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Phase and thermal stability of hydroxyapatite whiskers precipitated using amine additives

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Abstract

Two kinds of hydroxyapatite (HA) whiskers, prepared using urea and acetamide, were investigated to determine their thermal stability in air at 800–1200 °C. The thermal decomposition behavior and the phase stability of the whiskers upon heating were found to depend on the synthesis method, crystallinity and constitution of the whiskers. The phase transformation of the whiskers prepared using urea took place at a temperature below 800 °C due to low crystallinity and more carbonate and HPO_4 ions substitutions. Long rod-like particles appeared in the products treated at 1000–1200 °C. However, the whiskers prepared using acetamide were morphologically and structurally stable at 1200 °C due to their high crystallinity and low ions substitution, but with minor TCP caused by the decomposition of HPO_4 in the structure. Such whiskers would be useful and promising reinforcement for fabricating highly reliable HA ceramics or composites either in dense or porous form.

Keywords: Hydroxyapatite whiskers; Thermal stability; Crystallinity and constitution; Morphology

1. Introduction

Hydroxyapatite (HA) has the similar mineral composition as bone and teeth, and has been extensively considered as a promising bone reconstruction and replacement material because of its excellent biocompatibility and bioactivity [1,2]. However, acceptable HA bioceramics or composites, either in dense or in porous form, are restricted to areas free of dynamic load because of their weakness and brittleness [3]. Although short metal and ceramic fibers or whiskers, and oxide ceramic reinforcement have been proven to be useful and effective in improving the mechanical brittleness and reliability, most available fibers show decreased biocompatibility in the composites [4–6]; some have been found to be cytotoxic *in vitro* [7]. In the case of oxide reinforcement, the presence of zirconia or alumina in the composites accelerates the decomposition of HA, leading to second phase appearance such as tri-calcium phosphate (TCP) or calcium zirconate ($CaZrO_3$) when the sintering temperature is higher than about 1000 °C [4,8]. Consequently, bioactive and thermally stable HA whiskers or fibers appear to be a most appropriate reinforcement due to their good biocompatibility and non-cytotoxicity.

Heat treatments are always involved in sintering HA or HA-containing ceramic composites. Inappropriate preparation conditions, calcinations or sintering can result in dehydroxylation and decomposition of HA, giving rise to the change in physicochemical properties of the final implants through their mechanical performance and dissolution behaviour [9,10]. Thermal stability of reinforcements at high temperature is directly correlated with the processing route and their physicochemical characteristics, and this in turn directly affects the mechanical and biological properties of both dense and porous HA ceramics and composites [11,12]. Although the thermal stability of HA particles or HA ceramics and composites has been well documented over a wide range, including particles size, ions substituted HA materials, and different preparation routes [8,13,14], most of the research focus on the phase composition change of HA particles and composite materials [14,15]. The thermal stability of HA whiskers has received little attention. No further information has been provided in the literature. Suchanek et al. [3] reported that the fibrous microstructure of HA was retained in all cases after hot-pressing the HA whiskers at 800–900 °C. However,

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when the whiskers were hot-pressed at 1000–1100 °C (1 h, 30 MPa), only large equiaxed grains were present in the HA whisker ceramics; no toughening occurred. Therefore, the thermal stability of HA whiskers is of major importance to allow the sintering condition to be controlled and helpful for the design and preparation of HA-reinforced ceramics or composites for the repair or reconstruction of diseased or damaged parts of the skeleton, such as implants or bone tissue engineering scaffolds.

Wet precipitation from aqueous solution is a widely used route in preparing HA whiskers, but the obtained whiskers are always calcium-deficient, some of them contain carbonate or ion substitutions. Substitution in either phosphate or hydroxyl groups easily causes defects in the lattice structure of apatite. Possible decomposition or phase transformation of HA derived from these defects lead to the change in both phase composition and structure of the whisker-reinforced composites. Therefore, understanding the thermal behaviors of HA whiskers at elevated temperatures and finding one kind of highly thermal stable HA whiskers are greatly imperative. The chemical constitution and crystallinity of apatite play an important role in controlling the thermal behavior [16], thus, two different whiskers with similar Ca/P ratio prepared using amine additives were selected to study the possible effects on the phase composition and thermal stability of HA whiskers at high temperatures.

2. Materials and method

Aqueous solutions containing 42–84 mmol/L calcium and 25–50 mmol/L phosphate were prepared by dissolving analytical grade reagents $Ca(NO_3)_2{\cdot}4H_2O$ and $(NH_4)_2HPO_4$ in 0.05 mol/L HNO_3 (all AnalaR, BDH, Poole, England) solution, with a Ca/P ratio of 1.67. HA whiskers were prepared by conventional wet precipitation using 0.5 mol/L urea (AnalaR, BDH) or by hydrothermal homogeneous precipitation using 1 mol/L acetamide (AA) (99%, Alfa Aesar, Heysham, Lancashire, England), respectively, as previously reported [17,18]. The initial pH of solutions was adjusted to 3.00 using 0.1 mol/L HNO_3 or 1:1 ammonium hydroxide. After processing at 95 °C for 48 h or 180 °C for 10 h, the mixture was cooled naturally over 12 h to ambient temperature (~25 °C). The product was then filtered off, washed quickly with deionized water (Milli-RO, Milli-Q; Millipore, Bedford MA, USA) four times, and finally dried in air at 80 °C.

