



Facile preparation of hopeite coating on stainless steel by chemical conversion method

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ABSTRACT

Chemical conversion process has attracted more attention in recent years due to its significant potential use in biomedical areas such as surface modification of metal implants. In this study, uniform and fine coatings were fabricated on stainless steel 304 (304 SS) substrates using phosphate chemical conversion (PCC) treatment. The Fe^{2+} ions were introduced to initiate the coating formation. The experimental results showed that the coatings were composed of hopeite ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$) with minor phosphophyllite ($\text{Zn}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$), with a crystal size of 2–4 μm . The substrates were fully covered with the coatings after PCC treatment at 70 °C for 30 and 45 min with the coating mass of 4.08 and 6.48 g/m^2 , respectively. Adhesive test indicated that the PCC coating was strongly attached on the substrate. The electrochemical analysis revealed that the as-prepared coatings imparted better corrosion resistance to the substrate.

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1. Introduction

Stainless steels have been widely used in engineering and biomedical fields due to their good corrosion resistance, low cost, workability and excellent mechanical performances [1–3]. However, corrosion behavior of stainless steels has been observed in aggressive medium and in the body fluid, which can lead to the pitting corrosion and the release of undesirable ions [4–6]. Therefore, it is necessary to endow them with a protective and biocompatible coating through surface modification. Nowadays, there are many reported methods for surface modification, such as plasma spraying [7], electrochemical [8], electrodeposition [3] and ion implantation methods [9]. However, phosphate chemical conversion (PCC) is regarded as an ideal way to facilitate further coating and painting, and to improve surface corrosion resistance, wear resistance and so on [8,10,11] as it exhibits many advantages such as low-cost, rapid coating formation and suitable for treatment of irregular surface. Moreover, the resultant coatings are contiguous and highly adherent to the underlying metal [11].

As a potential versatile biomedical material, hopeite could enhance bone growth [12,13]. The main composition of zinc phosphate conversion coating is hopeite ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$), which is also an important phase in hardened zinc phosphate bone cement. Besides, hopeite powder could be transformed into hydroxyapatite (HA) by chemical treatment in calcium nitrate solution [12]. It is reported that the hopeite layer efficiently facilitated re-growth of HA in the simulated body fluid

(SBF) [14]. Therefore, it is expected that the hopeite conversion coating would improve protective and osteogenic performances of metal implants.

Usually, it is difficult to deposit a phosphate coating on stainless steels by a traditional chemical conversion method due to the passive oxide layer on their surface, even after 30 days of immersion [3]. For this reason, many methods including electroplating, electrophosphating and hydrothermal treatments were adopted to fabricate PCC coatings on stainless steels [8,10,11,15]. In this paper, we reported on the fabrication of uniform and fine hopeite coatings on a stainless steel 304 (304 SS) substrate by a traditional chemical conversion method with the addition of Fe^{2+} curing process. The morphology, phase and coating mass of the coating were investigated. The polarization curves were also examined. The aim of this study is to develop a facile PCC method for the surface modification of biomedical metals.

2. Materials and method

2.1. Chemical conversion process

Commercially available 304 SS specimens were used as substrates with the size of 10 mm × 10 mm × 1 mm. The specimens were abraded using a 240-grit emery paper, followed by degreasing in an 80 g/L sodium hydroxide solution at 60 °C for 15 min. Then, pickling was performed on the specimens in a solution containing 30%V/V of hydrochloric acid at room temperature for 1 min. Afterwards, activation was performed in a solution of 3 g/L Ti colloids ($\text{Na}_4\text{TiO}(\text{PO}_4)_2$, commercially obtained) at room temperature for 30 s.

The samples were then immersed in a bath with the composition of zinc oxide: 25 g/L, phosphoric acid (85%): 8 mL/L, nitric acid: 30 mL/L,

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nickel nitrate: 0.2 g/L and citric acid: 8 g/L at 60 °C and 70 °C for duration times of 5–45 min. Before the immersion process, the bath solution, with the pH value of 2.0, was cured with a 10 g/L pure iron powder (AR, 98%) at room temperature for 24 h. The aim of the curing process was to dissolve part of the iron powder and increase the concentration of Fe^{2+} in PCC bath. After curing, the remaining pure iron powder was removed. Finally, the coupons were washed with distilled water and dried by blowing air at room temperature.

2.2. Physical and microstructural characterization

A digital scale with an accuracy of ± 0.1 mg was used for the determination of the weight of the samples.

The coating mass (M , g/m^2) was calculated according to Eq. (1):

$$M = \frac{m_1 - m_2}{A} \quad (1)$$

Where m_1 and m_2 are the weights (g) before and after stripping the coatings in a stripping medium, respectively, and A is the area of the substrates (m^2). The stripping was performed in a solution containing 50 g/L of chromium trioxide at 70 °C for 10 min. The results were the average value of five measurements.

The microstructures of the coatings were studied using a SU-70 field emission SEM (FE-SEM) equipped with an energy dispersive spectrometer. The phase analysis of the coatings was carried out using a Rigaku D/max- γB X-ray diffractometer (XRD), with a scan speed of $4^\circ/\text{min}$ between 5 and 75° 2θ angle and $\text{CuK}\alpha$ radiation, operated at 40 kV and 100 mA. Scratch tests were carried out using a WS-2004 scratch tester. A maximum load of 100 N was applied at a loading speed of 8 N/min and a table speed of 4 mm/min.

