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ARTICLE

Influence of Alkali Treatment on Ti6Al4V Alloy and the HA Coating Deposited by Hydrothermal-Electrochemical Methods

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Abstract: The aim of this work is to investigate the influence of NaOH pretreatment time on the phases and morphologies of Ti6Al4V substrates and hydroxyapatite (HA) coatings. Ti6Al4V substrates were pretreated with a sodium hydroxide (NaOH) solution for different amounts of time (12, 24, 36, 48, and 60 h). After NaOH pretreatment, a three-dimensional porous network of sodium titanate gel was observed on the Ti6Al4V surface. Subsequently, HA deposition was achieved using the hydrothermal-electrochemical methods, while the electrolyte solution containing NaCl, $K_2HPO_4 \cdot 3H_2O$, and $CaCl_2$, was maintained at 120 °C and applied by a constant current density of 1.25 mA/cm^2 for 120 min. The results indicate that the growth pattern and micromorphology of the HA coating are all influenced by different pretreatment time. After pretreating Ti6Al4V substrates with NaOH for 12 h, needle-like structures are primarily formed on the HA coating, and some dandelion-like morphologies are presented. During 48 h NaOH solution pretreatment, the dandelion-like structures increase with the increase of time. However, the amount of the dandelion-shaped HA drops slightly, when pretreatment time is longer than 48 h. The orientation index of the (002) plane of HA reaches the minimum when Ti6Al4V substrates are pretreated for 48 h, whereas the crystallinity is the highest for this pretreatment time.

Key words: Ti6Al4V; hydroxyapatite coating; alkali pretreatment; hydrothermal-electrochemical methods

Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) is widely used for clinical applications in orthopedics and dentistry because of its excellent biocompatibility and security[1-4]. Unfortunately, the mechanical performance of a pure hydroxyapatite is poor, for instance, the material is brittle and its fatigue resistance is low, which severely limit its use in load-bearing areas. However, titanium alloys can be used as high-load-bearing bone substitutes owing to their excellent corrosion resistance and mechanical performance[5,6]. Therefore, the titanium-HA composites have been developed by depositing hydroxyapatite onto the surfaces of titanium alloys, which take advantage of HA's superior biocompatibility without sacrificing mechanical properties of the titanium alloys.

Hydroxyapatite can be deposited onto titanium alloy surfaces using various techniques, e.g., plasma spraying[7,8], ion plating[9], sol-gel films[10,11], microarc oxidation[12,13], electrophoresis[14], electrochemical methods[15], and hydrothermal-electrochemical methods[16]. Among them, the electrochemical method has some advantages, including their ease of application onto complexly shapes and microporous implants as well as their relatively low application temperatures, which protects the substrate's mechanical properties[17]. Hydrothermal-electrochemical method involves the electrochemical synthesis under high pressure and at temperature above 100 °C. It affords the advantages of both the hydrothermal method and the electrochemical methods. Ban and colleagues[18] reported

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the success in using the hydrothermal-electrochemical method to achieve hydroxyapatite coatings.

When a Ti6Al4V substrate is treated with NaOH, a three-dimensional porous hydrogel layer made of sodium titanate is formed on the Ti6Al4V surface. The gel can then be converted to Ti-OH groups during hydrothermal-electrochemical deposition, which will contribute to the formation of hydroxyapatite. In addition, the gel's porous structure can provide more nucleation sites, thus improving the adhesion strength between the Ti6Al4V substrate and the deposited HA coating[19-21].

The purpose of the present work is to investigate the effects of alkali treatment on the Ti6Al4V alloy substrate and the HA coating deposited on the substrate by hydrothermal-electrochemical method, so as to provide the clinical applications in orthopedics and dentistry etc with a technical base.

1 Experiment

Commercially available Ti6Al4V plates, with dimensions of *Φ*30 mm×2 mm, were mechanically polished with P200, P400, and P800 abrasive papers. Subsequently, samples were ultrasonically cleaned for 10 min in acetone, ethanol, and then distilled water. Then they were dried in an oven at 40 °C. Finally, the polished and cleaned Ti6Al4V plates were immersed in 8 mol/L NaOH solutions at 60 °C for 12, 24, 36, 48, and 60 h.

