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Electroformed iron as new biomaterial for degradable stents: Development process and structure–properties relationship ☆

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ABSTRACT

An electroforming technique was developed for fabricating iron foils targeted for application as biodegradable cardiovascular stent material. The microstructure, mechanical properties and corrosion of electroformed iron (E-Fe) foils were evaluated and compared with those of pure iron made by casting and thermomechanical treatment (CTT-Fe), with 316L stainless steel (316L SS) and with other candidate metallic materials for biodegradable stents. Electron backscattered diffraction revealed an average grain size of 4 μm for E-Fe, resulting in a high yield (360 MPa) and ultimate tensile strength (423 MPa) being superior to those of other metallic biodegradable stent materials. Annealing at 550 °C was found to improve the ductility of the E-Fe from 8% to 18%. The corrosion rate of E-Fe in Hanks' solution, measured by potentiodynamic polarization, was higher than that of CTT-Fe, which had been found to have a slow *in vivo* degradation. The results showed that E-Fe possesses fine-grain microstructure, suitable mechanical properties and moderate corrosion rate as a degradable stent material.

1. Introduction

Cardiovascular stenting is a catheter-based procedure in which a tiny, expandable wire mesh tube (stent) is intravascularly implanted, X-ray placed and deployed in a diseased artery, serving as a scaffold to hold it open. Current stent technology is based on the use of permanent implants made of corrosion-resistant materials such as 316L SS and nitinol. These permanent implants are intended to remain in the vessel wall for life, mainly because they cannot be removed without causing irreversible damage to the heart. However, it has been shown that the scaffolding effect of stents for prevention of the artery occlusion and arterial remodelling is only required for a set timeframe (6–12 months), and the permanent presence of stents would not provide any further benefit [1]. Therefore, development of biodegradable stents which provide the scaffolding effect and thereafter degrade could be the logical approach to avoid the potential complications observed with permanent stents [1,2]. In the search for biodegradable stent material, several polymers have been evaluated *in vivo*. However, polymers have special drawbacks, including low radial strength and inflammatory response, which limit their application as stents [3]. Magnesium alloys, iron–35% manganese alloy (Fe–35Mn) and pure iron are metallic materials which have been investigated for biodegradable stent application [4–8]. Magnesium alloys (AE21 and WE43) have been implanted in porcine models and in clinical studies in humans [4,5]. The implantation results showed that further improvements are required to lower the degradation rate and to increase the mechanical properties of Mg alloys [3–5]. Recently, Fe–35Mn alloy developed by powder metallurgy has been evaluated *in vitro*. It has shown good mechanical properties and slower degradation than Mg alloys and is currently under further development [6]. Pure iron made by casting and thermomechanical treatment (CTT-Fe) has been implanted in rabbit and porcine models. The results showed that iron had good biocompatibility and superior mechanical and degradation properties compared with Mg alloys. However, *in vivo* degradation of pure iron was slower than the calculated value from *in vitro* degradation tests. It was suggested that structural or compositional modifications should be made to iron to obtain higher *in vivo* degradation rates [7,8].

In this work, the feasibility of producing electroformed iron (E-Fe) suitable for application as a biodegradable material for stents was investigated. The following are the main reasons for such

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investigation. (1) Iron ion (Fe^{2+}) is an essential element for the body. It is an essential component of a variety of enzymes. Transport absorption and storage mechanisms for iron are also well known and make iron and iron-based alloys favourable candidates as biodegradable implant material [7]. (2) Iron has also shown moderate and uniform degradation, which is required for biodegradable stents to avoid the mechanical failure of the device in vessels [7,9]. (3) The mechanical properties of iron are also comparable with those of 316L SS and other stent materials. (4) One of the aims of this work was to modify the microstructure of pure iron to produce a material with a higher degradation rate and mechanical properties superior to those of CTT-Fe. Therefore, the fabrication method selected for production of iron was electroforming. This method uses the electrodeposition principle to produce complex metallic parts and components [10]. While electrodeposition is used to modify the surface of a substrate material by deposition of a metallic coating, in electroforming a metallic part is deposited to be used as a separate entity. As the structure of metallic parts is formed atom layer by atom layer, electroforming is an ideal process for fabrication of complex shapes and surfaces with dimensional precision, thin-walled materials and high-purity metals with different microstructures, thicknesses and properties [10,11]. Also, electroforming produces polycrystalline metals with exceptionally fine-grain structure with grain sizes much smaller than in bulk metals produced by other production methods. The microstructure of electroformed metals could be tailored by adjusting the electrodeposition parameters, including current density, electrolyte composition, pH and temperature [10].

Applications for electroforming include precious tools, mesh and foil products, space mirrors, metal optical parts, bellows, radar and wave guides, and micro-electromechanical systems using LIGA and SU-8 processes [12,13]. The most common current application of E-Fe is the production of foils used in microelectronic devices and electromagnetic recording devices [14,15].

