

Morphology and Formation Mechanism of Hydroxyapatite Whiskers from Moderately Acid Solution

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Hydroxyapatite (HA) whiskers with uniform morphology and good crystallinity were successfully prepared by a precipitation-hydrolysis method in moderately acid solution at 85-95 °C for 48-120 h, their lengths were in the range of 50-150 μm and aspect ratios (length/diameter) in the range of 40-100. The precipitates formed at each stage of the synthesis were characterized by XRD, FTIR, TEM and SEM. The morphology and crystallinity of the precipitates depended on the synthesis temperature and time as well as the concentrations of soluble calcium and phosphate ions. The HA whiskers were formed by the hydrolysis of precursors produced during the reactions and took over the morphology of fibrous octacalcium phosphate (OCP). The stoichiometric HA whiskers were improved with the increase of pH value of solution, the synthetic temperature and the duration.

Keywords: *hydroxyapatite whiskers, precipitation-hydrolysis, morphology, forming mechanism*

1. Introduction

Hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, is one of the most promising materials for the manufacture of osseous implants, because of its excellent biocompatibility, which is due to its chemical similarity with the mineral portion of hard tissues. However, the mechanical reliability of pure HA ceramics is the principal limitation as a load-bearing implant such as artificial teeth or bone. The fracture toughness (K_{IC}) of HA ceramics does not exceed a value of $\sim 1 \text{MPa} \times \text{m}^{1/2}$, as compared with $2-12 \text{MPa} \times \text{m}^{1/2}$ for human bone¹. Therefore, numerous studies have been developed to investigate the reinforcement of bioceramics materials. A common method to improve the mechanical brittleness and reliability of ceramic materials is toughening the ceramic matrix by the addition of short fibers or whiskers. At present, various fibrous materials or whiskers such as SiC, Carbon, Si_3N_4 , Al_2O_3 , ZrO_2 and metal fibers have been applied in the HA ceramics²⁻⁴. Unfortunately most of the available bioinert

ceramic and metal reinforcements decrease the biocompatibility and bioactivity of HA ceramics. Consequently the investigation of HA whiskers or fibers and their application have recently received much attention.

HA whiskers or fibrous HA have been synthesized by various methods such as hydrothermal synthesis, homogeneous precipitation, solid synthesis at high temperature and growth in the gel system⁵⁻⁹. But, these whiskers or fibers prepared by the solid reaction and in the gel system show a sensitive dependence on the preparation condition, their crystallinity and thermal stability are relatively inferior. It has been reported that the crystal shape of HA tends to become needle-like under hydrothermal condition; unfortunately, it is difficult to obtain a crystal possessing a controlled morphology. HA whiskers synthesized by hydrothermal treatment of β -tricalcium phosphate, $\beta\text{-Ca}_3(\text{PO}_4)_2$, with citric acid possess only a length of 20-30 μm and a width of 0.1-1 μm.

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Homogenous precipitation with a slow reaction rate is a relatively easy procedure for obtaining uniform HA particles. Many investigations in HA have covered a wide range of compositions and experimental conditions that produced the fibrous and rod-like HA⁹⁻¹¹. However these precipitated fibrous HA have a relatively low crystallinity, are not a pure HA phase, possess a low aspect ratio. Furthermore, no more information on the synthetic mechanism and the nature of the phase was provided in the literatures. As described in our previous work¹², we have successfully prepared single crystal HA whiskers with a length of 50-150 μm and an aspect ratio of 40-100 by the precipitation-hydrolysis method. In the present paper, a series of tests were conducted to investigate the morphology and the formation mechanism of HA whiskers.

