increased with an increasing duration time of the AC-flash state. It should be noted that the blue FL could be obtained in 3YSZ without any other cations as FL centers as described later. The impurities in the raw powders were not considered as the FL centers, because no FL was obtained from the conventionally-sintered compact prepared with the same raw powders, as shown in Fig. 3(b).

A number of studies have reported about the FL of doped zirconia polycrystals, single crystals and pure zirconia nanoparticles. For example, Nakamura et al. reported the blue FL of Tm2O3-doped zirconia ceramics. They confirmed a blue FL with a peak wavelength of 460 nm when exposed to UV light of 365 nm. Nakayama et al. also reported that zirconia ceramics, which included a small amount of Ti and P, emitted a blue FL of 475 nm under excitation at 280 nm. Pure zirconia nanoparticles also emitted FL with peak wavelengths of 470–490 nm. The details for the nature of this FL band observed in pure zirconia nanoparticles have not yet been clarified.
possible origins have been reported as the structure defects of singly ionized oxygen vacancies (F+ centers). Ashraf et al. have reported that FL intensity decreases with decrease in oxygen vacancies by annealing monoclinic nano/submicron-scale crystalline ZrO$_2$ powders. Meanwhile, Y$_2$O$_3$ is often used to stabilize high temperature phases, which is similar case for the present material of 3YSZ. The emission of blue FL has also been confirmed in zirconia single crystals and crystal particles including Y$_2$O$_3$. Smits et al. reported that red shift occurs by doping Y$_2$O$_3$. They claimed that FL centers are related to the oxygen vacancies but are not the origin of oxygen vacancies themselves. A quasi-continuum state of a deep trap level for electrons is related to the oxygen vacancies. The origin of blue FL has not been discussed from the viewpoint of doped yttrium ions, themselves. This is also confirmed in the present result. Conventionally-sintered 3YSZ polycrystal does not emit blue FL as shown in Fig. 3(b). The detailed diagram for the emission of FL observed in AC-flashed 3YSZ is still unknown at present state. However, it should be noted that the treatment of flashing is a key to induce the emission of blue FL for 3YSZ polycrystal.

In the present study, we have developed a simple technique to control a flash state at/after the occurrence of a flash event during AC-flash sintering. As results, a flash state could be controlled automatically using a conventional power supply even during AC electric field. 3YSZ compact with about 80% relative density could be obtained at furnace temperature of 820°C by AC-flashing. In addition, it was revealed that DC- and AC-flashed 3YSZ polycrystal emits blue FL excited by ultra violet light of 254 nm. The emission could be concluded to be closely related to the treatment of flashing for 3YSZ.

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References