FABRICATION OF DENSE HYDROXYAPATITE BY PULSE ELECTRIC CURRENT SINTERING (PECS)

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Abstract: Hydroxyapatite was sintered by either the pulse electric current sintering (PECS) process or pressureless sintering (PLS) process in this paper. Sintering by PECS process at 700°C with a heating rate of 100 °C/min under applied pressure of 30MPa led to the dense hydroxyapatite bodies without other calcium phosphate phases. Their samples of hydroxyapatite prepared at 700°C by PECS showed very fine microstructure with the average grain size of approximately 150 nm and very narrow grain size distribution, whereas samples sintered by PECS over 800°C revealed the tremendous grain growth in the matrix. Nevertheless, it was found that the significant decrease of sintering temperature for dense hydroxyapatites could be achieved by PECS, compared to the PLS process with a heating rate of 10 °C/min. The effect of the sintering process on the microstructure of hydroxyapatite bodies was discussed.

EXPERIMENTAL PROCEDURES

The starting powder of hydroxyapatite was provided from Taihei Chemical Corp (Nara, Japan). Hydroxyapatite powders (average particle size= 0.1μm, BET=39m²/g) were granulated by splay drying
The powder was subsequently sintered by using the PECS equipment (Dr Sinter: Sumitomo Coal Mining) or by the conventional pressureless heating method. 10 g of the powder was put in graphite mold and heat-treated by PECS method. PECS sintering was performed at 700 to 1200°C in pure Ar under an applied pressure of 30 MPa. The powders were heated at 100°C/min of heating rate and maintained for 5 min at the sintering temperature. After holding at the sintering temperatures, the electric power was shut off and then cooled to room temperature at about 100°C/min in the PECS furnace. The specimens prepared by PECS process were disk of 30 mm in diameter and 4 mm in thickness.

On the contrary, the conventional pressureless heating method was also conducted. Hydroxyapatite powder was pressed into pellet (30mm in diameter and 5mm in thickness) at 30 MPa with stainless steel mold. The pellets were cold-isostatic pressed with pressure of 200 MPa and then sintered at 800 to 1200°C in air with a heating rate of 10°C/min. After kept at the desired temperatures for 120 min, the samples were cooled to room temperature.

The samples prepared by both sintering methods were cut and ground with diamond wheels. The composition of the sintered samples was identified by X-ray diffractometry (XRD: RINT-2500, Rigaku Co., Tokyo, Japan) using Cu-Kα radiation. Relative density was determined by Archimedes' method. The cut specimens were polished with diamond pastes. The polished surface of sintered bodies was performed by a chemical-etching treatment in 0.2M-CH₃COOH solutions. The microstructures of the etched surface and fractured surface were observed with a scanning electron microscope (FE-SEM: S-800, Hitachi Ltd., Tokyo, Japan). At least 100 grains were chosen and evaluated by using image analyzer to determine the average grain diameter and size distribution of hydroxyapatite for the sintered samples.

RESULTS AND DISCUSSION

The relation of relative density of hydroxyapatite and sintering temperatures by PECS and PLS processes is shown in Figure 1. The sintering temperatures that full density over 98% was achieved depended on the sintering methods. For the samples sintered by PLS process, the full densification over 98% of the theoretical density was obtained at 1200°C, although 67% at 1000°C and 91% at 1100°C, respectively. This result was consistent with the results reported by others. However, in the case of PECS sintering, the fully densified hydroxyapatite samples were achieved at 700°C, whereas the specimens treated by PECS at 1000°C and 1200°C possessed approximately 90% of theoretical density. Conversely the density of samples prepared over 800°C by PECS tended to decrease with sintering temperatures. Nevertheless, PECS-sintering at 700°C led to the dense hydroxyapatite bodies. This densification of hydroxyapatite by PECS at lower temperatures is thought to be attributed to very fast mass transport rate due to the significantly rapid heating with 100°C/min of a heating rate. The results reported by Zhou et al. suggested that the localized heating would cause a rapid increase in the temperature of the particles since the electric discharge generated by on-off pulsed voltage might lead to localized heating between the particles. Kondo et al. studied the effect of PECS on densification of Al₂O₃-ZrO₂ composites and referred to the possibility of strong bonding between Al₂O₃ and ZrO₂ grains due to this localized heating effect of particles. In this work it is also speculated that the sintering by PECS causes the localized increase of the temperature between the hydroxyapatite particles. Therefore, another reason of sufficient densification at lower temperatures by PECS may be owing to this localized heating effect.