The thermal stability of the products was evaluated in a cabinet electric furnace (HTF 18/15, Carbolite, Hope Valley, UK) at 800–1200 °C for 2 h in air at a heating rate of 15 °C/min. The crystalline phases and possible decomposition of the products and their constitution change were then investigated using X-ray powder diffraction (XRD) (Philips X'Pert Pro, PANalytical BV, Almelo, The Netherlands) and Fourier-transform infrared spectroscopy (FTIR) (Magna-TRTM 750, Nicolet Instrument Corp., Madison, WI). The morphology of the products before and after thermal treatment was observed by scanning electron microscopy (SEM) (XL30CP, Philips Electron Optics, Eindhoven, The Netherlands; and JSM-6490, JEOL, Tokyo, Japan). XRD pattern-processing software (MDI Jade 5, Materials Data, Livermore CA, USA) was used for phase identification and lattice parameter calculations. The degree of crystallinity (X_c) of the HA whiskers was evaluated by the following equation according to the examined XRD diffractograms [19]:

$$X_c = 1 - \left(\frac{V_{112/300}}{I_{300}}\right)$$

where $V_{1\,1\,2/3\,0\,0}$ is the intensity of the hollow between (1 1 2) and (3 0 0) peaks and $I_{3\,0\,0}$ is the intensity of the (3 0 0) peak. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) observations, and selected-area electron diffraction (SAED) patterns (Tecnai G2 20 S-TEM, Philips, Hillsboro OR, USA) of whiskers were also taken. The Ca/P ratio was analyzed by energy dispersive X-ray spectroscopy (EDX) using a field emission-scanning electron microscope (FE-SEM) (LEO 1530, Oxford Instruments, Abingdon, UK). EDX results were believed to be accurate to within ~5%. Both thermogravimetric analyzer (TGA) and differential scanning calorimeter (DSC) (STA 449C Jupiter, Netzsch Selb, Germany) were employed to ascertain the thermal stability and decomposition process of the whiskers. The analyses were conducted in air from room temperature to 1250 °C.

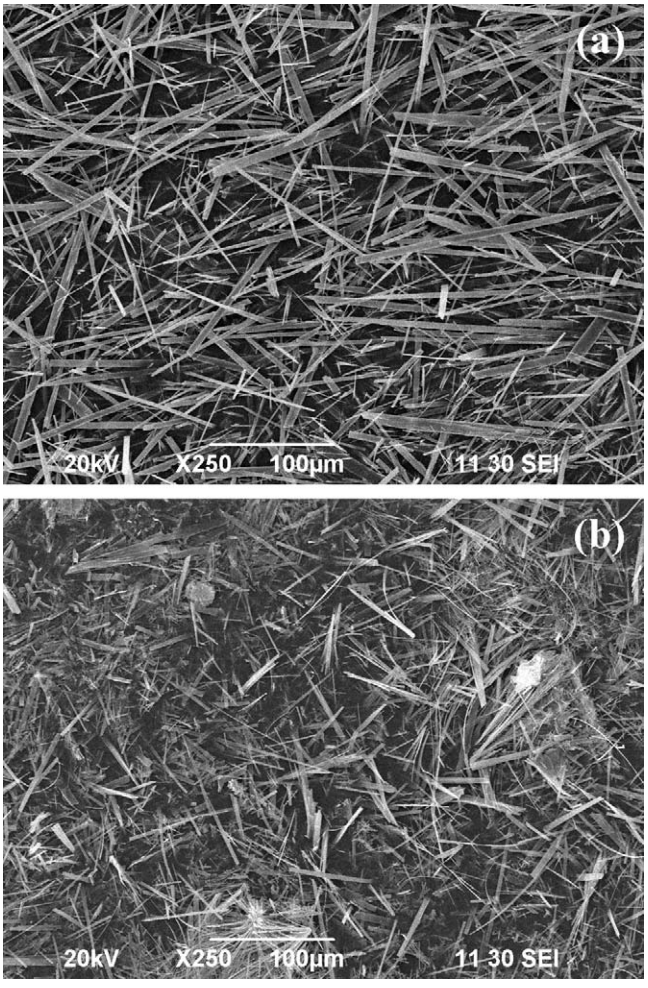

Fig. 1. SEM images of HA whiskers prepared using acetamide (a) and urea (b).

3. Results and discussion

3.1. Constitution and crystallinity

Fig. 1 shows the SEM images of the products prepared. They exhibited uniform morphology, but the mean length and aspect ratio of the whiskers prepared using AA (whisker-A) were significantly larger than those of the whiskers prepared using urea (whisker-U). Whisker-A had a mean length of 116 μm and an aspect ratio of 103, without obvious aggregation or entanglement; whereas the latter had a mean length of 88 μm and an aspect ratio of 55, with small particles and aggregation in the products.

