CORROSION PROPERTIES OF IRON BASED BIODEGRADABLE FOAMS

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Abstract
Pure iron foams were prepared from carbonyl iron and, in order to investigate the corrosion rate, iron-based metallic foams from phosphate layer coated carbonyl iron by the replication method on the basis of highly uniform foamed polyurethane. The specimens were tested with respect to microstructure, corrosion behaviour and hemocompatibility. The microstructures of the samples were investigated by scanning electron microscopy. The corrosion behaviour in simulated body fluid (Hank’s solution) at 37 °C was determined by potentiodynamic polarization. No corrosion inhibiting effect of phosphorus on degradation rate was observed. In contrast, degradation studies indicated that the presence of phosphorus in the phosphate form lowered the corrosion potential and slightly increased their corrosion rate compared to that of pure iron. Both samples were found to be hemocompatible.

Keywords: powder metallurgy, metallic foams, biodegradation, corrosion behaviour, hemocompatibility

INTRODUCTION
The development of biodegradable metals for temporary medical implants has been the subject of intensive research in recent years [1-8]. Biodegradable implant can be dissolved or adsorbed after implanting, thus eliminating the need for its removal in an additional operation. Nowadays, magnesium, iron and their alloys make up two classes of metals used in temporary medical implants [6-8]. Poor mechanical properties of magnesium, fast degradation rate in physiological environments and significant hydrogen evolution limit the application of Mg based alloy materials, especially in orthopaedic surgery [3]. When a higher load is required, the use of iron based materials appears to be a good alternative [5]. The results of the first in vivo animal test of pure iron stents showed suitability of iron as a biodegradable material [6]. However, the studies also showed that the corrosion rate of pure iron is fairly low [5-6]. The degradation rate of iron can be promoted by various alloying elements [7-9].

At the beginning of the healing process, the implant serves as a stabilizer, during the remodelling process, the implant is resorbed and the entire load is gradually transferred to the bone. To achieve the optimal bone remodelling, Young's modulus must not exceed the stiffness of the bone implant. This can be achieved by using cellular metals. The porosity of the material allows bone cells and veins to grow throughout the implant, which is essential for regeneration of the bone tissue [5]. When iron-based alloys are used as the
base material in cellular metal implants, high strength is needed for the load bearing implants. Phosphorus seems to be an appropriate alloying element. During sintering, phosphorus diffuses into iron, forming a liquid phase which assists rapid densification, increasing the sintered density and strength. Additionally, phosphorus is known as an essential element that maintains physiological homeostasis processes with balanced cell proportions [10].

Therefore, the aim of the present study was to design Fe-P materials with an open cell structure as degradable bone replacement implants. The effect of iron phosphate coating of carbonyl iron powder has been evaluated and corrosion properties and hemocompatibility of sintered materials studied.

**EXPERIMENTAL PROCEDURES**

Carbonyl iron powder fy BASF (type CIP CC, d50 value 3.8 – 5.3 μm), with the composition of 99.5% Fe, 0.05% C, 0.01% N and 0.18% O was used as the raw material. Using the modified precipitating method [11], the powder particles were phosphated in a phosphating solution consisting of orthophosphoric acid as a phosphating active agent and acetone as a solvent. Carbonyl iron powder with 0.5 wt.% phosphorus was prepared.

The metallic foams were fabricated by the replication method. The polyurethane sponge BULPREN S (fy POLYPRO) with cell size 1060-1600 μm was used as the template. The specimens with size of 15x10x8 mm were entirely impregnated by a slurry comprising iron and iron-coated particles. The polyurethane template was thermally removed in a laboratory furnace Aneta 1. The samples were heated at 1°C/min to 450°C in flowing nitrogen (approximately 4L/ min) and held at 450°C for 2 hours. The metallic foams were sintered at 1050°C for 1 hour in an H2-N2 atmosphere.

The corrosion behaviour was studied electrochemically in Hank's solution (pH = ~7.4), simulated body fluid, containing 8.00 NaCl, 1.00 glucose, 0.60 KH2PO4, 0.40 KCl, 0.35 NaHCO3, 0.14 CaCl2, 0.10 MgCl2.6H2O, 0.06 MgSO4.7H2O, and 0.06 NaH2PO4.2H2O (in g/l). The potentiodynamic curves were measured at 37°C using Autolab Potentiostat PGSTAT 302N. A conventional three-electrode system with the Ag/AgCl, served as the reference electrode, platinum as a counter electrode and our specimens were used as the working electrode. Five cycles of anodic potentiodynamic polarization were registered for each specimen. Polarisation curves were obtained by varying the applied potential from -1500 mV up to +1500 mV at a scan rate of 1 mV/s. The corrosion current, corrosion potential and corrosion rate were determined by the use of the Tafel extrapolation method. The microstructures and surface morphologies of the experimental samples, both before and after corrosion, were examined by a scanning electron microscope (JOEL JSM-7001J, Japan). The specific surface of prepared metallic foams was determined by the BET method.

Biocompatibility studies were carried out on cleaned and sterilized cellular samples. For this purpose, 1 ml of healthy sheep blood with 3.8wt. % sodium citrate (anticoagulant) in the ratio of 9:1 was used and diluted to 10 ml with regular saline. The haemolysis test, thrombus formation test and platelet adhesion test, described in detail in [12], were carried out.

**RESULT AND DISCUSSION**

The sintered metallic foams closely resemble the original polymer template structure.
Figure 1 shows the high porosity iron foam with density of about 0.55 g/cm$^3$, specific surface area of 0.39 m$^2$/g and cell size between 200-500 µm; the Fe-P foams have a density of 0.79 g/cm$^3$. The structures exhibit interconnected porosity, which is one of the most important requirements for tissue ingrowth. The structures of pure iron foams were very similar to those from phosphate carbonyl iron.

