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Precipitation of biocompatible hydroxyapatite whiskers from moderately acid solution

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Abstract

Hydroxyapatite (HA) whiskers with uniform morphology and good crystallinity were successfully prepared by a precipitation-hydrolysis method in moderately acid solutions at 85–95 °C for 48–120 h. A proper precipitation agent was selected to control the growth of HA crystal in a desired way. The lengths of HA whiskers 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, TG-DSC and SEM techniques. It is revealed that 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 obtained were morphologically stable at elevated temperatures below 1200 °C. They were formed by the hydrolysis of precursors produced during the reactions and took over the morphology of fibrous octacalcium phosphate [$Ca_8H_2(PO_4)_6{\cdot}5H_2O$, OCP]. The stoichiometric HA whiskers were improved with the increase of the synthetic temperature and the duration.

Keywords: Hydroxyapatite whiskers; Precipitation-hydrolysis; Morphology; Forming mechanism; Thermal stability

1. Introduction

Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, is one of the main calcium phosphate salts which have been studied extensively and used in clinically because of its excellent biocompatibility and bioactivity. At present, applications for synthetic HA are restricted to areas free of dynamic load bearing because synthetic HA is known for its weakness and brittleness [1–3]. On the other hand, the major requirement of acceptable bioceramics either in dense or in porous form are a good biocompatibility, high mechanical strength, good thermal stability at high temperature and easy of handing in an operating room environment [4,5]. Therefore, numerous studies have been developed to investigate the reinforcement of bioceramics materials. Generally, 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. Various fibrous materials or whiskers such as SiC, Carbon, Si_3N_4, Al_2O_3, ZrO_2 and metal fibers have been applied in HA ceramics [6]. 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, homogenous precipitation, solid synthesis at high temperature and growth in the gel system [7–11]. But, these whiskers or fibers prepared by the solid reaction and in the gel system show a sensitive dependence on the preparation condition, and their crystallinity and thermal stability are relatively inferior. Although well crystalline needle-like particles under hydrothermal condition can be synthesized, it is difficult to obtain a crystal possessing a controlled morphology. Homogenous precipitation with a slow reaction rate is a relatively easy procedure for obtaining uniform HA particles. Many investigations in fibrous and rod-like HA have covered a wide range of compositions and experimental conditions [11–13]. However these precipitated fibrous HA have a relatively low crystallinity, are not a pure HA

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phase, possess a low aspect ratio. Therefore, we have tried to improve the homogenous precipitation method, by which HA whiskers with a high crystallinity, uniform morphology and high aspect ratio could be obtained. In the present paper, a series of tests were conducted to investigate the preparation process and the effects of synthetic condition on the morphology and properties 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 and 0.1 mol/l phosphate ions. The typical experimental procedures were as follow: Soluble calcium ion and phosphate ion were prepared by dissolving the analytical grade reagents $Ca(NO_3)_2{\cdot}4H_2O$ and $(NH_4)_2HPO_4$ in distilled water together with desired amounts of 0.5 mol/l HNO_3. After mixture 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 °C for various lengths of time. After the reaction, the solid product was filtered and washed with distillated water, followed by an ethanol treatment to remove the residual ions and water. Final HA whiskers were dried at 80 °C.

2.2. Characterization of HA whiskers

The phase composition of the HA whiskers and the precipitates formed at different stages were identified by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The morphology and microstructure of HA whiskers were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Simultaneous Thermogravimetry and Differential scanning calorimetry (TG-DSC) were performed to analyze the phase transition. 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 spectra-photometer, respectively.