Figs. 2 and 3 show the XRD patterns and FTIR spectra of the products before and after heat treatment. Both products before thermal treatment were identified as HA by XRD and FTIR. All XRD peaks matched well those of the JCPDS PDF 9-432 diffraction pattern for synthetic HA. However, for whisker-A, the strongest peak intensity appeared for the (3 0 0) lattice plane, rather than for the (2 1 1) as is usual for HA. Furthermore, the peak intensity for (3 0 0) and (2 0 0) planes was rather stronger than for the reference pattern, indicating that the crystals were obviously elongated along the *c*-axis [20]. This was also confirmed by the TEM analysis results, spots in the SAED pattern near the (0 0 0) plane were identified as (0 0 2) or (0 0 $\bar{2}$), (1 1 0) and (1 1 2) of HA, which were taken from the [$\bar{2}$ 2 0] zone axis; they matched the vector relationship of the crystal planes. Reflections were very strong, and (0 0 $\bar{2}$), (0 0 2) and (0 0 4) spots were aligned perpendicular to the long axis of the HA whiskers (Fig. 4). Such whiskers had similar lattice constants in both *a* and *c* to those of the reference (PDF 9-432) (Table 1). Whereas for whisker-U, high baseline and wide XRD diffraction peaks clearly indicated low crystallinity [21]; they had a similar *a*-value and a slightly larger *c*-value than that of the reference by ~0.013 Å. The calculated crystallinity was 94.9 and 51.7% for whisker-A and whisker-U, respectively, coinciding with the XRD results.

This can be also supported by the FTIR analysis. Although the positions of the characteristic bands, assigned as the stretching and bending modes of phosphate, were similar for these two products, the absorption intensity of hydroxyl group at 3571 and 633 cm^{-1} for whisker-A was obviously stronger than those for whisker-U [2]. Due to the synthesis being conducted in a moderately acidic solution, the symmetrical stretching vibration band of HPO_4^{2-} group at 872 cm^{-1} was present in both whiskers. However, bands at 1420 and

