JOURNAL OF MATERIALS SCIENCE **39** (2004) 2531–2534

Thermal stability of hydroxyapatite whiskers derived from the hydrolysis of α-TCP

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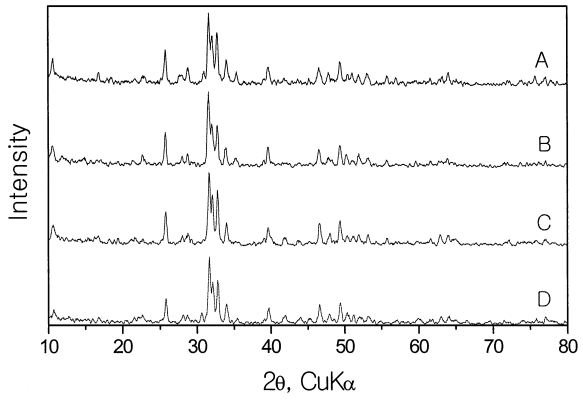

Figure 1 XRD patterns of the materials obtained by the hydrolysis of α-TCP at 90 °C for 6 h with pH: 9.1 (sample A), 10 (B), 10.7 (C) and 11.5 (D).

Whisker shaped hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAp) is a promising candidate material for reinforcing ceramic or polymer matrices to be used in the biomedical and dental fields [1]. Various techniques for preparation of whiskerlike or fibrous HAp have been reported [2–6]. Among these, the hydrolysis of α-$Ca_3(PO_4)_2$ (α-TCP) under controlled processing conditions (aqueous pH, temperature and time) is often adopted to generate a whisher shaped form of HAp [2, 3].

Several authors [7–10] have reported on the thermal stability of synthetic HAp but the results are not generally coincident. It is suggested that the reason for this that the thermal decomposition of HAp is inherently dependent on the crystallinity, stoichiometry and atmosphere conditions prevailing during the reactions