2. Experimental procedure

2.1 Preparation of HA whiskers

HA whiskers were synthesized by refluxing a mixture aqueous solution of 0.167 mol/l calcium ions, 0.1 mol/l phosphate ions and 0.5-1.0 mol/l urea. The typical experimental procedures were as follow: Soluble calcium ion and phosphate ion were prepared by dissolving the analytical grade reagents $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ in distilled water together with desired amounts of 0.5 mol/l HNO_3 . After mixing them with a stoichiometric Ca/P molar ratio of 1.67, they were put into a glass distillatory and refluxed together with the additive, urea, at 85-95 $^\circ\text{C}$ for various lengths of time. The pH value was measured continuously during the reaction. After the reaction, the solid product was filtered and washed with distilled water, followed by an ethanol treatment to remove the residual ions and water. Final HA whiskers were dried at 80 $^\circ\text{C}$.

2.2 Characterization of HA whiskers

X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) were employed to analyze the phase composition of HA whiskers. Scanning electron microscopy (SEM), Field emission Scanning electron microscopy (FE-SEM) and Transmission electron microscopy (TEM) were also used to observe the morphology and microstructure of the HA whisker. The pH value was measured by pH meter, and the calcium and phosphorus ion contents in the HA whiskers were measured by an atomic absorption spectrometer and an infrared spectrophotometer¹³, respectively.

3. Results and Discussion

3.1 Characteristics of HA whiskers

Figure 1 shows the SEM micrograph of the HA whiskers synthesized at 85-90 $^\circ\text{C}$. The HA whiskers had a uni-

form morphology, their lengths were in the range of 50-150 μm and aspect ratios in the range of 40-100. It is possible to obtain HA whiskers with a desired shape and size by selecting the synthetic conditions. All diffraction peaks of the precipitate were identified by XRD as HA phase only (Fig. 2). The selected area diffraction (SAD) pattern and TEM photograph indicated that the HA whiskers obtained were pure HA single crystal with a hexagonal structure, had good crystallinity and flat surface (Fig. 3). A chemical analysis of the HA whiskers obtained in our laboratory and the element analysis of FE-SEM revealed a slightly lower Ca/P molar ratio than in stoichiometric HA, and the Ca/P molar ratio was in the range of 1.60-1.62. The phase composition was also confirmed by the FTIR analysis (Fig. 4). There were bands at 1091, 1054, 601 and 563 cm^{-1} , which were assigned as the stretching and bending motion of phosphate in the HA whiskers. The bands at 3581 and

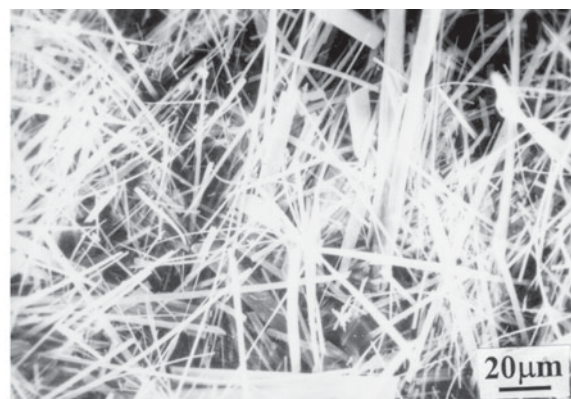


Figure 1. SEM micrograph of HA whiskers obtained at 85-90 $^\circ\text{C}$ for 72-120 h.

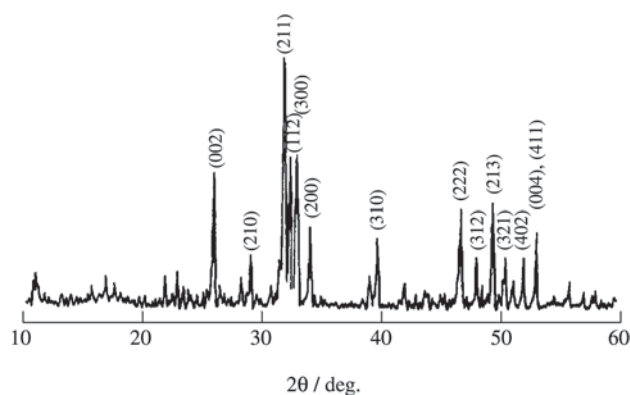


Figure 2. XRD pattern of HA whiskers obtained at 85-90 $^\circ\text{C}$ for 72-120 h.

