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Synthesis and Evaluation of Calcium-Deficient Hydroxyapatite with SiO_2

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ABSTRACT

Effect of SiO_2 addition on the microstructures of calcium-deficient hydroxyapatite prepared by the heat-treatments was examined. Obtained hydroxyapatites substituted with Si ion were characterized by XRD, FT-IR and XAFS measurements. XANES results of Si K-edge and P K-edge in these modified hydroxyapatites indicated the shift of peaks of P K-edge with the SiO_2 contents, although no change of Si local structures. In this study, the effect of Si ion on micro- and local structure of hydroxyapatite with SiO_2 addition was mainly clarified.

Keywords: *Hydroxyapatite, SiO_2, XAFS, Local Structure*

1. Introduction

It is well-known that hydroxyapatite (HAP) is a major inorganic component of bone and teeth. Since HAP possesses high bioactivity, osteoconductivity and bio-compatibility, it is extremely useful as a biomaterial for artificial implant parts, bone fillers, and bone-cements etc. [1-6].

On the contrary, HAP has also both the high ability of ion exchange against cations and anions and adsorbent for various amino acids and proteins among other inorganic materials [5-10]. In bone, HAP is usually calcium-deficient below Ca/P of 1.67, not stoichiometry "($Ca_{10}(PO_4)_6(OH)_2$) with Ca/P of 1.67", for the achievement of doping metal ions and control of the solubility. As a consequence, nonstoichiomeric HAP with Ca/P of less than 1.67 possesses the high ion-exchange ability of various cations. Therefore, calcium-deficient HAP is expected to be applicable as an ion-exchange media for solving environmental problems, such as the purification for water and soil polluted with heavy metals as well as biomedical applications [10,11]. Recently, the syntheses of HAP doped with functional elements (Zn and Fe) are also attempted for developing high performance bioceramics for biomedical application and the clarification of effects of functional elements on the properties and microstructures is carried out in order to develop the high performance bioceramics.

The syntheses of HAP substituted with other metals have been eagerly attempted by various synthetic processes, such as hydrothermal treatments, ion-exchange treatments, and normal heat-treatments at high temperature in order to enhance the ion exchange ability and bioactivity of HAP [9-15]. For example, Fe substituted HAP *i.e.* abbreviated by "HAP modified with Fe ions", synthesized by hydrothermal treatment indicated the good exchange ability against As and Pb etc., compared to monolithic HAP. However, in fact, monolithic HAP doped with metal ions is significantly difficult to synthesize without any other phase.

Since Bonefield reported that HAP containing with SiO_2 indicated high bioactivity and osteoconductivity [14], the synthesis of HAP with SiO_2 and tricalcium phosphate (TCP) with SiO_2 have been performed by many researchers. However, HAP with SiO_2 addition often results in the formation of reaction phase between HAP and SiO_2, such as calcium silicate, and phosphate glass etc, and unreacted SiO_2 residue. Thus, the SiO_2 doped HAP without reaction phases and SiO_2 residue is difficult to synthesize by the conventional methods. However, the successful synthesis of SiO_2 doped HAP will lead to understanding effect of SiO_2 element on the high bioactivity and osteoconductivity for SiO_2 doped HAP.

In this study, the main purpose is to synthesize SiO_2 doped HAP. As a strategy, the incorporation of Si ions into HAP was especially carried out by using whisker-like calcium-deficient HAP as a starting material, not stoichiometric HAP. Whisker-like calcium-deficient HAP powders were synthesized by the soft chemical processing for the hydrolysis of α-TCP. In addition, calcium-deficient HAP containing SiO_2 was normally heat-treated in air atmosphere and the effect of SiO_2 addition on micro- and local structure of HAP was examined. Furthermore, Si and P local structures of these substituted HAP were investigated by the XANES.

