Deposition of hydroxyapatite coating on biocompatible porous titanium by biomimetic method

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Biocompatible porous titanium was fabricated by powder sintering. Hydroxyapatite (HA) coating was deposited on surface of porous titanium by treatments of acid-alkali and immersion in simulated body fluid in turn. The pre-calcification treatment before immersion in SBF was performed to accelerate the HA formation process. The results show that pre-calcification assisted biomimetic method is an effective approach to deposit HA layer. The porous titanium with unique porous structure, proper mechanical property and bioactive HA coating is a promising candidate for hard tissue implant.

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Keywords: Porous titanium, Hydroxyapatite coating, Biomimetic method

1. Introduction

Pure titanium and its alloy have been used widely as metallic implants for replacement or repair of bone tissue due to excellent biocompatibility and mechanical property. But the solid metallic prosthesis may carry much loading and affect the bone remodeling, and then cause the osteoporosis phenomenon because of its high elastic modulus compared with that of bone tissue. The so-called "stress-shielding" effect has attracted the researchers' much attention [1-3]. Introducing pore structure into solid metal becomes an alternative approach to tailor its elastic modulus and strength to the requirement of bone tissue. In addition, permeable pore structure can contribute to the ingrowth of bone tissue as well as transportation of body fluid and nutrients.

Some processes have been developed to prepare porous metals. Porous titanium can be fabricated by metal injection molding or powder sintering [3-5]. Compared with the former, the latter is featured by convenient processing. In this paper, porous titanium was fabricated from TiH_2 powder and space holder of NH_4HCO_3 by powder sintering.

The biological response to implant materials is a property related directly to their surface conditions. The integrity of the interface between the metallic implant and bone tissue is vital to its permanent biocompatibility. Surface modification like depositing hydroxyapatite coating is a convenient route to improve its surface biocompatibility because the constituents of this bioactive layer are similar to those of bone [6-12]. Some surface modifying techniques like plasma spraying [6], ion beam-assisted deposition [7], sol-gel [8] and biomimetic method [9] have been developed to deposit HA layer on surface of titanium, magnesium and their alloys. Among these approaches, the biomimetic method is suitable to deposit HA coating on metallic implant with complex geometry. Additionally, it has other advantages like low temperature, good interface bonding between the layer and substrate, etc. In addition to the common biomimetic procedures of acid-alkali treatment and soaking in simulated body fluid (SBF), pre-calcification is proposed to accelerate apatite formation [10]. Biomimetic method of alkali- and heat-treatment and then immersion in SBF in turn was used to deposit HA coating on porous titanium (with thickness of 2mm) sintered on dense titanium substrate [11]. Acid-alkali and immersion in SBF was performed to form HA coating on porous NiTi alloy prepared by combustion synthesis [12].

However, there is no report on depositing HA coating on surface of porous titanium by pre-calcification assisted biomimetic method.

It is the objective of this paper to investigate the effect of pre-calcification treatment on formation a HA coating on porous titanium using biomimetic method.

2. Experiment details

As described in literature [5], porous titanium was prepared from powders of TiH_2 and space holder of NH_4HCO_3 by powder sintering. The porous titanium samples were spark cut into size of Φ9mm×3mm and cleaned ultrasonically with acetone, ethanol and distilled water, respectively.

Porous titanium samples were immersed in 37.5% HNO_3 aqueous solution at 60°C for 24h and then 1.5M NaOH aqueous solution at 60°C for 24h.

Half acid-alkli treated samples were soaked in 1M Na_2HPO_4 solution at 37.5°C for 24h and saturated $Ca(OH)_2$ solution at 37.5°C for 6h in turn to investigate the influence of pre-calcification on formation of HA on porous titanium before immersion in SBF at 37.5°C for 7 and 15 days, respectively. The concentrations of SBF (Hank's solution) with pH of 7.4 are listed in Table 1.

Table 1. Concentrations of simulated body fluid.