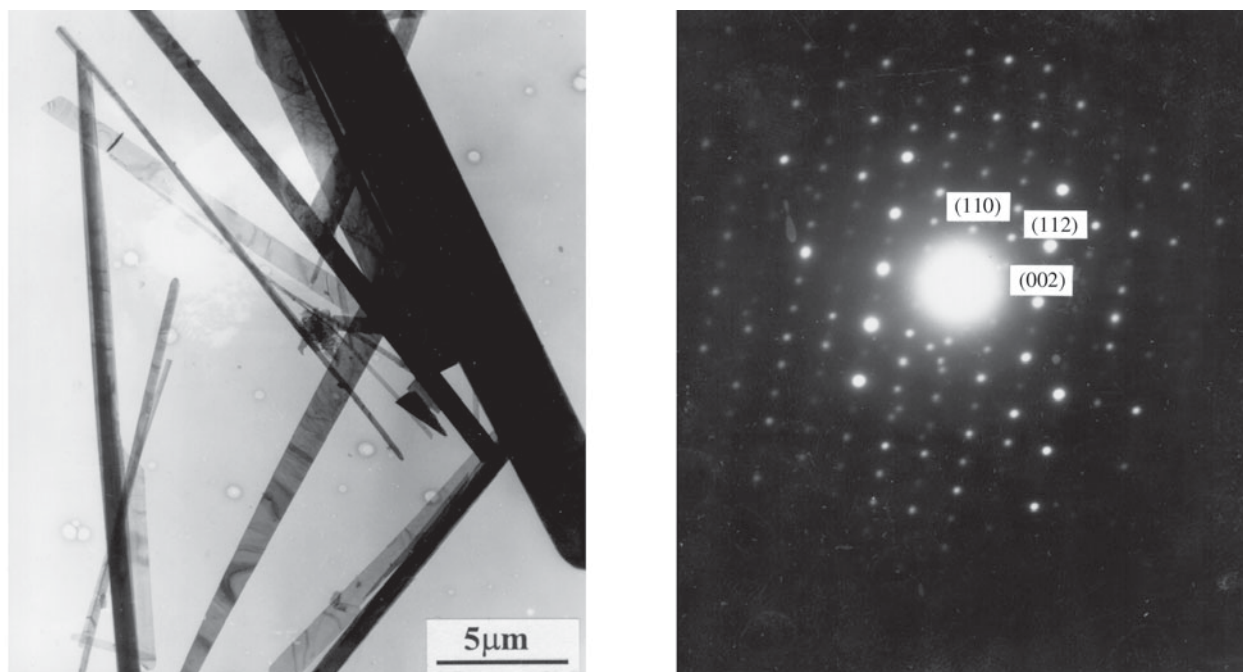


Figure 3. TEM photograph of HA whiskers obtained at 90 °C for 72 h and a SAD pattern

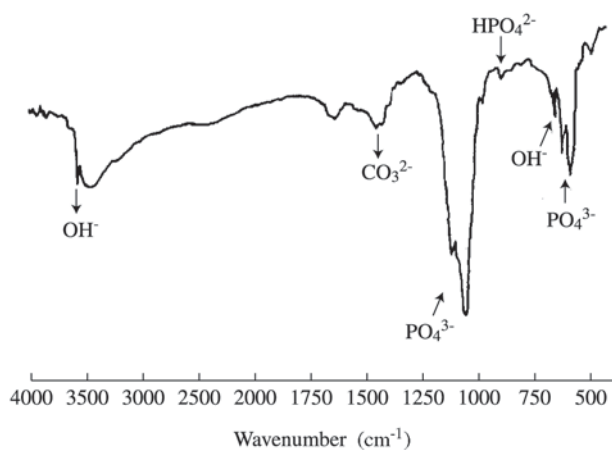


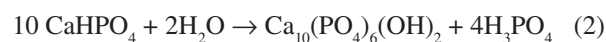
Figure 4. FTIR spectra of HA whiskers obtained at 85-90 °C for 72-120 h.