2. Experimental Procedures

2.1. Synthesis

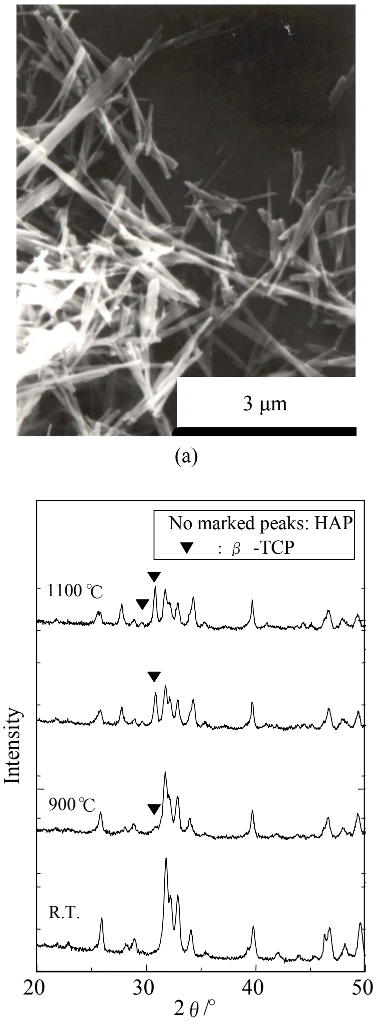
HAP powder was synthesized by the soft chemical processing for the hydrolysis of α-TCP [15]. 10 g of α-TCP powder was stirred in 200 ml of 1-octanol at 70˚C for 48 h. The solution during reaction was kept at pH11 with 0.1 M NH_4OH. The precipitation was filtered with the membrane and washed with ethanol and ion-exchange water sufficiently and then dried at 50˚C for 24 h. Commercial SiO_2 powder from Tokuyama Chemical (Tokushiru) was used as a source of Si ion. SiO_2 (3, 10, and 30 wt%) was added into HAP powder and mixed in ethanol with ball milling for 24 h. After mixing, the mixture was filtered with membrane and subsequently dried at 323 K. The dried powder was crashed with alumina mortal. Mixed HAP/SiO_2 powder was compacted with stainless mold. Dimension of pellets was 2 mm in thickness and 20 mm in diameter. Pellets were heated at 600˚C to 1200˚C in air atmosphere. Heating rate was 5˚C/min. After holding at the high temperature for 2 h, samples were cooled in furnace. Heat-treated samples were polished with diamond paste.

2.2. Evaluations

The component of samples was identified with XRD (Rint-2000: Rigaku, Tokyo, Japan). The microstructure of samples was observed by SEM (S-450: Hitachi, Tokyo, Japan) and TEM (FX-2010: JOEL, Tokyo, Japan). The samples were evaluated with FT-IR equipment (Shimazu, Tokyo, Japan). Si-K and P-K edge were measured at UVSOR in Okazaki.

3. Results and Discussion

Figure 1 shows XRD and SEM results of HAP samples synthesized by the soft chemical processing, *i.e.* the hydrolysis of α-TCP in 1-octanol at 70˚C for 48 h. XRD results indicated that products were composed of monolithic HAP and no other phase like calcium phosphate. From SEM observation, HAP particles synthesized by the hydrolysis of α-TCP were observed to be whisker-like. From ICP measurements, Ca/P ratio of calcium-deficient HAP added with SiO_2 (0 wt%, 3 wt%, 30 wt%) were evaluated for samples synthesized by the soft chemical processing. ICP results indicated that this whisker-like HAp had 1.580 of Ca/P ratio, suggesting that obtained whisker-like HAP was calcium-deficient. On the other hand, Ca/P ratio of calcium-deficient HAP added with 3 wt% SiO_2 and 30 wt% were 1.590 and 1.603, respectively. It was obvious that the addition of SiO_2 into calcium-deficient HAP samples resulted in the decrease of Ca/P ratio.



(a)

(b)

Figure 1. (a) XRD and (b) SEM image of whisker Ca-deficient HAP synthesized by the hydrolysis of α-TCP in 1-octanol at 70˚C for 48 h.

