Flash sintering of hydroxyapatite ceramics

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ABSTRACT

The flash sintering process has been regarded as a noble method to densify ceramic materials. The distinctive feature of the flash sintering is the reduced sintering time which is caused by the electric field. In this study, flash sintering of the hydroxyapatite bioceramics was carried out at temperatures of 900–1200°C and electric fields of 500–1200 V/cm. Dense sintered sample was prepared in a short time within 10 seconds. Electric field required for flashing became reduced as the furnace temperature increased. Abrupt rise of the sample temperature of up to 120°C was observed when the flash occurred. The incubation time for flashing became shorter with increasing temperature and electric field. The flashing was found to occur at lower temperature and lower electric field in vacuum than in air. Microstructure of the flash sintered sample was not different from that of conventionally sintered sample.

1. Introduction

Dense ceramics are usually produced from powders by sintering method. Normal sintering method requires high temperature and hour-long time for densification. Cologna et al. [1] successfully produced dense zirconia ceramics in just a few seconds by flash sintering method with an aid of electric field at a temperature of 850°C which was much lower than that of normal sintering. In addition to zirconia-based ceramics [2–13], flash sintering was also found effective to consolidate various ceramic materials such as yttria [14,15], alumina [16–20], spinel, titanium oxide, barium titanate, zinc oxide [21–33] and tricalcium phosphate [34,35]. It was suggested that the rapid densification was attributed to the generation of lattice defects and the temperature rise by Joule-heating. Still more additional research is required for the full understanding of flash sintering mechanism [7,36–42].

Hydroxyapatite or Ca\(_{10}\)(PO\(_4\))\(_6\)(OH)\(_2\) is a bio-ceramic material which has a similar chemical composition to that of the human bone. This material has excellent bio-friendly properties such as protein adsorption, bone binding, and cell adhesion, so it is widely used as an artificial bone and bio-implant for the human body [43–47]. Hydroxyapatite ceramics are also usually prepared by a sintering method. Muralithran et al. [48] were able to prepare a hydroxyapatite compact by sintering powders for two hours at a temperature of 1250°C or higher. They also reported that sintering for an extended time caused grain growth and the degradation of mechanical properties [49–51]. In addition to normal sintering, studies using hot pressing [52–55] and spark plasma sintering [56,57] have been reported [58–60]. The spark plasma sintering method was found to be effective, but it is an expensive route because it required an individual mold and a pressurizing device on a large scale. Recently, Yun et al. have attempted a flash sintering of hydroxyapatite, and have successfully prepared a dense sample in a short time of 10 seconds without an application of pressure [51,61]. In this study, hydroxyapatite ceramic was sintered using the flash sintering method. The flash onset temperature, voltage, incubation time, flash current and the increase in temperature were investigated. When the flash was observed, the sample temperature increased due to the internal heating of the sample, and a dense sintered body was prepared within a few seconds. The rapid sintering mechanism was discussed.

2. Experiment procedures

Hydroxyapatite powders (Junsei, Japan) were uniaxially pressed to rectangular plate-shaped green sample, with a size of 20 × 5.4 × 1 mm. The scanning electron microscopy showed that the raw powders had a mean particle size of 60 to 100 nm. Two holes having a diameter of 1 mm were drilled onto the pressed green sample in a thickness direction at an interval of 10 mm in the longitudinal direction. The green sample was placed in a furnace and heated up to a constant temperature while applying a voltage through a platinum wire. The sample was hung by a platinum wire hooked in two holes and a platinum paste was applied to the
holes to lower the contact resistance. DC power supply (Magna Power, USA) was used for the power source. Current limit was set to 5 mA for the most of the flashing experiments. During flash sintering, voltage, current, video image and sample surface temperatures were monitored and recorded using a digital multimeter, a CCD and a pyrometer.

The furnace was heated up at a rate of 10°C/min and when a temperature reached 900°C voltage began to be applied. When the flash event occurred as the temperature went up, the onset temperature was recorded. Then another sample was heated up at the same heating rate, and when the flash temperature previously recorded was reached, a voltage was applied and the incubation time or the period of time from the instance of voltage application to the flash onset was recorded. Finally, flash sintering was carried out in vacuum (5 torr) and the effect of the atmosphere was investigated. A control sample was prepared using a normal sintering method for comparison.