The electrolyte was heated in a stainless steel autoclave. The cathode consisted of the pretreated Ti6Al4V plate, and the anode was a platinum plate. The electrolyte contained a given amounts of 137.8×10^3 mol/L NaCl, 1.67×10^3 mol/L $K_2HPO_4\cdot3H_2O$, and 2.5×10^3 mol/L $CaCl_2$. The electrolyte was heated to 120 °C and the current density was maintained at 1.25 mA/cm^2 for 120 min.

The crystal morphologies were observed by scanning electron microscopy (SEM: Quatan 450; FEI, Holland). The surface phase structures were analyzed by X-ray diffraction meter (XRD: D8-Advanced; Bruker, Germany) using Cu Kα radiation at a scanning speed of 4.00°/min and a scanning range (2θ) from 10° to 60°.

2 Results and Discussion

2.1 Alkali pretreatment of Ti6Al4V substrates

Fig.1 shows the SEM images of the Ti6Al4V substrates immersed in NaOH solution for 12 h to 60 h. The images show that a porous and three-dimensional network structure is formed on the Ti6Al4V surface. According to XRD analysis results (Fig.2), the submicron-scale network structure is composed of sodium titanate hydrogel[22]. After 48 h pretreatment, the sizes of the pores in the network increase remarkably. It is found that the pore sizes increase as pretreatment time increases. In addition, another porous layer with smaller pore sizes is located below the outermost porous gel layer. This phenomenon becomes more and more obvious as pretreatment time increases. It can be concluded that the thickness of the sodium titanate gel on the surface of the Ti6Al4V substrate increases with the increase of pretreatment time. However, for the pretreatment time longer than 48 h, the size of the network structure decreases. It is possible that the pore structures on the outer surface of the gel are corroded away when immersion time is too long. Particularly, the presence of a three-dimensional network structure will significantly increase the substrate surface area, which may provide more nucleation sites for the hydroxyapatite anchored to the substrate. As a result, the gel layer can improve the adhesion strength between the Ti6Al4V substrate and the HA coating[20].