XRD results of calcium-deficient HAP samples containing 3 to 30 wt% SiO_2 heat-treated at 600˚C to 1200˚C are shown in **Figure 2**. HAP samples without SiO_2 heat-treated at 600˚C were composed of HAP phase without another calcium phosphate phase, although HAP samples heat-treated at 1000˚C have the mixture of HAP and

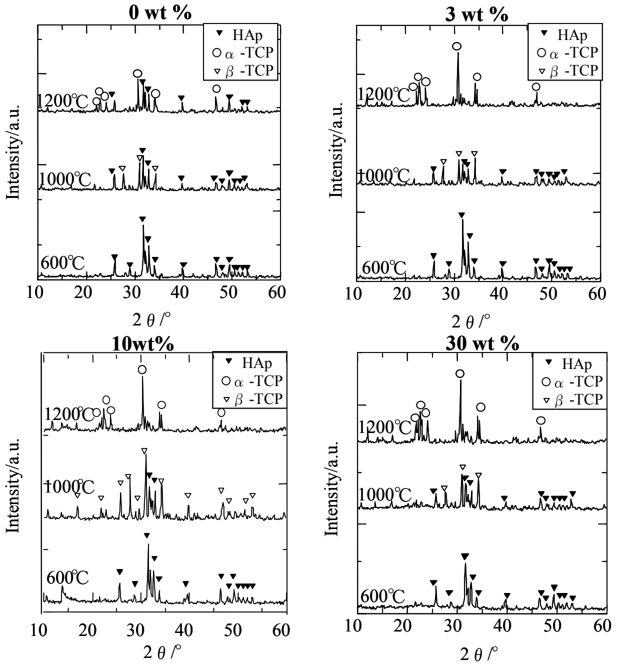


Figure 2. XRD results of Ca-def HAp added with SiO_2 (0 wt%, 3 wt%, 10 wt%, and 30 wt%) heat-treated at various temperatures.

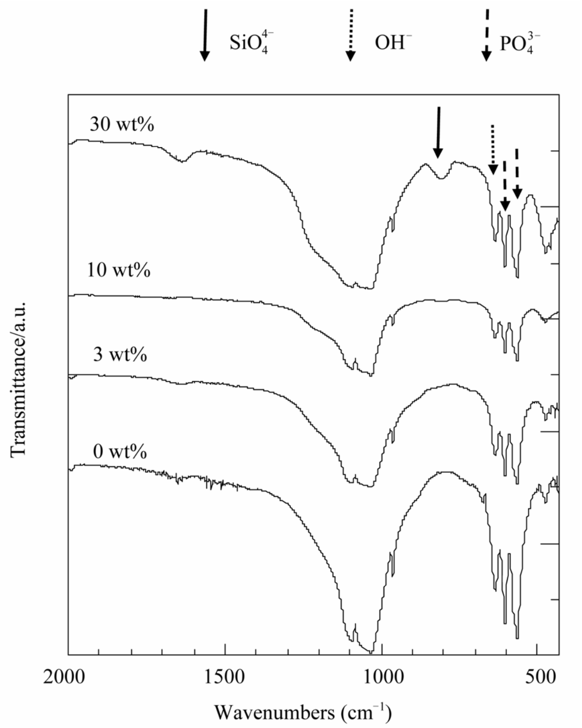


Figure 3. FT-IR results of Ca-def HAp added with SiO_2 (0 wt%, 3 wt%, 10 wt%, and 30 wt%) heat-treated at 600˚C.

α-TCP. The component of samples heat-treated at 1200˚C was the mixture of HAP and α-TCP. In case of HAP/3%SiO_2, samples heat-treated at 600˚C contained HAP monophase. HAP/3%SiO_2 samples heat-treated at 1200˚C were composed of mainly α-TCP and in part HAP, although the component of samples heat-treated at 1000˚C were HAP and α-TCP. HAP/10%SiO_2 and HAP/30% SiO_2 samples indicated the same dependence of heat-treatment temperatures for XRD results. For HAP/10% SiO_2 and HAP/30%SiO_2, samples heat-treated at 600˚C were composed of monolithic HAP and ones at 1200˚C were of α-TCP, respectively. On the other hand, both HAP/10%SiO_2 and HAP/30%SiO_2 samples heat-treated at 1000˚C were composed of HAP and α-TCP. Thus, it was found that the addition of SiO_2 into calcium-deficient HAP enhanced the formation of α-TCP above 1000˚C.

