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Fabrication and characterization of a hydroxyapatite–methylcellulose composite coating on the surface of AZ31 magnesium alloy

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ABSTRACT

Magnesium alloys are attracting attention as materials for use in biological applications. In this work, Ca$(OH)_2$ and $Ca(H_2PO_4)_2 \cdot H_2O$ are used as raw materials, and methylcellulose is used as an additive, to prepare a hydroxyapatite–methylcellulose composite coating on the surface of AZ31 magnesium alloy using a sol–gel technique. Phase analysis, a surface morphology study, and cross-section and microstructure characterization of the hydroxyapatite–methylcellulose composite coating are presented. Potentiodynamic polarization curves and corrosion morphologies of the coating are also presented. The results indicate that the thickness of the hydroxyapatite–methylcellulose composite coating is approximately 60 μm and the composite coating could improve the biodegradation property of AZ31 magnesium alloy effectively.

1. Introduction

AZ31 magnesium alloy has attracted extensive interest in the field of biological materials due to its small density and high mechanical strength [1,2]. However, its application in the biomedical field is limited by its poor corrosion resistance and high degradation rate [3]. To solve this problem, some surface modification methods [4,5], such as electrophoretic deposition [6], electrodeposition [7,8], and chemical conversion [9], have been researched recently. Hydroxyapatite (HAP) has received widespread attention as a bioactive material [10–12]. A HAP coating on the surface of a magnesium alloy not only improves the corrosion resistance of the magnesium alloy and delays its degradation rate, but it also gives the material some excellent mechanical properties [3,4,13]. Methylcellulose (MC) can be used to stabilize the HAP coating because of its good viscosity and film properties.

The purpose of this study was to develop a stable composite coating on the surface of AZ31 to slow down the biodegradable rate. $Ca(OH)_2$ and $Ca(H_2PO_4)_2 \cdot H_2O$ were utilized as raw materials to prepare the HAP–MC composite coating on the surface of AZ31 via the sol–gel technique. Comparison and analyses of the phase compositions, surface morphologies, and cross sections of the HAP and HAP–MC coatings are presented. The corrosion resistances of the specimens were also investigated.

2. Experimental procedure

Rolled AZ31 alloy of dimensions 20 mm × 20 mm × 1 mm was used as the substrate material in this study. The samples were prepared by grinding with successively finer silicon carbide abrasive paper up to grit #1000, and the samples were ultrasonically cleaned in acetone for 10 min. Then, the specimens were immersed into 4% phosphoric acid solution for 10 s and successively cleaned in alcohol and double distilled water for 10 min.

A supersaturated aqueous solution of $Ca(OH)_2$ was placed in a water bath at 70 °C. Then, the $Ca(H_2PO_4)_2 \cdot H_2O$ solution was added dropwise to the Ca precursor to prepare a solution containing Ca:P at a ratio of 1.67:1. The final solution was stirred at 500 rpm for 1 h and then divided into two solutions: one was used for preparing the HAP coating and the other was added to a moderate 2% MC aqueous solution for preparing the HAP–MC coating. The substrates were dipped into the solutions for 2 min and then withdrawn at a continuous speed of 0.5 mm/s. The two coated samples (one for each solution) were gradually heated to 80 °C and preserved for 1 h. The two samples were heated to 200 °C for 30 min and then cooled in a furnace.

TD-3500 X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectra were used to analyze the phase compositions of the coatings. A JSM-6700F scanning electron microscope (SEM) was utilized to observe the microstructures and morphologies of the coatings. A CS-350 electrochemical workstation was used to provide polarization curves of the coatings in NaCl solution. The biodegradable behavior was measured by immersion tests in the

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stimulated body fluid (SBF) at 37 °C with exposed area 1 cm^2. SBF is composed of 8.0 g/l NaCl, 0.4 g/l KCl, 0.14 g/l $CaCl_2$, 1.0 g/l $C_6H_{12}O_6$, 0.35 g/l $NaHCO_3$, 0.1 g/l $MgCl_2 \cdot 6H_2O$, 0.06 g/l $MgSO_4 \cdot 7H_2O$, 0.06 g/l KH_2PO_4 and 0.06 g/l Na_2HPO_4 [7].

3. Results and discussion

Fig. 1a depicts the XRD patterns of the HAP and HAP–MC coatings on the surface of the AZ31 alloy. The curve (a) shows sharp diffraction peaks of magnesium, while the peaks of HAP are inconspicuous, which suggests that the thickness of the HAP coating is thin. The curve (b) reveals typical diffraction peaks of hydroxyapatite (PDF no. 09-0432) at diffraction angles (2θ) of 25.9°, 31.8°, 32.2°, 32.9°, 39.8°, and 49.5°, which demonstrates that the MC is good for increasing the thickness of the coating and the binding force between the coating and substrate. Fig. 1b shows the FTIR spectra of the samples. The FTIR curve of pure MC powder is shown in the curve (a). It is noted that the peak at 3486 cm^{-1} is the O–H (stretching mode) band and the peaks at 2981 cm^{-1} and 2887 cm^{-1} are the C–H (stretching mode) band, while the peak at 1645 cm^{-1} [4] is the O–H (bending mode) band. The curve (b) shows