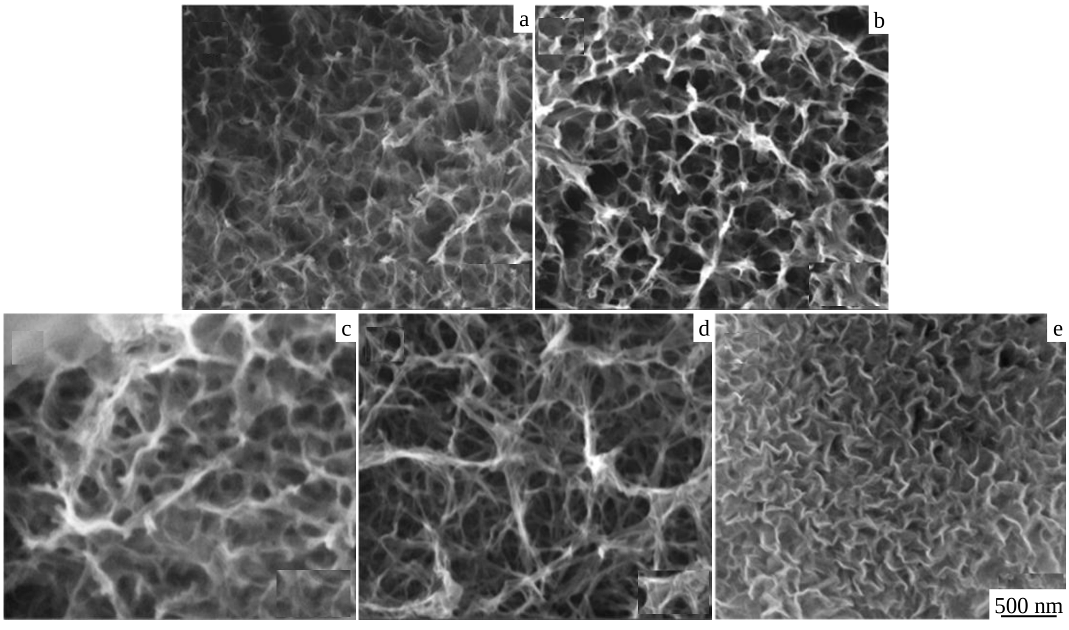

Fig.1 SEM images of Ti6Al4V substrates immersed in the NaOH solution for 12 h (a), 24 h (b), 36 h (c), 48 h (d), and 60 h (e)

The XRD results are shown in Fig.2. It is clear show that new broad diffraction peaks appear at 2*θ* angles of 23°~30° and 47°~49° after pretreatment with the NaOH solution. These peaks can be ascribed to a microcrystalline or an amorphous phase, indicating that the sodium titanate hydrogel is formed on the Ti6Al4V substrates[23,24]. Sepahvandi et al. explained the formation mechanism of this hydrogel layer, which is summarized briefly below[25]. After a Ti6Al4V surface is mechanically polished, a thin titanium dioxide film quickly appears on its surface. When immersed in a NaOH solution, this superficial TiO_2 layer dissolves, according to the following reaction (1):

$$\mathrm{TiO_2{+}OH^- \rightarrow HTiO_3^-} \tag{1}$$

Simultaneously, the titanium also reacts with the NaOH solution, and these reaction mechanisms are as follows:

$$\mathrm{Ti{+}3OH^- \rightarrow Ti(OH)_3^+{+}4e^-} \tag{2}$$

$$\mathrm{Ti(OH)_3^+{+}e^- \rightarrow TiO_2 \cdot H_2O{+}1/2H_2} \uparrow \tag{3}$$

$$\mathrm{Ti(OH)_3^+{+}OH^- \leftrightarrow Ti(OH)_4} \tag{4}$$

$$\mathrm{TiO_2} \cdot n\mathrm{H_2O + OH^- \leftrightarrow HTiO_3^-} \cdot n\mathrm{H_2O} \tag{5}$$

2.2 Hydrothermal-electrochemical deposition method

Fig.3 shows the SEM images of HA deposition on the Ti6Al4V substrates. The figures show that the layered growth pattern and the micromorphology of hydroxyapatite are all influenced by NaOH solution pretreatment time. Almost only one full layer of hydroxyapatite is presented when Ti6Al4V plate is pretreated for 12 h. The microstructure of this layer is compact, and HA forms needle-like shapes growing in a direction perpendicular to the Ti6Al4V surface. Furthermore, the needle-like hydroxyapatite as a defined hexagonal crystal habit appears. What is more, when the first needle-like hydroxyapatite layer grows to a certain degree, a large number of nucleation happens again at the top of the needle of HA, and this phenomenon can be seen at a higher SEM magnify-cation. With the growth of new nuclear, a new layer of small-grained HA is formed. It is defined as the second layer, which appears as dandelion-like shape. The amount of hydroxyapatite in the second layer increases as pretreatment time increases, until the 48 h pretreatment time is reached. Then, the amount marginally decreases. One possible mechanism that explains why the layered growth of hydroxyapatite is influenced by different pretreatment time may have to do with the amount of Ti-OH groups that form at different pretreatment time. When the Ti6Al4V substrate is soaked in the NaOH solution for a relatively short time, such as 12 h, almost only a small amount of sodium titanate gel appears on the substrate. Consequently, only a few Ti-OH groups are formed during hydrothermalelectrochemical deposition. These few Ti-OH groups promote the formation of a HA layer. Moreover, because of the limited three-dimensional network structure, the HA layer produces a selective growth, forming needle-like hydroxyapatite. As the pretreatment time increases, the sodium titanate gel layer becomes thicker, allowing for the generation of more Ti-OH groups during hydrothermal-electrochemical deposition. The greater numbers of Ti-OH groups will provide additional nucleation positions, thus promoting the formation of the second layer, which produces dandelion-like hydroxyapatite. The dandelion-like shape of this second layer might arise because of less space constraints.