XRD patterns of crashed powder of hydroxyapatite by PECS at 700, 1000 and 1200°C are shown in Figure 2. As the patterns of crashed samples agreed with the main peaks of hydroxyapatite, they were
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identified as a hydroxyapatite phase. All patterns of crashed specimens by PECS showed that the component was only hydroxyapatite and no other phases were detected even at 1200°C by PECS process. Furthermore, in the case of the bulky samples prepared by PECS at high sintering temperature, the preferred orientation (not shown here) was confirmed, such as (211) and (300), although (002) was disappeared for samples prepared by PECS above 1000°C, which suggest the grain growth of hydroxyapatite to c-axis. On the contrary, XRD patterns prepared by PLS at 1000°C and 1200°C are shown in Figure 3. The patterns prepared by PLS at 1000°C showed mainly hydroxyapatite peaks and a small trace of tetracalcium phosphate (TTCP: Ca₄(PO₄)₂O). However, a trace of tetracalcium phosphate was not confirmed for the samples by PLS over 1100°C. The small peaks of CaO were observed for the samples by PLS at 1100 and 1200°C. The following solid-state reaction at high temperatures was reported:

$$3Ca_4(PO_4)_2O + H_2O \rightarrow Ca_{10}(PO_4)_{6}(OH)_2 + 2CaO$$

Therefore, the formation of CaO for the samples prepared at 1100 and 1200°C was thought to be due to this solid state reaction. No preferred orientation was shown for the bulky bodies of hydroxyapatite by PLS. Suchanek et al. reported that the formation of α-TCP was caused by strong reducing hot-pressing conditions such as graphite dies and Ar atmosphere. According to their results, the optimum sintering temperature for hot-pressing was 1000°C for 2h, although the small (approximately 5%) quantities of α-TCP was contained. Also, Champion et al. also showed the trace of α-TCP for the hydroxyapatite/Al₂O₃ composites hot-pressed above 1100°C.

Microstructural observations of samples treated by PECS and PLS processes were conducted by SEM. Figure 4(A), (B) and (C) shows the photographs of etched surfaces for samples prepared by the PECS. The microstructure of sintered by PECS at 700°C showed very fine microstructure of hydroxyapatite with the equi-axed shape. The microstructures of specimens sintered by PLS at 1200°C are shown in Figure 4(D). Their microstructures were coarse and partly large grains. Figure 4 shows the grain size of samples prepared by PECS at 700°C and by PLS at 1200°C. The average grain size of hydroxyapatite matrix sintered by PECS at 700°C was below approximately 150nm. Furthermore, the particle size distribution of hydroxyapatite by PECS at 700°C was very narrow. On the contrary, samples prepared by
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PLS at 1200°C, as clearly shown in Figure 4(D), showed larger average grain size and broader distribution, compared to those by PECS at 700°C. It was reported that rapid PECS sintering resulted in minimal grain growth for each Al2O3, Si3N4 and ZrO2 ceramics. These fine-microstructured hydroxyapatites could be obtained owing to rapidly heating by PECS. Fanovich25 reported that the hydroxyapatite in the absence of a-TCP by PLS at 1100-1200°C showed homogeneous microstructures with the average grain size of 1-2 μm, whereas samples containing α-TCP showed the abnormal grain growth over 1200°C of sintering temperature by PLS. In XRD results, the samples prepared at 1000°C showed a trace of tetracalcium phosphate, not α-TCP. Therefore, the relatively homogeneous sintered bodies were thought to be obtained by PLS in the present study. From these results, the significantly fine-microstructured hydroxyapatite bodies with high density over 99% were achieved by PECS processing at a low sintering temperature.

