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Microwave assisted deposition of hydroxyapatite coating on a magnesium alloy with enhanced corrosion resistance

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ABSTRACT

In this work, a thick, dense and uniform microstructural hydroxyapatite coating was deposited on a magnesium alloy in an aqueous solution under microwave irradiation at 100 °C in a short time of 10 min. The results showed that the high driving force of interfacial growth under microwave irradiation greatly promoted the growth of hydroxyapatite nuclei into rod-like crystals, and the thickness of obtained hydroxyapatite coating was ~9.9 μm, larger than that of ~6.3 μm derived by water-bath heating. The coating derived by microwave heating offered preferable corrosion resistance for the magnesium alloy compared with the coating derived by water-bath heating. The corrosion current density of the coated magnesium alloy was reduced by 100-fold as compared to the naked magnesium alloy.

1. Introduction

Biodegradable magnesium alloys have attracted significant concerns as promising temporary implants by virtue of their excellent mechanical compatibility and biocompatibility [1]. Unfortunately, severe corrosion, as an intrinsic response of these alloys with human body fluids, results in a quick decline of mechanical integrity and high level of local pH surrounding human tissues [2,3]. Among bioactive ceramics, hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) has been proved effective to be protective coatings on magnesium alloys to improve the corrosion resistance and biocompatibility [4].

Recently, a mild aqueous chemical route has been developed to synthesize HA coatings on magnesium alloys [5,6]. However, the synthetic route is rather time-consuming and usually takes hours to days. Many researchers reported that microwave irradiation can remarkably shorten the reaction time in polar molecules involved systems [7]. Thus, in order to facilitate a rapid deposition of HA coatings on the substrates, microwave heating was applied as an alternative to the conventional electric heating in the aqueous chemical route. In this work, the influence of heating methods, i.e., microwave heating and water-bath heating, on the phase, morphology and corrosion resistance performance of the deposited HA on magnesium alloys was investigated.

2. Experimental procedure

Commercial AZ31 magnesium alloy strips of 10 mm × 10 mm × 2 mm were used as substrates, which were ground with SiC papers to 2000 grit. Then the naked magnesium alloys were immersed in 1.5 M NaOH solution at 80 °C for 1 h. The coating solution was prepared using 0.153 g $Ca(NO_3)_2 \cdot 4H_2O$ and 0.050 g $Na_2HPO_4 \cdot 12H_2O$ as raw materials, which were consecutively added to 100 ml distilled water under continuously magnetic stirring at room temperature for 2 h, meanwhile pH of the solution was adjusted to 6.3 using 1 M HNO_3. The pretreatment process of the both types of samples (water-bath heating and microwave heating) was exactly the same. Total 10 alkaline-treated magnesium alloy strips were immersed into 100 ml coating solution in a beaker, which was covered by a Teflon lid. A thermocouple was inserted into the solution to measure temperature and microwave power was changing constantly between 0 and 2000 W to maintain the temperature of the solution at 100 °C for 10 min in a microwave chemical reactor with 2.45 GHz microwave frequency (Tangshan nano source microwave thermal instrument, China). Moreover, samples were also prepared by water-bath heating at 100 °C for 10 min for comparison. The phase and morphology of the samples were characterized using X-ray diffraction (XRD, D/Max-2500 Rigaku) and scanning electron microscopy (SEM, S-4800, Hitachi). The electrochemical corrosion behavior was investigated in simulated body fluid (SBF) at 37 °C and five parallel samples were tested to ensure repeatability. The

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detailed process was recorded in our previous study [8].

3. Results and discussion

XRD patterns of the coated magnesium alloys prepared by microwave heating and water-bath heating and the naked magnesium alloy were shown in Fig. 1. Except for magnesium diffraction peaks (JCPDS no. 35-0821), HA diffraction peaks at 2θ of 25.9° and 32.2° were observed for both coated magnesium alloys, indicating that impurity-free HA coatings were successfully deposited on the magnesium alloys by the two different heating methods. Furthermore, it was found that the relative intensity of diffraction peaks of $(002)_{HA}$ plane to $(300)_{HA}$ plane of the HA coating derived by microwave heating was higher than that of the standard powder diffraction profile of hexagonal HA (JCPDS no. 74-0566), suggesting an orientated growth to the *c*-axis direction of HA crystals under microwave irradiation.

Although the obtained coatings had the same phase composition, the morphologies of HA coatings prepared by microwave heating and water-bath heating are significantly different as shown in Fig. 2. At low magnification, a relative uniform and dense structure was observed for the microwave heating derived coating (Fig. 2a), while the coating derived by water-bath heating exhibited a flat morphology with a few large globules randomly dispersed on the coating surface (Fig. 2d). At high magnification, it was found that rod-like HA crystals with diameter of ~80 nm and length of ~500 nm were stacked to form a flower-like structure (Fig. 2b). However, the large HA globules obtained by water-bath heating were constituted by plate-shaped grains (Fig. 2e). As for cross-section morphologies of the HA coatings, the thickness of the microwave heating derived coating was ~9.9 μm and no remarkable interface between the coating and magnesium alloy substrate was observed in Fig. 2c. However, the coating derived by water-bath heating exhibited a lower thickness of ~6.3 μm (Fig. 2f). Interestingly, a HA globule was embedded and some micro-cracks occurred in the whole coating matrix (indicated by the white arrows), which might result from the residual stress involved due to the difference of Young's modulus between the large HA globules and coating matrix. The large HA globules dispersed on the surface of the water-bath heating derived coating seriously decreased the homogeneity of the coating, probably having a negative effect on the protective effect of the HA coating to the underlying magnesium alloy.

