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Short communication

Preparation of hydroxyapatite coating by the use of a sacrificial Mg anode method

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Abstract

A sacrificial anode method was introduced into the preparation process of a hydroxyapatite (HAP) coating on a Ti alloy (TAMZ) surface. Fourier transform infrared spectra (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM) were applied to characterize the coatings. A $CaHPO_4{\bullet}2H_2O$ layer formed on TAMZ at the initial stage, and later it was transformed into HAP through a steam treatment. According to SEM, the HAP coating was composed of needle-like, feather-like and sheet-like crystals.

Keywords: Hydroxyapatite coating; Sacrificial Mg anode; Hydrothermal treatment; TAMZ Ti alloy

1. Introduction

Due to their excellent bio-compatibility and corrosion resistance, bioactive ceramic hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAP) coatings are extensively applied onto surgical metallic implants, and their preparation techniques have been a subject of extensive research. The most widely applied method is plasma spray. During the spraying operation, however, HAP may decompose due to the high temperature involved, which can result in a complex coating composition and lower properties.

Several low temperature preparation methods of HAP coating had been developed [1–3]. Electrochemical deposition and the hydrothermal synthesis method, which was proposed by Shirkhanzadeh [4] in 1995, showed obvious advantages owing to its low temperature operation. During deposition, a potential or impressed current was applied to the metallic substrate to induce coating deposition. Since this process involves an electrochemical reaction, i.e. electrons translate from the other electrode, it is reasonable to expect that it can be modified by introducing a sacrificial anode. Rather than providing electrons by a power supply, the sacrificial anode could transfer electrons to the substrate directly. Based on this concern, a sacrificial Mg anode method was introduced into the preparation of HAP coating on a Ti alloy (TAMZ) in the present work. In addition, Fourier transform infrared spectra (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to examine the coatings.

2. Experimental

The experimental materials were TAMZ (Ti 92.5%, Al 2.5%, Mo 2.5% and Zr 2.5%, wt.%) and a standard sacrificial Mg anode (GB/T 17731-2004, China). The electrolyte used for coating deposition was prepared by mixing 0.042 mol/L $Ca(NO_3)_2$ and 0.025 mol/L $NH_4H_2PO_4$ solutions. All solutions were prepared by analytical reagents and distilled water.

TAMZs were machined into slices 60 mm × 10 mm × 1 mm in size; the size of the Mg anode was 30 mm × 20 mm × 20 mm. All the samples were polished by silicon carbide abrasive paper, rinsed with deionised water, degreased with pure alcohol and dried by air. Then a TAMZ sample and an Mg anode were immersed into the solution after the temperature reached the designed value (40 °C). The schematic diagram for the experimental set-up is displayed in Fig. 1. After several hours, the TAMZ sample was removed from the solution. The obtained coating, termed as initial coating, was then steam treated at 150 °C for 8 h in an autoclave. The finally obtained coating was termed as treated coating. Both coatings were examined by FTIR and XRD. The morphology of the treated coating was observed by SEM.

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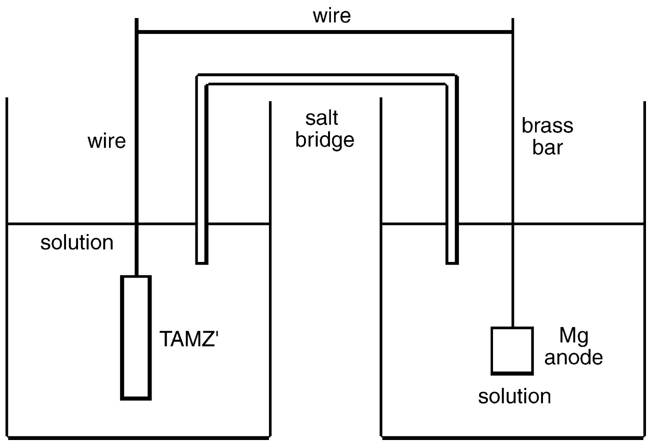

Fig. 1. Experimental set-up schematic diagram.

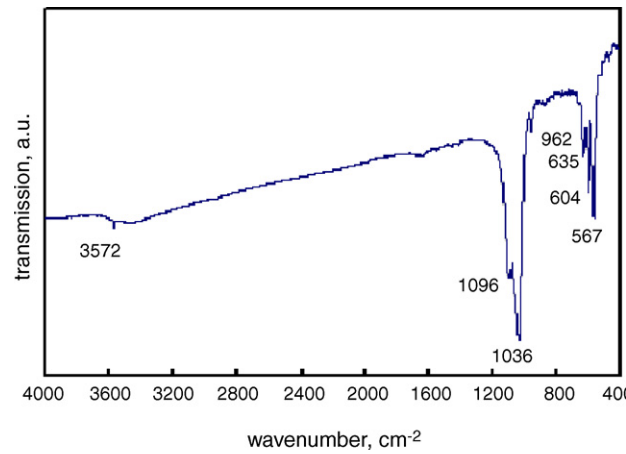

Fig. 4. FTIR spectrum of the treated coating on TAMZ surface.

3. Results and discussion

Fig. 2 shows the FTIR spectrum of the initial coating. The bands at 1649, 3165, 3289, 3489 and 3543 cm^{-1} were modes of adsorbed water. The band shown at 874 cm^{-1} was due to the vibration of HPO_4^{2-}, and the peaks around 500–700, 900–1200 cm^{-1} are characteristic of PO_4^{3-}. Fig. 3 displays the XRD pattern of the initial coating, which greatly matches the XRD pattern of $CaHPO_4{\bullet}2H_2O$. From the results of FTIR and XRD, it can be confirmed that the initial coating is composed of $CaHPO_4{\bullet}2H_2O$ crystals.