Ion	Na^+	Ca^{2+}	K^+	Mg^{2+}	Cl^-	HCO_3^{2-}	HPO_4^{2-}	SO_4^{2-}
Concentration	142.0	2.5	5.0	1.5	147.8	4.2	1.0	0.5

The surface morphology of the specimens was observed by scanning electron microscopy (SEM, Hitachi S3400N). The surface chemical analysis was conducted by energy dispersive X-ray (EDX) spectroscopy. Phase constituents of the coating were analyzed by X-ray diffraction (XRD, Rigaku D/max).

3. Results and discussions

Fig. 1 shows the pore morphology of porous titanium prepared from powder sintering. It is characterized by some small closed pores distributed on the walls of big open interconnected pores. Mean pore size of 137 μm is in the optimal pore size range for attachment and ingrowth of bone tissue. Elastic modulus in compressive of 8.1GPa is close to that of cancellous bone. In addition, pore size and elastic modulus can be regulated by amount of space holder [5].

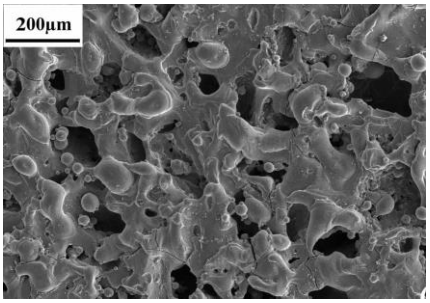

Fig. 1. SEM image of pore morphology of porous titanium compact.

Fig. 2 presents SEM micrographs of HA coating deposited on porous titanium samples subjected to different treatments. For the porous titanium sample subjected to treatments of acid-alkali and immersion in SBF for 7 days, some small and sparsely scattered granular substances can be seen on the substrate in Fig. 2(a). When the immersion period in SBF is extended to 15 days, granular substances distributed densely on the porous sample can be shown in Fig. 2(b). For the sample subjected to treatments of acid-alkali, pre-calcification and then immersion in SBF for 7 days in turn, some big spherical substances formed on the surface can be seen in Fig. 2(c). When the immersion period in SBF is extended to 15 days, some big and densely distributed spherical substances can be shown in Fig. 2 (d). The HA coating with thickness within about 3μm can be deposited on the surface or inside the pores of porous titanium sample by this approach. The porous structure of porous titanium with mean pore size of 137μm would remain interconnectivity, favoring ingrowth of bone tissue and transportation of human body fluid. The results suggest that pre-calcification treatment plays a significant role in the morphology of the coating formed on porous sample.

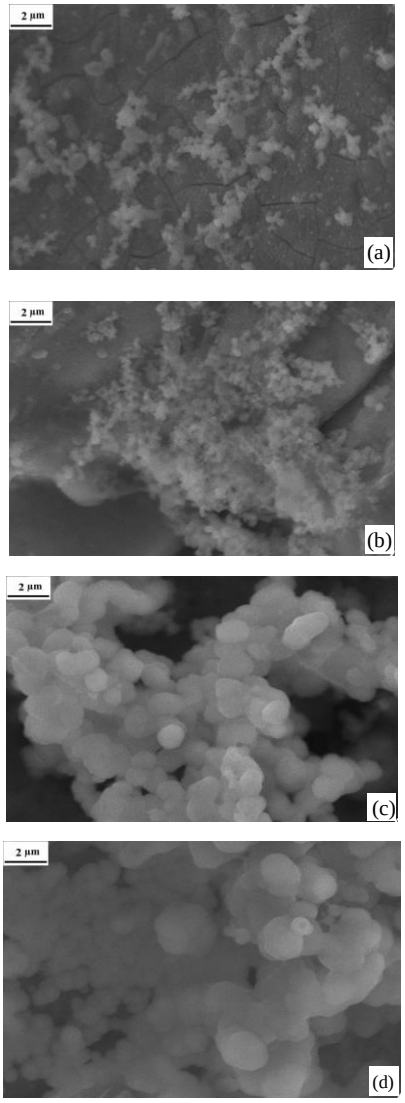

Fig. 2. SEM micrographs of the porous titanium samples subjected to different treatments (a) acid-alkali, immersion in SBF for 7 days, (b) acid-alkali, immersion in SBF for 15 days (c) acid-alkali, pre-calcification and immersion in SBF for 7 days, (d) acid - alkali, pre-calcification and immersion in SBF for 15days.