Figure 3 shows the variation of FT-IR spectra of calcium-deficient HAP/SiO_2 samples heat-treated at 600˚C with SiO_2 content. HAP/SiO_2 samples with higher SiO_2 content indicated the stronger peak from SiO_4^{4-} with SiO_2 content. However, as obviously shown in figure, the peak form phosphate (PO_4^{3-}) for HAP/SiO_2 samples decreased with increase of SiO_2 content. In addition, the peak from OH^- for HAP/SiO_2 samples decreased with high SiO_2 content of 30%. In this study, XRD results indicated no formation of calcium silicate for HAP/SiO_2 samples heat-treated at 600˚C. These FT-IR results, in conjunction with XRD and FT-IR results, indicate that SiO_2 was incorporated into calcium-deficient HAP structures, although the excess addition of SiO_2 (e.g. 30 wt% addition) and heat treatment at high temperatures have the possibility of formation of calcium silicate. Therefore, these results indicate that SiO_4^{4-}, below the optimum SiO_2 contents, was substituted for PO_4^{3-} site in calcium-deficient HAP structure during the heat-treatment at 600˚C.

The microstructures of these calcium-deficient HAP/3 ~ 10 wt% SiO_2 heat-treated at 600˚C were observed with SEM. **Figure 4** shows SEM images of calcium-deficient HAP samples containing 0, 3 and 10 wt% SiO_2 after the heat-treatment at 600˚C. Although calcium-deficient HAP/3 ~ 10 wt% SiO_2 were whisker-like as well as calcium-deficient HAP samples without SiO_2, the length of whisker-like products decreased with SiO_2 content. Also, no agglomerate and grain growth of HAP grains were confirmed after heat-treatment at 600˚C. Thus, the addition of SiO_2 into calcium-deficient HAP resulted in the inhibition of HAP grain growth, which was caused by the substitution of SiO_4^{4-} for PO_4^{3-} site in hydroxyapatite structure during the heat-treatment.

Figures 5 and **6** shows the spectra of XANES of P *K*-edge and Si *K*-edge for calcium-deficient HAP/3 ~ 10 wt% SiO_2 heat-treated at 600˚C, compared to monolithic HAP and samples heat-treated at 600˚C and quartz as a reference material. From measurement in Si *K*-edge,

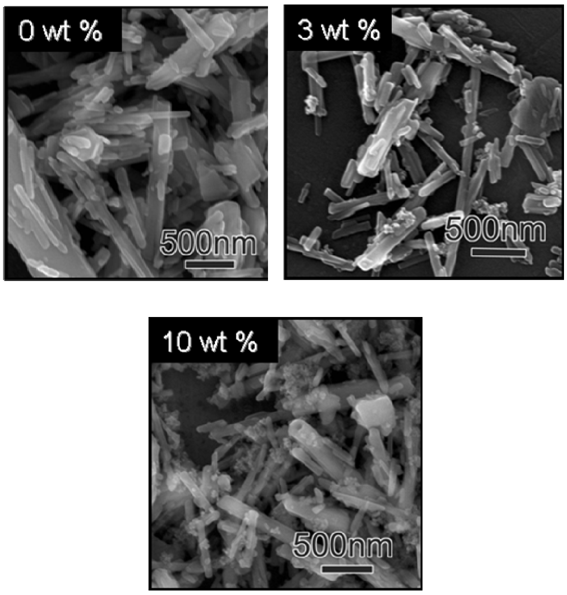


Figure 4. SEM images of calcium-deficient HAP samples containing 0, 3 and 10 wt% SiO_2 after the heat-treatment at 600˚C.