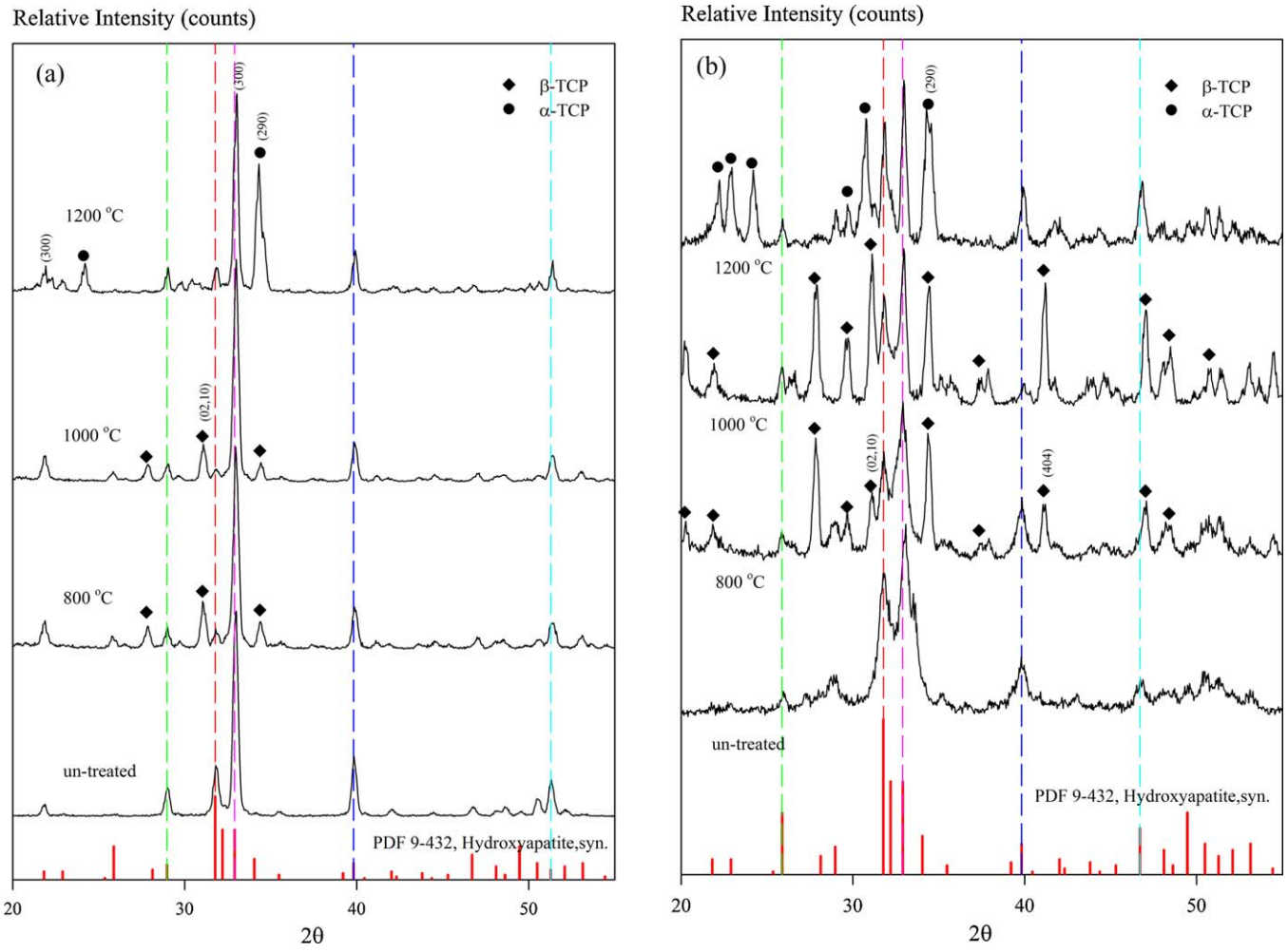

Fig. 2. XRD patterns of HA whiskers, prepared using acetamide (a) and urea (b), before and after treatment at 800–1200 °C for 2 h.

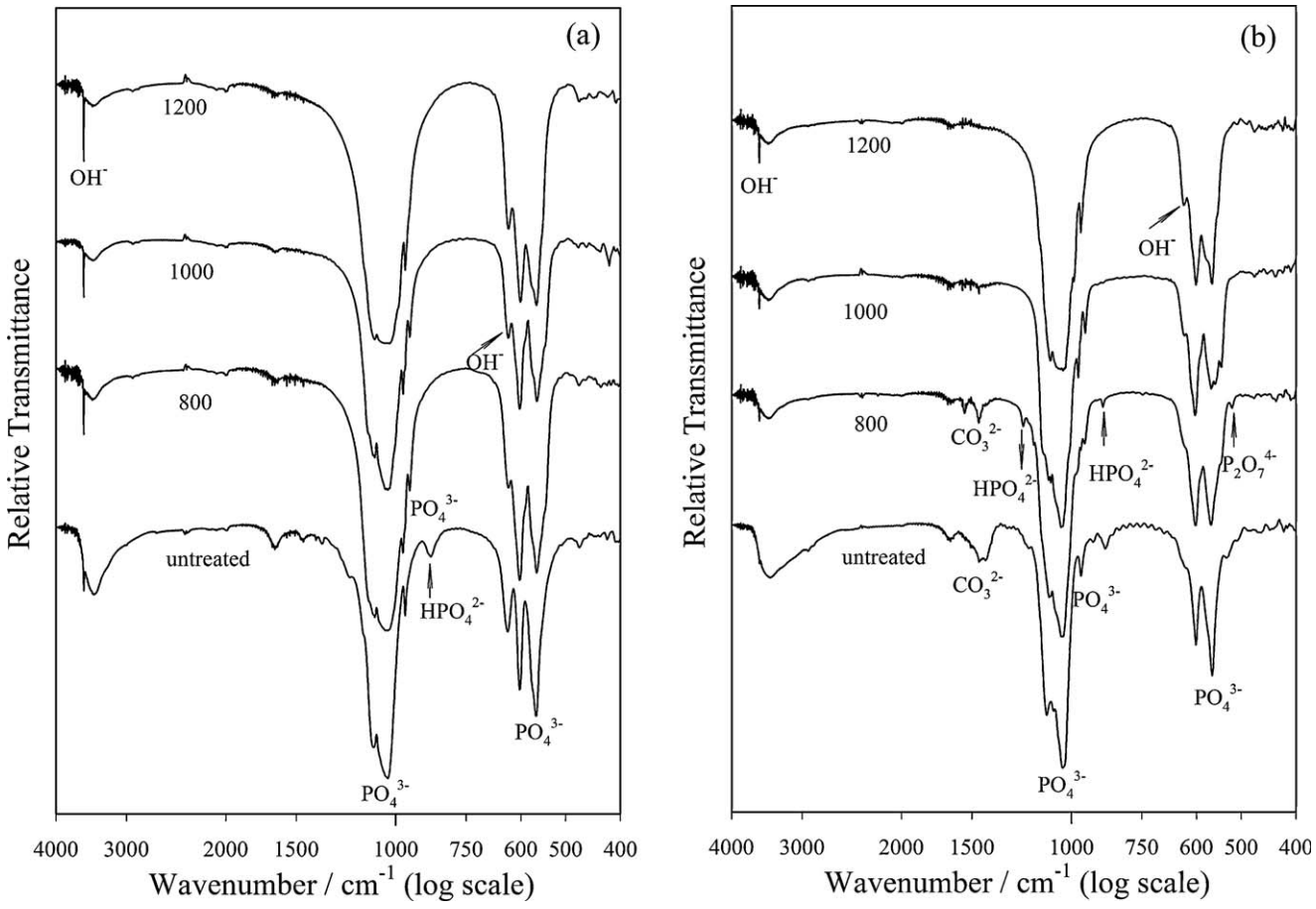

Fig. 3. FTIR spectra of HA whiskers, prepared using acetamide (a) and urea (b), before and after treatment at 800–1200 °C for 2 h.

