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Electric current assisted microstructure evolution of bioceramic materials: Intragranular pore containing bulk hydroxyapatites

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ABSTRACT

We successfully fabricated a controllable intragranular pore containing hydroxyapatite (HA) by the combination of an electric current assisted sintering and pre-heat treatment process. The microstructure and mechanical properties of the sintered HA bulk with and without intragranular pores were investigated in this study. Fully densified HA fabricated by the combination of an electric assisted sintering and pre-heat treatment process showed extremely superior mechanical properties. Meanwhile, hierarchically structured porous HA consisting of nanosized intragranular pores without macropores in the grain boundary showed dramatically decreased elastic modulus by different fracture mechanism compared with fully densified HA.

Artificial microstructure design of bulk ceramic materials is crucially important due to their microstructure dependent mechanical and physical properties. Especially, an understanding of the porous structure in ceramic materials is extremely important for adjusting their mechanical properties including the elastic modulus, hardness, toughness, and strength.

Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) has attracted much attention as the main inorganic structural component of the skeleton and dentition because of its superior biocompatibility, osteoconductivity, bioactivity and transparency [1–7]. However, the relatively poor mechanical properties of single phase bulk HA still prevent its application as bone graft materials in load-bearing sites [5,8]. The literature revealed that the values for the mechanical characteristics of HA ceramics are very diverse. The compressive strength of HA in the literature has been reported to be between 200–918 MPa [9]. The thermal decomposition of HA, pores, and defects in sintered HA affect the physical, mechanical, chemical and biological properties of HA. Therefore, a fully dense microstructure with a fine grain size and low residual pores is required to enhance the mechanical properties of bulk HA ceramics which can be achieved by controlling the fabrication conditions. It has been shown in various studies that the processing conditions have a crucial role in determining the microstructure and mechanical properties of HA [7–17]. Diverse fabrication processes, such as microwave sintering [10–12] and electric current assisted sintering (ECAS, commonly known as spark plasma sintering; SPS) [2,13–17] have been widely used to increase mechanical properties of bulk HA by controlling the grain size, porosity, and densification. The pulsed DC current effect on the densification of ceramic materials, which is one of the interesting phenomena with advanced microstructures, has been developed and is currently in use. Therefore, the use of electric current is believed to alter the interfacial properties of the HA interface and increase the driving force for sintering.

Dehydroxylation of HA [18–21] producing oxyapatite ($Ca_{10}(PO_4)_6O$) has been reported, and it is a concern in terms of maintaining the HA structure. The dehydroxylation of HA has not been totally avoided in all processes because it usually starts at a low temperature or very close to the applied sintering temperature for HA densification [17,19,21]. Therefore, the most promising method for designing the mechanical or physical properties of HA is by controlling the dehydroxylation phenomenon during the sintering process. Because the pore structure is expected to be deeply related with the dehydroxylation of

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HA, this study precisely analyzed the pore structure of HA, which was dependent on the process conditions used, and suggests successful manufacturing conditions for controllable intragranular pore containing bulk HA produced by the combination of an electric ECAS and pre-heat treatment process. The mechanical properties including the hardness, elastic modulus, compressive strength and fracture toughness related to the microstructure changes are discussed. The densification phenomenon during the DC current assisted densification process was also investigated in detail.

As a raw material, HA powder (Central Glass Co., Ltd. Tokyo, Japan), which has an average particle size of 2.1 μm, was prepared. HA powders were mildly milled to crushed agglomerated HA powders by a planetary ball mill (planetary mono-mill Pulverisette 6, Fritsch GmbH, Germany) for 24 h in ethanol at 250 rpm using ∅5 and ∅10-mm zirconia balls and a bowl to yield a fine HA powder. We used 1.5:1 ball to powder weight ratio with agate balls and vial at a 650 rpm rotation speed. Milled HA powders were consolidated by spark plasma sintering (SPS) (SPS-S515, SPS Syntex Inc., Japan), which enables sintering by Joule heating using a spark plasma generated by a high pulsed electric current applied through the compact. The HA powders were placed in a graphite die and sintered at 900–1200 °C for 10 min. at a uniaxial pressure of 75 MPa in a vacuum. The heating rate up to the sintering temperature was 50 °C min^{-1}. The fabricated bulk HA had a cylindrical shape with a diameter and height 10 and 5 mm, respectively. The XRD patterns were obtained by a RINT-2400 diffractometer (Rigaku Co. Ltd., Japan) using Cu K α radiation. The compressive strength of the HA samples was measured on cube samples ($3 \times 3 \times 6$ mm^3) using a universal testing machine (UH-500kN, Shimadzu Co. Ltd., Japan) with a strain rate of 0.5 mm/min at room temperature. Vickers hardness measurements were performed on the polished surface of the specimens. A load of 29.42 N was applied for 12 s using a diamond Vickers indenter (Hardness testing machine:HM-102, Mitutoyo, Japan). The bulk density of the composites was measured with a method based on the Archimedes principle and then compared with the theoretical density. The reported values are the average of over five reliable measurements. The molecular vibrational frequencies of PO_4 in the HA powder and sintered HA were analyzed by Raman spectroscopy (STR250, Seki Technotron Corp., Japan) using a 532 nm green diode laser. The microstructures of the samples were determined with a field-emission scanning electron microscope (FESEM 6500, JEOL Co. Ltd., Japan) and transmission electron microscope (TEM, HF-2000EDX, Hitachi, Japan). TEM specimens were prepared by mechanical polishing followed by an ion-thinning process using a precision ion polishing system (PIPS; dual penning Ar-ion gun, Gatan 691, USA).