2.3. Electrochemical evaluation

The corrosion resistance of the samples was evaluated by electrochemical measurements, which were carried out using a classical three electrode cell with platinum as the counter electrode, saturated calomel electrode (SCE) as the reference electrode and the uncoated or coated samples with an exposed area of 1 cm^2 as the working electrode. The corrosive mediums of 0.9 wt.% sodium chloride were used. The potentiodynamic curves were obtained using a Parstat potentiostat model 2273 at a constant voltage scan rate of 1 mV/s.

3. Results and discussion

3.1. Coating mass

Fig. 1 shows the coating mass of PCC samples conducted at 70 °C for different times. It is clearly observed that the coating mass increases with the reaction time. As time increased from 5 min to 45 min, the coating mass increased from 1.33 to $6.48 \text{ g}/\text{m}^2$. However, the coating formation shows a non-linear fashion. It was a slow increase initially, and then the growth rate quickly increased with time. This is due to a relatively low nucleation rate at the initial stage, owing to the remaining oxide film on the substrate surface. Afterwards, the rate of nucleation increases rapidly with time [11]. At the same time, the crystal growth, reorganization and the secondary crystallization contributed to the increase of coating mass [11]. Usually, the coating mass rather than the coating thickness has been adopted to measure the coatings due to the uneven nature of the substrate and the coating [11]. A coating mass versus time curve can reveal the efficiency of the pretreatments of the substrate and that of the conversion solution. However, it is noticeable that no coating formed on the substrates if there was no Fe^{2+} ion introduced into the PCC solution.

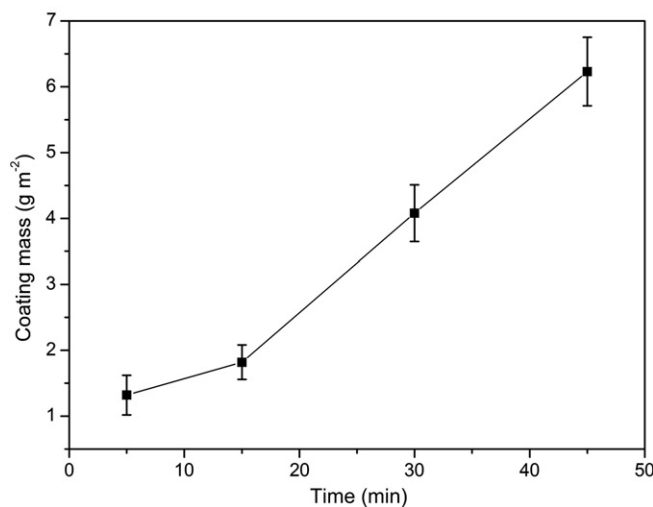


Fig. 1. The relationship between coating mass and time for 304 SS samples PCC treated at 70 °C.

3.2. Phase analysis

The typical XRD pattern of the PCC coatings is shown in Fig. 2, which was obtained at 70 °C for 30 min. It can be seen that the coating consists of hopeite and minor phosphophyllite. It is reported that hopeite is biocompatible, which could facilitate bone growth [12]. Based on this, more efforts have been paid on chemical conversion coating with hopeite formation [3,8,12,15–18]. Besides, hopeite is thought to be a potential versatile biomedical material [12,13] and an alternative to HA [19]. Phosphophyllite has better corrosion resistance than that of hopeite due to its chemical stability [20].

3.3. Microstructural characterization

Fig. 3 shows the FE-SEM micrographs of PCC coatings treated at 60 and 70 °C for 30 min, respectively. It is obvious that the coatings exhibited a fine structure with granular crystals of about 2–4 μm . It can be seen that the substrate surface was fully covered with crystals at 70 °C whereas the substrate surface could not be fully covered with crystals at 60 °C. Moreover, the coating obtained at 70 °C shows a finer structure than that obtained at 60 °C.

The microstructural images of the coatings obtained at 70 °C for different times are shown in Fig. 4. It reveals that all the coatings show

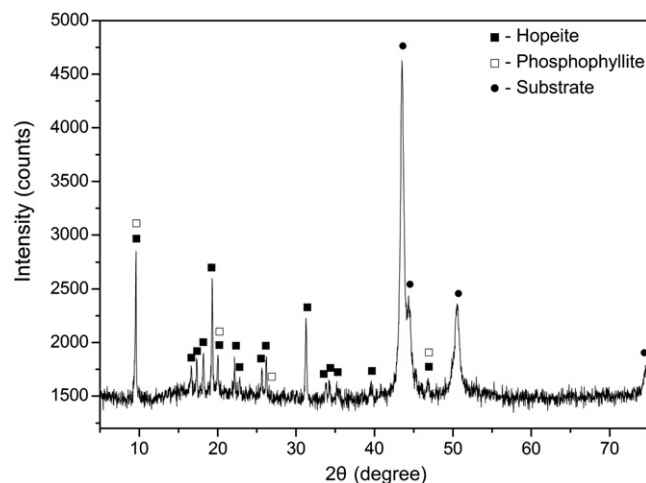


Fig. 2. XRD pattern of 304 SS samples PCC treated at 70 °C for 30 min.

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