1457 cm^{-1}, attributed to the CO_3^{2-} group, only appeared in the spectra of whisker-U, indicating that these two whiskers were calcium deficient, but the whisker-U had a low crystallinity and contained carbonate ion substitution.

Amide additives can be hydrolyzed in both acidic and basic aqueous solution to release ammonia, hence they can be used to control the solution pH and to modify the growth habit of HA [18,22,23]. The constitution, crystallinity and morphology of whiskers greatly depend on their hydrolysis behavior and on the resulting products. Our previous study found that the hydrolysis rate of both additives was accelerated at higher temperature, and the solution pH increased steadily with time [24]. Urea hydrolysed rapidly beginning at ~80 °C, and the pH quickly rose above 9; therefore, preparing HA whiskers under hydrothermal conditions is infrequently conducted using such additive [17,21]. While, AA showed a relatively low hydrolysis rate even at 120–180 °C. The pH gradually and continuously rose with increasing temperature and duration. A rapid rise in pH could be avoided to allow the quick growth of HA whiskers at a low supersaturation, without any interference, thereby giving non-aggregated whiskers with high crystallinity, controllable aspect ratio, high purity and low dislocation density [1,25].

In addition, because the structure and properties of HA crystals are highly sensitive to the preparation conditions [26,27], the resulting CO_3^{2-} ions caused by urea decomposes are easily incorporated into the structure of HA, being located in the position of OH (A-type) or PO_4 (B-type), which easily causes the variation in constitution and the distortion of apatite structure. As shown in Fig. 3b, the absorption bands at 1420 and 1454 cm^{-1} indicated that the substitution of CO_3^{2-} mainly occurred in the B-site of the apatite structure. Such substitution was reported to be responsible for the decreased crystallinity of the products [2]. In the case of whisker-A, CH_3COO^- ions hydrolyzed from AA could neutralize the H^+ ions, effectively preventing the precipitation of acid calcium phosphate. Moreover, the adsorption and incorporation of Ca on the surface of apatite crystal were supposed to be enhanced because of less competition with hydrogen ions, giving rise to the quick growth of HA crystals. The hydrolysis product of AA does not affect the crystal growth habit but also favors the rapid growth along the *c*-axis of the HA crystals [18]. Therefore, these two whiskers exhibited observable differences in their constitution and in their degree of crystallinity.

3.2. Phase and thermal stability

The phase change of the whiskers after heat treatment was analyzed by XRD and FTIR, as shown in Figs. 2 and 3. Thermal stability was intimately related to the constitution and degree of crystallinity [28], though the Ca/P ratio characterized

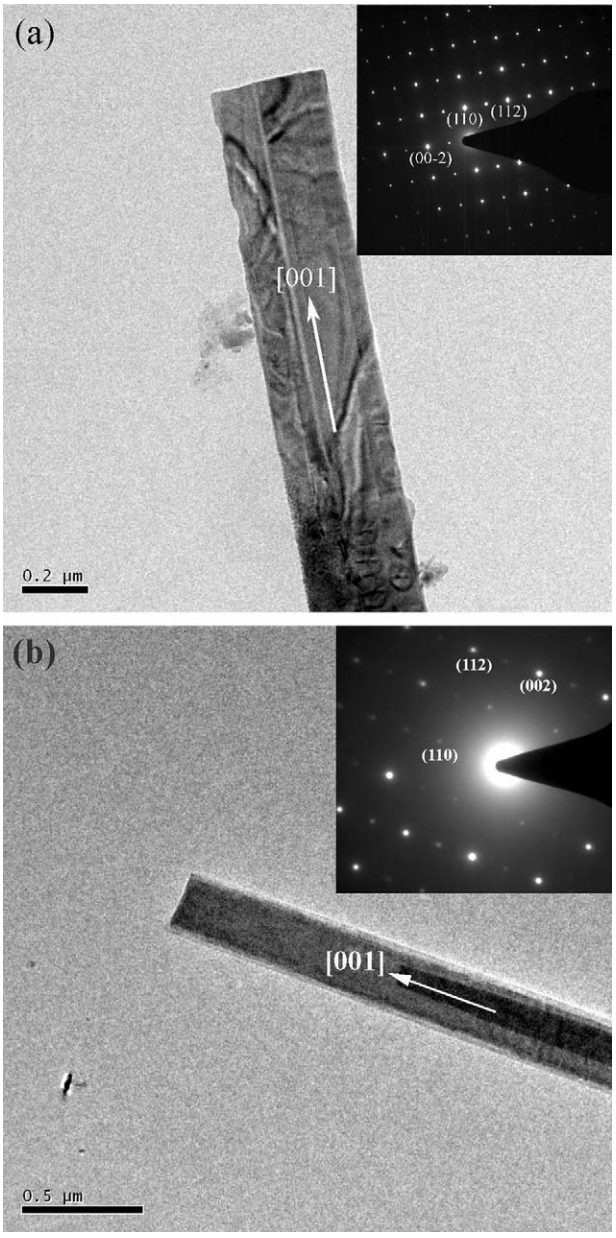

Fig. 4. TEM images and SAED patterns of HA prepared using acetamide at 180 °C for 10 h and using urea at 95 °C for 48 h.

