

Enhancement of Apatite-Forming Abilities of Calcium Phosphate Ceramics by Autoclaving

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Abstract. Apatite-forming abilities of $60\text{CaO}\cdot 30\text{P}_2\text{O}_5\cdot 7\text{Na}_2\text{O}\cdot 3\text{TiO}_2$ glass-ceramic, $\beta\text{-Ca}_3(\text{PO}_4)_2$ (β -TCP), $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ (β -CPP) and hydroxyapatite (HA) after surface modification by autoclaving were estimated by immersion tests using simulated body fluid (SBF). Each sample was autoclaved in DW at 100-180°C, and then immersed in SBF for 10 days. The apatite-formation on the glass-ceramic and β -TCP were enhanced by autoclaving at 140-180°C and the formation was not observed on the non-autoclaved and autoclaved β -CPP. The apatite nucleation on HA was enhanced by autoclaving. Ti-OH group inducing the apatite-formation was formed on the glass-ceramic surface by autoclaving. Surface potentials of the β -TCP and HA was decreased by autoclaving. These changes in surface properties of the samples by autoclaving are expected to cause the enhancement of the apatite-formation.

Introduction

Apatite-forming ability has been regarded as one of the important factors for biocompatibility of bone substitute [1,2]. The apatite formed on bioactive materials was reported to provide good interaction between implanted materials and host bone through cell activation. The apatite-formation can be demonstrated in simulated body fluid (SBF). The SBF have been applied as a biomimetic method to coating with the apatite on bioinert materials, such as titanium, zirconia and alumina.

Bioactive glass and glass-ceramics containing silica, such as Bioglass[®] and Cerabone A-W[®], have the excellent apatite-forming ability in SBF [3,4]. On the other hand, it has been regarded to be difficult for glasses and glass-ceramics containing no silica to form the apatite on their surfaces in SBF. In our earlier study, $60\text{CaO}\cdot 30\text{P}_2\text{O}_5\cdot 7\text{Na}_2\text{O}\cdot 3\text{TiO}_2$ glass-ceramic has been reported to have the apatite-forming ability [5]. However, the apatite-formation was observed after 14-days of immersion.

In the present study, we proved the enhancement of the apatite-forming ability of the $60\text{CaO}\cdot 30\text{P}_2\text{O}_5\cdot 7\text{Na}_2\text{O}\cdot 3\text{TiO}_2$ glass-ceramic by a simple method of autoclaving in

distilled water. In addition, an effect of the autoclaving on the apatite-forming abilities of various calcium phosphate ceramics, such as β - $\text{Ca}_3(\text{PO}_4)_2$ (β -TCP), β - $\text{Ca}_2\text{P}_2\text{O}_7$ (β -CPP) and hydroxyapatite (HA), was estimated by SBF immersion tests.

Materials and Methods

A phosphate glass composed with $60\text{CaO}\cdot 30\text{P}_2\text{O}_5\cdot 7\text{Na}_2\text{O}\cdot 3\text{TiO}_2$ was prepared using reagents of CaCO_3 , H_3PO_4 , Na_2CO_3 and TiO_2 . The mixed reagents were heated in a platinum crucible at 1350°C for 0.5 hr to be melted. The melt was poured on a stainless-steel plate, and then immediately pressed with an iron plate, finally formed into glass plates with 0.5-1 mm in thickness. The prepared glass plates were reheated at 800°C for 1 hr to be crystallized. The obtained glass-ceramic was characterized by X-ray diffractometry (XRD).

β -TCP and HA reagents were provided from Taihei Chemical Industrial Co. Ltd., and β -CPP reagent was purchased from Kishida Chemical Co. Ltd. The reagents were pressed in a 10- μm diameter mold, and then isostatically pressed under 98 MPa for 15 min to be formed into discs. The discs were heated at a ramp rate of 5°Cmin^{-1} and held at the temperatures of 1070°C for β -TCP, 1000°C for β -CPP and 1100°C for HA for 3 hr in a furnace.

The obtained samples of the glass-ceramics, β -TCP, β -CPP and HA were autoclaved in DW at 100 - 180°C for 1 hr. The autoclaved and non-autoclaved samples were immersed in SBF and incubated at 37°C for 10 days. The samples after the incubation were washed with DW and dried at room temperature. Surface morphologies of the samples were observed by field emission scanning electron microscopy (FE-SEM). Surface characterization of the samples before and after autoclaving was examined by XRD, laser electrophoresis spectroscopy and X-ray photoelectron spectroscopy (XPS).

