Journal of Ceramic Processing Research. Vol. 14, No. 6, pp. 700~702 (2013)

J O U R N A L O F
Ceramic Processing Research

Synthesis of rod-like titanium doped hydroxyapatite nanopowder

Li-li Wang*, Xiu-feng Wang, Cheng-long Yu and Yan-qi Zhao
School of Material Science and Engineering, Shaanxi University of Science & Technology, Xi'an, Shaanxi, People's China 710021

Rod-like titanium doped hydroxyapatite (Ti-doped HA) nanopowder was synthesized using $Ca(NO_3)_2 \cdot 4H_2O$, $(NH_4)_2HPO_4$ and tetraethylorthotitanate as precursor materials via a combination of chemical co-precipitation and microwave techniques route. The effect of the content of titanium in Ti-doped HA (0.2-2.4 wt.%) on sintering behavior, crystal size, shape and morphology was investigated. The results suggested that the addition of titanium to HA structure did restrain HA decomposition and thermal reaction between HA and titanium, which resulted in improved thermal stability of HA at high sintering temperature. The grain size of sintered Ti-doped HA, which was much smaller than that of pure HA. 0.8 wt.% addition of titanium to HA, was optimum for producing nanometer-sized rod-like Ti-doped HA crystal with improved thermal stability.

Key words: Hydroxyapatite, Titanium, Rod; Nanoparticles, Microwave.

Introduction

Hydroxyapatite (HA) is a good candidate for bone substitutes due to its chemical and structural similarity to bone mineral. Apatite used in biomedical applications is always available as micron- or nanometre-sized crystals of HA [1, 2]. Fully developed mature dental enamel is a highly organized structure of enamel prisms that consist of bundles of nanorod-like HA crystals arranged roughly parallel to each other [3-4]. The properties of these materials depend on the orientation of the crystals. Many attempts have been reported to fabricate nano- or micro-structured scaffolds to mimic structural and three-dimensional details of natural bone or teeth consisting of tiny HA crystals in the nano-regime, in order to understand the natural biomineralization process and relationship between their unique structure and physicochemical properties [5, 6]. Various techniques have been employed to prepare the nano-sized HA, including precipitation, hydrothermal [7], sol-gel [8], crystal conversion [9] and microwave techniques [10]. The crystal size, shape, chemical composition, defect concentration and assemblage all depend on the manufacturing technology. It is established that the resulting microstructure and properties vary considerably from one preparation route to another. However, no one has been successful in arranging such HA nanocrystals to mimic the fine and complex structure of real bone and teeth.

At the same time, it is found that in most of the sintered samples, HA decomposes completely into β-TCP and CaO. The decomposition of HA results in changes in the physical and chemical properties of the material and thus affects the performance of implant material in a living body [11]. HA decomposition is, therefore, an important problem both from a scientific and a biomedical application viewpoint. Titanium-based metals and alloys have achieved great success as medical implants [12]. However, so far there is only limited literature available on the incorporation of Ti into the HA structure. In this study our concern was focused on the fabrication of nanometer-scale rod-like Ti-doped HA which simulates bone or "enamel-like" structure. Due to incorporation of titanium, the decomposition of HA was restrained and made sliced HA convert into rod-like.

Experimental Procedure

Commercially available $Ca(NO_3)_2 \cdot 4H_2O$, $(NH_4)_2HPO_4$ and tetraethylortho titanate were used in the present study as raw materials to fabricate Ti-doped HA, containing 0, 0.2, 0.8, 1.6, and 2.4 wt.% of titanium, where tetraethylortho titanate was used for the source of titanium. $Ca(NO_3)_2 \cdot 4H_2O$ and $(NH_4)_2HPO_4$ solution were mixed together using continuous magnetic stirring for 2 hrs at room temperature with adding tetraethylortho titanate according that the Ca/(Ti + P) ratio was fixed at 1.667. The pH was kept 10 by the addition of ammonia solution. The mixtures were then put into the microwave oven for 30 min, which power was 500 W. The Ti-doped HA precipitation with different content of titanium produced was aged, filtered, dried and then sintered at various temperatures in the range of 800-1200 °C which firstly heated at 500 °C and dwelled for 2 hrs,

*Corresponding author:
Tel : +86-137-09101367
Fax: +86-029-86168688
E-mail: mariawanglili@126.com