by EDX analysis was similar for these two whiskers (1.62 for whisker-A and 1.65 for whisker-U). The marked changes in phase composition were visible in both the XRD pattern and the FTIR spectra of whisker-U. β-Tricalcium phosphate (β-TCP) appeared in the XRD pattern after treated at 800 °C; such phase was identified as one of the main compositions up to 1000 °C, with strong XRD peak intensities for (0 2 10) and (4 0 4) planes of β-TCP. It subsequently transformed to α-TCP at 1200 °C. For whisker-A, due to the whiskers having high crystallinity, only a minor β-TCP was found in the products after treated at 800–1000 °C; no significant difference in the XRD intensity ratio $I_{HA(3\,0\,0)}/I_{\beta-TCP(0\,2\,10)}$ (varied from 4.35 to 5.37) was found. Further phase transition of the TCP from β- to α-phase at 1200 °C also did not decrease the peak intensity of the HA, indicating that such whiskers possessed good phase and thermal stability.

The crystallinity of the whisker was improved with the rising temperature, the absorption band at 3570 cm^{-1} for the stretching mode of OH^- became sharper and stronger; moreover, the librational mode at 633 cm^{-1} was enhanced for whisker-U after heat treatment at 800–1200 °C. The new bands for PO_4 group at 948 and 972 cm^{-1} indicated the formation of β-TCP at <1000 °C, and the bands at 961 and 987 cm^{-1} revealed the phase transformation of the newly formed β-TCP to α-TCP after treated at 1200 °C, in agreement with the XRD analysis. On the other hand, the absorption bands for CO_3 and HPO_4 groups exhibited obvious differences between these two whiskers. For whisker-U, the bands attributed to these two groups became weak after treated at 800 °C, subsequently disappeared at 1000 °C. Meanwhile, two new bands at 1545 and 1456 cm^{-1}, attribute to A-type substitution of CO_3^{2-}, drastically appeared in the FTIR spectra after treatment at 800 °C, in place of B-type CO_3^{2-}, which implies that CO_3^{2-} substitution actually occurred in both A- and B-sites. B-type carbonate in the apatite has been reported to easily cause a highly disordered orientation in the OH^- channel and a high Ca-deficiency, resulting in the diminution of OH^- bands before heat-treatment, decreased crystallinity and low thermal stability [29,30], The bands for the bending mode of A-type carbonate in the structure were supposed to be shielded due to their low crystallinity and high B-type carbonate substitution. For whisker-A, the strong absorption band intensity at 3571 cm^{-1} and slight changes in FTIR spectra clearly proved that whisker-A had higher crystallinity and lower Ca-deficiency than whisker-U. The phase composition change of the whiskers was hardly affected by the formation of β-TCP and its phase transformation to α-

Table 1
Ca/P ratio, crystallinity and lattice parameters of products prepared using AA and urea.

Sample	Ca/P	Crystallinity (%)	Lattice parameter			
			a (Å)		c (Å)	
			$a_{cal.}$	$a_{obs.} \pm$ S.D.	$c_{cal.}$	$c_{obs.} \pm$ S.D.
Whisker-A	1.65	94.9	9.418	9.4267 ± 0.0017	6.884	6.8874 ± 0.0132
Whisker-U	1.62	51.7		9.4151 ± 0.0092		6.8977 ± 0.0132

Note: $a_{cal.}$ and $c_{cal.}$: calculated from PDF 9-432, $a_{obs.}$ and $c_{obs.}$: determined using image processing software.

