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In Vitro Bioactivity of Potassium Titanate Whiskers

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Abstract. The bioactivity of potassium titanate whiskers (PTW) was evaluated by soaking in simulated body fluids (SBF, Kokubo solution). At first, PTW was chemically treated by 1 M HCl and 1 M NaOH solutions at 60 °C for 48 h, respectively. Then PTW before and after treated were soaked in SBF solution and cultured at 37 °C for different times. The apatite deposit on PTW was examined by FTIR and SEM/EDX. The results showed that there was not apatite deposit on the raw PTW even after soaked for 14 days while apatite appeared on the treated PTW after soaked for only 7 days. This implies that treatment by HCl/NaOH solutions can improve the *in vitro* bioactivity of PTW. The possible mechanism is that more Ti–OH groups occur after treatment and induce Ca^{2+} and PO_4^{3-} aggregate and accelerate to deposit of apatite. The bioactive PTW with good biocompatibility is a potential candidate as reinforcing agent to improve the mechanical properties of calcium phosphate ceramics or cements.

Introduction

The potassium titanate whiskers (PTW) as multi-disciplinary materials have attracted much attention amongst material researchers. PTW has thermal durability, chemical resistivity, ion-exchange ability and dispersibility, and has been used as reinforcing agent for plastics, ceramics and metals, heat-insulating paints and filter materials, and is potential to apply as catalyst supports, gas sensors and lithium-ion-battery materials [1-4]. PTW can be easily synthesized by the solid state reaction and hydrothermal method [1, 4, 5]. The former method can prepare mass product [5], while the latter one can produce the monodisperse PTW with adjustable size in diameter [1].

Recently, titanates have been introduced to use as biomaterials, which include calcium titanates, barium titanates and sodium titanates in form of fillers, particles, films and ceramics [6-8]. These materials have good bioactivity. Moreover, it has been reported that potassium titanates are biocompatible and potassium titanate nanorod arrays can induce formation of apatite in 4 days in SBF solution [9]. However, to the best of our knowledge, bioactivity of PTW has not been investigated. PTW can be use as a reinforcing agent to improve the mechanical properties of calcium phosphate-based biomaterials in order to extend to apply in the load conditions. In this paper, the bioactivity of PTW before and after acid and alkaline treatment was investigated by soaking in SBF solution.

Experimental procedure

PTW was offered by Prof. Xin Feng from Nanjing University of Technology. All chemicals in reagent grade used to prepare SBF solution were purchased from Shanghai Chemical Co. Ltd, China and used as received without further purification. SBF solution was prepared according to the reference [10]. Deionized water was employed to prepare the solution.

PTW was treated by soaking in 1M HCl solution at 60 °C for 48 h and in 1 M NaOH solution at 60 °C for 48 h, respectively. The treated PTW was collected by centrifuge and washed by deionized water for three times to remove adsorbed ions, and dried at room temperature for more than 48 h. PTW before and after treatment was cultured in SBF solution with a solid/liquid ratio of 100mg/50ml at 37 °C for the different times. The SBF solution was changed by the fresh SBF solution at every 12 h. After cultured, PTW was collected and washed by deionized water for several times and dried at room temperature until its weight did not change.

The Fourier Transform Infrared (FTIR) spectroscopy was conducted in a Nicolet magna-IR FTIR system 550 spectrophotometer with 2 cm^{-1} resolution from 4000 to 400 cm^{-1} using KBr pellet method. Powder X-ray diffraction (XRD) patterns were recorded on an ARL X'TRA diffractometer (Thermo Scientific, USA) using CuKα radiation over the range $10^{o} \leq 2\theta \leq 70^{o}$ with a step of 0.02^{o}. The surface morphologies of the PTW before and after treatment were performed on a JSM-5900 scan electron microscope (SEM) operating at 10 kV with a Thermo Noran EDX system. The SEM specimens were prepared by placing a drop of calcium phosphate precipitates dispersed in ethanol solution on a specimen stage and evaporating the solvent completely at room temperature. The SEM specimens were coated an Au film to prevent their discharge during the observation.

Results and discussion

The raw PTW was examined by XRD as showed in Fig.1. Its diffraction peaks agree well with the standard card of $K_2Ti_6O_{13}$ (JCPDS Card 040-0403). The SEM (Fig. 2a) results show that the potassium titanates are whiskers with a diameter of 300-500 nm.