After sintering, the sample was cut and the section between two electrode holes was taken for the density measurement. Bulk density was measured using Archimedes method. A cross-section of the sample was cut, polished, and thermally etched at 900°C for 30 min in air, and then microstructure was analyzed by scanning electron microscopy (SEM). Transmission electron microscopy (TEM) samples were prepared by a focused ion beam (FIB) technique (Auriga, Carl Zeiss, Germany), and aberration-corrected TEM (JEM-ARM200F, Jeol, Japan) was used to observe grains, grain boundaries, and nanovoids in the sample. Phase analysis was performed using an X-ray diffractometer (Smart Lab, Rigaku, Japan) with Cu Kα radiation source at a scan speed of 0.5°/min and a step scan of 0.02°

3. Results and discussions

Figure 1 shows the onset temperature and electric field conditions in which the flash occurred in air or in vacuum atmosphere. Regardless of the atmosphere, the flash onset temperature tended to decrease as the electric field increased. The flash onset temperature was 70–80°C lower in vacuum than in air, and the flash onset electric field was about 400 V/cm lower in vacuum than in air for the same temperature, indicating that the flash phenomenon occurs more easily in an atmosphere with a lower gas partial pressure [62,63].

After applying the electric field, the incubation time, or the time taken to generate the flash, was measured and is shown in Figure 2. The flashing occurred in most of the samples within 30 seconds, but in some samples where the flash condition was not satisfied, the flash did not occur even though it was maintained for 3600 seconds (an hour). In that case, it was judged as “no flash occurrence”. The incubation time became shorter as the electric field or the temperature increased. Flash did not occur in the electric field range of 1200–1400 V/cm at a temperature of 992°C.

Electric current flowing and the temperature rise of the sample during flash are shown in Figure 3. When the flash occurred, the electric current increased from zero to 1–10 mA which corresponds to 0.5–1.85 mA/mm² of current density. The sample temperature measured by pyrometer abruptly rose to a maximum by 42–120°C in stage II and decreased. The amount of temperature rise was found to increase with the increasing electric field and current value.

Figure 4 shows the densities of the sample flash-sintered for 10 seconds and of the sample normal
sintered for 5 minutes. Densities of the flash sintered samples remained same with varying furnace temperature. And the densities of normal-sintered samples were significantly lower compared to flash sintered samples, indicating that flash sintering was effective for low-temperature sintering.

X-ray diffractometry (XRD) pattern of flash sintered sample showed only peaks of hydroxyapatite without any traces of tricalcium phosphate (TCP) or tetracalcium phosphate (TTCP) phase indicating that no phase transformation occurred during flash sintering (Figure 5).

Scanning electron microscopic observation of the cross-section of the sample flash-sintered at 1051°C for 10 seconds showed that it was similar to that of the sample normal-sintered for one hour at 1192°C as shown in Figure 6 even though duration of time was quite different. Transmission electron microscopic image shows that grains are of a size of 100–300 nm, and voids are of a size of 5–10 nm located in grains (Figure 7).

As shown in Figure 8, it was found that some samples partially melted. Melt trace was formed on the surface with the shape of a narrow band between two electrode holes. Recrystallized grains were observed at the melt trace by SEM. Melt trace was formed on a front surface near an electrode hole but connected to another one on the back near the other hole, showing that melting was done not only on the surface but also extended to the inside of the sample. An instantaneous temperature rise of 400–700°C was recorded during flashing in the sample with a partial melting in contrast to 120°C of the sample without. The current measured was 42 mA in the sample with a partially melting which was very high compared to 5 mA in the sample without. Even though the trace shows non-uniform melting in a route, flashing seems to
Figure 4. Density of samples prepared by flash or normal sintering.

Figure 5. X-ray diffractometry pattern of the samples produced by flash sintering in the condition of (a) 1192 °C 0 V/cm, (b) 1192 °C 600 V/cm, (c) 1142 °C 800 V/cm, (d) 1093 °C 1000 V/cm, (e) 1042 °C 1200 V/cm, and of (f) hydroxyapatite powders, and (g) JCPDS file (9-432) of hydroxyapatite.

Figure 6. SEM image of the cross-sectional microstructure of the samples prepared by (a) flash sintering at 1051 °C 1000 V/cm for 10 seconds, and (b) normal sintering at 1192°C for one hour.
occur uniformly because the cross-sectional microstructure was dense and uniform. Once the local temperature exceeds melting point, sample begins to melt locally. Since the resistivity of liquid melt is much lower than that of solid phase [64], electric current preferentially flows through melt, and further melting would be accelerated, finally forming a melt trace. It is easier for the surface to melt than inside because the sample surface has a higher defect concentration and no restriction on volume expansion during melting. However, the melting was regarded as a non-uniform erroneous densification and was avoided by limiting the maximum current to 5 mA in a current control mode of power supply.