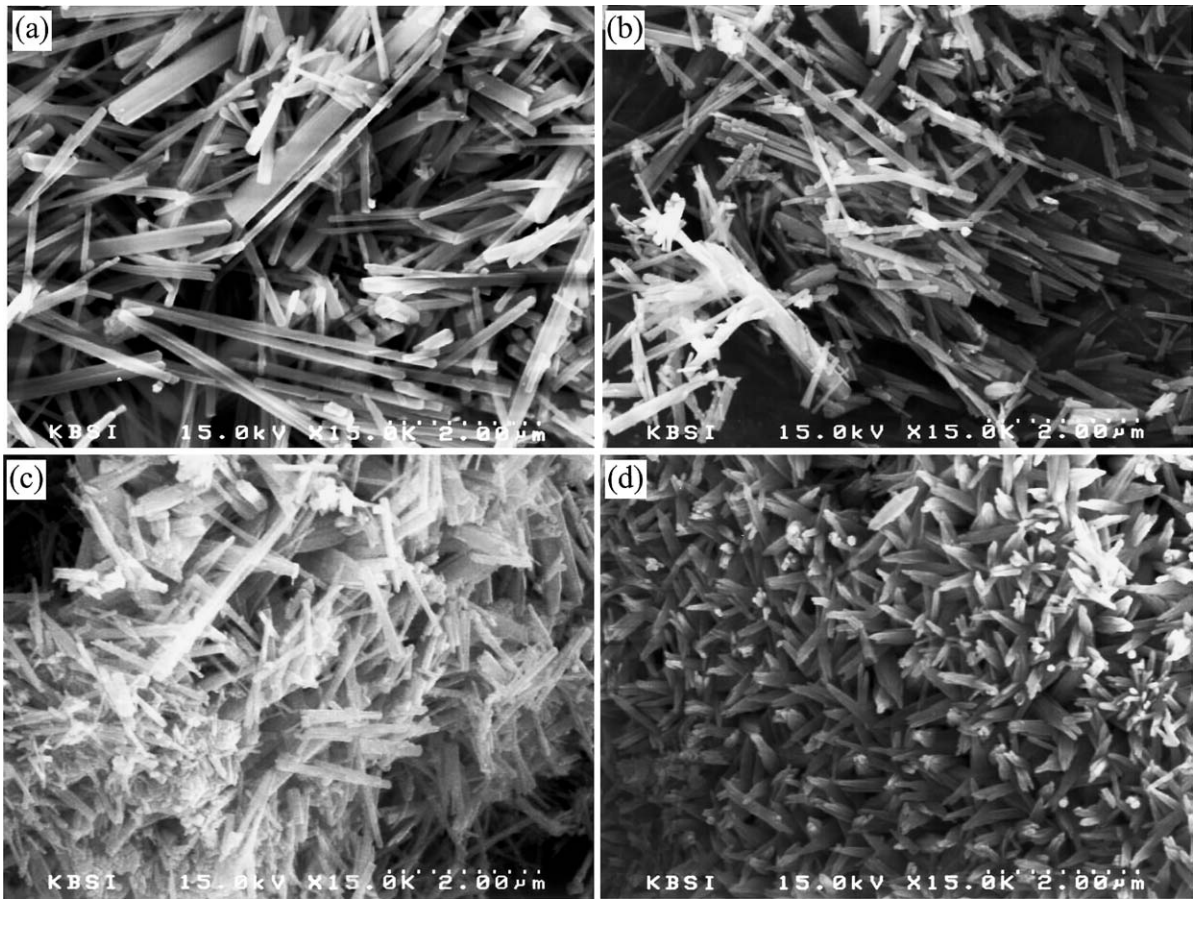

Figure 2 SEM micrographs of sample: (a) A, (b) B, (c) C and (d) D.

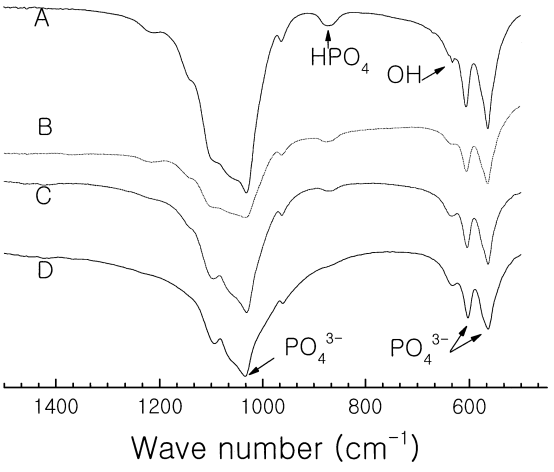

Figure 3 FTIR spectra of the HAp materials obtained by the hydrolysis of α-TCP at 90 °C for 6 h with different pHs: (A) 9.1, (B) 10, (C) 10.7 and (D) 11.5.

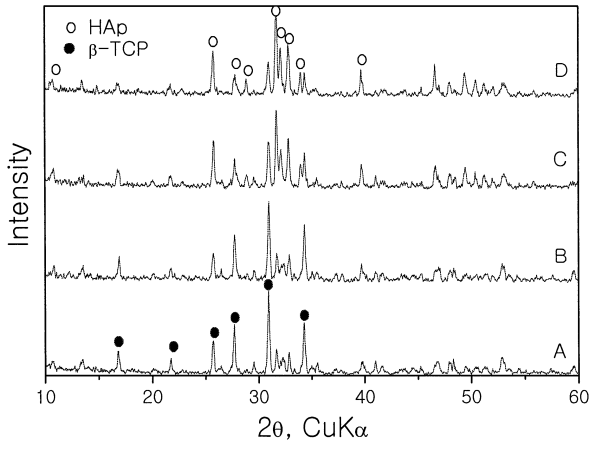

Figure 4 XRD patterns of sample A, B, C and D, after heating at 800 °C for 2 h in air.