630 cm^{-1} corresponded to the stretching mode of hydroxyl group of HA. This further demonstrated the analytical result of XRD. Meanwhile there were also bands at 874 cm^{-1} and 1401-1458 cm^{-1} , which were assigned to the acidic phosphate group (HPO_4^{2-}) and the carbonate group (CO_3^{2-}) in the HA whiskers respectively^{10,11,14}. It is indicated that the HA whiskers synthesized were of carbonate containing HA whiskers and contained trace calcium deficiency.

3.2 Phase transition and changes of the pH value

The changes of the pH value of aqueous solutions during the synthesis of HA whiskers at various temperatures with the time are shown in the Fig. 5. It is apparent that these curves could be divided into three stages and highly dependent on the synthetic temperature. The precipitates obtained from the solution at different temperatures for various lengths of time were identified by XRD and the results are shown in the Table 1. The first and second peaks of pH value were associated with the appearance of dicalcium phosphate anhydrate (CaHPO_4 , DCPA) and fibrous OCP ($\text{Ca}_8\text{H}_2(\text{PO}_4)_6$) respectively, and the last stage corresponded to the phase transition of the precursors into HA whiskers.

With the decomposition of urea, the pH value of solution was raised. The first appearance of solid phase, DCPA, was separated out after 12 min at 95 °C, 28 min at 90 °C, and 46 min at 85 °C, respectively. Due to the hydrolysis behavior of DCPA in the solution¹⁵, DCPA hydrolyzed to HA as follows:



Nevertheless, the compound of H_3PO_4 produced resulted in the decrease of pH. Due to the dissolution of DCPA and HA formed by the reactions (1) and (2) rapidly, the suspended solution maintained only for 10-30 min after the

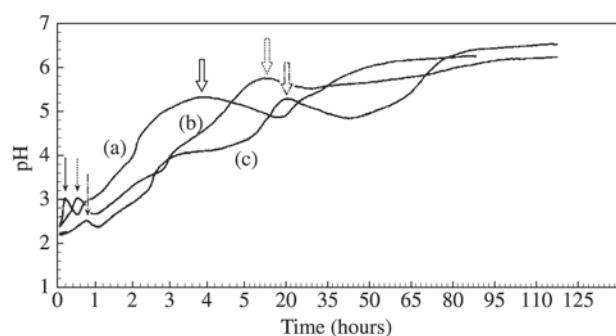


Figure 5. Time dependence of pH value of solution at the different temperature: (a) 95 °C; (b) 90 °C; (c) 85 °C.

Table 1. XRD analysis results of the precipitation obtained at the different temperatures and the duration.

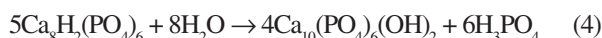
Temp.(°C)	Time (h)	Ca/P ratio	Phase composition
85	8	1.59	HA OCP DCPA
	100		HA
90	6	1.61	HA OCP DCPA
	72		HA
95	4	1.62	OCP DCPA
	20		HA OCP DCPA
	48		HA

appearance of first precipitation. The first peak of pH value, corresponding to the different temperature, presented at the range of 2.4-3.1, which agreed with the solubility diagram and other literatures^{16,17}.

When the pH value of solution rose above 3.8, some of white fibrous precipitates that corresponded to the formation of fibrous OCP¹⁸ at the pH range of 3.8-5.2 appeared in the solution according to the reaction:



Because of the presence of H_3PO_4 caused by the reaction (3) and the hydrolysis of OCP, the second peak of pH value was formed after the synthesis of 4 h at 95 °C, 12 h at 90 °C, 18 h at 85 °C respectively, and the maximum pH value maintained at the range 5.2-5.7. But in this stage the decreasing rate of pH value was lower and the extent was slight, which lasted 13 h at 95 °C, 18 h at 90 °C, and 25 h at 85 °C respectively. On the other hand, since the low pH environment favored the precipitation of DCPA, OCP was accompanied by the appearance of DCPA. Subsequently the pH value rose slowly until the end of reaction and was steady at the range of 6.2-6.5, where OCP and DCPA hydrolyzed and transformed into HA whiskers as the reaction (2) and the following reaction:



