PREPARATION OF BIOLOGICALLY DERIVED HA/TCP COMPOSITES

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Introduction

Hydroxyapatite (HA) is the main mineral constituent of the vertebrate skeletal systems, and has an approximate chemical composition of $Ca_{10}(PO_4)_6(OH)_2$. HA has been used widely as a biocompatible bioceramic in bone and tooth implants since the 1960s [1]. Tricalcium phosphate (TCP, $Ca_3(PO_4)_2$) is another successful material for resorbable, hard tissue replacements for some repairs of the jaw or head [1]. In recent years, biphasic calcium phosphate (BCP) bioceramics consisting of a mixture of HA and TCP are commercially available as a bone-graft or bone substitute materials for orthopaedic and dental applications [2].

Biologically derived calcium phosphates have advantages of low production cost and similar composition to human bone [3]. Therefore, a variety of biomaterials from natural bone has been developed. Some calcium phosphates directly derived from bovine bone have been applied for bone graft substitution materials [4].

Bone ash imported from foreign countries has mainly been used as an animal feed or raw material for bone china [5]. HA is an inorganic component of bone ash with a similar chemical compositions to human bone and teeth, suggesting that bone ash derived-HA should be biocompatible. However, there were few studies on fabrication of calcium phosphate substances from bone ash for biomedical application, whereas animal bone-derived calcium phosphates have been reported elsewhere [6]. Therefore, we in this study prepared biologically derived HA/TCP composite ceramics using bone ash and the effect of sintering condition on microstructure and dissolution behavior of bone ash-derived HA/TCP composites.

Experimental

Bone ash powder was obtained commercially and used as a raw material. The organics in bone ash were removed by soaking in a 0.1 M NaOH solution at 80 ˚C for 4 h and by calcination at 1000 ˚C for 1 h. Organic-free powder was obtained by attritor-milling the calcined bone ash for 24 h. The HA/TCP composites were prepared by pressureless sintering and hot-pressing. For pressureless sintering, the powders were uniaxially and cold isostatically pressed into pellets. The pellets were sintered at 1200 ˚C for 1 h. In the case of hot-pressing, sintering was carried out at 1000 ˚C for 0.5 h under a pressure of 30 MPa in Ar atmosphere. For the dissolution test, the polished disks were soaked in distilled water of pH 7.4 (buffered using 0.05 M tris(hydroxymethyl)-aminomethane) at 37 ˚C for 3-14 days. At the end of the time periods, the samples were washed with distilled water and ethanol, and then dried overnight at 80 ˚C for further analysis.

Results and Discussion

Fig. 1 shows the bone ash-derived HA powder after calcination and milling. The powder had a wide size distribution of 0.5-1.0 μm with an irregular particle shape and agglomeration. XRD showed that the powder consisted a mixture of HA and α-TCP (α-$Ca_3(PO_4)_2$). According to element analysis, the bone ash had a Ca/P ratio of 1.73, which is higher than the stoichiometric composition. HA decomposed thermally to α-TCP at elevated temperature due to the non-stoichiometry.

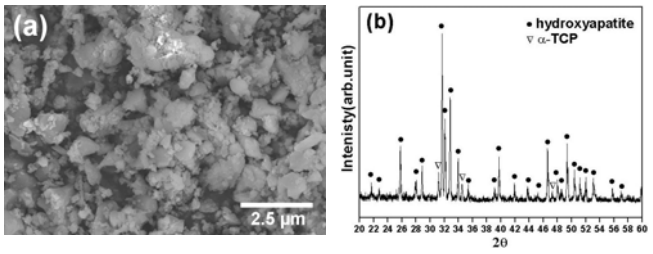

Fig. 1 (a) SEM micrograph and (b) XRD pattern of HA/TCP composite powder calcined at 1000 ˚C.