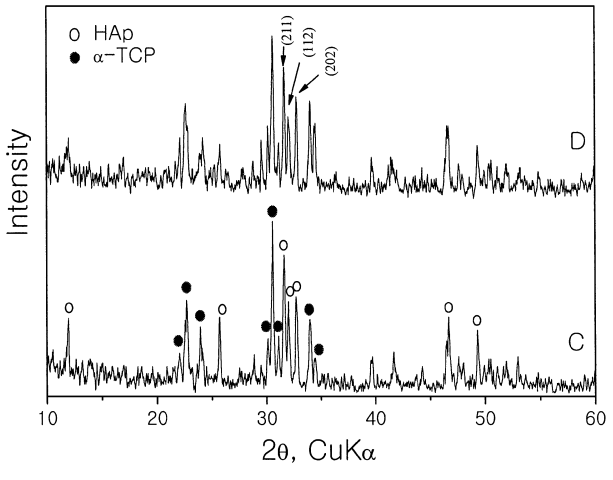

Figure 5 XRD patterns of sample C and D after heating at 1200 °C for 2 h in air.

[11]. Most studies on the thermal stability of HAp are concentrated on the particulate phase, whereas few papers on whisker and fibrous morphology HAp have been reported. In the present work, the thermal stability of the HAp with a whisker type morphology, derived from the hydrolysis of α-TCP is examined by means of XRD, TGA, FTIR and SEM instruments.

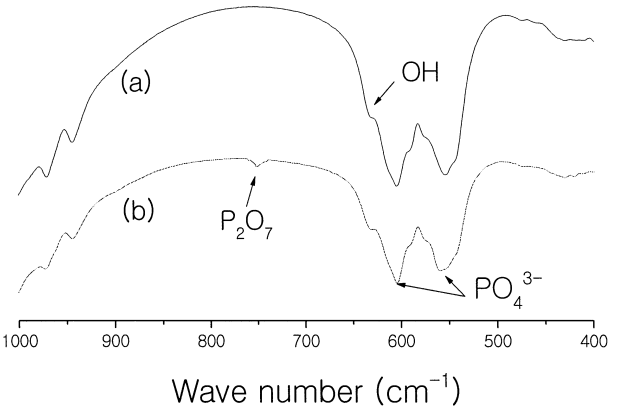

Figure 6 FTIR spectra of sample A after heating at: (a) 300 and (b) 600 °C for 2 h in air.

3 grams of α-TCP powder (d_{50}: 9.3 μm; S_{BET}: 5.3 m^2/g; Ca/P = 1.50, molar ratio) in 100 cc of deionized water was hydrolyzed at 90 °C for 6 h. The pH of the suspension was adjusted in the range 9.1–11.5 with 0.2 M NH_4OH. The hydrolyzed product was washed successively four times with deionized water and dried at 40 °C for 12 h in an oven. In order to investigate the thermal stability of the materials which had been hydrolyzed at different pH values, they were subsequently heated at 600, 800 and 1200 °C for 2 h in air.

The crystallographic characteristic was examined using XRD (D/max-IIA, Rigaku) and FTIR (Impact 400D, Nicolet), and the morphological evaluation was carried out using a SEM (JSM 840A, Jeol). The Ca/P molar ratio was determined by ICP (ICP-IRSI, Thermo Jarrel Ash). The changes of functional groups and weight loss in the reaction product during heating were investigated by FTIR and TG/DTA (PTC-10A, Rigaku), respectively.

XRD patterns of the reaction products obtained at 90 °C for 6 h at a pH of 9.1 (sample A), 10 (B), 10.7 (C) and 11.5 (D) are shown in Fig. 1. Sharp peaks showing high crystallinity of HAp regardless of pH value had appeared. The microstructure of sample A shows whisker shaped particles (length: ~5 μm, diameter: ~0.5 μm) (Fig. 2a) similar to B and C, apart from the development of whisker phase and the degree of agglomeration. However, the sample D (Fig. 2d) obtained at pH 11.5 showed ellipsoidal shaped grains to be different from the whisker shape obtained at lower values of pH. The Ca/P molar ratio increased in the range 1.53–1.61 with increasing pH value: A (1.53), B (1.55), C (1.56) and D (1.61). This infers that the whisker shaped HAp derived from the hydrolysis of α-TCP is calcium deficient compared with stoichiometric HAp (Ca/P = 1.67, molar ratio). By use of FTIR analysis of the resultant materials, the absorption bands of HPO_4^{2-} (827 and 1208 cm^{-1}) and OH^-(634 cm^{-1}) group were confirmed (Fig. 3), which indicated a conversion into the calcium deficient HAp by the hydration of α-TCP. The absorption strength of HPO_4^{2-} increased somewhat with decreasing pH.

