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Effect of electrolyte composition and deposition current for Fe/Fe-P electroformed bilayers for biodegradable metallic medical applications

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ABSTRACT

With its proven biocompatibility and excellent mechanical properties, iron is an excellent source material for clinical cardiac and vascular applications. However, its relatively low degradation rate limits its use for the healing and remodeling of diseased blood vessels. To address these issues, a multi-purpose fabrication process to develop a bilayer alloy composed of electroformed iron (E-Fe) and iron-phosphorus (Fe-P) was employed. Bilayers of Fe/Fe-P were produced in an electrolytic bath. The effects of electrolyte chemical composition and deposition current density (i_{dep}) on layer structure and chemical composition were assessed by scanning electron microscopy, electron probe microanalysis, X-ray diffraction and X-ray photoelectron spectroscopy. The corrosion rate was determined by potentiodynamic polarization tests. The bilayers showed an increasing amount of P with increasing $NaH_2PO_4 \cdot H_2O$ in the electrolyte. Fe-P structure became finer for higher P amounts. Potentiodynamic polarization tests revealed that the corrosion rate was strongly influenced by deposition conditions. For a P amount of ~2 wt. %, the corrosion rate was 1.46 mm/year, which confirms the potential of this material to demonstrate high mechanical properties and a suitable corrosion rate for biomedical applications.

1. Introduction

In the last decade, degradable metallic biomaterials have become increasingly relevant in such biomedical applications as cardiovascular devices and orthopedic replacements [1,2]. Due to their temporary nature, these devices are designed to effectively integrate physiological sites during the healing process, provide mechanical support for a specific time period, and gradually dissolve thereafter. To tailor the chemical, physical, and biological properties of these biomaterials, key factors including the materials' selection, device design, and fabrication processes must be considered. Moreover, degradation of the metal is expected to begin slowly (weeks to months) and gradually accelerate until the metallic device completely disappears. In the majority of cardiac and vascular applications, a period of 6 to 12 months for vessel remodeling is deemed acceptable from a clinical standpoint [3] and approximately 6 to 8 months [4] for bone remodeling.

Today, most of the degradable metals developed are magnesium-based [5] and iron-based alloys [6]. Typically, magnesium-based alloys display mechanical properties that are inferior to those of SS316L stainless steel, the reference alloy for permanent metallic devices [1]. SS316L demonstrates a plastic deformation higher than 50% [7], while Mg alloys attain a plastic deformation of 25–30% post-microalloying with rare earths (RE) [8]. In addition, Mg alloys generally dissolve in pseudo-physiological solutions with H_2 production and a higher corrosion rate [5] than that of iron-based alloys. RE microalloying has also been shown to increase corrosion resistance [8].

Two strategies commonly adopted to increase mechanical properties and control the degradation rate are modifications to the material's microstructure [9] and chemical composition [1]. Iron has been shown to possess good mechanical properties, although its low degradation rate does not meet clinical needs and standards. Studies have combined several different alloying elements with iron to enhance its clinical efficacy as degradable implants; most notable among these are Fe-Mn [1, 10], Fe-Mn-Pd [11], and Fe-X, with X = Mn, Co, Al, W, Sn, B, C, and S [12] or X = C, P, B, and Ag [4].

Semi-finished products can be obtained through several fabrication methods, such as casting [13], powder metallurgy [14], forging [15], and electroforming [9]. Recently, Moravej et al. [9] developed the

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electroforming of pure iron (E-Fe) as a new fabrication technique to develop semi-finished products for biomedical applications such as small diameter tubes and other small-sized pieces. For small devices, including pediatric implants and coronary stents, electroforming has an advantage over other fabrication methods in that it allows for the production of materials with complex geometries that do not require additional processing, thus generating an effective, near "ready-to-use" device. For example, research has shown that small diameter tubes (minitubes) for stents can be produced with this technique, thereby reducing the number of fabrication steps usually required for production through casting and powder metallurgy processes. Furthermore, this technique can lead to a controlled metallurgical microstructure influencing corrosion behavior. The *in vivo* dissolution rate of electroformed iron is greater than that measured for devices produced with traditional methods [13]. Because its potential in the fabrication of semifinished products with tailored properties [16,17], studies on the use of electroforming for the production of binary alloys remain a highly relevant research domain.

In this study, phosphorus was selected as the alloying element in the iron-based alloy layer because of its good biocompatibility and its favourable effect on iron degradation rate [4]. The ductility and strength of Fe-P alloy are influenced by P concentration and by alloy phase composition and distribution. However, studies have thus far failed to address the direct effect of simulated body solutions on the corrosion properties of the material. In the case of Fe-P alloys, the effect of the material's chemical composition, microstructure, and present phases on mechanical and corrosion properties have been studied [18–23].