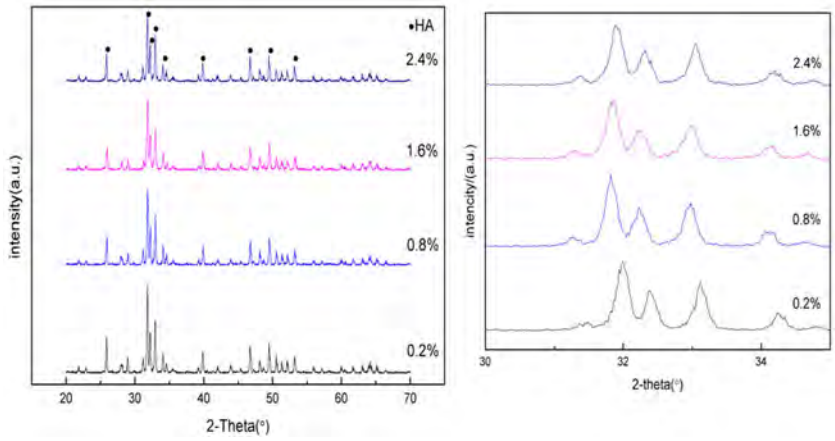

Fig. 1. XRD patterns and local magnified patterns of Ti-doped HA sintered at 1200 °C for 2 hrs with various addition of titanium.

then heated to 800-1200 °C for 2 hrs.

The sintered Ti-doped HA specimens were tested by X-ray diffraction (D/max-2200PC) for the constituent phases and the morphology of Ti-doped HA was evaluated using scanning electron microscopy (Cambridge, UK).

Results and Discussion

XRD measurements

Fig. 1 shows the XRD patterns of Ti-doped HA nanopowder with various content of titanium sintered at 1200 °C for 2 hrs. It showed that the presence of all the expected major HA peaks and no additional phases such as β-TCP, CaO and calcium titanite observed, which demonstrated that the addition of titanium to HA restrained the decomposition of HA and thermal reaction between HA and titanium. It is well known that HA started to decompose to the mixture of β-TCP and α-TCP at 1000 °C; at 1200 °C, this decomposition was nearly complete and the TCP was entirely α-TCP phase and above about 1200 °C, calcium titanite was formed [8]. From this discussion, it can be concluded that the addition of titanium to HA structure did restrain HA decomposition and thermal reaction between HA and titanium, even when the sintering temperature was about 1200 °C, which resulted in improved HA thermal stability at high sintering temperature.

Fig. 1 also shows that the local magnified X-ray diffraction patterns of Ti-doped HA nanopowder with various content of titanium sintered at 1200 °C for 2 hrs. It can be found that the peaks of HA shifted significantly, indicating that titanium atoms did enter the structure of HA and replaced the phosphorus atoms, which resulted in the change of HA crystal lattices. The addition of titanium to HA affected the lattice parameters and crystallinity, which in turn influenced the thermal stability of HA.

It also can be seen that with increasing of the content of titanium in Ti-doped HA nanopowder from 0.2 wt.% to 2.4 wt.%, the intensity of all HA peaks reduced somewhat, indicating that crystallinity of Ti-doped HA decreased. The reason for this phenomenon was that when titanium incorporated into HA, titanium atoms replaced the phosphorus atoms and excess titanium atoms entered interstitial of HA structure, which reduced the crystallinity of HA. It can be concluded that the addition of titanium to HA restrained HA decomposition and thermal reaction between HA and titanium. At the same time, with increase the content of titanium in Ti-doped HA, crystallinity of Ti-doped HA decreased, which showed that 0.8 wt.% content of titanium in Ti-doped HA was optimum.