3.3 Forming mechanism of HA whiskers

The precipitation of calcium phosphate from aqueous solutions is somewhat complicated due to the possible occurrence of several solid phases depending on the solution composition and the pH. Owing to the low pH value of solution at the beginning of synthesis, the HA whiskers could not be synthesized directly from the solution despite the fact that the supersaturations of HA, OCP and DCPA are often in the order $\text{HA} \gg \text{OCP} \gg \text{DCPA}$. As soon as the critical pH value is obtained, the precursor of DCPA and OCP particles were produced respectively before the HA whiskers¹⁹.

Paul. W. Brown¹⁶ had investigated the phase relationships in the ternary system $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$, and found that CaHPO_4 could form a stable invariant point with HA and that CaHPO_4 could hydrolyze to HA. However, the HA formed would be more calcium deficient. In addition, M.T. Fulmer¹⁵ also found that the formation of HA was indicative of incongruent dicalcium phosphate dihydrate (DCPD) dissolution, the formation of HA significantly reduced the rate of DCPD hydrolysis, and the extent and rate of DCPD hydrolysis were dependent on the proportion of solution. Therefore, during the synthesis of HA whiskers, DCPA always accompanied the HA phase in the initial and middle stages. In order to avoid the formation of irregular HA particles and obtain the pure HA whiskers, the amount of DCPA should be decreased in the initial stage by selecting the appropriate synthetic conditions. When the solution presented a weak acid environment ($4.0 < \text{pH} < 5.2$), a large quantity of fibrous OCP was separated out from solution. Since OCP is one of thermodynamically metastable phase, it would hydrolyze and transform to HA whiskers.

Because of the similarities between the structure of OCP and HA, the hydrolysis of OCP to pseudomorphs, whose properties progressively approach those of HA, took place. Fibrous OCP provided one formwork for the growth of HA whiskers. One unit cell of OCP could be hydrolyzed to two unit cells of HA, HA whiskers took over the morphology of fibrous OCP and were formed by the epitaxial overgrowths²⁰⁻²². However, because the molar ratio of Ca/P of OCP is 1.33 and there is no OH^- in the OCP structure, the HA whiskers formed by the hydrolysis of OCP presented a calcium deficiency and should be viewed as a structure which existed over the composition range $\text{Ca}_{(10-x)}(\text{HPO}_4)_x(\text{PO}_4)_{(6-x)}(\text{OH})_{(2-x)}$, where $x \leq 1$ ^{10,16}. Compared with the stoichiometric HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, there were many Ca^{2+} vacancies and some of OH^- vacancies in the columns that existed in the structure of calcium deficient HA whiskers. The Ca^{2+} vacancies that are surrounded by six oxygen atoms belonging to PO_4 groups and an OH group are the stronger absorption sites, they adsorbed Ca^{2+} ions from the solution. Whereas, the Ca^{2+} vacancies that are sur-

rounded by three oxygen atoms, the weaker absorption sites, were partially filled by the Ca^{2+} ions in the solution and the others retained in the structure²³. For the OH^- vacancies in the calcium deficient HA, they could absorb PO_4^{3-} , OH^- and CO_3^{2-} groups, affecting the characteristic of HA whiskers and resulting in the appearance of CO_3^{2-} group in the infrared spectra. Because calcium deficient HA is more acidic than stoichiometric material, more and more composed ions such as Ca^{2+} , PO_4^{3-} and OH^- ions were absorbed by calcium deficient HA whiskers with the rise of pH of solution and the duration, which made calcium deficient HA transform to the stoichiometric HA. These agreed with the research of Young and Brow indicating that high pH favors the formation of stoichiometric HA¹⁶.