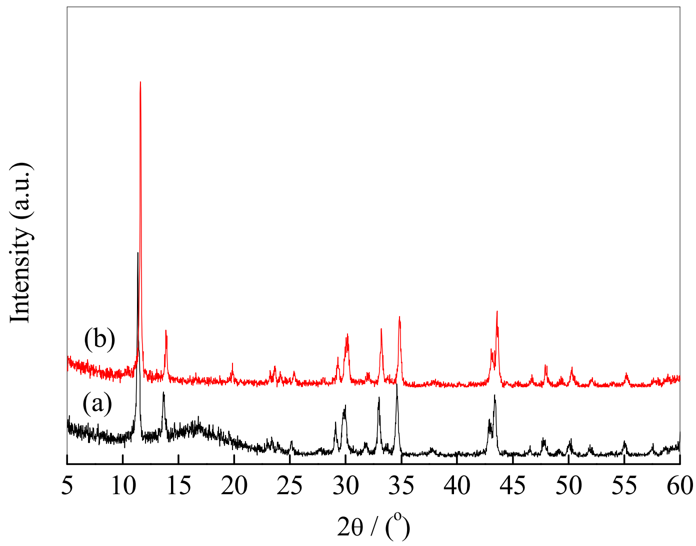

Fig.1 XRD patterns of PTW before (a) and after (b) treated by 1M HCl solution at 60 °C for 48 h and in 1 M NaOH solution at 60 °C for 48 h, respectively.

Unfortunately, the surface of PTW is still smooth after soaked in SBF solution for 14 days, which implies it has low or even no ability to form apatite. In another word, the raw PTW has low or even no bioactivity. However, potassium titanate nanorods arrays growing on the titanium substrates can induce deposition of apatite in 4 days reported by Liu *et al* [9]. Moreover, apatite deposit on sodium titanate ceramic can be accelerated by alkaline treatment using 5 M NaOH [6]. Acid and/or alkaline treatment is usually used to improve the ability of apatite formation on the titanium or titanium oxide. So, acid and alkaline treatment was employed to improve the surface properties. Crystalline phase of PTW after treated by 1M HCl solution at 60 °C for 48 h and 1 M NaOH solution at 60 °C for 48 h, respectively, retained $K_2Ti_6O_{13}$ phase (JCPDS Card 040-0403) as shown in Fig.1b. Furthermore, the amorphous background in the raw PTW disappeared after acid and alkaline treatment. The surface morphology is still smooth as showed in Fig. 3a after treated by acid and alkaline solutions, respectively. These results indicate that acid and alkaline treatment did not affect the structure and morphologies of PTW because of the lower concentration of the acid and alkaline solution used in this work than the ones in the literature [6].

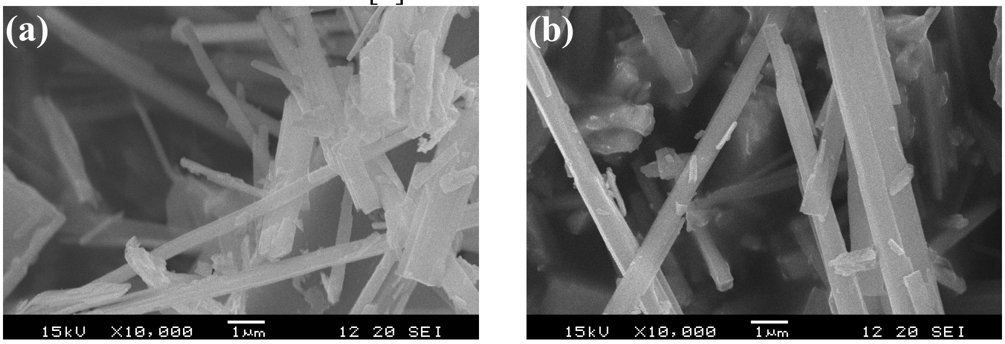

Fig. 2 SEM micrographs of PTW without treatment after soaked in SBF solution for 0 day (a) and 14 days (b).