**Corrosion behaviour**

The values of corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$) and corrosion rate ($CR$) calculated from the intersection of the anodic and cathodic Taffel lines extrapolation and determined biodegradation rates are summarized in Table 1.

It is assumed that uniform corrosion is occurring and the process of oxidation does not occur selectively for any component of the alloy. Then the corrosion rate $CR$ (mm/y), is given as

$$CR = \frac{i_{corr}}{\rho F \sum c_i n_i M_i}$$

where $i_{corr}$ = corrosion current density ($\mu$A/cm$^2$), $\rho$ = alloy mass density (g/cm$^3$), $F$ is the Faraday constant, $c_i$ is the mass fraction of the $i$th component of the alloy, $M_i$ is the molar mass of the $i$th component and $n_i$ is the number of electrons lost when oxidizing the $i$th component atom under conditions of the corrosion process (the valence of the $i$th component element).

<table>
<thead>
<tr>
<th></th>
<th>$E_{corr}$ [mV]</th>
<th>$i_{corr}$ ($\mu$A/cm$^2$)</th>
<th>CR (mm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1. cycle</td>
<td>2. cycle</td>
<td>3. cycle</td>
</tr>
<tr>
<td>Fe</td>
<td>-546</td>
<td>-599</td>
<td>-612</td>
</tr>
<tr>
<td>Fe-P</td>
<td>-415</td>
<td>-647</td>
<td>-675</td>
</tr>
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</table>

Figure 2 shows typical potentiodynamic polarization curves. The corrosion potential moved towards negative values before stabilization. This negative shift indicates an increased corrosion susceptibility of the foams. Generally, it was found that the corrosion resistivity decreased with increasing number of cycles.
The passive layer on the foam sample top surface, which to some extent protected the material, was dissolved during the first cycle of polarisation. Thereupon, in the next cycle, specimens showed a higher tendency to corrode. Corrosion potential of the Fe-P foams was shifted to a lower value than that of the pure Fe foam, while the corrosion current remained similar.

![Fig.2. Polarisation curves for Fe and Fe-P foams in Hank's solution at 37°C, semilogarithmic form.](image)

The significant shift of corrosion potential to less negative values for Fe-P foam in the first cycle could be associated with existence of passive P-containing layer, which inhibits direct contact of samples with the solution. The presence of $PO_4^{3-}$ ions in the sintered structure [13], $Ca^{2+}$ and $SO_4^{2-}$ ions in Hank's solution could cause precipitation and consequently influence the shifting [10]. In the following cycles, when protective layer was dissolved, the corrosion potential of Fe-P foam is slightly shifted to more negative values. It indicates worse corrosion resistance. Calculated corrosion rates are 0.682 and 0.711 mm/year for Fe and Fe-P foams, respectively. Wegener [5] reported the corrosion rate of microporous carbonyl iron samples and those with 0.6 wt.%P in SBF solution after 7 days immersion of 0.25 and 0.27 mm/y, respectively. Corrosion rates of porous samples are higher than those of the nonporous iron-based. This could be ascribed to higher surface area, roughness and penetrable structure of cellular material.

The surfaces of the foams exposed to Hank's solution after electrochemical corrosion are illustrated in Fig.3. The surfaces of all specimens are covered by a relatively compact brown layer of corrosion products. Due to internal stress, these layers are cracked. When iron-based alloys are used as the base material in cellular metal implants, high strength is needed for the load bearing implants.
The strength of cellular foams can be increased by increasing either the structural density or the strength of the basic material. The structural density should be kept low in order to decrease the total mass to be resorbed. For this reason, the strength increase of basic material is essential. Phosphorus seems to be an appropriate alloying element. During sintering, phosphorus diffuses into iron, forming a liquid phase which assists rapid densification and strength. Maximum addition of phosphorus is limited, because the content above 0.6% phosphorus leads to forming a eutectic Fe$_3$-P phase at grain boundaries, which results in an embrittlement of the material [5]. Phosphorus is known to inhibit corrosion of steels, but in this work, no corrosion inhibiting effects of phosphorus on the degradation rate has been observed. Results are in good agreement with Wegener's previous work [5].

**Biocompatibility studies**

The calculated values of the hemolysis percentage were 7.00% and 5.33% for Fe and Fe-P foams, respectively. Addition of phosphorus to the iron powder resulted in lowering of the haemolytic activity compared to pure iron foams. The samples can be categorized as hemocompatible. The slight decrease in thrombus formation was observed for Fe-P foam as compared to pure carbonyl iron foam [14].
Figure 4 shows SEM micrographs of platelets adhering to the experimental samples. It is clearly visible that more platelets were present on the pure iron surface as compared with Fe-P material. Platelets adhering to the iron surface have more affinity to the metal surface and form pseudopodia-like structures, whereas those present on the Fe-P material surface maintained their integrity, as shown by arrows.

CONCLUSIONS

Cellular Fe and Fe-P structures with interconnected porosity, density of about 0.55 and 0.79 g/cm³ respectively, cell size between 200-500 µm, were manufactured by the replication method based on powder metallurgy. Corrosion behaviour of the prepared samples was determined by the anodic polarisation curves in Hanks solution at 37°C. It was found that the corrosion potential of Fe-P foam is shifted to more negative value in comparison with the pure iron foam. The corrosion rate of Fe-P foam is higher than that of pure iron foam; the presence of phosphorus has no corrosion inhibiting effects. The foams were found to be hemocompatible.

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