4. Conclusion

Hydroxyapatite (HA) whiskers with uniform morphology and good crystallinity could be prepared by the precipitation-hydrolysis method in moderately acid solution at 85-95 °C for 48-120 h, their lengths were in the range of 50-150 μm , aspect ratios in the range of 40-100 and the Ca/P molar ratio in the range of 1.60-1.62. The morphology and crystallinity of the products depended on the synthesis temperature and time. The HA whiskers were formed by the hydrolysis of precursors. Because of the similarity in the structure of HA and OCP, fibrous OCP provided one formwork for the formation of HA whiskers. HA whiskers took over the morphology of fibrous OCP and were formed by the epitaxy of OCP. During the period of the formation of HA whiskers, the stoichiometric HA whiskers were improved with the increase of pH value of solution and the duration. The phase transition between HA whisker and the OCP as well as DCPA was related with the changes of pH value of solution.

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References

1. Suchanek W.; Yaashima M.; Kakihana M. *et al. J. Am. Ceram. Soc.*, v. 80, n. 11, p. 2805-2813, 1997.
2. Park K.; Sundaresan S.; Vasilos T. *et al. J. Mater. Res.*, v. 9, n. 10, p. 2476-2479, 1994.
3. Rubs A.J.; Wei M.; Milthorpe B.K. *et al. J. Australia Ceram. Soc.*, v. 29, n. 1, p. 51-56, 1993.
4. With G. de; Corbijn A.J. *J. Mater. Sci.*, v. 24, p. 3411-3415, 1989.
5. Asaoka N.; Suda H.; Yoshimura M. *The Chemical Society of Japan*, n. 1, p. 25-29, 1995.
6. Ota Y.; Iwashita T.; Kasuga T. *et al. J. Am. Ceram. Soc.*, v. 81, n. 6, p. 1665-1668, 1998.
7. Kamiya K.; Yoko T.; Tanaka K. *et al. J. Mater. Sci.*, v. 24, p. 827-832, 1989.
8. Fujishiro Y.; Yabuki H.; Kawamura K. *et al. J. Chem. Tech. Biotechnol.*, v. 57, p. 349-353, 1993.
9. Suzuki S.; Ohgaki M.; Ichiyonagi M. *et al. J. Mater. Sci. Lett.*, v. 17, p. 381-383, 1998.
10. Kandori K.; Horigami N.; Yasukawa A. *et al. J. Am. Ceram. Soc.*, v. 80, n. 5, p. 1157-1164, 1997.
11. Yasukawa A.; Takase H.; Kandori K. *et al. Ployhedron*, v. 13, n. 22, p. 3071-3078, 1994.
12. Yan Y.; Wang Y.; Zhang H., in "Bioceramics", Giannini S. and Moroni A., Switzerland, Trans Tech Publications Ltd., v. 13, p. 311-314, 2000.
13. Department of Chemistry of Hangzhou University, *Chemical Analysis Manual*, Chemical Industry Press, Beijing, China, 1997.
14. Roy D.M.; Eysel W.; Dinger D. *Mat. Res. Bull.*, n. 9, p. 35-40, 1974.
15. Fulmer M.T.; Brown P.W. *J. Mater. Sci.: Mater. Med.*, v. 9, p. 197-202, 1998.
16. Brown P.W. *J. Am. Ceram. Soc.*, v. 75, n. 1, p. 17-22, 1992.
17. Ito A.; Nakamura S.; Aoki H. *et al. J. Crystal Growth*, v. 163, p. 311-317, 1996.
18. Monma H. *J. Mater. Sci.*, v. 15, p. 2428-2434, 1980.
19. Boistelle R.; Valero I.L. *J. Crystal Growth*, v. 102, p. 609-617, 1990.
20. Nancollas G.H.; Tomazic B. *J. Phy. Chem.*, v. 76, n. 22, p. 2218-2225, 1974.
21. Boskey A.L.; Posner A.S. *The Journal of Physical Chemistry*, v. 80, n. 1, p. 40-45, 1976.
22. Graham S.; Brown P.W. *J. Crystal Growth*, v. 165, p. 106-115, 1996.
23. Sheng W.; Gu Y.; Liu C. *et al., Bulletin of the Chinese Ceramic Society*, n. 1, p. 45-52.