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Effects of temperature and voltage on formation of electrolysis induced chemical conversion coating on titanium surface

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ABSTRACT

Zinc phosphate chemical conversion technology (PCC) has attracted more attention as a potential surface modification method of biomedical metal. However, it is difficult to prepare a phosphate coating on titanium (Ti) by the traditional PCC methods due to the presence of the passive oxide layer on its surface. In this research, a practical phosphate chemical conversed coating was prepared on Ti by means of electrolysis induced phosphate chemical conversion (EPCC) method. The effects of temperature as well as voltage on the formation, microstructures, properties and the deposition mechanism of coatings are investigated. The results show that the temperature and voltage play important roles in determining the phase composition and crystal structure of the coatings. The coatings obtained by EPCC treatments at 30 °C mainly consist of Zn while that of 90 °C are mainly composed of hopeite grown preferentially along (020) and (040) planes. The results also show that the mechanism of formation of different coatings can be attributed to the influence of process parameters on hydrogen overpotential. Besides, the corrosion resistance of the EPCC coatings is improved by increasing temperature and decreasing voltage.

1. Introduction

With the development of load-bearing metallic implants, quality of the biological characteristics appraisal has become more and more important, which leads to extensive research on its surface modification methods [1–4].

As the most commonly used load-bearing metallic implants, titanium (Ti) and its alloys can provide effective solutions to the clinical orthopedic wound and dental restoration [5–7], due to the outstanding performance such as low density, high strength, high corrosion resistance, low modulus, inertness to human body environment and high capacity to bond with bone and other tissues [8–10]. After implantation of the implant, an interface is formed between the surface of the embedded implant material and the living tissue. Thus, various phenomena may appear at the interface when the biological material is implanted into the biological system [11]. The most remarkable impact is the corrosion of metallic implants, which has been observed in the aggressive biofluid [12,13]. This means that the leaching Ti ions and Ti particles release into the peri-prosthetic environment. Because the release of Ti ions may cause allergic, toxic and potentially carcinogenic responses, the bare pure Ti and its alloys cannot be proposed as the 'golden standard' for medical implants [14]. In addition, Ti and its alloys are inert materials without bioactivity in order to prevent ion release and improve biological activity of Ti. It is effective to endow the surface with chemically-stable and biocompatible coatings by various modification methods [15–17]. In view of the above-mentioned coatings, the hydroxyapatite (HA) coating is the most widely used in the clinical application of titanium implants [18–22]. However, the brittle HA coating has its disadvantages during the long-term service [23–26], which leads to cracking of composite coatings and peeling off from the substrate owing to the weak adhesion between HA and implants. In summary, these deficiencies limit its widespread application and popularization [27–30].

Besides, various methods have been used to improve surface performances of Ti implant [31–35], which are roughly divided into three different categories according to their characteristics. Although many of the methods mentioned above have been clinically applied, there are still many existing limitations such as interfacial separation, substrate deformation, spallation and cracking of compound layer. In order to solve this problem, the development of new modification techniques and new coating technologies is an effective way to improve the surfaces performance of Ti and its alloys.

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It is well established that the phosphate chemical conversion (PCC) method is widely used in engineering to manufacture protective coatings for steel and magnesium alloy [36–38]. This approach offers many attractive features, such as low-cost, easy operation, high corrosion resistance, rapid deposition and applicability to irregular shapes. What is more, the PCC coatings are chemically-stable and strongly combined to the metal surface [39].

Furthermore, it is a tendency that zinc (Zn) PCC technology is introduced as a new method to modify surface of medical implants, because the Zn PCC coating has already been proved safe and effective in the enhancement of the surface performance of metallic implants [40–43]. Noteworthily, the main product of Zn PCC is hopeite, which has been reported to enhance bone growth and facilitate formation of HA efficiently in the simulated body fluid (SBF) [44,45]. As a potential material for biomedical applications, hopeite has recently been identified to be osteogenic and biocompatible [46]. It has been confirmed that cells can adhere and spread well on the hopeite prepared by Zn PCC on Ti.

In addition, hopeite can be fabricated into various coatings with different roughness microstructure by adjusting the technological parameters, which is helpful for the attachment and proliferation of various cells [47,48]. Therefore, it can be suggested that Zn PCC can play a critical role in enhancing the protectivity and biocompatibility of titanium-based implants.

Although Zn PCC technology has attracted more attention as a potential surface modification method of biomedical metal. However, it is almost impossible to prepare a phosphating film on Ti by the conventional PCC methods due to the presence of the passive oxide film on its surface. In view of this, several methods such as hydrothermal treatment, induction deposition by galvanic coupling and Fe^{2+} ions are developed to prepare PCC coatings on titanium [49–51]. High temperature and longtime conversion still limit its application, although the above methods for preparing PCC on titanium surface are feasible.