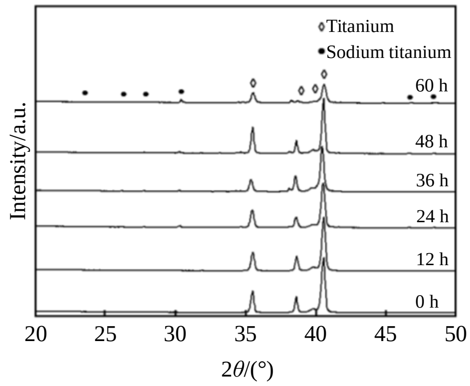

Fig.2 XRD patterns of Ti6Al4V substrate treated with 8.0 mol/L NaOH solution at 60 °C for 0~60 h

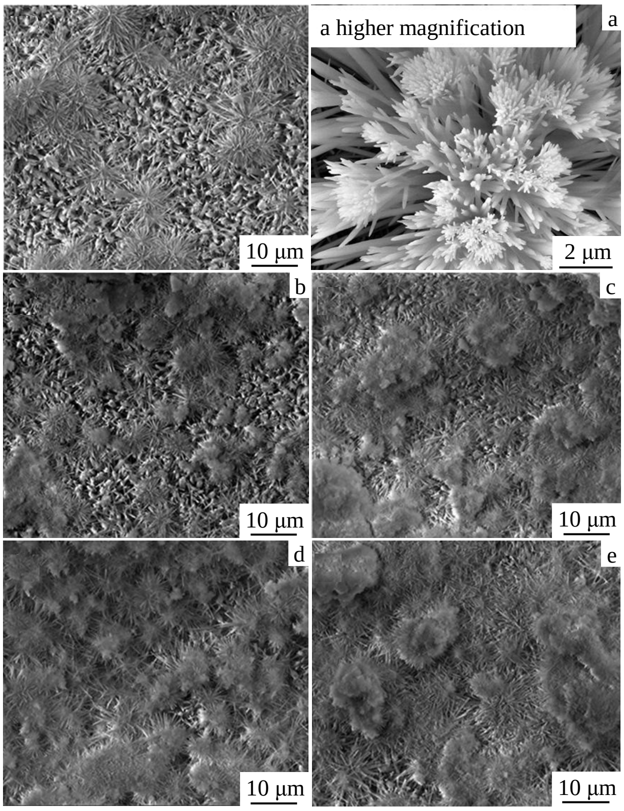

Fig.3 SEM images of the Ti6Al4V substrates pretreated in NaOH solution for12 h (a), 24 h (b), 36 h (c), 48 h (d), and 60 h (e), and HA deposition by hydrothermal-electrochemical method

Fig.4 shows the XRD patterns of HA-coated substrates after hydrothermal-electrochemical deposition. They indicate that hydroxyapatite is formed according to standard JCPDS file No.09-0432[26]. After NaOH solution treatment, the mechanism of hydroxyapatite formation can be explained as follows[22,23]: soaking a Ti6Al4V substrate in NaOH solution results in the formation of a porous sodium titanate gel layer on the substrate surface. These hydrogels turn into Ti-OH groups during hydrothermal-electrolyte deposition, which can promote hydroxyapatite formation. At the same time, these groups can also strengthen the chemical bonds between the Ti6Al4V substrate and the HA coating, thereby increasing their bonding strength.

Moreover, the diffraction peak corresponding to (002) at 2θ=25.8° has a stronger-than-normal intensity compared with the standard XRD pattern, which suggests that the hydroxyapatite crystal orientation is on the c-axis[27, 28]. It is consistent with the SEM results that hydroxyapatite has a needle-like morphology.

