Electrocrystallization, growth and characterization of calcium phosphate ceramics on magnesium alloys

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ABSTRACT

In order to make biodegradable magnesium alloys corrosion resistant for a potential orthopaedic and bio-implant application, their surface should be modified with bioactive bone-like hydroxyapatite (HA) coatings. In the present paper, the initial step of coating formation on Mg alloy was studied by electrochemical techniques. The electrocrystallization and growth of the surface film occur as an instantaneous 3D nucleation under diffusion control, as was extracted from a fitting procedure of current-time transient data to the various nucleation models. Electrodeposited calcium hydrogenphosphate coatings were converted into bone-like HA (calcium deficient HA) in an alkaline treatment. The bioactive properties of HA coatings have been directly identified with a Ca/P mole ratio. Their morphology, composition and barrier properties were identified using scanning electron microscopy (SEM), energy dispersion spectroscopy (EDS), Fourier transform infrared spectroscopy (FTIR), electrochemical impedance spectroscopy (EIS), and voltammetry.

1. Introduction

The development of degradable implants is an important research area in medical science because they are attractive for temporary orthopaedic application. They are expected to degrade at a slow rate, but to maintain the mechanical integrity until the healing of the tissues. The products of their degradation must be dissolved and consumed or excreted without causing any biological problem. The current biodegradable implants are mainly made of polymers, but their mechanical properties are not satisfactory [1]. Mg is the best potential material for biodegradable implants for many reasons: (i) Mg is an essential element to humans and beneficial for bone strength; (ii) Mg degrades in physiological solutions; and (iii) the mechanical properties of Mg are similar to those of natural bone. Unfortunately, Mg is very susceptible to corrosion in physiological solutions and its mechanical properties decrease before the new tissue has healed. Mg dissolution is accompanied by hydrogen evolution and formation of gas pockets, which significantly deteriorate the healing process [1]. Alloying Mg with elements like Al has shown some improvements in its degradation resistance, but not significant [1–6]. Various surface treatments have been applied to magnesium and its alloys to improve their corrosion resistance and

the lifetime of implants [5–7]. However, besides the improving chemical stability of implants, the biocompatibility of modified surfaces plays an important role in implants medical application and should be considered. One of key techniques to combine inorganic material with bioorganic matter is the use of self-assembled monolayers (SAM) of biomolecules like alkylcarboxylic acids [4,8] and alkylphosphonic acids [8,9]. These molecules, consisting of head groups that are able to react with a surface oxide layer, arrange themselves on the implant surface. In these monolayers the driving forces for self-assembly are both the covalent bond of the head group with the substrate and the Van der Waals interaction between the hydrocarbon chains that lead to the parallel alignments of the individual chains. The other important type of biomaterials is HA ($Ca_{10}(PO_4)_6(OH)_2$) due to its structural and chemical similarities to mineral components of natural bones [7,10]. Its main characteristics are the Ca/P mole ratio of 1.67, very high stability and low solubility; among calcium orthophosphates (CaP), HA is the most stable and least soluble [11]. Therefore its bioresorption kinetics is very slow; the implants of calcined HA of high crystallinity have been found years after implantation in a virtually unchanged form [12]. To increase bioresorption more soluble CaP, having a lower Ca/P mole ratio, have been favoured as an implant coating/material. After implantation these coatings undergo degradation simultaneously with the formation of a new bone. Such material is calcium-deficient hydroxyapatite (CDHA), which Ca/P mole ratio is 1.5–1.67. The HA and CDHA coatings on titanium alloys and stainless steels can be prepared by

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many methods including the sol–gel process [13], electrophoretic deposition [14], various plasma-assisted methods [15], and biomimetic methods [16]. However, these methods are not convenient for deposition of HA/CDHA on Mg and its alloys due to their low melting point and poor heat resistance. The cathodic deposition has been used for coating calcium phosphates on various metals/alloys including magnesium and its alloys [17–21]. This method has some advantages such as deposition at low temperature, controlled chemical composition, simple set up, and low expense. Electrochemical reactions taking place during coating deposition depend on the applied cathodic potential, and are discussed in literature [22,23].

In this paper we report the preparation of bone-like HA coatings on magnesium AZ91D alloy by cathodic deposition at constant potentials followed with a treatment in NaOH. The nucleation process of coatings was investigated using chronoamperometry. The chemical composition and morphology of alkali treated coatings were examined using SEM, EDS, and FTIR, while their barrier properties were investigated using EIS and voltammetry methods.

2. Experimental

The AZ91D alloy (wt.%: Al 8.6, Mn 0.19, Zn 0.51, Si 0.05, Cu 0.025, Fe 0.004 and balance Mg) was used in this study. The working electrodes, having the surface area of $0.235\ cm^2$, were sealed into glass tubes with Polirepar S. Before CaP deposition the electrodes were abraded with fine emery paper, polished with alumina powder down to 0.05 μm, degreased in ethanol in an ultrasonic bath, kept immersed in 1.0 M solution of NaOH at 80 °C for 1 h, and rinsed with distilled water. Electrodeposition of CaP was carried out at constant potential values ranging from −1.90 to −2.10 V for different periods of time in a solution ($100\ cm^3$) containing 0.05 M $Ca(NO_3)_2$ and 0.03 M $NH_4H_2PO_4$. The pH value of solution was 5 (adjusted with 0.5 M HNO_3). During deposition the solution was stirred with a magnetic stirrer. After deposition, the electrodes were immersed in 1.0 M solution of NaOH at 80 °C for 2 h, rinsed with distilled water and dried in air.