To investigate the effect of initial pH in the reaction system on the thermal stability of reaction products, the samples A, B, C and D were heated at 600, 800 and 1200 °C for 2 h in air and then analyzed

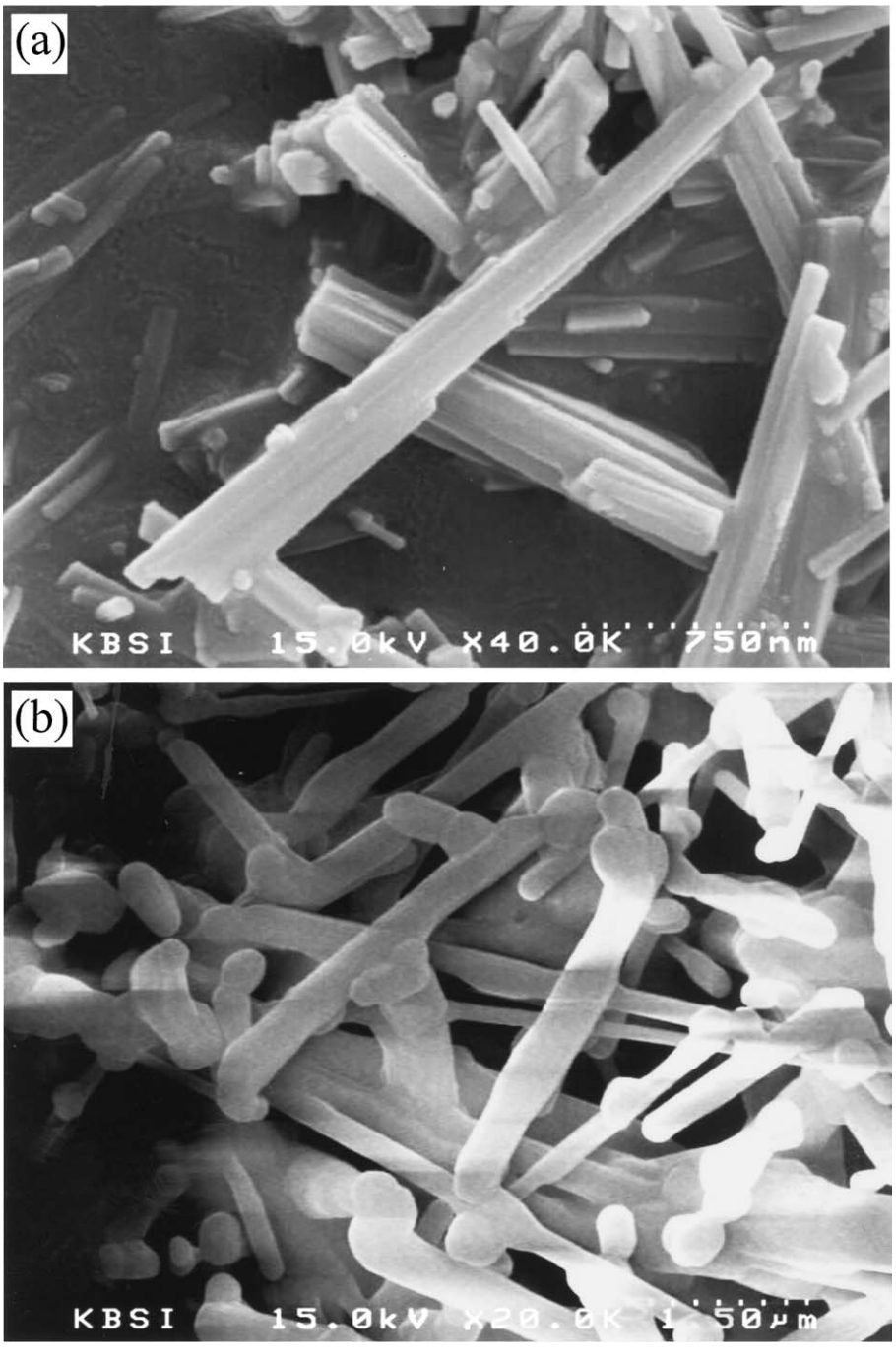

Figure 7 SEM photographs of sample A after heating at: (a) 300 and (b) 800 °C for 2 h in air.

for different phases by means of XRD. After heating at 800 °C, β-TCP was identified as a main phase in sample A and B but HAp was present in sample C and D (Fig. 4). The XRD patterns were similar to those of samples heated at 600 °C. On increasing the maximum heating temperature up to 1200 °C, the XRD peaks (211), (112) and (202) of HAp disappeared in sample A and B, but they remained in C and D (Fig. 5). At 1200 °C, the transformation of β-TCP to α phase was found. The FTIR spectra of the sample A heated at 300 and 600 °C are shown in Fig. 6. After heating at 600 °C, the weak absorption peak at 750 cm^{-1} was confirmed, rather different from that found on heating at 300 °C. The result is in good agreement with the earlier report [12] that the $P_2O_7^{2-}$ formed by the thermal decomposition of HPO_4^{2-}, reacts with OH^- to form β-TCP. After heating at 800 °C, the shrinkage in the endpoints of whisker due to the partial decomposition of HAp was observed, differently from the result obtained at 300 °C (Fig. 7). The TGA analysis for sample A which exhibited relatively low thermal stability was undertaken (Fig. 8). A small weight loss (∼0.2%) from