Fig. 3 shows the surface EDX spectra of the HA coating deposited on porous titanium samples subjected to different treatments. Major elements like Ca, P and O in HA phase can be detected for all samples. The composition percentages of Ca and P peaks become bigger when the immersion time in SBF extends from 7 to 15 days. Additionally, the Ca/P ratio becomes bigger for the pre-calcified sample.

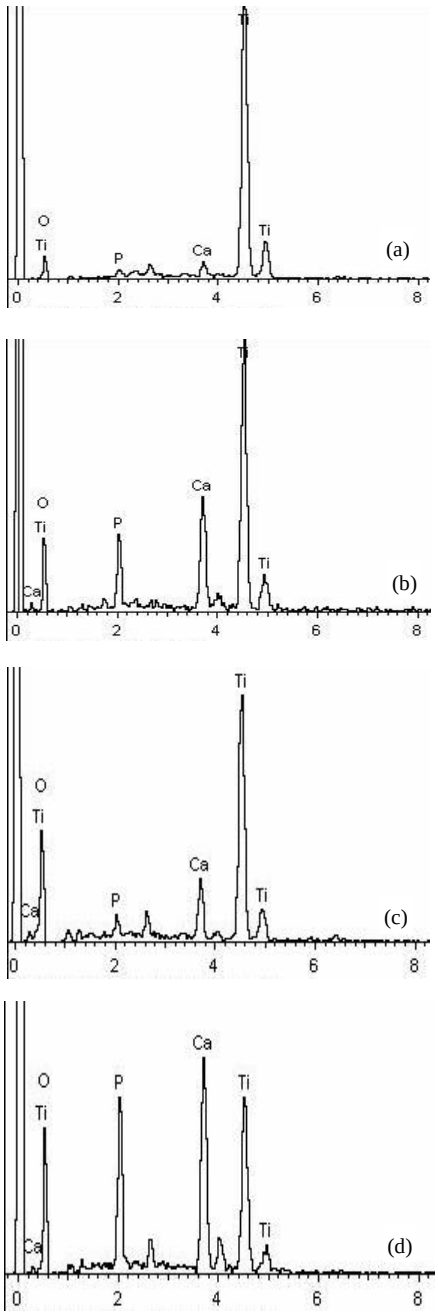

Fig. 3. Surface EDX spectra of the porous titanium samples subjected to different treatments (a) acid-alkali, immersion in SBF for 7 days, (b) acid-alkali, immersion in SBF for 15 days, (c) acid-alkali, pre-calcification and immersion in SBF for 7 days, (d) acid - alkali, pre-calcification and immersion in SBF for 15 days.

Fig. 4 exhibits the XRD patterns of the coating deposited on surface of porous titanium sample by treatments of acid-alkali, pre-calcification and immersion in SBF for 15 days in turn. Compared with the peaks of titanium phase, the weaker intensity of peaks for HA phase indicates that the coating is thin.

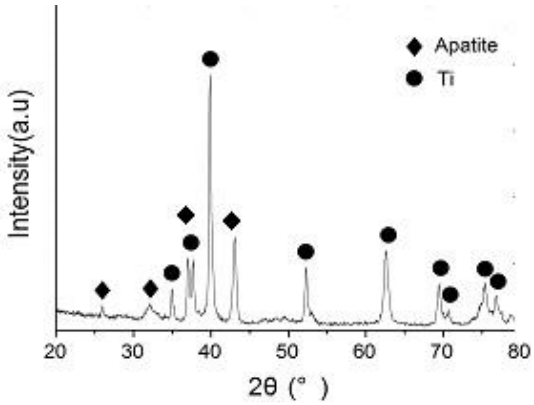

Fig. 4. XRD patterns of porous titanium sample deposited with hydroxyapatite coating.