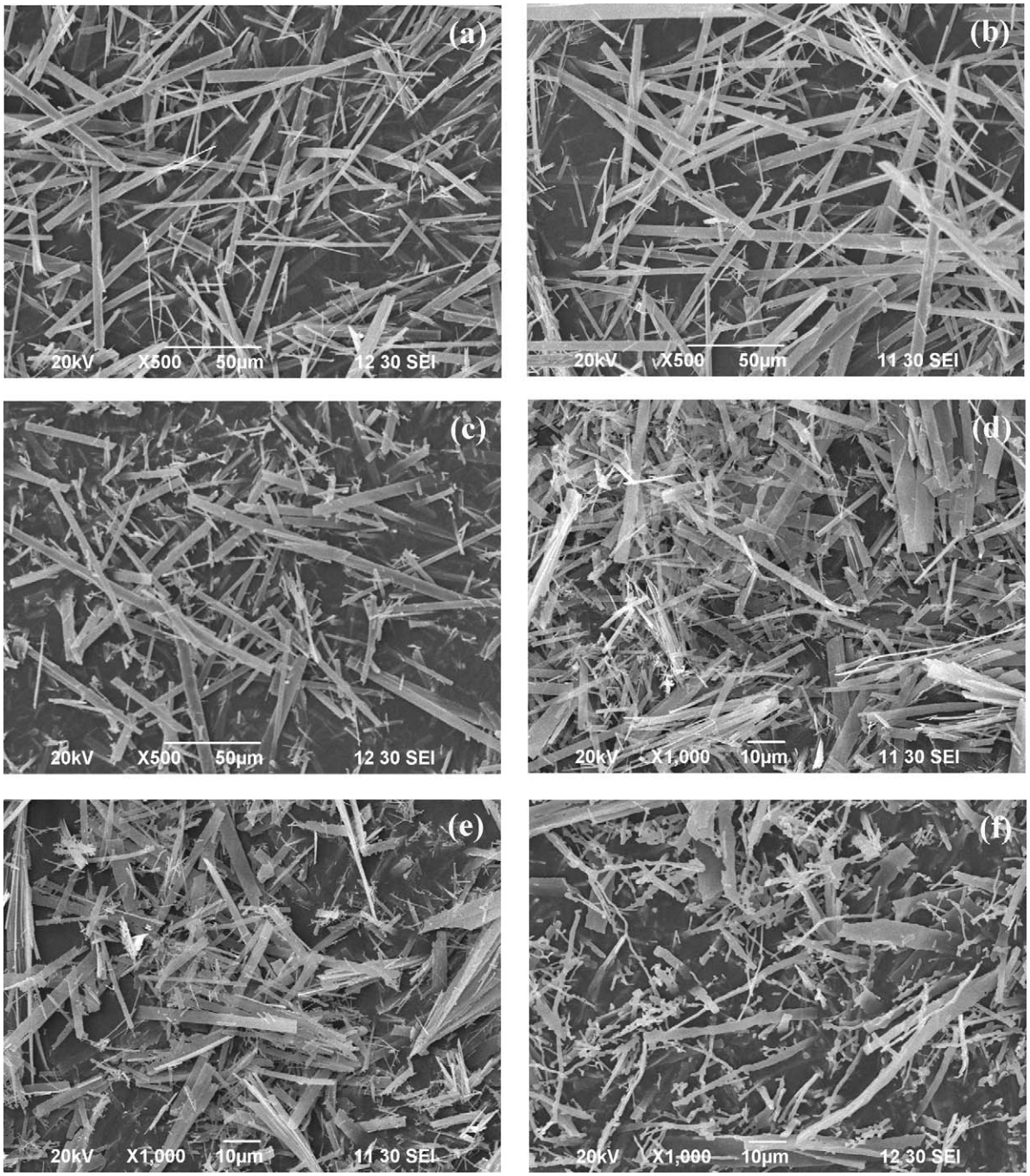

Fig. 5. SEM images of HA whiskers prepared using acetamide (a–c) and urea (d and e) after heat-treatment. (a) and (d): 800 °C, 2 h; (b) and (e): 1000 °C, 2 h; and (c) and (f): 1200 °C, 2 h.

TCP after treated at 800–1200 °C, conferring high thermal stability.

In addition, the thermal decomposition performed on commercial HA has been reported that HA gradually released its OH^- ions and transformed into OHAP at 1000–1360 °C [31]. This case seems not occur here in the studied temperature ranges. The OH^- stretching band at 3571 cm^{-1} was enhanced with the heating temperature, without any decrease in its absorption intensity even at 1200 °C. The β-TCP was mainly caused by the partially decomposition of HPO_4 or carbonate in the structure, especially for the whiskers prepared using AA under hydrothermal conditions.

3.3. Morphological change and decomposition process

Fig. 5 shows the SEM images of the HA whiskers after heat-treated in air at 800, 1000 and 1200 °C for 2 h, respectively. Both whiskers retained their morphology after heat-treated at 800 °C (Fig. 5a and d). However, small rod-like particles appeared in whisker-U after treated at 1000 °C; moreover, pores and bubble-like grains were also visible in

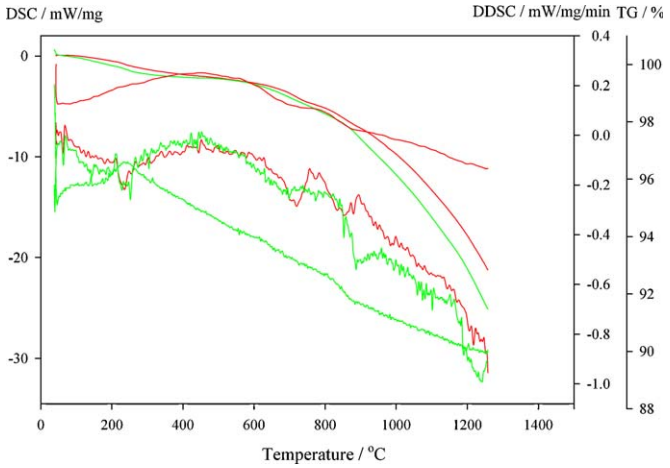

Fig. 6. TG/DSC curves of HA whiskers heated from room temperature to 1250 °C.

the whisker surface (Fig. 5e), which was supposed to have been caused by the partially decomposition of carbonate and the condensation of HPO_4 in the apatite between 850 and 900 °C. After treated at 1200 °C, the whiskers appeared to break from the aforementioned pores and eventually formed long rod-liked particles (Fig. 5f). While, whisker-A showed good structurally and morphologically stable at an elevated temperature below 1200 °C due to its high crystallinity and phase purity, they, although small rod-like particles appeared after heat-treatment at 1200 °C (Fig. 5c).