The treated coating was also analysed by FTIR and XRD methods. As shown in Fig. 4, the stretching and librational modes of hydroxyl in HAP, i.e. the peaks at 3572 and 635 cm^{-1}, both appeared, although the band at 3572 cm^{-1} was not quite sharp. Also, in the XRD pattern of the treated coating (Fig. 5) 002, 102, 211 and 112 reflections of HAP could be indexed. According to these results, it could be concluded that the coating formed during the initial stage had transformed into HAP after the steam treatment.

The treated coating (Fig. 6) is composed of needle-like, feather-like and sheet-like crystals. Pores are also observed.

Based on the above results, the reaction mechanism involved in the formation of the initial coating was as follows.

$$\text{Anodicreaction}: \quad Mg \rightarrow Mg^{2+} + 2e$$

$$\text{Cathodicreaction}: \quad H_2O \rightarrow H^{+} + OH^{-}$$

$$2H^{+} + 2e \rightarrow H_2\uparrow$$

$$OH^{-} + H_2PO_4^{-} \rightarrow HPO_4^{2-} + H_2O$$

$$Ca^{2+} + HPO_4^{2-} + 2H_2O \rightarrow CaHPO_4{\bullet}2H_2O\downarrow$$

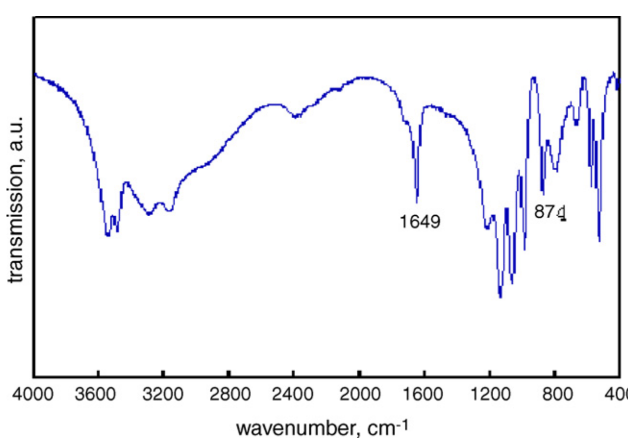

Fig. 2. FTIR spectrum of the initial coating on TAMZ surface.

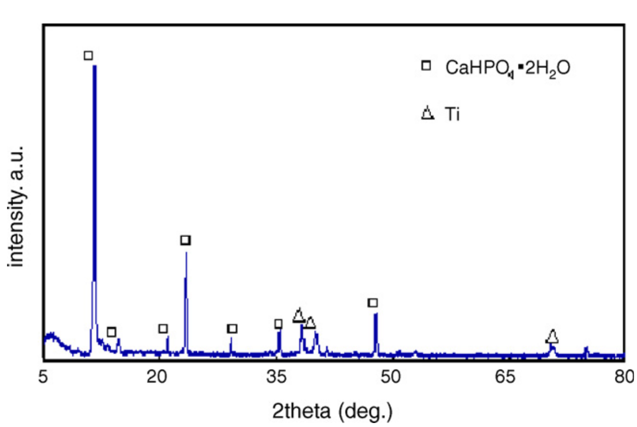

Fig. 3. XRD pattern of the initial coating on TAMZ surface.

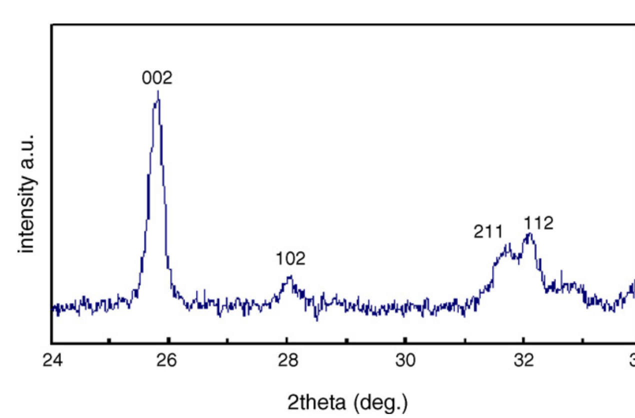

Fig. 5. XRD pattern of the treated coating on TAMZ surface.

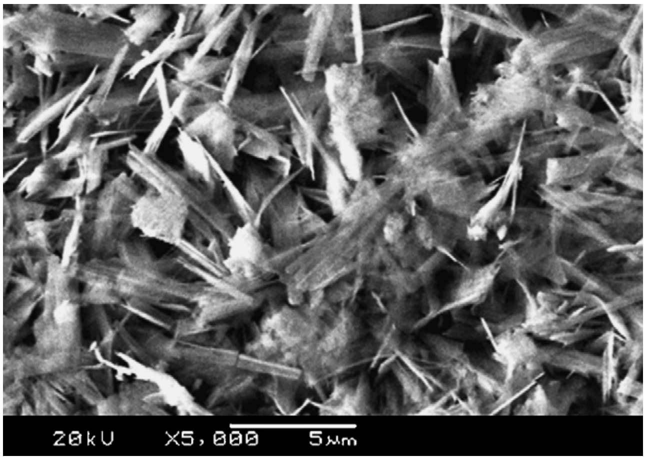

Fig. 6. Morphology of the treated coating on TAMZ surface.

The initial coating transformed into HAP after steam treatment by the following reaction:

$$10CaHPO_4{\bullet}2H_2O + 12OH^- \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 4PO_4{}^{3-} + 30H_2O$$

4. Conclusions

(1) An HAP coating was successfully prepared on a TAMZ alloy by using a low temperature sacrificial anode method.
(2) The HAP coating was composed of needle-like, feather-like and sheet-like crystals.

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