Iron phosphides have been produced as a result of electrodeposition with several demonstrated phases, including Fe_2P and FeP. Their presence and concentration in the alloy depend on electrolyte composition as well as deposition method. The formation of phosphides, or more generally, the various phases with a corrosion potential different from that of the matrix, can be beneficial for the induction of microgalvanic effects [11,24] that increase the degradation rate of the alloy. Appropriate thermal treatments can be further used to alter the microstructure of the material to increase toughness and ductility and promote the formation of a smooth P gradient at the interface by diffusion. This allows for the precipitation of Fe_xP which can affect both the mechanical and corrosion properties of the material, as previously described. Thermal treatments can also be used to release residual stresses typical of electroforming processes and homogenize chemical composition. The produced material can also be inserted as an inter-layer between two consecutive layers of different materials.

In this study, E-Fe/Fe-P bilayers were produced by electrodeposition to assess the influence of bath composition and deposition current on the structure, chemical composition, and corrosion properties of the deposited alloy. The technique potential was explored by means of a double bath system which allowed for the deposition of alternate layers of different composition (E-Fe and Fe-P). This system exhibited impressive versatility, as it enabled the tuning of properties at both the microscopic (microstructure and chemical composition by deposition parameters) and macroscopic levels (deposition of layers with different properties and thickness).

A new material was thus designed according to the following specific parameters: (1) sufficient mechanical properties to adapt to the deformation during implantation; (2) a degradation rate superior to that of pure electroformed iron; and (3) adequate biocompatibility. The galvanic corrosion of the alloy could be stimulated by depositing electroformed layers of iron and iron-based alloy. More specifically, the goal was to elucidate the interactions between the deposition parameters and the structure and properties of the electroformed materials.

2. Materials and methods

2.1. Electroforming process

Electroformed Fe/Fe-P bilayers were prepared using a dual bath electrodeposition technique. Fig. 1 and Table 1 describe the experimental setup, which consisted of three beakers, each one containing 300 mL of electrolyte, a temperature controller, a pH controller and a power source providing a DC current. Beaker no. 1 containing electrolyte 1 was used for E-Fe electrodeposition, while beakers 2 and 3 containing electrolyte 2 were used for the rinsing and electrodeposition of the Fe-

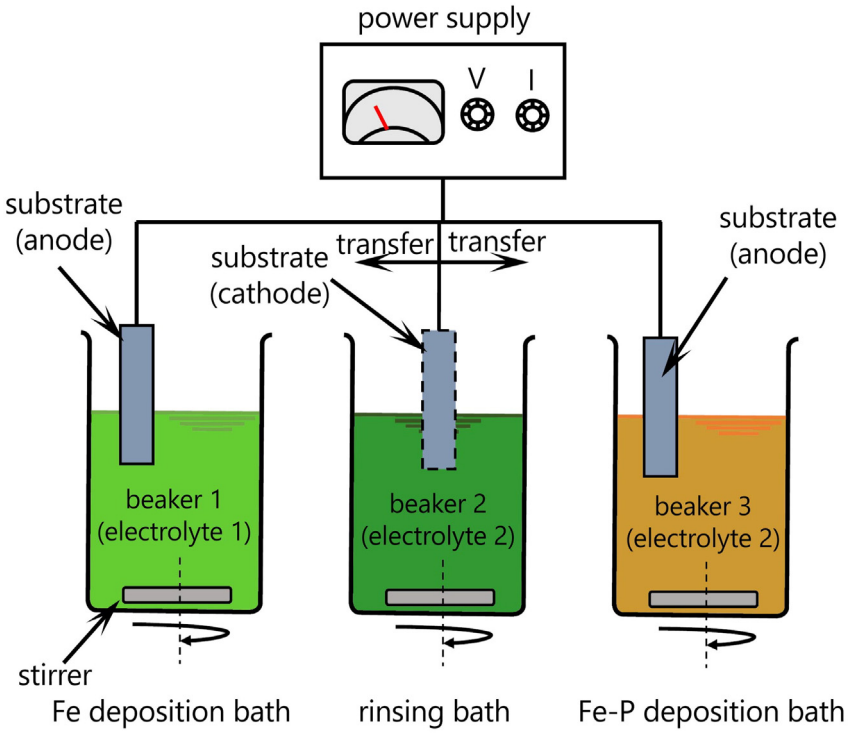

Fig. 1. Layout of the deposition system.