3. Results and discussion

3.1. Effects of synthesis condition and preparation process

The synthetic temperature and time, the pH value of solution and the concentration of Ca^{2+}, PO_4^{3-} ions were the main effective factors on the formation and morphology of HA whiskers. Maintaining the same concentration of Ca^{2+}, PO_4^{3-} ions and the fixed time, the precipitates formed at different temperatures showed the different phase composition and morphology. The HA whiskers having the desired aspect ratios were obtained under the condition of 95 °C for 48 h, 90 °C for 72 h and 85 °C for 120 h, respectively, which were related to the pH value of solution and the rate of hydrolysis of precursor phases. Our experiment also

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

Temp (°C)	$[Ca^{2+}]{\cdot}[PO_4^{3-}]$ (mM^2)	Time (h)	pH		Ca/P ratio	Phase composition
			Initial	Final		
85	16.7	8	2.22	4.40		HA, OCP, DCPA
		100		6.40	1.51	HA
90	16.7	6	2.32	5.60		HA, OCP, DCPA
		72		5.82	1.61	HA
95	16.7	4	2.36	5.32		OCP, DCPA
		20		4.95		HA, OCP, DCPA
		48		5.92	1.62	HA

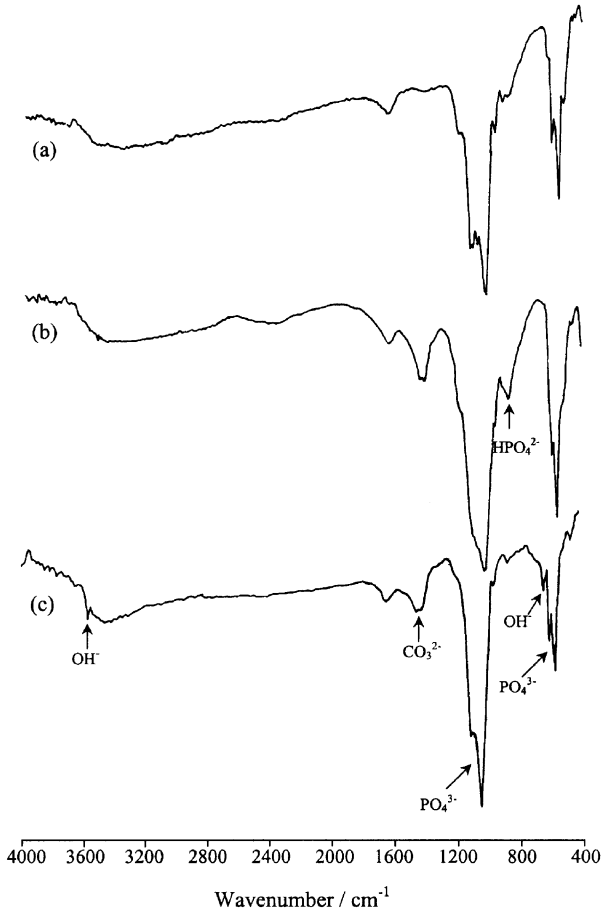

Fig. 1. FTIR spectra of HA whiskers obtained at 95 °C for various times. (a) 4 h, (b) 8 h, (c) 48 h.

found that HA whiskers could be synthesized at 82 °C, but it needed more than 180 h.

The precipitates obtained from the moderately acid solution at different temperatures for various lengths of time were identified by XRD and the results are shown in Table 1. The synthetic temperature had obvious effects not only on the decomposition of urea but also on the formation and growth of HA whiskers. The higher the synthesis temperature was, the more quickly the pH value rose with the duration. Meanwhile more precursors, such as dicalcium phosphate anhydrate ($CaHPO_4$, DCPA) and fibrous OCP, were produced in the solution, and the HA whiskers could be formed quickly by the hydrolysis of the precursors. Fig. 1 shows the FTIR spectra of the precipitates formed at 95 °C for various lengths of time. The bands at 3581 and 630 cm^{-1} which were assigned to the stretching mode of hydroxyl group of HA and the bands at 1401–1458 cm^{-1} that corresponded to the carbonate group (CO_3^{2-}) in the HA whiskers [12–14] increased with the duration, whereas the bands at 874 cm^{-1} that were assigned to the acidic phosphate group (HPO_4^{2-}) in the HA whiskers [12,13] decreased. These were related to the change of structure of the precipitates.