Biocompatible HA can be deposited on the bioinert porous titanium using biomimetic route. HA formability and growth rate are crucial to the bioactivity of metallic implant. During the treatment used in this paper, the HA coating formation mechanism may be similar to that proposed for solid titanium [9]. The acid treatment is performed to refresh the surface and thicken TiO_2 layer on the porous titanium sample [9]. In 1.5M alkali solution, the negatively charged $HTiO_3^-\cdot nH_2O$ species react with positively charged Na^+ ions to form sodium titanate hydrogel layer on the surface of acid treated porous titanium sample. In SBF, $Ti{-}OH^-$ groups are formed on the surface of porous sample to induce the apatite nucleation. The nuclei grow spontaneously by adsorbing Ca^{2+} and HPO_4^{2-} ions from SBF solution and then a HA layer can be deposited on the surface of porous titanium [9].

For the pre-calcified porous titanium sample, the Ca^{2+} and HPO_4^{2-} ions can be sufficiently adsorbed onto the surface of porous sample [10]. According to Eq.1, the free energy (ΔG) of apatite nucleation would decrease due to the increase of the local supersaturation (S) of these ions.

$$\Delta G = -RT \ln S + \sigma A \tag{1}$$

Where R, T, σ and A is a constant, temperature, interface energy and surface area, respectively.

Consequently, apatite nucleation and HA formation would be accelerated significantly.

The investigation results indicate that porous titanium deposited with HA coating is a promising implant candidate for cancellous bone because of good combination of appropriate mechanical properties, porous

structure and biocompatible HA layer.

4. Conclusions

Porous titanium with suitable pore size and elastic modulus can be fabricated from powders of TiH_2 and NH_4HCO_3 by powder sintering. By treatments of acid–alkali, pre-calcification and immersion in SBF in turn, HA coating can be deposited on surface of porous titanium. Pre-calcification treatment can accelerate significantly the apatite formation.

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References

[1] L. L. Hench, E. C. Ethridge, Biomaterials: An interfacial Approach, Academic Press, New York, 1982.
[2] Y. H. Li, R. B. Chen, G. X. Qi, Z. T. Wang, Z. Y. Deng, J. Alloys Compd. **485**, 215 (2009).
[3] I. Oh, N. Nomura, N. Masahashi, S. Hanada, Scripta Mater. **49**, 1197 (2003).
[4] L. J. Chen, T. Li, Y. M. Li, H. Hao, Y. H. Hu, Trans. Nonferrous Metal Soc. China, **19**, 1174 (2009).
[5] Y. H. Li, T. Fan, N. Zhang, Rare Metal Mater. Eng., **40**(S2), 84 (2011).
[6] X. B. Zheng, M. H. Huang, C. X. Ding, Biomaterials, **21**, 841 (2000).
[7] C. X. Wang, Z. Q. Chen, M. Wang, Z. Y. Liu, P. L. Wang, S. X. Zheng, Biomaterials, **22**, 1619 (2001).
[8] M. F. Hsieh, L. H. Perng, T. S. Chin, Mater. Chem. Phys., **74**, 245 (2002).
[9] T. Kokubo, F. Miyaji, H. M. Kim, J. Am. Ceram. Soc., **79**, 1127 (1996).
[10] H. B. Wen, Q. Liu, W. J. R. De, G. K. De, F. Z. Cui, J. Mater. Sci. Mater. Med., **8**, 765 (1997).
[11] F. H. Liang, L. Zhou, K. G. Wang, Surf. Coat. Technol., **165**, 133 (2003).
[12] H. C. Jiang, L. J. Rong, Surf. Coat. Technol., **201**, 1017 (2006).

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