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Dehydroxylation of hydroxyapatite in dense bulk ceramics sintered by spark plasma sintering

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Abstract

Dense transparent hydroxyapatite (HAp) nanoceramic samples were prepared by spark plasma sintering of a commercial available granulated nanopowder. This made it possible for investigating the dehydroxylation behaviours of HAp in fully dense bulks. Post-SPS thermal annealing was performed in a temperature interval of 800 to 1100 °C in air. The phase analysis and microstructural characterization revealed that the dehydroxylation in fully dense HAp was initiated above 900 °C and its kinetics seems to be determined by the water vapour diffusion. Accordingly, a gradient structure consisting of porous interiors and a peculiar surface topography reflecting the water vapour escaping patterns were observed in samples experienced severe dehydroxylation.

Keywords: Bioceramics; Hydroxyapatite; Dehydroxylation; Microstructure

1. Introduction

Having good biocompatibility with human body hydroxyapatite ceramics, HAp, are ideal candidates for the replacement of damaged hard tissues, i.e. bone and teeth.[1,2] However, the applications of single phase HAp in clinic are rather limited due to its poor mechanical properties. New strategies have been developed accordingly to overcome these drawbacks. For example, HAp has been used as coatings on the metal substrate or as fillers in the bio-inert ceramic matrix.[3,4] Another strategy to improve the mechanical properties of HAp ceramics is to add a second-phase for reinforcement.[5–7] In all these approaches, the thermal stability of HAp has been a major concern. Once decomposition takes place during thermal processing of HAp, the physical, chemical, mechanical and biological properties of HAp will be affected.[8]

The dehydroxylation of HAp takes place ahead of the decomposition that occurs at a higher temperature. Dehydroxylation yields the formation of hydroxyoxyapatite (OHAp) and oxyapatite (OAp),[8–10] whereas decomposition gives rise to tricalcium phosphate (TCP) and tetracalcium phosphate (TTCP)[8,11–14] by following the equation 1 listed below.

$$\text{HAp} \rightarrow \text{OHAp} \rightarrow \text{OAp} \rightarrow \text{TCP} + \text{TTCP} \quad (1)$$

These compounds show higher solubility than HAp in aqueous environment,[15] which deteriorates the chemical stability and mechanical properties but enhance in vivo degradation of the HAp products. Therefore, in order to get the dense HAp ceramic or its composite without decomposition, low sintering temperatures have to be applied. So far, this goal has been achieved by two-step sintering,[16] morphology enhanced sintering,[17] microwave sintering,[18,19] hot pressing[20] or spark plasma sintering (SPS).[5,21] In all these processes the dehydroxylation of HAp has not been totally avoided, as it starts already at about 800 °C[12,22] or even lower,[9,10] a temperature lower or very close to the applied sintering temperature.

As known, dehydroxylation occurring during the sintering is a dynamic process determined by the water vapour releasing speed, which in turn depends on the microstructure developed. In sintered bodies with close pores the water vapour releasing from the dehydroxylation will be trapped inside the close pores. A local hydrothermal environment is accordingly established inside these pores filled with high pressure steam, which will influence the sintering and grain growth behaviour of HAp. Even before the total isolation of the pores, the atomic diffusion

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responsible for densification may also be influenced because of the steam flows inside the sintering compact. However, investigations on the dehydroxylation behaviour of HAp ceramics have only been focused on the kinetic processes until now.[8,10] No work has been done to study the effect of dehydroxylation on the microstructure evolution.

In the present work, fully dense transparent HAp ceramics were firstly prepared by spark plasma sintering, SPS, at a minimized temperature by applying a high heating rate and a short holding time. The as prepared HAp ceramics are almost free from dehydroxylation. This makes it possible for us to follow the dehydroxylation process in fully dense ceramics and study its effect on the microstructure evolution by post-SPS thermal annealing in air.