room temperature to 250 °C, probably resulting from the dehydration of adsorption water was confirmed. Also, a relatively large weight loss (∼6%) due to the decomposition of HAp occurred in the range 250–600 °C. On further increasing the heating temperature up to 870 °C, an additional weight loss (∼0.8%) occurred. Considering the above results, in general, the thermal stability of the synthetic whisker shaped HAp seems to be relatively low, compared with the particulate grains [7, 11], a consequence of the

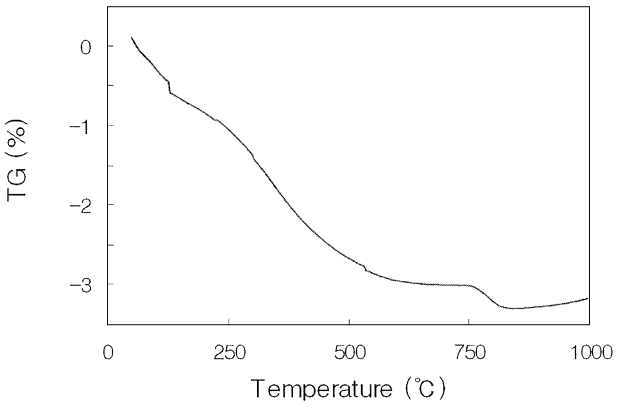

Figure 8 Weight loss of sample A With heating in air (heating rate: 4 °C/min).

relatively large surface area and corresponding surface energy.

In summary, the calcium deficient and different morphological whisker shaped hydroxyapatite has been prepared by the hydrolysis of α-TCP under controlled pH. As the chemical composition approached stoichiometry and became structurally agglomerated to a dense ceramic, the thermal stability of the synthetic hydroxyapatite whiskers increased. The ellipsoidal shaped particles showed relatively superior thermal stability, compared with the whisker shaped particles.

Acknowledgments

This study was supported financially by the Pusan Metropolitan City Government through the Institute for Environmental Technology and Industry (IETI), Pusan National University, Korea (Project number: R12-1996-015-00047-0).

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Received 23 July
and accepted 29 October 2003