Because of the orientation of the (002) plane, the sum of six diffraction peak intensities (002, 102, 211, 112, 300 and 202) are used as the intensity value for hydroxyapatite[29]. The intensity factor (IF) is calculated according to the following equation (6):

$$\mathrm{IF}=\frac{I_{002}}{I_{002}+I_{102}+I_{211}+I_{112}+I_{300}+I_{202}} \qquad (6)$$

A similar IF fraction (termed IFR) is calculated using random intensity data of hydroxyapatite from JCPDS No.09-432, yielding an IFR=0.1932. The orientation index can be obtained by dividing the IF term by the IFR term[26].

Fig.5 shows the orientation index of the (002) plane of hydroxyapatite derived from the XRD patterns. It can be seen that the orientation index decreases with the increase of pretreatment time, and reaches a minimum at 48 h. Then, it marginally increases when the pretreatment time is longer than 48 h. This oriented growth was also observed in the study of mimicking the biomineralization of hydroxyapatite. In the patite layer was induced by an organized hydroxylated surface, which was prepared through an interaction between an aqueous hydrogen peroxide solution and a fresh titanium oxide layer[30].

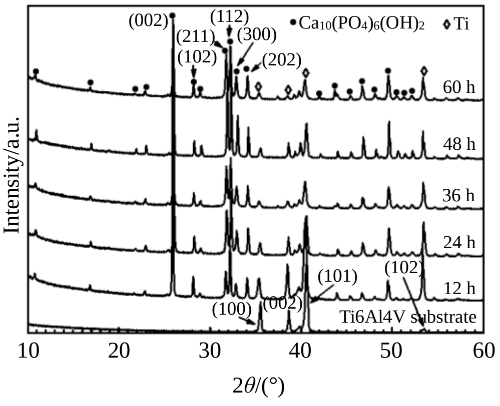

Fig.4 XRD patterns of HA-coated substrates after hydrothermal-electrochemical deposition

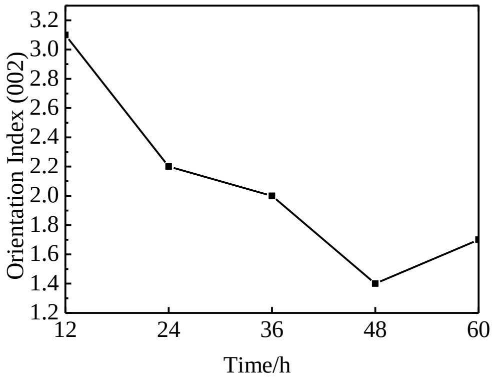

Fig.5 Orientation index of the (002) plane of hydroxyapatite derived from the XRD patterns

It can be seen that the orientation index of dandelion-like hydroxyapatite is smaller than that of the needle-like hydroxyapatite. This may be because the dandelion-like HA grows in a radial direction, while the needle-like hydroxyapatite growth direction is upright. Thus, the diffraction peak corresponding to (002) of the needle-like HA has a larger intensity ratio[18] than that of the dandelion-like HA. Based on the findings of our study, the following conclusions can be drawn: The variable nature of the orientation index is study, the nucleation and the growth of an oriented hydroxyaconsistent with the observed hydroxyapatite morphologies. Hydroxyapatite has a higher orientation index when it grows in a single layer consisting of needle-like HA. The orientation index decreases gradually with the emergence and further growth of the second HA layer, consisting of dandelion-like HA. Finally, the orientation index for the substrates pretreated for 60 h slightly increases because of the moderate decrease in dandelion-like hydroxyapatite.

The hydroxyapatite crystallinity X_C, dependent upon the arrangement of ions deposited on the electrode[29], is evaluated using the following relationship (7)[31]:

$$X_C \approx 1 - (V_{112/300}/I_{300}) \qquad (7)$$

where, I_{300} is the intensity of the (300) reflection peak, and $V_{112/300}$ is the intensity of the hollow between (112) and (300) reflection peaks, which completely disappears in noncrystalline samples.

