Corrosion performances of a Nickel-free Fe-based bulk metallic glass in simulated body fluids

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1. Introduction

Biomedical 316L SS is prone to localized attack in long-term applications due to the aggressive biological effects [1]. It has been reported that more than 90% of the implants fabricated with 316L SS were subject to localized corrosion, such as pitting corrosion, on the surface of the implants removed from patients [2,3]. Nickel ion releasing is of particular interest since it may not only cause adverse biological effects but also the most widespread contact allergy [4]. These biocompatibility concerns deriving from clinical use of Ni-containing biomedical alloys for extended periods of time have prompted the study of alternative materials [5].

Recent works on BMGs proved their excellent corrosion resistance, exceptional mechanical properties and precise net-shaping ability. These superior properties over currently used metallic biomaterials make BMGs promising biomaterials, however, limited work has been carried out to characterize the biocompatibility of BMGs. They are actually newcomers to the metallic biomaterials family. Schroers et al. summarized the possibilities for BMGs to be used in biomedical areas and reported the in vitro and in vivo biocompatibility evaluation of a Zr-based BMG and a Pt-based BMG. And they found BMGs are in general nontoxic to cells and compatible with cell growth and tissue function [6].

Many electrochemical studies have proved Fe-based BMG could be excellent corrosion resistant materials used in aggressive media [7–9]. However, there is no report on the corrosion behavior of Fe-based BMG in simulated body fluids. In the present study, a Fe-based BMG (Fe41Co7Cr15Mo14C15B6Y2) with high GFA was chosen for its Nickel-free feature, and relatively larger size of critical maximum diameter ($r_{\text{max}} = 16$ mm) [10]. Various electrochemical measurements were carried out to reveal the corrosion performance and ion release behavior of this alloy.

2. Materials and methods

2.1. Materials preparation and characterization

Fe41Co7Cr15Mo14C15B6Y2 (in at.%) BMG samples (hereafter, called FeY BMG) with diameter of 5 mm were prepared by suction casting of the molten alloy into a copper mold. Crystalline FeY alloy with the same composition was obtained from FeY BMG after annealed at 1073 K for 5 h and followed furnace cooling. 316L SS rod samples were purchased from Goodfellow Cambridge Ltd. (Huntingdon, England) and cut into wafers with the same size of FeY BMG samples. The surfaces of the experimental specimens were mechanically grinded to a SiC paper of 2000# grit.

X-ray diffraction (XRD) for phase analysis was conducted with a scan rate of 4°/min using Rigaku-D/maxR diffractometer operated at 40 kV and 100 mA at room temperature.
2.2. Electrochemical measurements

The electrochemical measurements were performed using an electrochemical analyzer (CHI 650C, CHI, Austin, TX). The sample was set as a 'working' electrode, a platinum electrode acting as an auxiliary electrode and a saturated calomel electrode (SCE) was used as the 'reference' electrode. The OCP (open circuit potential) measurement was maintained up to 7200 s. The cyclic polarization curves were measured from 300 mV under the OCP value (vs. SCE) to 1500 mV (vs. SCE) with a scan rate of 1 mV/s after dipping the specimen into the corresponding electrolyte for 7200 s. The simulated body liquid electrolytes were Hank’s solution with pH value 7.4[11] and artificial saliva solution with pH value 6.3[12]. EIS data were obtained with signal amplitude of 10 mV around OCP values in the frequency range of $10^{-2}$ to $10^{4}$ Hz. Data were shown as the mean ± SD ($n = 3$).

2.3. ICP test

The inductively coupled plasma atomic emission spectrometry (Leeman, Profile ICP-AES) was employed to measure the concentrations of ions which had dissolved into the electrolytes.

3. Results and discussion

3.1. Microstructure

For FeY BMG, as shown in Fig. 1, there is only one diffuse peak and with no sharp diffraction peak among the XRD pattern, indicating a fully glassy phase formed. For the 316L SS, typical austenite (1 1 1), (2 0 0) and (2 2 0) peaks can be observed.

3.2. OCP measurement

From OCP measurements, the following data could be obtained: in Hank’s solution, the OCP value of FeY BMG is ($-0.178 ± 0.016$) V, while 316L SS is ($-0.18 ± 0.012$) V; in artificial saliva, the OCP value of FeY BMG is ($-0.185 ± 0.022$) V, while 316L SS is ($-0.144 ± 0.003$) V.

3.3. Electrochemical impedance measurement

The impedance spectra for the FeY BMG and 316L SS samples after 7200 s immersion time in simulated body fluids are shown in Fig. 2. The fitted curves are obtained using the $R_s(Q_pR_p)$ model with only one time constant. Very good agreement between simu-

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Fig. 1. XRD pattern of FeY BMG and 316L SS.

Fig. 2. Representative EIS spectra diagrams of experimental data and fitted curves. (a) Nyquist diagram in Hank’s solution; (b) Bode diagram in Hank’s solution; (c) Nyquist diagram in artificial saliva solution; and (d) Bode diagram in artificial saliva solution.
lated and experimental data is achieved, with chi-square values below $1 \times 10^{-3}$. It is obvious from Nyquist plots that the diameter of the semicircle for FeY BMG is bigger comparing to that of 316L SS in both simulated body fluids, which indicates the enhancement of the corrosion resistance [13]. It also can be observed that both samples have a similar pattern of Bode–log|$Z$ plots in the low and middle frequency ranges, and the impedance spectra display a linear slope of about $-1$, which is the characteristic response of a capacitive behavior of passive film [14–16]. In the Bode-phase plots in Fig. 2, the phase angle drops to near $0^\circ$ with the response of electrolyte resistance in the high frequency region; in the middle frequency range, the phase angles remain near to $-80^\circ$ indicating a typical passive film presented on the surface.