Fig. 6 shows the TG/DSC curves of the whiskers heated from room temperature to 1250 °C. Whisker-A exhibited a significantly lower weight loss and endothermic capacity than whisker-U. The weight loss slowly increased with increasing temperature above ~250 °C, yielding a total loss of about 3.1% and 6.5% from 300 to 1200 °C for whisker A and whisker-U, respectively. Accompanying the weight loss, three evident endothermic processes for both whiskers were observed from the DSC derivative curve: the initial DSC change took place before 300 °C, representing the loss of surface moisture; the second change occurred from 400 to 780 °C, resulting in a weight loss of about 1.21% and 2.52% for whisker-A and whisker-U, respectively; the third change occurred between 780 and 860 °C for whisker-A and between 780 and 900 °C for whisker-U, giving a weight loss of 0.55% and 1.15%, respectively. The weight loss and the variation in the heating flow that occurred in the last two stages were associated with the dehydration of HPO_4^{2-} group and the decomposition of Ca-deficient HA whiskers.

HA precipitated from aqueous solution is usually Ca-deficient and can be expressed by $Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$ $(0 < x < 2)$ [2,32,33]. Both whiskers here were identified to be Ca-deficient. By increasing the heating temperature, the evaporation of adsorbed water in the whiskers caused weight loss at the initial stage. At higher temperature, dehydration and decomposition of the whiskers would gradually take place, depending on their constitution and crystallinity. The phase transformation of Ca-deficient apatite would occur upon heating the sample in the temperature range of 250–720 °C, as the proposed reactions [32,33]:

$$Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x} \rightarrow Ca_{10-x}(P_2O_7)_x(PO_4)_{6-2x}(OH)_2 \quad (1)$$

$$2HPO_4^{2-} \rightarrow P_2O_7^{4-} + H_2O \quad (2)$$

Further increasing the temperature to 900 °C, the $Ca_{10-x}(P_2O_7)_x(PO_4)_{6-2x}(OH)_2$ formed by the condensation of HPO_4 was transformed to HA and β-TCP by the reactions:

$$Ca_{10-x}(P_2O_7)_x(PO_4)_{6-2x}(OH)_2 \rightarrow 3x\beta\text{-}Ca_3(PO_4)_2 + (1-x)Ca_{10}(PO_4)_6(OH)_2 + xH_2O \quad (3)$$

$$P_2O_7^{4-} + 2OH^- \rightarrow PO_4^{3-} + H_2O \quad (4)$$

The XRD, FTIR and TGA/DSC analysis of the samples, after treated at 800–1200 °C, were coincident well with these reports. In the case of whisker-U, since both HPO_4^{2-} and CO_3^{2-} ions substitutions heavily decreased the crystallinity and the degree of channel ions order, vacancies, lattice distortion, microstresses, and crystal defects caused by ion substitution accordingly enhanced the chemical activity and depressed the thermal stability [34,35]. Reactions (3) and (4) could take place before 800 °C and might last up to 900 °C due to more ions substitution and low crystallinity (Fig. 6). The newly formed β-TCP in turn accelerated the further decomposition of HA [19]. Further increasing the temperature up to 1240 °C caused a big endothermic process for whisker-U (Fig. 6), where the transformation of β-TCP to α-TCP and the decomposition of the whiskers took place according to the following reaction (2):

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow Ca_4(PO_4)_2 + 2\alpha\text{-}Ca_3(PO_4)_2 + H_2O \quad (5)$$

When such materials are used as precursors to prepare block porous or dense biomedical ceramics or composites, the sintering behavior and biological performance of materials as well as their dissolution and mechanical properties will be affected. Thus, although HA whiskers prepared using urea are most interesting in view of their clinical application due to their similarity in composition to bone mineral, their poor chemical and thermal stability may limit their application in the preparation of both dense and porous ceramic blocks.

4. Summary

The morphology, constitution and crystallinity of HA whiskers were markedly dependent on synthesis techniques and precipitation agents. The whiskers precipitated hydrothermally had good crystallinity and high phase purity; they were also structurally and morphologically stable at elevated temperatures below 1200 °C, showing better thermal stability than those synthesized by conventional wet precipitation using urea. The constitution and the crystallinity of HA whiskers had obvious effects on both the phase transformation and

morphology change. The substitution of carbonate and hydrogen phosphate in the structure of HA could accelerate the decomposition of whiskers.

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