Using the bone ash-derived HA powder, the sintered bodies were prepared by pressureless sintering and hot pressing. Fig. 2 shows bone ash-derived HA/TCP

composite prepared by pressureless sintering. The composite consisted of grains of 1-2 μm in size and there were small and large sizes of pores among the grains corresponding to low sintered density of 71% of the theoretical. The composite fractured by transgranular mode and there were interconnected pores similar to the surface morphology. XRD pattern was almost similar to the case of the calcined powder.

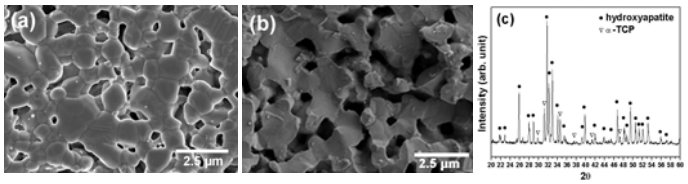

Fig. 2 Pressureless-sintered HA/TCP composites; (a) surface microstructure, (b) fracture surface and (c) XRD pattern.

Fig. 3 shows bone ash-derived HA/TCP composite by hot pressing. Sintered density of the composite was about 95% of theoretical, meaning that densification can be obtained by hot pressing at much lower sintering temperature than by pressureless sintering. Surface microstructure revealed that the ceramics mostly consisted of small grains of 0.5 μm with presence of relatively large grains of 1.0 μm above.

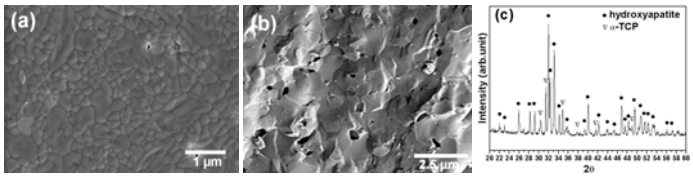

Fig. 3 Hot-pressed HA/TCP composites; (a) surface microstructure, (b) fracture surface and (c) XRD pattern.

Fig. 4 shows the surface morphology of the hot-pressed HA/TCP composite after different immersion periods. The polished surface was smooth with a low density of surface defects. Grain boundaries began to appear due to dissolution (marked by arrows in Fig. 4(b)). Grain boundary dissolution was pronounced after immersion for 7 days. After 14 days, the extent of grain boundary dissolution increased and bonding between the grains became weak and some grains were separated and moved away from the surface.

Mixtures of HA and TCP can allow changes in the implant resorption rates while maintaining useful bioactive properties. In addition, the presence of a secondary TCP phase in HA ceramics helps enhance the mechanical properties because of the tougher TCP phases.

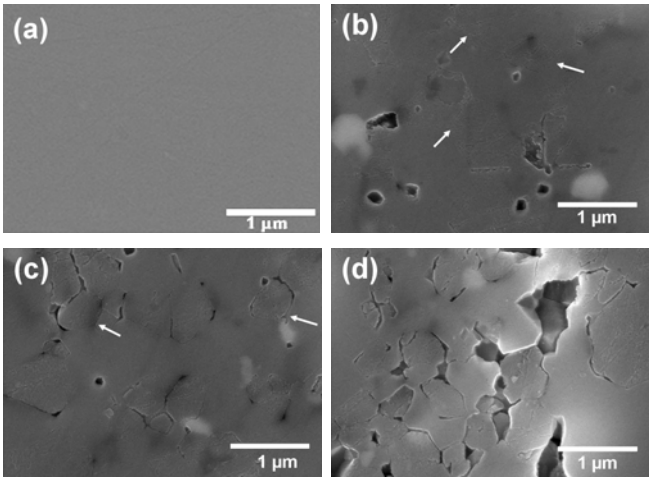

Fig. 4 Dissolution of hot-pressed HA/TCP composites; (a) as-sintered, and immersed for (b) 3 days, (c) 7 days and (d) 14 days.

Conclusion

It was possible to obtain dense HA/TCP composite ceramics by hot pressing. The presence of α-TCP in the composites was responsible for the surface dissolution in which the grain boundaries were included. However, HA/TCP composites can be a useful substance in terms of improving the mechanical and biological properties of HA-based bioceramics.

Acknowledgements

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