It has been known that the flash phenomenon is caused by thermal runaway and the generation and movement of defects in the material. Generally defect concentration of the oxide ceramics is a function of the oxygen partial pressure, and the flash occurrence temperature changes with a redox reaction depending on the oxygen partial pressure [7,36–40]. In case of zirconia ceramics oxygen vacancy is a major defect [65], and it has been reported for example that the addition of yttrium oxide with trivalent cations to zirconia with tetravalent cations, increases the oxygen vacancy concentration, and significantly lowers the flashing temperature [66,67]. However, in case of hydroxyapatite ceramics, hydroxide and hydrogen ions are major defects contributing to electrical conduction [68–71] while the oxygen-type defects rarely contribute [69]. When dehydration reaction occurs and hydroxyl groups are decomposed at high temperatures, lattice defects of hydroxyl and hydrogen vacancies and water vapor are generated as shown in Equation (1) with

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**Figure 7.** Transmission electron microscope image of hydroxyapatite sample prepared by flash sintering.

**Figure 8.** A sample with partial melting during flash sintering. (a) Front and back surface images of the flash sintered sample under the condition of 1000 V/cm. One can see band-like melt trace between the two electrode holes. (b) A cross-sectional microstructure under the melt trace (c) low magnification (x50) image of the melt trace. One can see splash.

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a square sign for OH vacancy and Equation (2) with Kroger-Vink notation \([51,59,71,72]\). Although the claims of previous researchers are not in agreement and unclear as to which of these two defects is more important in terms of their effect on the electrical conductivity at high temperatures, at least it is obvious that the dehydration reaction is an important defect-generating reaction for electrical conduction in hydroxyapatite \([51,71]\).

\[
\text{Ca}_{10}({\text{PO}}_4)_6(\text{OH})_2 \rightarrow \text{Ca}_{10}({\text{PO}}_4)_6(\text{OH})_2 - 2x\text{O}_x + x\text{H}_2\text{O} \tag{1}
\]

\[
2\text{OH}_{\text{OH}} \rightarrow \text{O}_x + \text{V}_{\text{OH}} + \text{V}'_\text{H} + \text{H}_2\text{O} \tag{2}
\]

The decomposition of hydroxyl groups starts at or above 800°C \([59]\). As temperature increases, defect concentration increases by enhanced dehydration. Defect mobility also and finally electrical conductivity increases with temperature. Indeed, it was found in this study that as the temperature increased, the flash occurred more easily. In addition, the dehydration reaction is accelerated in vacuum, increasing the defect concentration and making the flash easier, being consistent with the result of this study.

Temperature can be more sensitive factor for the flash occurrence than the voltage in the sense that defect concentration is more sensitive to the former than the latter. In fact 40% higher voltage was required when temperature decreases by 8% as shown in Figure 2. As the temperature increases, the defect concentration increases, and when the defect concentration exceeds a threshold, current begins to flow, causing heat generation inside the sample, and again making the temperature rise. An increase in the temperature further increases the defect concentration, resulting in a synergistic effect of increasing heat generation. Such a chain reaction makes a flash. If the chain reaction is not properly controlled, the temperature of the sample rises rapidly, causing the sample to melt as we observed.

There are two reasons why the densification occurs very rapidly during flash sintering: an increase in the diffusion rate and a change in the sintering mechanism. Since the diffusion rate is a function of temperature, it is clear that a high diffusion rate at high temperatures will contribute to rapid densification. However, Raj \([36]\) and Qin et al. \([8]\) reasoned that the increase in sintering rate cannot be explained only by temperature effect and there must be a fundamental change during flash sintering. Frenkel defects model was proposed for the high conductivity and diffusion rate \([36]\) but its validity was suspicious because the electric field for their formation was much higher than the reported one for the flash sintering experiments. Grain boundary may be an effective path for the current and diffusional flow and plays a role of a heat source resulting in a rapid densification. Further study is on the way.

4. Conclusions

The dense sample of hydroxyapatite ceramics was successfully prepared by flash sintering. Flash occurred in the conditions of an electric field of 500–1200 V/cm and a temperature of 925°C–1200°C. Flash occurred more easily in vacuum than in air. As the temperature increased, the flash occurrence electric field decreased, while the flash generation temperature decreased as the electric field increased. The incubation time required for a flash occurrence was shortened with increasing temperature or electric field. With the occurrence of flash, the sample temperature rose abruptly over the furnace temperature with an amount of up to 120°C. The microstructure of the flash sintered sample was not different from that of the normal sintered sample despite of the rapid sintering. No phase transformation was found during flash sintering. The flash phenomenon was due to a joule heating induced by a defect generation at high temperatures and an increase in current flow. Hydroxyl or hydrogen type of defects generated by dehydration reaction attributed to the increase in the electric current.

Acknowledgments

Authors are grateful to Dr. S. Y. Kim (Yeungnam University, Korea) for his technical advice and Mr. Jisoo Kim (Gumi Electronics & Information Technology Research Institute, Korea) for his technical assistance in transmission electron microscopy.

Disclosure statement

No potential conflict of interest was reported by the authors.

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