Research Article

Preparation and Characterization of Hydroxyapatite Coating on AZ31 Mg Alloy for Implant Applications

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Magnesium alloys as biodegradable metal implants in orthopaedic research received a lot of interest in recent years. They have attractive biological properties including being essential to human metabolism, biocompatibility, and biodegradability. However, magnesium can corrode too rapidly in the high-chloride environment of the physiological system, losing mechanical integrity before the tissue has sufficiently healed. Hydroxyapatite (HAp) coating was proposed to decrease the corrosion rate and improve the bioactivity of magnesium alloy. Apatite has been cathodically deposited on the surface of Mg alloy from solution that composed of 3 mM Ca(H₂PO₄)₂ and 7 mM CaCl₂ at various applied potentials. The growing of HAp was confirmed on the surface of the coatings after immersion in SBF solution for 7 days. The coating obtained at −1.4 V showed higher corrosion resistance with bioactive behaviors.

1. Introduction

Metal materials, including stainless steels, titanium, and cobalt-chromium-based alloys, are commonly used for implant devices due to their high strength, ductility, and good anticorrosion properties [1]. It is more suitable for load-bearing applications compared with ceramics or polymeric materials due to their combination of high mechanical strength and fracture toughness [2]. The release of toxic metallic ions or particles by corrosion or wear processes leads to undesirable effects on cell and bone tissues [3]. Moreover, these metallic materials are not biodegradable in the human body and can cause long-term complication (infection) [4]. The elastic modules of current metallic biomaterials are not well matched with that of natural bone tissue, resulting in stress shielding effects that can lead to reduced stimulation of new bone growth and remodeling which decreases implant stability [5]. Comparing to commonly approved metallic biomaterials, magnesium alloys have many outstanding advantages due to their attractive biological property including being essential to human metabolism, biocompatibility, and biodegradability [6].

The mechanical properties of magnesium alloys are similar to those of natural bone (40–57 GPa) [7]. Moreover, magnesium is one of the most important bivalent ions associated with the formation of biological appetites and plays an important role in the changes in the bone matrix that determines bone fragility [8]. On the other hand, implants made of magnesium alloys were degraded in vivo, eliminating the need for a second operation for implant removal. Good biocompatibility was observed in clinical studies [9]. Unfortunately, magnesium can corrode too rapidly in the physiological pH (7.4–7.6) and high-chloride environment of the physiological system, loosing mechanical integrity before the tissue has sufficiently healed and producing hydrogen gas in the corrosion process at a rate that is too fast to be dealt with by the host tissue [10].

Recently, some researches have been done to slow down the biodegradation rate of magnesium alloys, including fluoride conversion coating [11], alkali-heat treatment [12], and plasma immersion ion implantation [13]. Besides improving the biodegradation rate of magnesium alloys, the biocompatibility should also be considered. The hydroxyapatite [Ca₁₀(PO₄)₆(OH)₂], hereafter (HAp), coating can satisfy
the dual properties. Synthetic HAp ceramics was routinely used as porous implants, powders, and coatings on metallic prostheses to provide bioactive fixation. Therefore, HAp coatings led to bone tissue response and bone growth along the coating in vitro. The presence of sparsely soluble HAp coatings improved the bioactivity property and effectively improved in vitro bioactivity in simulated body fluid.

2. Materials and Methods

2.1. Specimens Preparation. Commercially available AZ31 Mg alloy (3 mass% Al, 1 mass% Zn) was used as the substrate. The chemical composition of the alloy is listed in Table 1. The alloy (3 mass% Al, 1 mass% Zn) was used as the substrate.

2.2. The Film Formation. The specimens were immersed in 3 mM Ca(H₂PO₄)₂ + 7 mM CaCl₂ solution at 37°C and pH 6 for 30 min. The electrodeposition was performed at −1.4, −1.6, and −1.8 V applied potentials using a conventional electrochemical cell equipped with three electrodes. Platinum, Ag/AgCl sat. KCl, and magnesium alloy specimen served as the counter, the reference, and the working electrode, respectively.

2.3. Characterization Methods. The morphology and microstructure of the films were observed with Hitachi S-800 scanning electron microscope (SEM). The crystal structure of the coated films was identified using X-ray diffraction (XRD) analysis using a Shimadzu XRD-6000 X-ray diffractometer with Cu Kα radiation with scan step 0.02° and scan speed 2°/min. from diffraction angle of 10 to 60 at 30 kV and 20 mA. The elemental composition of the coating was identified using Energy Dispersive Spectroscopy (EDS).

2.4. Anticorrosion Measurements. The anodic polarization and electrochemical impedance spectroscopy tests were carried out using a Solartron 1285 Potentiostat from Solartron Analytical, Farnborough, United Kingdom. The measurements were controlled by Scribner Associates Corrware and Z polt electrochemical experiment software, respectively. The polarization curves were measured in phosphate buffered saline PBS(−) solutions with a scanning rate of 1 mV/s.