Results and Discussion

Figure 1 shows an XRD spectrum of the glass-ceramic. The glass-ceramic included a large amount of β -TCP and β -CPP crystals. TiO_2 and Na_2O were suggested to be included in a residual glassy phase of the glass-ceramic. No significant change in the crystallinity of the glass-ceramic after

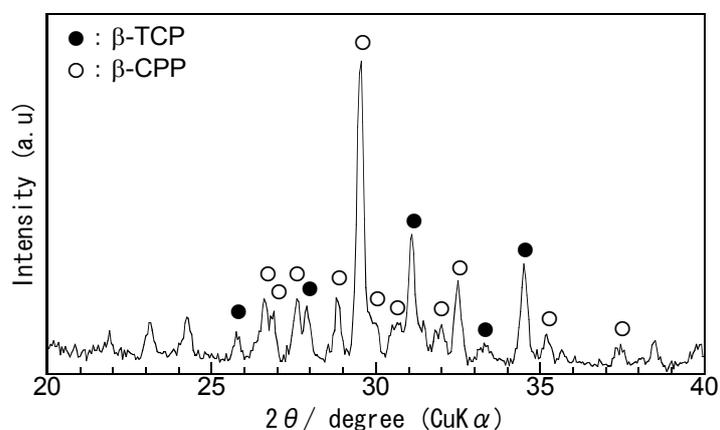


Fig. 1 XRD spectrum of $60\text{CaO}\cdot 30\text{P}_2\text{O}_5\cdot 7\text{Na}_2\text{O}\cdot 3\text{TiO}_2$ glass-ceramic

autoclaving was seen (data not shown here).

Figure 2 shows surface morphologies of the non-autoclaved and autoclaved samples after SBF-immersion for 10 days. Enhancement of the apatite-formation by autoclaving was confirmed on the surfaces of the glass-ceramic, β -TCP and HA. The apatite crystals in the shape of leaf covered on the surface of the glass-ceramic autoclaved at 140°C and 180°C (Fig. 2 [c], [d]), while no deposit was observed on the surface of the glass-ceramic autoclaved at 100°C and non-autoclaved (Fig.2 [a], [b]). All of the autoclaved β -TCP showed the apatite-forming ability and the quantity of the apatite crystals increased with increasing of the autoclaving temperature (Fig. 2 [f-h]). The non-autoclaved β -TCP showed no apatite-forming ability (Fig. 2 [e]). The apatite crystals dispersedly deposited on the non-autoclaved HA. On the autoclaved HA, the apatite crystals densely deposited and covered on the surface; the apatite nucleation on HA was enhanced by autoclaving (Fig. 2 [m-p]). No deposition was observed on the