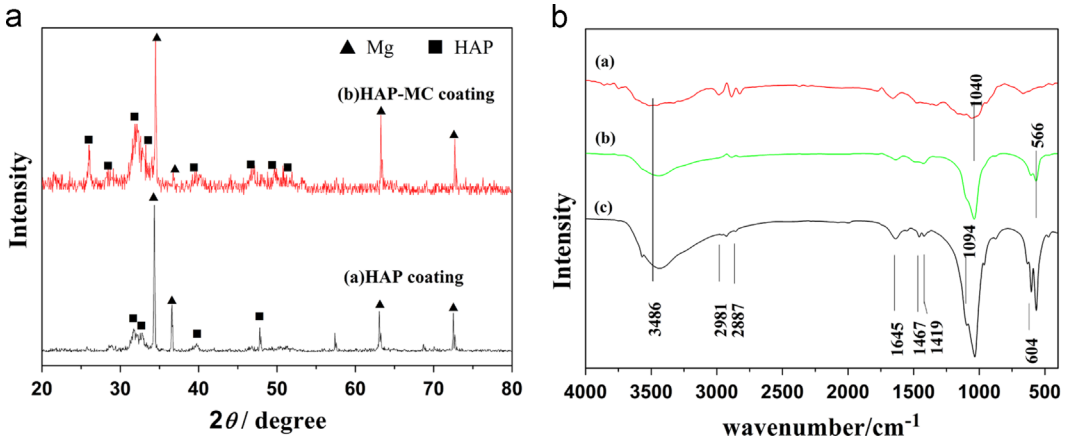

Fig. 1. a: X-ray diffraction patterns of different samples (a) HAP coating; (b) HAP–MC coating; b: FTIR spectra of different samples (a) MC; (b) HAP; (c) HAP–MC.

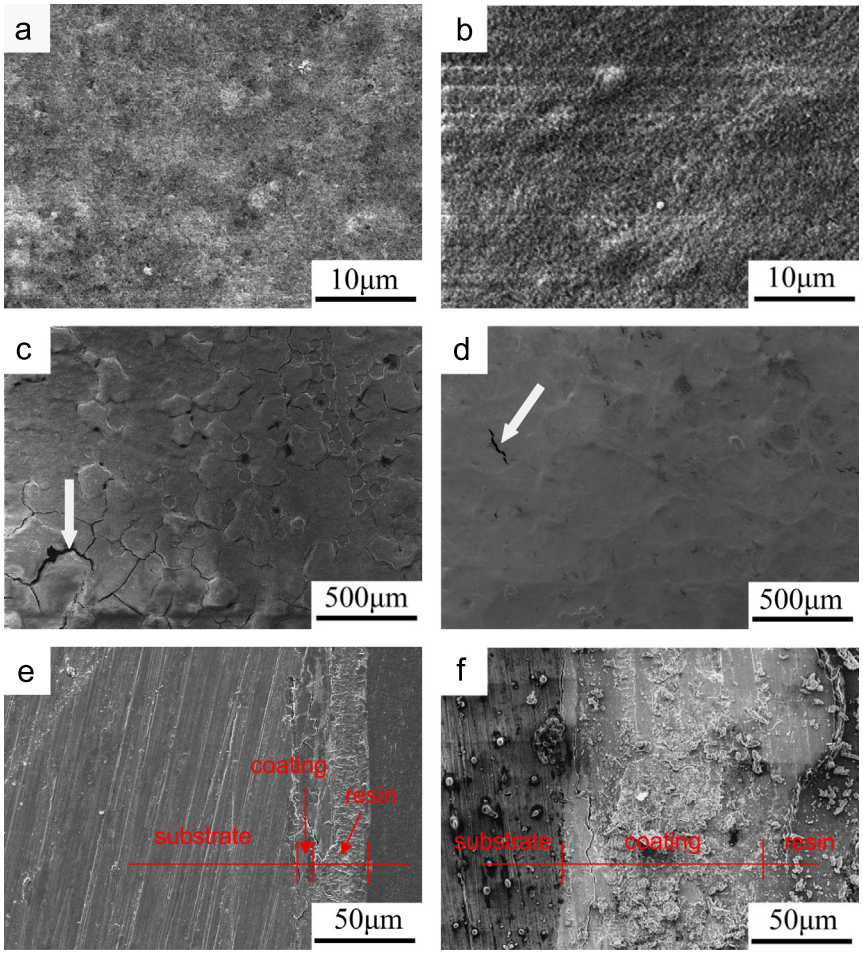

Fig. 2. SEM micrographs of HAP coating and HAP–MC coating: (a, b) microstructure; (c, d) macrostructure; (e, f) cross section.