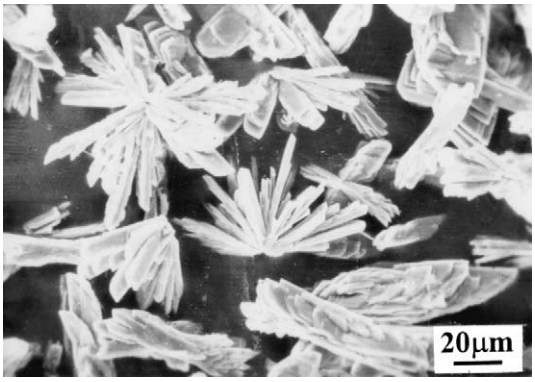

Fig. 2. SEM micrograph of precipitates formed at 95 °C for 50 h with the concentration product of 67 mM^2.

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 HA > > OCP > > DCPA [15]. With the decomposition of urea, the pH value of the solution was raised. As soon as the critical pH value is obtained, 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 in a pH range of 2.4–3.1, respectively. Due to the hydrolysis behavior of DCPA in the solution [16], DCPA hydrolyzed to HA as follows:

$$Ca^{2+} + HPO_4^{2-} \rightarrow CaHPO_4 \quad (1)$$

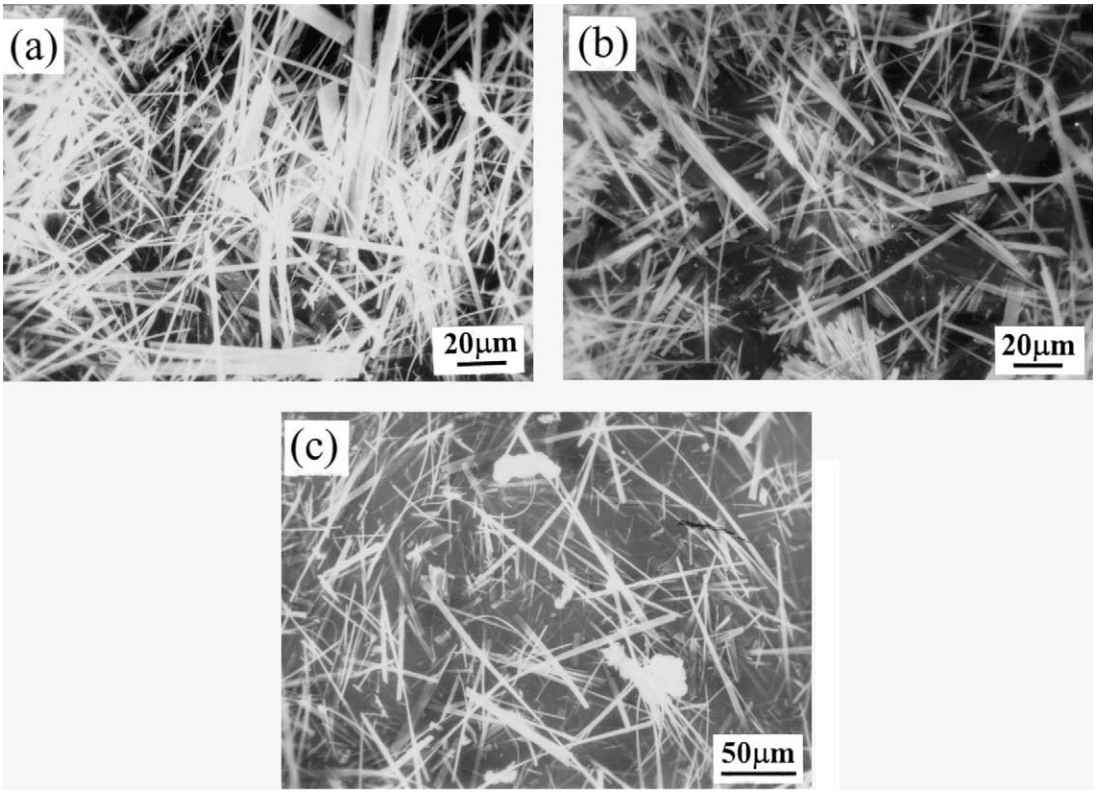

Fig. 3. SEM micrographs of HA whiskers obtained at different temperatures and times. (a) 85 °C for 120 h, (b) 90 °C for 72 h, (c) 95 °C for 48 h.