### Table 1: Results of electrochemical parameters.

<table>
<thead>
<tr>
<th></th>
<th>$R_s$ (Ω cm$^2$)</th>
<th>$R_p$ (10$^5$ Ω cm$^2$)</th>
<th>$Q_p$ (l F cm$^{-2}$)</th>
<th>$n$</th>
<th>$E_{corr}$ (V)</th>
<th>$E_{pit}$ (V)</th>
<th>$E_{pp}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>316L SS Hank's</td>
<td>16.67 ± 0.13</td>
<td>3.31 ± 0.17</td>
<td>58.26 ± 0.044</td>
<td>0.8809 ± 0.0018</td>
<td>4.537 ± 0.691</td>
<td>0.262 ± 0.026</td>
<td>0.27 ± 0.09</td>
</tr>
<tr>
<td>316L SS Saliva</td>
<td>226 ± 1.75</td>
<td>7.06 ± 0.28</td>
<td>18.15 ± 0.016</td>
<td>0.9095 ± 0.0026</td>
<td>1.763 ± 0.412</td>
<td>0.225 ± 0.012</td>
<td>0.23 ± 0.09</td>
</tr>
<tr>
<td>FeY BMG Hank's</td>
<td>11.35 ± 0.14</td>
<td>0.14</td>
<td>5.44 ± 0.39</td>
<td>37.76 ± 0.38</td>
<td>0.8846 ± 0.0093</td>
<td>0.276 ± 0.016</td>
<td>0.28 ± 0.09</td>
</tr>
<tr>
<td>FeY BMG Saliva</td>
<td>234 ± 0.59</td>
<td>2.40</td>
<td>8.47 ± 0.095</td>
<td>3.18 ± 0.041</td>
<td>0.8755 ± 0.0049</td>
<td>0.381 ± 0.025</td>
<td>0.39 ± 0.09</td>
</tr>
<tr>
<td>Annealed FeY Hank's</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>3.591 ± 3.189</td>
<td>0.286 ± 0.026</td>
<td>0.57 ± 0.03</td>
</tr>
<tr>
<td>Annealed FeY Saliva</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.461 ± 0.778</td>
<td>0.290 ± 0.023</td>
<td>0.31 ± 0.25</td>
</tr>
</tbody>
</table>

![Fig. 3. Representative cyclic polarization curves of FeY BMG, annealed FeY and 316L SS (a) in Hank's solution; and (b) in artificial saliva solution.](image)

![Fig. 4. Metal ion releasing concentration into the electrolytes after cyclic polarization.](image)
and a near capacitive response for passive film; in the low frequency, the phase angles decrease to lower value because of the contribution of the passive film resistance \[14–16\]. These results show that the one-layer model could describe satisfactorily the oxide films formed on the alloy surfaces in simulated body fluids. Table 1 shows the parameter values obtained from the fitting results. As can be seen in Fig. 2 and Table 1, FeY BMG sample presents higher \( R_p \) value and smaller \( Q_p \) value than that of 316L SS in both simulated body fluids, which could be attributed to the amorphous feature and the composition difference.

### 3.4. Cyclic polarization measurement

EIS results proved FeY BMG has higher impedance values than that of 316L SS and further indicated that oxide film of FeY BMG might be more corrosion resistant than 316L SS. Fig. 3 presents the cyclic polarization curves for FeY BMG, annealed FeY and 316L SS measured in Hank’s solution and artificial saliva solution. The corrosion potential \( (E_{corr}) \), the pitting potential \( (E_{pit}) \) and the corrosion current density \( (i_{corr}) \) can be calculated from the polarization curves and are shown in Table 1. Apparently, with smaller \( i_{corr} \) values and higher pitting potentials in both simulated body fluids, FeY BMG is more corrosion resistant than annealed FeY and 316L SS.

To reveal the stability of passive films after anodic polarization, negative scans were recorded during the polarization measurements, and \( E_{pp} \) values were obtained, the potential at which the current density returns to the passive value, as shown in Table 1. In both simulated body fluids, FeY BMG owes much higher \( (E_{pp} - E_{corr}) \) and \( (E_{pit} - E_{corr}) \) values than that of annealed FeY and 316L SS. It would be less risky for FeY BMG to meet pitting problems in body fluids under normal condition. These results also proved that the excellent corrosion resistance of FeY BMG is not only contributed to its composition, but also to its amorphous structure feature, mostly.

Fig. 4 shows the metal ions releasing concentration from the tested samples into the electrolytes after cyclic polarization, error bars indicate standard deviation. For 316L SS, significant Ni ion is detected at the level of 1 µg/ml. Comparing their common metal constituents (i.e. Fe, Cr, Mo) release of 316L SS and FeY BMG in Hank’s solution, obvious Fe ion is detected for 316L SS after pitting corrosion, however, no Fe ion is detected for the case of FeY BMG after pitting corrosion. Cr ion concentrations are even for both alloys. FeY BMG has higher Mo ion releasing into the solution. In artificial saliva solution, even though FeY BMG has higher Cr and Mo constituent in its composition, the Cr and Mo ions released are less than those released from 316L SS.

### 4. Conclusions

In summary, because of the amorphous structure feature, FeY BMG displays higher pitting potential values and lower corrosion current density values than that of 316L SS both in Hank’s solution and in artificial saliva solution, making them quite safer than 316L SS for the biomedical applications. And it is also interesting to see that FeY BMG has better corrosion resistance in artificial saliva solution than in Hank’s solution, suggesting more positive prospective applications in dental areas.

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### References