In principle, precipitation of HA coatings from aqueous solution consists of two processes: nucleation and crystal growth. The driving force for the above two processes can be expressed as the relative supersaturation [9] and will increase with the increase of solution temperature and pH [10]. Once the coating solution boiled (100 °C), HA nuclei would be immediately formed (solution changing from clear to milky). It can be assumed that at this stage the driving force in the two different heating methods was equivalent with the same pH and solution temperature.

In the case of crystal growth, the driving force in the two heating methods seemed different. According to Cahn's theory [11], low driving force promotes the interface to move laterally resulting in a face by face growth and the obtained HA exhibits a plate-shaped morphology. However, high driving force facilitates the interface to move normal to itself leading to a spiral growth and rod-like HA is achieved. In water-bath heating of this work, the driving force was considered not high enough, thus plate-shaped HA crystals were precipitated, then continuously wrapped and agglomerated into large globules to reduce the overall surface energy. In microwave heating, higher driving force of interfacial growth was gained, which was manifested by Haque et al. that microwave heating could decrease the activation free energy (ΔG)

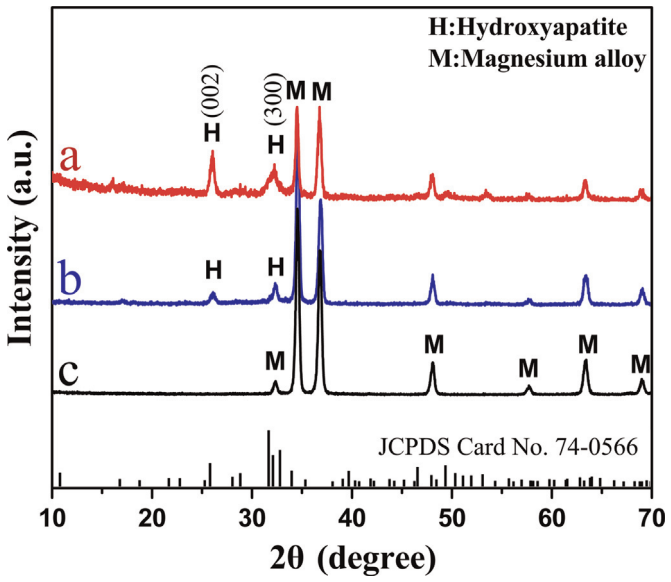

Fig. 1. XRD patterns of the coated magnesium alloys prepared by microwave heating (a), water-bath heating (b), and naked magnesium alloy (c).

compared with the conventional heating [12]. Consequently, rod-like HA crystals were formed. Moreover, the deposition process was accelerated due to the enhanced HA nuclei transport rate in the solution under microwave irradiation [13], thus a thicker HA coating was deposited on the substrate.

In general, proper compactness and thickness endow protective coatings with favorable corrosion resistance for magnesium alloys [14]. In order to evaluate the protective effects of the obtained HA coatings, electrochemical impedance spectroscopy and potentiodynamic polarization tests were conducted in SBF and the results were shown in Fig. 3. Compared with water-bath heating, the sample derived by microwave heating exhibited larger E_{corr} of −1.37 V (−1.42 V for water-bath derived sample), smaller i_{corr} of 1.51 μA cm^2 (~2.6 times lower than that of water-bath derived sample) and larger charge transfer resistance (R_t) of 43,292 Ω cm^2 (16,811 Ω cm^2 for water-bath derived sample). In addition, taking into consideration of the micromorphology of the two types of HA coatings, microwave heating provided a more uniform and denser surface structure. More importantly, the coating derived by microwave heating showed a large thickness and an ideal Mg alloy/coating interface without microcracks. It was convinced that the coating derived by microwave heating could retard the cracking and peeling of HA coatings and finally avoid the penetration of body fluids into the magnesium alloy during implantation, thus obtaining an excellent long-term corrosion resistance performance.

4. Conclusion

In summary, the high driving force of interfacial growth under microwave irradiation promoted the growth of hydroxyapatite nuclei into rod-like crystals, stacking to form a flower-like structure. The deposited HA coating with a large thickness and uniform structure provided high corrosion resistance performance for the magnesium alloy. Therefore, this microwave assisted approach may find a wide range of applications in preparing other bioactive coatings, such as MgP on magnesium alloys to improve the corrosion resistance and biological properties.