$$CaHPO_4 + H_2O \rightarrow Ca_{10}(PO_4)_6(OH)_2 + H_3PO_4 \quad (2)$$

while the compound of H_3PO_4 produced resulted in the decrease of pH and the dissolution of DCPA and HA formed rapidly. When the pH value of solution rose above 3.8, some of white fibrous precipitates that corresponded to OCP [17] appeared in the solution at a pH range of 3.8–5.7 after synthesis of 4 h at 95 °C, 90 °C for 12 h, 85 °C for 18 h respectively. Since OCP is one of the thermodynamically metastable phases, the hydrolysis and transformation of OCP into HA whiskers took place as follows:

$$Ca^{2+} + HPO_4^{2-} \rightarrow Ca_8H_2(PO_4)_6 \cdot 5H_2O + H_3PO_4 \quad (3)$$

$$Ca_8H_2(PO_4)_6 \cdot 5H_2O + H_2O \rightarrow Ca_{10}(PO_4)_6(OH)_2 + H_3PO_4 \quad (4)$$

On the other hand, because of the similarities between the structure of OCP and HA, the precipitates hydrolyzed by fibrous OCP were one of calcium-deficient HA with the composition range $Ca_{(10-x)}(HPO_4)_x(PO_4)_{(6-x)}(OH)_{(2-x)}$ where $x \leqslant 1$, whose properties progressively approach those of HA. Fibrous OCP provided one formwork for the growth of HA whiskers, and HA whiskers were formed by the epitaxial overgrowths [18–20]. With the rise of pH and the duration, the Ca^{2+} vacancies in the calcium deficient HA whiskers absorbed Ca^{2+} ions from the solution, which made calcium deficient HA whiskers transform to the stoichiometric HA. So the intensity of bands of hydroxyl group increased with the time and that of HPO_4^{2-}group decreased. Whereas the OH^- vacancies in the calcium deficient HA absorbed PO_4^{3-}, OH^- and CO_3^{2-} ions, affecting the characteristic of HA whiskers and resulting in the appearance of CO_3^{2-} groups in the infrared spectra with the duration.

In addition, the concentration of Ca^{2+}, PO_4^{3-} ions would effect the morphology and crystallinity [21]. In order to obtain scattered whiskers with a great aspect ratio, a low supersaturation should be maintained and an ideal concentration product of Ca^{2+}, PO_4^{3-} ions ranged from 4 to 50 mM^2. It was found that when the concentration product of Ca^{2+} and PO_4^{3-} ions was more than 50 mM^2, the HA whiskers synthesized were characterized with the bundle HA fiber other than the single distributed HA whiskers (Fig. 2).

3.2. Morphology and characteristics of HA whiskers

Fig. 3 shows the SEM micrographs of the HA whiskers synthesized at 85–95 °C. The HA whiskers had a uniform 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 the HA whiskers with a desired shape and size by selecting the synthetic conditions. The crystalline phase of the precipitate was investigated by XRD and identified as HA phase only (Fig. 4), and the HA whiskers obtained had good crystallinity and high purity. The Ca/P molar ratio was in the range of 1.60–1.62.