Scanning electron microscopy

Fig. 2 shows SEM images of sintered Ti-doped HA with various content of titanium sintered at 1200 °C for 2 hrs. When the content of titanium in Ti-doped HA was about 2.4 wt.%, a considerable amount of agglomerate sliced HA could be detected clearly with bigger and nonuniform grain size. With the content of titanium in Ti-doped HA decreasing from 2.4 wt.% to

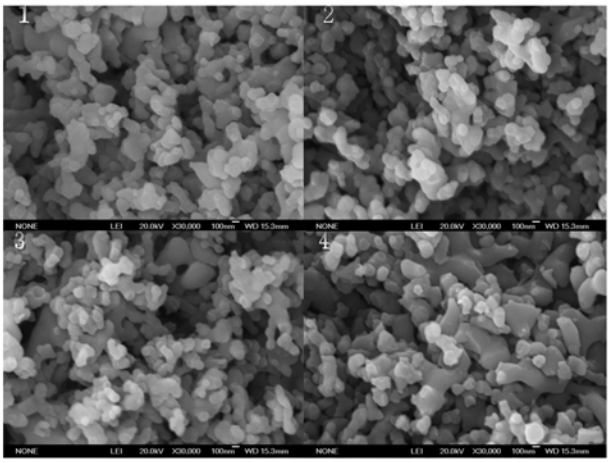

Fig. 2. SEM images of Ti-doped HA sintered at 1200 °C for 2 hrs with various addition of titanium; (1) 0.2 wt.%, (2) 0.8 wt.%, (3) 1.6 wt.% and (4) 2.4 wt.%.

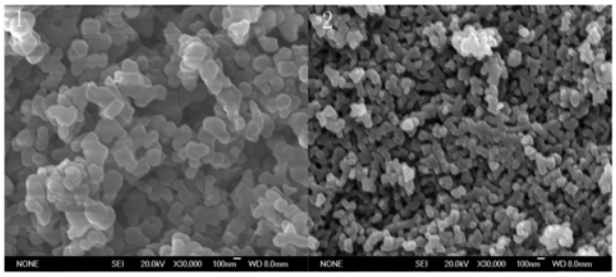

Fig. 3. SEM images of HA sintered at 1200 °C for 2 hrs; (1) without the addition of titanium (2) with the addition of 0.8 wt.% titanium.

0.8 wt.%, more uniform, less agglomerate and much more amount of small rod-like HA with smaller grain size was yielded. With the content of titanium in Ti-doped HA decreasing from 0.8 wt.% to 0.2 wt.%, rod-like HA became fewer instead of agglomerate sliced HA with bigger grain size. It can be concluded that the addition of titanium to HA structure had a great influence on the crystal size and morphology. Meanwhile, an increase of the content of titanium in Ti-doped HA leaded to change in the grain size and shape of the HA crystal. 0.8 wt.% content of titanium was optimum for producing rod-like HA nanpowder.

It can also be found from Fig. 3 that the grain size of sintered Ti-doped HA was much smaller than that of pure HA, which was due to the addition of titanium restraining grain growth during sintering. A smaller grain size and more uniform grains were obtained as microwave route was used. The direction of grain growth of HA involves two major axes, which are c-axis and a-axis, as it is identified as a hexagonal system. Needle-like crystallites are likely obtained when the c-axis is the growing direction, while plate or petal-like crystallites are yielded when they grow in preference to the a-axis direction, as found for carbonated apatite [10]. When plate-or petal-like crystallites are yielded, the crystallites sometimes are agglomerated. In this case, with the content of titanium increasing, more plate-like HA were formed, which showed that the growing direction of HA changes from c-axis to a-axis. However, when the content of titanium was about 0.8 wt.%, more rod-like HA were formed, indicating that grain grows in preference to the a-axis direction. Although, so far it couldn't be confirmed which factors played a dominant role in growth direction, the content of titanium could be one reason in this case. Also note that at the beginning of crystallization of HA, homogeneous nucleation occurs, which results in their orientation are random and agglomerated plate-like of HA are obtained.

Conclusions

In summary, the addition of titanium to HA had a profound influence on sintering behavior, crystal size, shape and morphology of HA. The addition of titanium to HA structure restrained HA decomposition and thermal reaction between HA and titanium, even when the sintering temperature was at 1200 °C, which resulted in improved thermal stability of HA at high sintering temperature. The grain size of sintered Ti-doped HA was much smaller than that of pure HA. Meanwhile, with the addition of titanium to HA, slice-like HA converted into rod-like gradually, which structural is similar to bone mineral and is hopeful to be used in biomedical applications.

Acknowledgments

This work was supported by science and technology plan of Weiyang district, Xi'an city (201204), Department of education of Shaanxi province (12JK0468) and Yulin city science and technology bureau research plan for 2011.

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