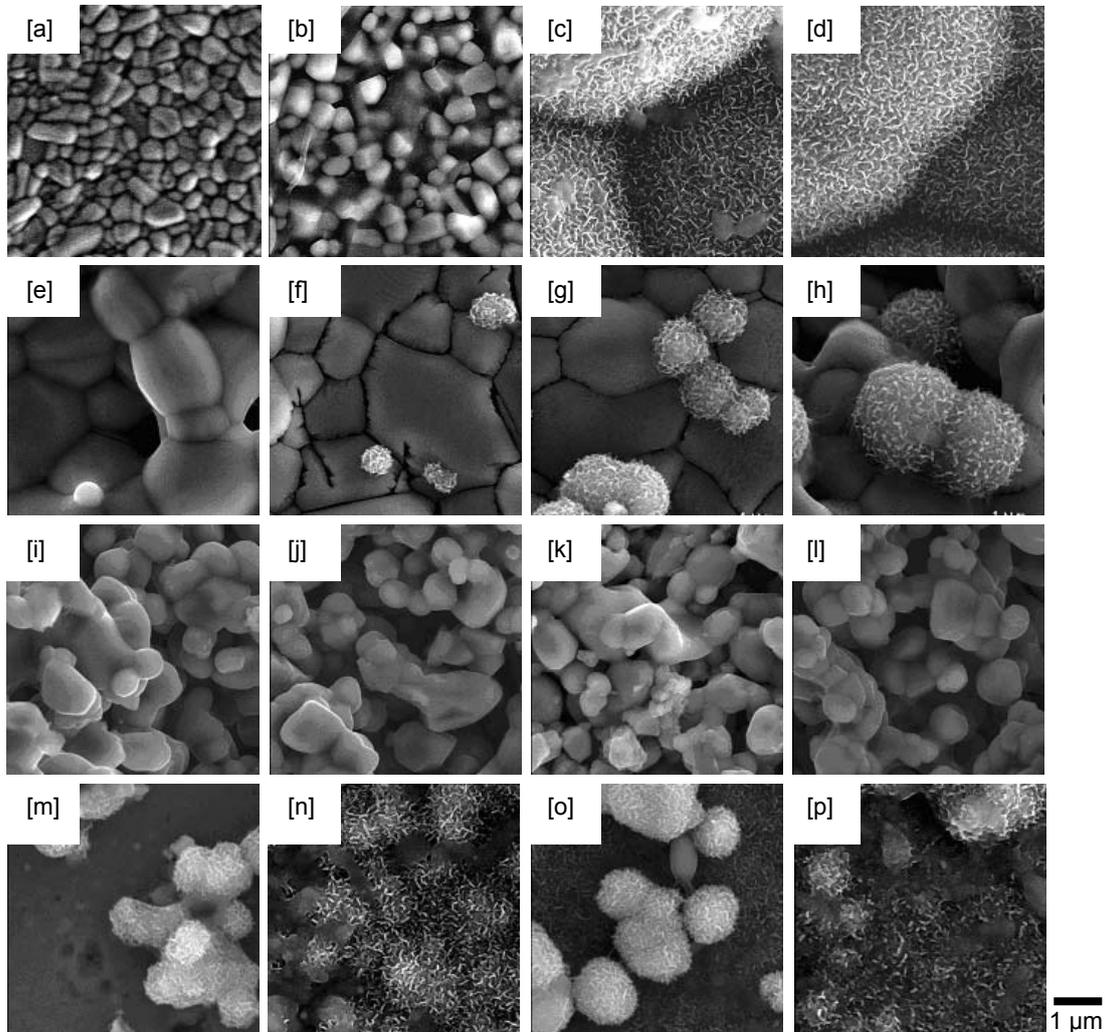


Fig. 2 Surface morphologies of glass-ceramic, β -TCP, β -CPP, and HA after 10-days SBF immersion. [a-d]; glass-ceramic, [e-h]; β -TCP, [i-l]; β -CPP, [m-p]; HA, [a,e,i,m]; non-autoclaved samples, [b,f,j,n]; samples autoclaved at 100°C, [c,g,k,o]; autoclaved at 140°C, [d,h,l,p]; autoclaved at 180°C.

surfaces of the non-autoclaved and autoclaved β -CPP.

Effect on the surface of the glass-ceramic by the autoclaving was estimated by XPS. After the autoclaving, peaks in Ti spectra shifted to 458.5 eV and 464.2 eV from 459.6 eV and 465.5 eV, respectively. This result indicates that Ti-O bond in the residual glassy phase was reformed new Ti-O bond, which is the same with that in TiO₂ crystal of anatase phase, after break during the autoclaving. Anatase has been regarded as a significant factor for the apatite-formation. Since the surface of the glass-ceramic was exposed to water during the autoclaving, Ti ions may make Ti-OH groups. The Ti-OH groups were reported to be one of the important factors for inducing the apatite nucleation in SBF [6]. In the case of β -TCP and HA, surface potentials were decreased by the autoclaving. The lower surface potential may induce plus ions, such as Ca²⁺ playing a significant role in the apatite nucleation.

The glass-ceramic, β -TCP and HA were improved in surface properties by the autoclaving. On the other hand, β -CPP suffered no effect on its surface property and apatite-forming ability by the autoclaving. The enhancement of the apatite-forming ability by the autoclaving depended on the autoclaved material.

Summary

The apatite-forming abilities of the calcium phosphate ceramics were improved by a simple method of the autoclaving in DW. The glass-ceramic and β -TCP acquired the apatite-forming ability by the autoclaving. In addition, the apatite nucleation and growth on HA was enhanced by the autoclaving. The autoclaving is expected as one of the significant methods to enhance the biocompatibility of materials.

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