Fig.6 shows the crystallinity of the hydroxyapatite, which increases with the increase of pretreatment time and attains its maximum at a pretreatment time of 48 h. With further pretreatment, the crystallinity value marginally decreases. These results suggest that the crystallinity of hydroxyapatite is influenced by its surface morphology. Compared with needlelike hydroxyapatite crystals, dandelion-like hydroxyapatite crystals are better

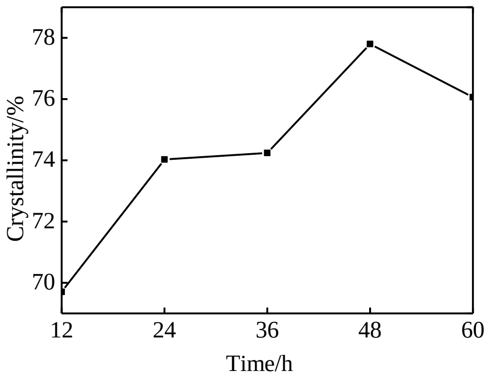

Fig.6 Crystallinity of hydroxyapatite derived from the XRD patterns

and consequently, have a higher crystallinity. The crystallinity of hydroxyapatite is relatively low upon short pretreatment time. Owing to the fact that the amount of dandelion-like hydroxyapatite gradually increases with increasing pretreatment time, the crystallinity also gradually increases. Finally, the crystallinity value decreases because of the marginal decrease of dandelion-like hydroxyapatite at the 60 h pretreatment time.

3 Conclusions

1) A layer of sodium titanate gel is formed on the Ti6Al4V surface after pretreatment with NaOH solution, and the hydrogel layer consists of a three-dimensional porous network. The size of the network structure increases as the NaOH solution pretreatment time increases, until the pretreatment time reaches 48 h. Then with longer pretreatment time, the size of the network structure decreases.

2) The growth pattern of hydroxyapatite and its micromorphology are affected by pretreatment time. After a 12 h pretreatment, hydroxyapatite consists mainly of a needle-like hydroxyapatite layer and a small amount of dandelion-like HA. The amount of dandelion-like hydroxyapatite increases as pretreatment time increases, whereas the most dandelion-like HA is presented after the 48 h pretreatment. Longer pretreatment time results in a marginal decrease of the amount of dandelion-like HA.

3) The orientation index of hydroxyapatite first decreases with increasing of pretreatment time, reaching a minimum when the pretreatment time is 48 h, and then increases with prolonging of pretreatment time.

4) The crystallinity of HA increases with increasing pretreatment time, reaching a maximum when the pretreatment time is 48 h. Increasing the pretreatment time beyond 48 h results in a marginal decrease in crystallinity.

References

1 Djošić M S, Panić V, Stojanović J *et al*. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*[J], 2012, 400: 36

2 Sepahvandi A, Moztarzadeh F, Mozafari M *et al*. *Colloids Surf B Biointerfaces*[J], 2011, 86(2): 390

3 Fatehi K, Moztarzadeh F, Solati-Hashjin M *et al*. *Surf Eng*[J], 2009, 25(8): 583

4 Wang Yingchun, Huang Wenhai, Yao Aihua *et al*. *Rare Metal Materials and Engineering*[J], 2011, 40(5): 930 (in Chinese)

5 Huang Chuanhui, Wang Qingliang, Shi Xingling. *Rare Metal Materials and Engineering*[J], 2012, 41(7): 1161 (in Chinese)

6 Wu Bo, Liang Chenghao, Wang Peng. *Rare Metal Materials and Engineering*[J], 2010, 39(12): 2069 (in Chinese)

7 Lu Y P, Li M S, Li S T *et al*. *Biomaterials*[J], 2004, 25(18): 4393

8 Guo Yuanjun, Ning Chengyun, Tan Guoxin *et al*. *Rare Metal Materials and Engineering*[J], 2012, 41(8): 1447 (in Chinese)

9 Struts V K, Petrov A V, Matvienko V M *et al*. *Journal of Surface Investigation-X-Ray Synchrotron and Neutron Techniques*[J], 2011, 5(3): 497

10 He Daihua. *International Conference on Information Engineering for Mechanics and Materials (ICIMM 2011)*[C]. Switerland: Trans Teach Publications, 2011: 426