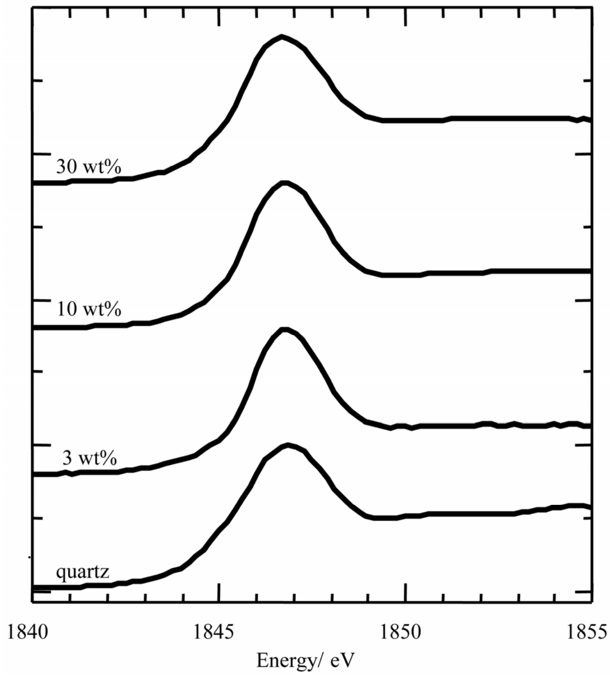


Figure 5. Results of Si *K*-edge XANES spectra of calcium-deficient HAP/0 ~ 30wt%SiO_2 heat treated at 600˚C.

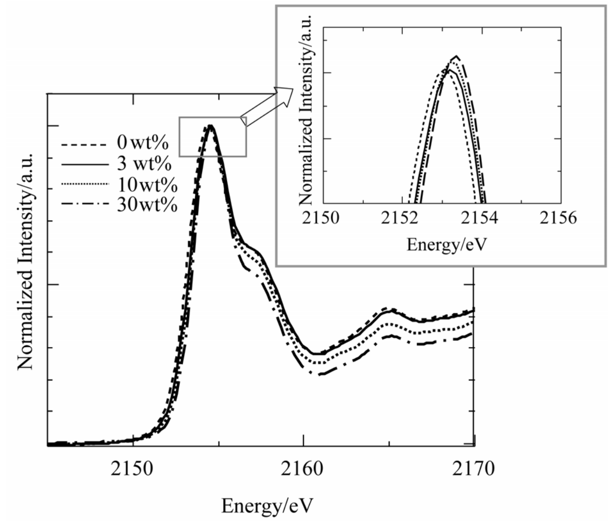


Figure 6. Results of P *K*-edge XANES spectra of calcium-deficient HAP/0 ~ 30 wt%SiO_2 heat-treated at 600˚C.

Si-local structures of calcium-deficient HAP/3 ~ 10 wt% SiO_2 heat-treated at 600˚C was the same as the quartz and had no peak shifts, as shown in **Figures 5**. However, in case of P local structures, the peak of P *K*-edge was shifted to higher energy with the SiO_2 contents. This result indicated that local structure around P *K*-edge for calcium-deficient HAP/3 wt% SiO_2 heat-treated at 600˚C was slightly different from monolithic HAP and HAP with a large amount of SiO_2. On the contrary, calcium-deficient HAP/10 ~ 30 wt% SiO_2 heat-treated at 600˚C had the significantly different local structure around P *K*-edge compared to monolithic HAP and HAP/3 wt% SiO_2. These XANES, XRD and FT-IR results also suggest that SiO_4^{4-} was substituted for PO_4^{3-} in hydroxyapatite structure. The difference in XANES spectra between HAP/3 wt% SiO_2 samples and others are thought to be caused by the electron state. According to results reported by Harris *et al.* [16], the substitution of PO_4^{3-} site by carbonate (2 to 6 wt%) produced marked change in EXAFS (extended X-ray absorption fine structure), leading to the structural distortion in hydroxyapatite structure due to the incorporation of carbonate into hydroxyapatite. This phenomenon and furthermore the theoretical defect energetics in hydroxyapatite is under investigation. Thus, these results indicated the noticeable structural changes accompany the substitution of SiO_4^{4-} into PO_4^{3-} site in hydroxyapatite structure.

4. Conclusions

Effect of SiO_2 addition on the microstructures of calcium-deficient HAP prepared by the soft chemical processing was investigated. HAP substituted with Si ion was synthesized by the normal heat-treatment at 600˚C to 1200˚C for 2 h in air atmosphere. The results of FT-IR measurements for modified HAP indicated that the peak from PO_4^{3-} decreased with the SiO_2 contents. Microstructural observations indicated that the incorporation of SiO_2 inhibited the growth of HAP grain. Evaluation of P

K-edge indicated the XANES spectra of HAP/10 ~ 30 wt% SiO_2 heat-treated at 600˚C were different from that of monolithic HAP and HAP/3 wt% SiO_2 samples. These results of micro- and local structure of modified HAP suggest that SiO_4^{4-} was substituted for PO_4^{3-} in hydroxyapatite structure.

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