Fig. 5 shows the FTIR spectra of the HA whiskers obtained at the different temperature and time. The position of bands at 1091, 1054, 601 and 563 cm^{-1} and bands at 3581 and 630 cm^{-1}, which were assigned as the stretching and bending motion of phosphate and the stretching mode of hydroxyl group in the HA whiskers respectively, was similar. Increasing of the synthetic temperature, the intensity of the bands of HPO_4^{2-} group at 874 cm^{-1} and the bands at 1421–1458 cm^{-1} decreased. These meant that the HA whiskers synthesized were one of carbonate containing HA whiskers and contained trace calcium deficiency despite the fact that the stoichiometric HA whiskers could be improved and the amount of carbonate group in the lattice of calcium-deficient HA whiskers decreased with the increase of temperature.

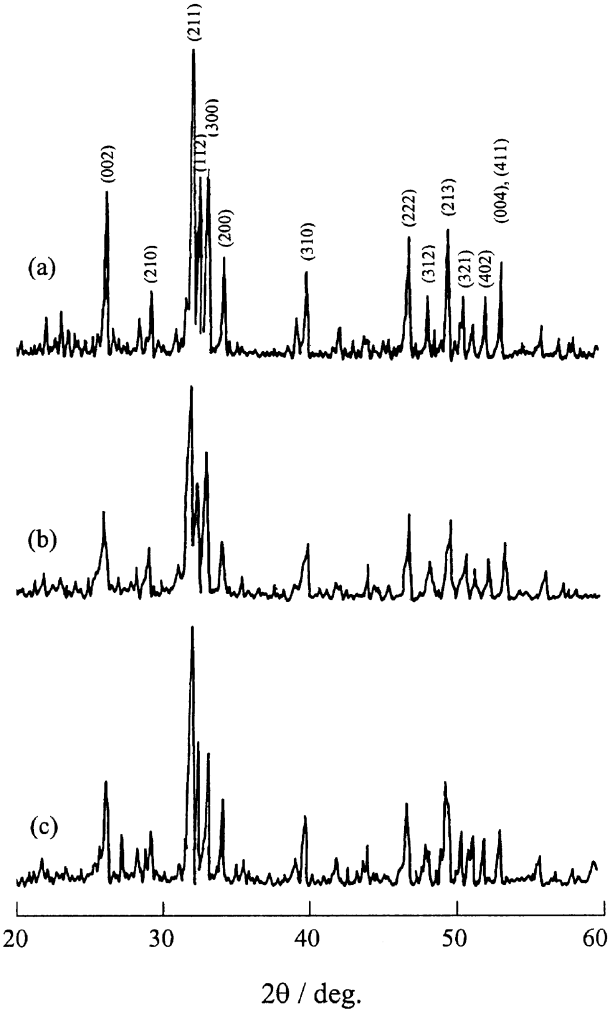

Fig. 4. XRD patterns of HA whiskers obtained at different temperatures and times. (a) 85 °C for 120 h, (b) 90 °C for 72 h, (c) 95 °C for 48 h.