In this work, E-Fe was investigated as a structural material for biodegradable cardiovascular stent application. Electroformed Fe specimens were fabricated in flat form to facilitate the study of microstructure, mechanical properties and corrosion behaviour. After deposition, the foils were removed from their substrate and evaluated. The properties of E-Fe compared with those of CTT-Fe, Mg alloys, Fe–35Mn alloy, which have previously been studied as biodegradable stent materials, and 316L SS, which is the gold standard material for cardiovascular stent fabrication.

2. Materials and methods

2.1. Specimen fabrication by electroforming

A ferrous chloride–calcium chloride aqueous solution was used as electrolyte for iron electroforming. The electrolyte was prepared by dissolving $FeCl_2$ (Alfa Aesar, MA, USA) and $CaCl_2$ salts (Alfa Aesar, MA, USA) in deionized water. The composition of the bath was 400 g L^{-1} $FeCl_2$–80 g L^{-1} $CaCl_2$, which is known as Fischer–Langbien solution and is reported to produce more ductile iron foils compared with other electrolytes [16]. One gram per litre of sodium saccharine and 0.25 gram per litre of sodium dodecyl sulfate were added to the electrolyte as stress-reducing and anti-pitting agents, respectively. Ti6Al4V titanium alloy was selected as the substrate because it can be separated easily from deposits after electrodeposition. The substrate had a rectangular surface area of 14 cm^2, which was mechanically polished with 120–3000 grit SiC abrasive paper and then with 0.05 μm alumina paste for a mirror-like finish prior to electrodeposition. Armco® iron sheet was used as a soluble anode to provide Fe^{2+} ions in the electrolyte. The solution pH was adjusted to 1 with the addition of HCl and NaOH, and the temperature was kept at 90 °C. Electrodeposition were carried out for 4:30 h with a direct current density of 2 A dm^{-2}, which was found to produce Fe foils with the lowest surface roughness. The deposition time was calculated based on Faraday's law in order to obtain films 100 μm thick. Fig. 1 shows a schematic of the electrodeposition cell used in this work. Iron films ~100 μm thick were deposited on the titanium alloy substrate and removed after electrodeposition. To study the effect of heat treatment on properties, Fe foils were annealed at 550 and 650 °C for 1 h in high-purity argon atmosphere. The annealing temperatures were selected to be higher than the recrystallization temperature of pure iron, which is ~450 °C [17]. It has also been reported that annealing of E-Fe at 550 °C for 1 h removed the internal stress produced by electrodeposition and improved ductility [18].

In order to compare the microstructure, mechanical properties and corrosion behaviour of E-Fe with those of CTT-Fe, pure Fe foils with similar thickness to those of E-Fe (Fe > 99.9–0.125 mm thick, as-rolled, Goodfellow, USA) were annealed at 550 °C and tested along with the E-Fe foils.

2.2. Composition, phase and morphology characterization of E-Fe

The chemical composition of E-Fe was measured using inductively coupled plasma and the fusion gas analysis method, by means of a LECO TCH-600 gas analyser according to ASTM D1976 [19] and E1019 [20] standards, respectively. The surface morphology and cross section of E-Fe were observed using scanning electron microscopy (SEM; JOEL JSM-840A). For cross-section observation, an E-Fe specimen was mounted in acrylic resin and polished using 1000–4000 SiC paper and then 0.05 μm alumina

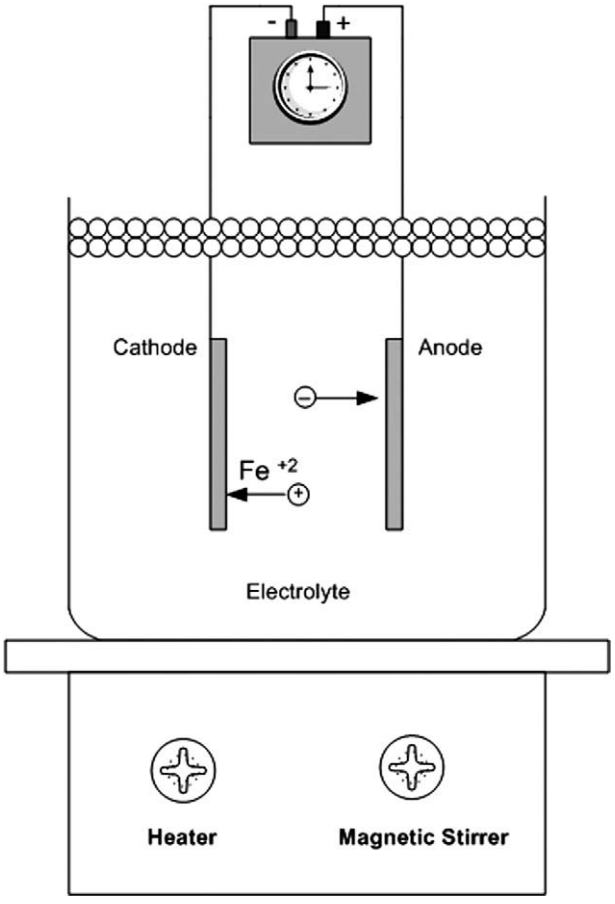

Fig. 1. Schematic of electroforming apparatus.

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