11 Wang Shaohong, Wang Hao, Hou Zhaoxia *et al*. *Rare Metal Materials and Engineering*[J], 2011, 40(S1): 44 (in Chinese)

12 Ma Fengcang, Liu Ping, Li Wei *et al*. *Rare Metal Materials and Engineering*[J], 2012, 41(S1): 478 (in Chinese)

13 Wang Fengbiao, Di Shichun. *Rare Metal Materials and Engineering*[J], 2012, 41(2): 298 (in Chinese)

14 Park J H, Lee D Y, Oh K T *et al*. *Mater Lett*[J], 2006, 60(21-22): 2573

15 Zhao X H, Yang L F, Zuo Y *et al*. *Chin J Chem Eng*[J], 2009, 17(4): 667

16 Ban S, Hasegawa J. *Biomaterials*[J], 2002, 23(14): 2965

17 Yang X J, Hu R X, Zhu S L *et al*. *Scr Mater*[J], 2006, 54(8): 1457

18 Ban S, Maruno S. *J Biomed Mater Res*[J], 1998, 42(3): 387

19 Luo R, Liu Z, Yan F *et al*. *Appl Surf Sci*[J], 2013, 266: 57

20 Qiang W, Yang Z, Ke Y *et al*. *Surf Rev Lett*[J], 2009, 16(5): 775

21 Raman V, Tamilselvi S, Rajendran N. *Electrochim Acta*[J], 2007, 52(26): 7418

22 Zhao Q M, Guo X, Dang X Q *et al*. *Colloids Surf B Biointerfaces*[J], 2013, 102: 321

23 Wang C X, Wang M, Zhou X. *Biomaterials*[J], 2003, 24(18): 3069

24 Fatehi K, Moztarzadeh F, Solati-Hashjin M *et al*. *Bull Mater Sci*[J], 2008, 31(2): 101

25 Kim H M, Miyaji F, Kokubo T *et al*. *J Biomed Mater Res*[J], 1996, 32(3): 409

26 Ban S, Maruno S, Harada A *et al*. *Dent Mater J*[J], 1996, 15(1): 31

27 Hu R, Shi H Y, Lin L W *et al*. *Acta Physico-Chimica Sinica*[J], 2005, 21(2): 197 (in Chinese)

28 Huang Chunpeng, Wang Jian, Che Daochuang. *Rare Metal Materials and Engineering*[J], 2011, 40(S2): 233 (in Chinese)

29 Ban S, Maruno S. *Biomaterials*[J], 1995, 16(13): 977

30 Mao C B, Li H D, Cui F H *et al*. *J Cryst Growth*[J], 1999, 206(4):

308

31 Landi E, Tampieri A, Celotti G *et al*. *J Eur Ceram Soc*[J], 2000, 20(14-15): 2377

碱预处理对水热电化学在钛合金表面沉积羟基磷灰石的影响

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摘　要：Ti6Al4V 基体经 NaOH 溶液恒温预处理不同的时间（12、24、36、48、60 h），然后分析了不同的碱预处理时间对 Ti6Al4V 基体及羟基磷灰石（HA）形态、物相的影响。经碱预处理后 Ti6Al4V 表面呈现三维网状结构，并检测到了钛酸钠凝胶的存在。随后采用水热电化学方法得到了 HA 涂层，水热反应电解质包括 NaCl、$K_2HPO_4 \cdot 3H_2O$、$CaCl_2$，在恒温 120 ℃、电流密度为 1.25 mA/cm^2 的条件下保持 120 min。结果表明：HA 的生长模式及形态均受预处理时间的影响：当基体经过 12 h 的预处理后，水热反应形成一层针状 HA 及少量蒲公英状 HA。而蒲公英状 HA 的数量随预处理时间的增加而增多。但预处理时间大于 48 h 时，其数量稍有减小。HA 在（002）晶面的取向指数、结晶度在预处理时间为 48 h 时分别达到了最小值、最大值。

关键词：Ti6Al4V；羟基磷灰石涂层；碱预处理；水热电化学

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