The surface morphology and composition of coatings were identified by SEM, EDS, and FTIR. SEM images were performed using *Jeol Ltd.* FE SEM, model JSM-7000F, while ED spectra wee recorded using *Oxford Instruments Ltd.* EDS/INCA 350 in addition to SEM. The FTIR spectra were recorded in the $4000–650\ cm^{-1}$ region using Horizontal Attenuated Total Reflectance (HATR) method on a Perkin-Elmer Spectrum One FTIR spectrometer.

The potentiodynamic ($\nu = 10\ mV\ min^{-1}$) and potentiostatic measurements with the Mg-alloy electrode were performed in a deposited solution in a standard three-electrode cell. The counter electrode was a large area platinum electrode and the reference electrode, to which all potentials are referred, was an Ag/AgCl/3 M KCl (209 mV vs. SHE). The barrier properties of CaP coatings were investigated at 37 °C in the Hanks' solution, pH 6.67, of the following composition ($g\ L^{-1}$): NaCl 8.00, KCl 0.40, $NaHCO_3$ 0.35, $NaH_2PO_4 \cdot H_2O$ 0.25, $Na_2HPO_4 \cdot 2H_2O$ 0.06, $CaCl_2 \cdot 2H_2O$ 0.19, $MgCl_2$ 0.19, $MgSO_4 \cdot 7H_2O$ 0.06, and glucose 1.00. All chemicals were analytical grade reagents. Five repeated experiments were always performed as a control. Before measurements the electrodes were stabilized for 1 h in the Hanks' solution. EIS measurements were performed at the open circuit potential (E_{OCP}) in the frequency range from 100 kHz to 0.1 Hz with an ac signal ±10 mV. Measurements were carried out using a Solartron Frequency Response Analyzer SI 1255 and Solartron Electrochemical Interface 1287 controlled by a PC. The experimental data were fitted using the complex non-linear least squares fit analysis software Zview. The numerical values of impedance parameters were determined with a standard deviation χ^2 of the order of 10^{-5}, and the relative error of each element was <5%.
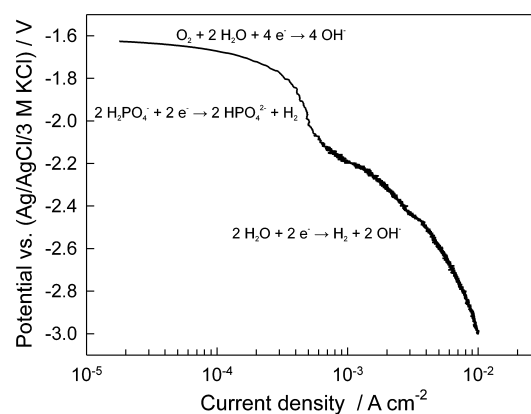

Fig. 1. The potentiodynamic polarization curve for Mg-alloy recorded in a solution containing $0.05\ mol\ L^{-1}\ Ca(NO_3)_2$ and $0.03\ mol\ L^{-1}\ NH_4H_2PO_4$; $\nu = 10\ mV\ min^{-1}$.

3. Results and discussion

3.1. Cathodic reactions and CaP nucleation

The cathodic polarization curve recorded with Mg alloy immersed in a deposition electrolyte is presented in Fig. 1. The curve can be divided into two potential regions. In the first region (up to ca. −2.05 V), the predominant cathodic reaction is reduction of $H_2PO_4^-$ (present in the electrolytic solution) to HPO_4^{2-}

$$2H_2PO_4^- + 2e^- \rightarrow 2HPO_4^{2-} + H_2 \tag{1}$$

It is expected that HPO_4^{2-} ions produced completely or partially react with Ca^{2+} ions and form insoluble coating on the electrode surface ($CaHPO_4 \cdot 2H_2O$). At higher cathodic potentials ($E > -2.10\ V$), reduction of water becomes a dominant cathodic reaction

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \tag{2}$$

This cathodic reaction causes an increase in pH of a solution and enables neutralization of $H_2PO_4^-$.

The numerical values of current density corresponding to the first potential region range up to $0.5\ mA\ cm^{-2}$. According to Zhang et al. [24] the current densities lower than $1\ mA\ cm^{-2}$ are not large enough to increase the interfacial pH in the electrodeposited solution used above 6.7, and under these condition the precipitation of $CaHPO_4$ takes place. According to these authors the precipitation of hydrated calcium phosphate, $Ca_3(PO_4)_2 \cdot nH_2O$ occurs at pH values 6.9–7.3, while the interfacial pH values greater than 7.4 are appropriate to produce bone-like HA coatings.

To obtain a deeper insight into the nucleation and formation of $CaHPO_4$, the potentiostatic transients were recorded on Mg-alloy electrodes at potential values ranging from −1.95 to −2.05 V. Fig. 2 shows examples of a general response of Mg-alloy held at constant potential values (E_t) in an electrodeposited solution. The shape of transients is characteristic of the nucleation and growth process. After a short period of time, the current reaches its maximum (in absolute values) j_m in time t_m and starts decreasing. This is due to the independent growth of each individual nucleus and/or due to the increase in number of nuclei. During this stage, the transport of electroactive species (Ca^{2+} and HPO_4^{2-} ions) to nuclei formed on the surface occurs through hemispherical diffusion zones developed around each isolated nucleus. However, the radius of these hemispherical diffusion zones increases with time and the zones start to overlap, finally forming a planar-like diffusion layer towards which the same amount of material diffuses by a linear diffusion mechanism [25]. This results in reduced mass transport to the electrode surface, i.e., the current starts to decline after reaching a maximum value. The current maximum increases markedly as the