It is very surprised to find that PTW after treatment by acid and alkaline solution was covered by the precipitates as showed in Fig. 3b after soaked in SBF solution at 37 ^{o}C for only 7 days. The EDX spectrum shows that the precipitates are composed of Ca and P elements. It can be concluded that the precipitates are apatite. Fortunately, The FTIR results can also support this conclusion. There are four absorption peaks at 935, 758, 721 and 456 cm^{-1} (in Fig. 4a), which are assigned to Ti-O and Ti-O-Ti group from potassium titanates [4]. The intensity of the absorption peaks at 935, 758, 721 and 456 cm^{-1} become weaker after soaked the treated PTW in SBF solution at 37 ^{o}C for 7 days (in Fig. 4b) because PTW was covered by the apatite precipitates. Moreover, there are three new absorption peaks at 1490, 1420 and 1030 cm^{-1} in the treated PTW after soaked in SBF solution (in Fig. 4b). The absorption peak at 1030 cm^{-1} is ascribed to PO_4^{3-} group, which comes from the apatite precipitate, and the absorption peaks at 1490, 1420 cm^{-1} are ascribed to carbonate group, which comes from B-type carbonate-substituted apatite [11, 12]. These results indicate that the precipitate is B-type carbonate substituted apatite, which is similar to the composition of the bioapatite in the bone. It needs to point out that the morphology of the apatite deposit in this work is flake-like, not needle-like as reported in the literature [10]. The acceleration of bioactivity after treatment by acid and alkaline can be attributed to the formation of Ti-OH groups, which can induce Ca^{2+} and PO_4^{3-} aggregate and accelerate to deposit of apatite [6].

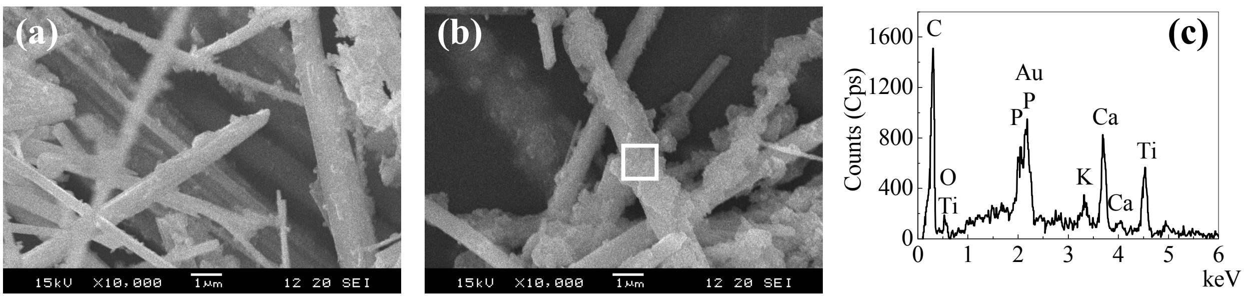

Fig. 3 SEM micrographs of PTW with treatment by 1 M HCl and 1 M NaOH solutions, respectively, after soaked in SBF solution for 0 day (a) and 7 days (b), and the EDX spectrum (c) of the precipitates marked by a white square in the Fig. 3b.

Conclusions

The bioactivity of potassium titanate whiskers (PTW) was accelerated by treatment using 1 M HCl and 1M NaOH solutions at 60 ^{o}C for 48 h, respectively. The flake-like carbonate-substituted apatites deposited on the treated PTW after soaked in SBF solution for 7 days. The bioactive PTW with the high mechanical properties is a potential candidate as a reinforcing agent in calcium phosphate based biomaterials in order to extend to apply in the load conditions.

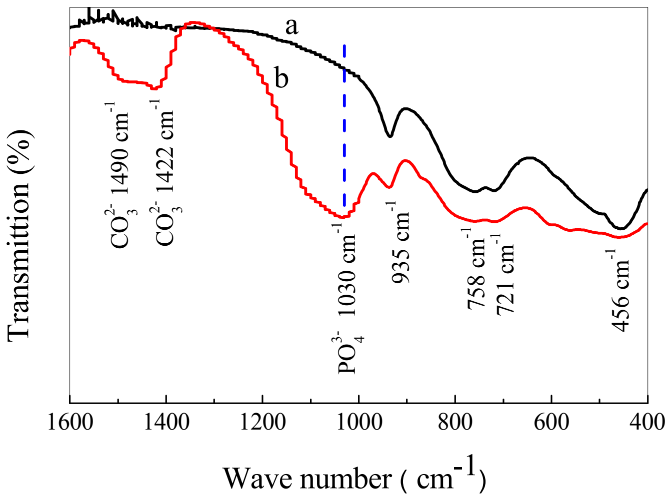

Fig.4 FTIR spectra of PTW treated by 1 M HCl and 1 M NaOH solutions, respectively, after soaked in SBF solution for 0 day (a) and 7 days (b).

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