The microstructure of samples treated by PECS over 800°C showed the elongated hydroxyapatite grains, as shown in Figure 4(B) and (C). The etched surface of specimens sintered at 800°C by PECS revealed the bi-modal structure composed of elongated hydroxyapatite grains and partly equi-axed grains with a few micron. These elongated grains showed the diameter of 5-10 μm and length of 20-40 μm with aspect ratio of 10-30 (average 15). However, the microstructure of specimens by PECS at 1200°C was found to be composed of elongated hydroxyapatite grains with the diameter of 10-20 μm and length of 30-50 μm. Aspect ratio of these specimens was in the range of 5-20 (average 10). According to the results by Zhou et al19 in the case of sintering ultrafine SiC by PECS, the sintered SiC bodies exhibited the enormous grain growth because of very fast mass transport rate. Therefore, this fast mass transport rate is thought to be a reason why the abnormal grain growth was observed over 800°C of a sintering temperature by PECS, whereas the homogeneous and fine-microstructured hydroxyapatite was achieved at optimum sintering temperature by PECS process. As shown in Figure 4(D), specimens sintered by PLS at 1200°C showed the fairly dense microstructure with the grain size of a few μm and some pores at grain boundaries. The samples sintered at 1200°C revealed the dense microstructure and a little grain growth of hydroxyapatite, which grain size was approximately 3-5 μm (Figure 4(D)). Hydroxyapatite containing α-TCP was reported to be heterogeneous by Fanovich25. These homogeneous microstructures by PLS were thought to be caused by the absence of α-TCP.

As clearly shown in Figure 4, all samples sintered by PECS at 700, 800 and 1200°C revealed the dense microstructure without pores in the hydroxyapatite matrix. However, as above-mentioned, the density of samples sintered by PECS over 800°C decreased with the sintering temperature. The observation of microstructures of samples by PECS shows no pores at grain boundary of hydroxyapatite even at 1200°C. The possibility of oxyapatite (Ca1o(PO4)2(OH)) existence during the partial dehydration of hydroxyapatite at high temperature has been pointed out:

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Ca1o(PO4)2(OH)2 → Ca1o(PO4)2O + H2O
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The possibility of this partial dehydration of hydroxyapatite at high temperature is present in the heat treatment such as sintering. Furthermore, Fanovich25 reported that a slight density decrease was confirmed at higher temperatures might be due to the partial decomposition of hydroxyapatite. Therefore, the decrease of density of hydroxyapatite by PECS over 800°C may be explained that the above-mentioned localized heating effect would lead to the partial dehydration of hydroxyapatite and slight formation of calcium phosphate between the hydroxyapatite grains, although they could not be confirmed by XRD.

Daculsi et al26 reported the presence of void type lattice defects in addition to other defects structure in the grain of hydroxyapatite sintered at 950°C by TEM. Under vacuum at high temperature around 950-1000°C, there was a small uptake of water to form Ca1o(PO4)2(OH)2·Oδ·Ca0.75δ2.75 where δ represents an OH- ion vacancy. Generally OH- ions were proposed as the charge carriers at high temperature with 1400°C.27 In the case of sintering temperatures over 800°C by PECS process, the significant grain growth of hydroxyapatite matrix was confirmed in the present study. Therefore, these OH- ions may play an important role on the densification in the process of PECS especially at high temperatures, because of the electric discharge generated by on-off pulsed voltage in the present study. However, the reasonable reason why the density decreased with the sintering temperature by PECS over 800°C is under investigation. It is thought that this localized heating effect and the behavior of OH- ion vacancy would be connected with the properties, e.g. thermal and electric conductivity of materials. The evaluations of thermal and electric properties are needed for the further investigation.

CONCLUSION

The effect of the sintering process on the microstructure of hydroxyapatite bodies was investigated. Hydroxyapatite was sintered by the pulse electric current sintering (PECS) process or by pressureless sintering (PLS) process in the present study. The following results were obtained:

1. XRD results showed that the specimens sintered by PECS were composed of only hydroxyapatite without another phases in the PECS temperature range of 700 to 1200°C. XRD patterns by PLS at 1000°C showed mainly hydroxyapatite peaks and a small trace of tetracalcium phosphate.
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2. The full densification over 98% of the theoretical density for samples by PLS process were achieved at 1200°C. On the contrary, the fully densified hydroxyapatite samples were obtained at 700°C by PECS process, whereas the density of samples prepared by PECS over 800°C decreased with sintering temperatures. The decrease of density with sintering temperature by PECS was speculated to be attributed to the partial dehydration of hydroxyapatite by this localized heating effect and the formation of OH− ion vacancy.

3. SEM observation showed that samples sintered by PECS at 700°C possessed very fine microstructure of hydroxyapatite with the equi-axed shape and sharp grain size distribution. The specimens sintered by PECS over 800°C revealed the bi-modal structure composed of elongated hydroxyapatite grains and partly equi-axed grains with a few micron. In the case of samples prepared by PLS at 1200°C showed larger average grain size and broader distribution.

4. From these results, the significantly fine-microstructured hydroxyapatite bodies with high density were achieved by PECS processing at a low sintering temperature, compared to PLS process.

REFERENCES