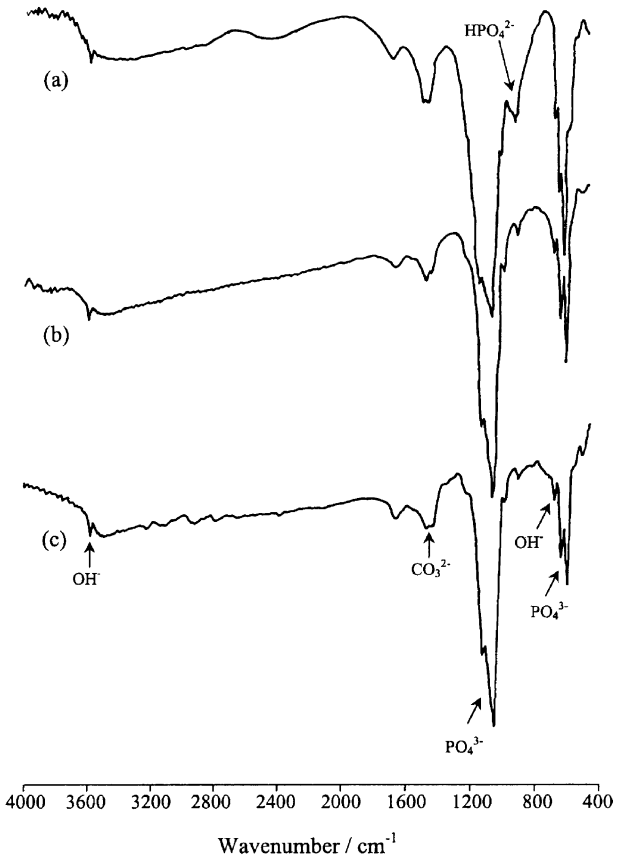

Fig. 5. FTIR spectra of HA whiskers obtained at different temperatures and times. (a) 85 °C for 120 h, (b) 90 °C for 72 h, (c) 95 °C for 48 h.

3.3. Thermal stability of HA whiskers

Studies of XRD and SEM revealed that the HA whiskers synthesized at 85–90 °C transformed partially into β-tricalcium phosphate, β-$Ca_3(PO_4)_2$, after the heat treatment in air at 800 °C for 2 h, which was related to the Ca-deficiency in the lattice of HA whiskers and agreed with the research of Yoshimura [6], indicating that Ca-deficient HA tends to precipitate β-$Ca_3(PO_4)_2$ on heating at 900 °C depending on the deficiency of calcium. When HA whiskers were heat-treated at 1200 °C, α-tricalcium phosphate, α-$Ca_3(PO_4)_2$, and β-calcium metaphasphate, β-$Ca_2P_2O_7$, presented obviously and remained a trace of HA phase. The HA whiskers had begun to decompose before 1200 °C. Small equiaxed grains precipitated on the whisker surfaces and some of the HA whiskers transformed into rod-liked particles, but retained their fibrous morphology after heat treatment in air below 1200 °C. However, when the heat-treatment was conducted at 1300 °C, the HA whiskers disappeared and turned into irregular grains entirely, exhibiting a new structure consisting of α-$Ca_3(PO_4)_2$ and tetracalcium phosphate, $Ca_4O(PO_4)_2$, as well as a trace of β-$Ca_2P_2O_7$. In addition, the FTIR analysis also revealed the appearance of β-$Ca_2P_2O_7$ at the bands 955–989 cm^{-1}. The shoulder about 1220 cm^{-1} that related to the phosphate group of HA disappeared after the heat-treatment about 1200 °C. Meanwhile the intensity and position of these bands about 557–608 cm^{-1} had a few changes, which were related with the presence of α-$Ca_3(PO_4)_2$ and $Ca_4O(PO_4)_2$. A possible explanation for such an effect is that the antisymmetric bending motion of phosphate in HA was effected by $P_2O_7^{4-}$ and oxygen atoms in $Ca_4O(PO_4)_2$.

4. Conclusion

HA whiskers with high crystalline, uniform morphology and high aspect ratio could be synthesized at 95 °C for 48 h, 90 °C for 72 h and 85 °C for 120 h by a precipitation-hydrolysis method in moderately acid solution. Their lengths were in the range of 50–150 μm and aspect ratios in the range of 40–100. The morphology and crystallinity of the products depended on the synthesis temperature and time as well as the concentrations of soluble calcium and phosphate ions. During the synthesis of HA whiskers, the precursors of DCPA and OCP were precipitated from the solution one after another. Because of the similarities between the structure of OCP and HA, HA whiskers with a chemical formula of $Ca_{(10-x)}(HPO_4)_x(PO4)_{(6-x)}(OH)_{(2-x)}$ were formed by the hydrolysis of precursors and took over the morphology of fibrous OCP. The stoichiometric HA whiskers was improved with the increase of temperature and the duration. Since the HA whiskers obtained was one of carbonate containing and contained trace calcium deficiency with Ca/P molar ratio of 1.60, some of the HA whiskers transformed into rod-like particles when they were heat treated about 1200 °C in air, but retained their fibrous morphology.

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