2. Experimental

2.1. Spark plasma sintering

Commercially available granulated HAp nanopowders (PLASMA BIOTAL Ltd) were directly used for SPS without any treatment. 0.6 g powders were loaded into a graphite die with an inner diameter of 12 mm and then the sintering was carried out in an SPS apparatus (Sumitomo Coal Mining Co., Japan) in the vacuum of 4 Pa. The temperature was measured by an infrared pyrometer that was focused on the surface of the graphite die. The transparent HAp ceramics were sintered at 925 °C for 3 min under a uniaxial pressure of 100 MPa. After sintering, the samples were grinded and polished down to 1 μm surface finishing.

2.2. Post-SPS thermal annealing in air

Each polished transparent HAp ceramic sample was cut into four small pieces. A single piece was used in each thermal annealing test conducted in the ambient air within the temperature range of 800–1100 °C with an interval of 100 °C. The samples were heated to 700 °C at a heating rate of 10 °C/min and then a heating rate of 2 °C/min was adopted until the final temperature. After reaching the final temperature, the power of the furnace was turned off and the samples were cooled down rapidly as the furnace cooling. We chose to not apply any holding in order to follow a continuous microstructure evolution when the annealing temperature linearly increased from 800 °C to 1100 °C.

2.3. Characterizations

Density was measured using the Archimedes' principle. Each sample was measured three times and the mean value is presented. Relative densities (RD) were calculated by assuming the theoretical density of HAp to be 3.156 g/cm^3.

Powder X-ray diffraction (XRD) technique was used to identify the phase transformation of the samples sintered at different temperatures. The XRD data were collected by a PANnalytical X'Pert instrument using CuK$_{\alpha1}$ radiation over a 2θ range of 20–55° at a step size of 0.02°. Fourier-transform infrared spectrometry (FTIR) spectroscopic measurements were carried out from 4000 to 400 cm^{-1} using a spectrometer (FTIR Varian 670-IR) equipped with a single-reflection Golden Gate ATR accessory with a diamond ATR element. The FTIR spectrum was used to estimate the dehydroxylation in connection with the thermal histories. For the sake of comparison, the spectrums were normalized using the $\nu4$ band of the phosphate group at 600 cm^{-1} as outlined in Ref.[23]

Microstructural observations of all the samples were conducted using a field emission scanning electron microscope (FE-SEM, JSM-7000F, JEOL, Tokyo, Japan). For the thermal annealed samples, both fresh surfaces and fractural surfaces paralleled to the direction of pressure were observed. Prior to examination, the samples were carbon-coated to prevent charging in the electron microscope. In order to check the possible pores inside the transparent HAp ceramic, the transmission electron microscope (JSM-2100, JEOL, Tokyo, Japan) was employed.

3. Results and discussions

3.1. Fully dense transparent HAp ceramics with stoichiometric composition

Fig. 1(a) shows a photo of the dense HAp ceramic sample prepared by SPS at 925 °C under a uniaxial pressure of 100 MPa. The apparent high transparency indicates that the density of the prepared HAp ceramic is sufficient high, which agrees well with the result of measured RD of 99.8%. TEM investigation was performed to check the possible presence of any residual pores and the grain size. One image from this study is presented in Fig. 1(b). It clearly reveals that no pores can be found along the grain boundary or inside the grains. Furthermore, it appears that the entire view of microstructure shows a homogeneous distribution of grains with a mean size of about 100 nm. It can thus be concluded the high density and small grain size are responsible for achieved high optical transparency.

In order to examine the possible phase changes during SPS, the XRD and FTIR were conducted. The obtained XRD pattern and IR spectrum are shown in Fig. 2. It is obvious that all the XRD peaks belong to the HAp phase. No any other phases such as TCP, TTCP or CaO can be found, which indicates that decomposition did not occur when sintered at 925 °C by SPS. The absorbance peaks at 629 cm^{-1} and 3569 cm^{-1} in IR spectrum ascribes to the OH bond in HAp lattice. The presence of these two peaks gives the possibility to study the dehydroxylation in the next thermal annealing.

3.2. Density decrease accompanied with no weight loss during thermal annealing

Fig. 3 shows the variation of sample density with the annealing temperature. It appears that the relative density starts to decrease when annealed at 900 °C and shows a rapid drop at 1000 °C. This variation of densities is also associated with a change in sample colour, see Fig. 4. It is evident that the transparency of the sample was deteriorated by annealing above