2.5. Bioactivity Experiment in Simulated Body Fluid. The coating was immersed for 7 days in the SBF (Kokubo solution) with ion concentrations nearly the same as those of the body blood plasma. The pH of the SBF solution was adjusted to 7.4. The phase structure, surface morphology, and the anticorrosion property were examined every day by removing the specimens from SBF solution, rinsed with distilled water, and air-dried.

### Table 1: Chemical composition (mass%) of AZ31 Mg alloy.

| Al  | Zn  | Mn  | Si  | Cu  | Ni  | Fe  | Mg  |
|-----|-----|-----|-----|-----|-----|-----|-----|
| 3.0 | 1.0 | 0.43 | 0.01 | <0.01 | <0.001 | 0.003 | Bal. |

![Figure 1: Current change during cathodic electrodeposition on AZ31 Mg alloy in 3 mM Ca(H₂PO₄)₂, 7 mM CaCl₂ for 30 min.](image-url)
3. Results and Discussion

High bioactivity can be achieved by performing the coating in the condition that is near to the human internal environment. Some research groups have applied various ranges of temperatures (room temperature; 45, 50, and 80°C) and initial pH (5.8, 6.5, and neutral) [25].

To achieve pure apatite coating on magnesium alloy, the initial pH and temperature should be carefully chosen. In our previous work, the optimum solution pH and temperature were defined [26]. The HAp peaks could be observed only at the temperature of 37°C or higher. It has been reported that the growth rate of apatite layer increased with the increasing temperature due to the decreasing in the solubility product of HAp [27].

HAp coating was deposited on the AZ31 alloy using the electrophoresis method. Fixed potential was set to −1.4, −1.6, and −1.8 V, so that the Mg alloy substrate became negatively charged (as a cathode). Magnesium dissolution takes place immediately after immersion of the specimen in 3 mM Ca(H₂PO₄)₂ and 7 mM CaCl₂ solution for 30 min at pH 6, according to reaction (1). Water is reduced at the cathode surface to produce hydrogen gas and hydroxide ions,
**Figure 5**: SEM images of coating obtained at $-1.4 \text{ V}$ before and after immersion in SBF solution for 1 day and 7 days.

**Figure 6**: xrd patterns of coatings obtained at $-1.4 \text{ V}$ before and after immersion in SBF solution for 1 day and 7 days.

**Figure 7**: EDS patterns of coatings obtained at $-1.4 \text{ V}$ before and after immersion in SBF solution for 1 day and 7 days.
which will lead to an increase in the solution pH according to reaction (2):

\[
\begin{align*}
    \text{Mg} &= \text{Mg}^{2+} + 2e^- \quad (1) \\
    2\text{H}_2\text{O} + 2e^- &= 2\text{OH}^- + \text{H}_2 \quad (2)
\end{align*}
\]

Figure 1 shows the current-time curves during the electrodeposition treatment at various potentials. At $-1.8$ V, the current density sharply decreased indicating the early formation of the coating film. On the other hand, the current density has a slight decrease at $-1.6$ V and has nearly a stable rate at $-1.4$. The local increase in the pH value and availability of Ca and P ions in the solution are expected to encourage the deposition of HAp and dicalcium phosphate dihydrate [CaHPO$_4$·$2\text{H}_2\text{O}$], hereafter (DCPD) on the magnesium alloy surface as shown in reactions (3) and (4):

\[
\begin{align*}
    5\text{Ca}^{2+} + 3\text{PO}_4 + \text{OH}^- &\rightarrow \frac{1}{2} (\text{Ca}_{10} (\text{PO}_4)_6 (\text{OH})_2) \quad (3) \\
    \text{Ca}^{2+} + \text{HPO}_4 + 2\text{H}_2\text{O} &\rightarrow \text{CaHPO}_4 \cdot 2\text{H}_2\text{O} \quad (4)
\end{align*}
\]

Figure 2 shows the SEM images of coating films formed at $-1.4$, $-1.6$, and $-1.8$ V. Flake-like particles were observed on all surfaces after cathodic deposition, while the size of crystallites becomes finer with increasing the cathodic potential to more negative side.

4. Conclusions

The hydroxyapatite coating was successfully electrodeposited on magnesium alloy surface by immersing in $3 \text{mM Ca(H}_2\text{PO}_4)_2$ and $7 \text{mM CaCl}_2$ solution for 30 min and at temperature of $37^\circ\text{C}$. The anticorrosion property of AZ31 magnesium alloy was improved with hydroxyapatite coating, and the best anticorrosion properties were obtained at $-1.4$ V. Hydroxyapatite was grown on the coating with immersion in SBF solution for 7 days, which proves its bioactivity.

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