Taking into account the above requirements, electrolysis induction may be beneficial for chemical deposition of Zn phosphate on titanium surfaces. Electrolysis intervention leads to the polarization of the titanium surface. When the polarization potentials reach a certain value where hydrogen evolution reaction can occur, the pH around the electrode interface changes [52], which would accelerate nucleation and growth of the PCC coating. According to the relevant literature, electrochemical approaches have been successfully applied to the surface treatment of metallic materials, such as the modification of protective coatings on the surface of metallic materials [53], the formation of quenched layers on metal surfaces [54], and the phosphating of passivated steels and other materials [55–59].

In this paper, the effect of electrolysis induced rapid formation of PCC coatings on Ti is investigated. The effects of voltage as well as temperature on the microstructures and properties of coating are researched. We also explained the detailed transformation mechanism of the EPCC coating. The aim of this study is to develop a simple and efficient method for surface modification of titanium-based biomedical materials.

2. Experimental

2.1. Materials and preparation

The matrix material of this paper was commercially available pure titanium, whose diameter and thickness were 10 mm and 2 mm, respectively. The pure titanium disks pretreatment methods are the same as our previous work [43,60]. Firstly, it was sanded to a 600 mesh silicon carbide with the purpose of retaining a certain degree of roughness to facilitate chemical conversion. Then degreasing with NaOH solution at 60 °C for 15 min. Afterwards, the samples after ultrasonic cleaning in acetone and deionized water were placed in HF aqueous solution for activation at room temperature for 30 s, rinsed with deionized water. Finally, the samples were activated in 5 g/L Ti colloids solution ($Na_4TiO(PO_4)_2$) at room temperature for 30 s before EPCC process.

2.2. Chemical conversion procedure

In the present work, the Ti disk were treated with PCC solution composed of ZnO: 7 g/L, H_3PO_4: 35 g/L, $Zn(NO_3)_2{\cdot}6H_2O$: 5 g/L, $Ca(NO_3)_2{\cdot}4H_2O$: 5 g/L and accelerants: 5.5 g/L. The PCC process was assisted with a DC voltage-stabilized Source, which is called EPCC. The as-prepared titanium samples were set as the cathode while the platinum electrode was used as the anode. The EPCC were performed at 30 °C and 90 °C for different times between 1 min and 15 min, respectively. Meanwhile, the cell potential was held constant at 3 V and 5 V, respectively. During the EPCC process, the pH of the conversion solution was controlled between 2.5 and 3.0 using sodium hydroxide or phosphoric acid. After the EPCC treatments, the samples were rinsed with deionized water and dried in warm air.

2.3. Characterization methods

The phase composition was observed through a X-ray diffractometer (XRD, Rigaku D/max-γB) equipped with CuKα radiation with a scan speed of 4°/min. The operating voltage and current of XRD were 40 kV and 100 mA, respectively. The microstructures of the EPCC coatings were characterized using SU-70 field emission scanning electron microscope (FE-SEM) operating at 15 kV. Besides, an energy dispersive spectrometer (EDS) configured on the FE-SEM was also used.

In addition, the functional groups of the EPCC coating were characterized using a Fourier transform infrared spectrometer (FTIR, BRUKER TENSOR 37), and the tested spectrum ranged from 4000 to 400 cm^{-1}. In the FTIR analysis, the coating scraped off the Ti surface is thoroughly ground and mixed with KBr. The adhesion of the coating was measured by a scratch meter (WS-2005, CAS, China). Scratch method is carried out with friction force mode using continuously increasing load to 40 N in 1 min. In this study, a JEM-2100 high-resolution transmission electron microscope (HRTEM, JEOL) with an accelerating voltage of 200 kV was used to observe the morphology of the samples and the electron diffraction pattern of the selected region. Electrochemical measurements with a classical three-electrode setup (Autolab PGSTAT302N) were performed to identify corrosion characteristics of EPCC coatings. Which were carried out in 0.9 wt% NaCl aqueous solution. In the three-electrode system, the working electrode is a sample with an exposed area of 1 cm^2, the reference electrode is saturated calomel electrode (SCE), and the counter electrode is platinum.

3. Results and discussion

3.1. The phase composition

The XRD analysis of the electrolysis conversion coating prepared with different temperature and time is presented in Fig. 1. For comparison purposes, the main indices of crystal face have been marked on the XRD spectrum. The result shows that there is obvious difference in phase composition at different temperature. Another notable phenomenon is that the coatings formed at the same temperature for different times have the similar phase structure.

Fig. 1(a) shows the XRD patterns of the EPCC coatings formed at 30 °C for 1 min and 15 min, respectively. When the conversion time is 1 min, it reveals that the XRD peaks of Ti substrate are visible, while the diffraction peak of the coating is very slight. This proves that the coating formed at 1 min is extremely thin.

As the conversion time increases from 1 min to 15 min, the corresponding diffraction peaks of coatings are enhanced. Obviously, regardless of the conversion time, the coatings formed at 30 °C are mainly