Fig. 1a shows a TEM image of the intragranular pore containing HA (IPc-HA) sintered at 1100 °C for 10 min. The sintered HA has an intriguing microstructure with both porous regions and dense grain boundary regions. A magnified TEM image of one HA grain clearly shows that the porous center area consists of regular tetragonal and rectangular pores, which have a size ranging from nanometers to one hundred nanometers in Fig. 1b and S2. Circular shaped porosities are commonly generated due to their energy efficient configuration in an isotropic condition; however, the pore shape is dominantly affected by the crystal structure of the matrix in solid materials. The generation of tetragonal and rectangular shaped pores indicates that the lattice diffusivity of the vacancy to be anisotropic and the HA sustains its origin hexagonal crystal structure during ECAS as shown in Fig. 1e and f. Thus, diffusion and densification between the HA powders mainly occurred at only the grain boundary region during the ECAS process. Furthermore, these pores have a preferred orientation. The selected area electron diffraction (SAED) pattern of the porous HA structure (Fig. 1c) clearly shows that the rectangular pores are oriented to ⟨001⟩ direction (C-axis of the HA) shown in Fig. 1c. HA has a hexagonal crystal system with a rod-like structure (Fig. 1f) shown in the SEM image of the HA powder (Fig. 1d). The high-energy state of the side surface of the HA, mainly comprised of {001} planes, generates the morphology change from the cylindrical shape to equiaxed grains by a preferred densification during the sintering shown in Fig. 1a and b [22]. Yun et al. reported a similar porous structure in sintered HA, which had equilibrium or quasi-equilibrium boundaries with the HA crystal structure [16]. It was previously reported that dehydroxylation of HA occurs during heating because vacancies at the hydroxyl sites (□) are formed shown in Eq. (1) [17–21,23,24].

$$Ca_{10}(PO_4)_6(OH)_2 \Leftrightarrow Ca_{10}(PO_4)_6(OH)_{2-2x}O_x\square_x + xH_2O\uparrow \qquad \square: \text{Vacancy} \tag{1}$$

Therefore, it is assumed that the discovery of the intragranular pores in the sintered HA across all samples is attributed to the diffused vacancies, which originated from the dehydroxylation of HA. The HA powders heat treated at various temperatures in an air atmosphere were imaged using TEM to verify the dehydroxylation induced pore generation and to characterize the formation mechanism of the intragranular pores in the HA powders. Fig. 2a–d show the TEM images of the as-received and heat-treated HA powders at 200, 700, and 1000 °C for 1 h, respectively. The TEM images of the as-received HA powder and heat treated HA powder at 200 °C reveal a high crystallinity; furthermore, many nano-sized pores are observed in Fig. 2a and b, respectively. Fig. 2c clearly shows that the HA powders heat treated at 700 °C have a fully nanoporous structure. The pore size increased as the sintering temperature was increased shown in Fig. 2c and d. These pores are similar to the intragranular pores of the sintered HA. Furthermore, the heat treated HA powders at 1000 °C show necked powders while maintaining the entire porous structure, which is thought to be related with the dehydroxylation induced pore formation and growth. Fig. 2e shows the DC current variation as a function of the sintering temperature. The DC current increased as the temperature was increased and reached up to over 1100A. The inset in Fig. 2e shows the pulse condition

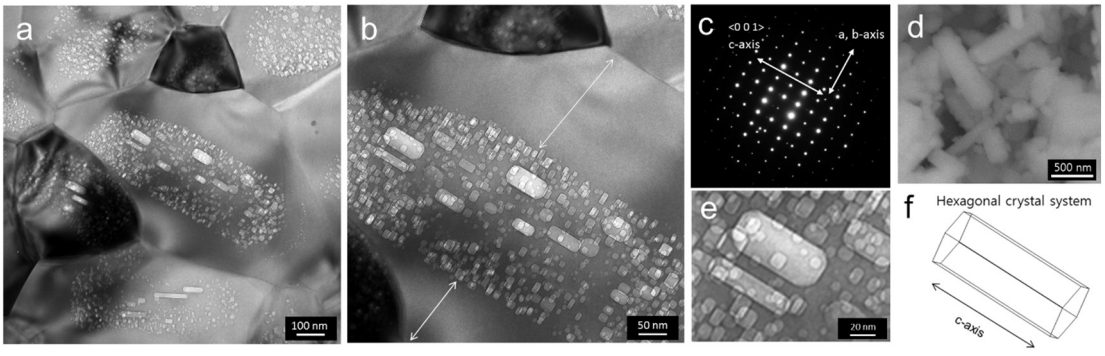

Fig. 1. (a) TEM image of IPc-HA consolidated by ECAS; (b) Magnified TEM image showing the center porous and dense grain boundary region of HA; (c) SAED pattern of the porous area (Panel b); (d) SEM image of the HA powder; (e) Magnified TEM image of the intragranular pores; (f) Schematic of the hexagonal crystal system of HA.