Simulated body fluid electrochemical response of Zr-based metallic glasses with different degrees of crystallization

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The bio-electrochemical response in simulated body fluid of the Zr53Cu30Ni9Al8 metallic glasses with different degrees of partial crystallization was systematically examined and discussed. Through thermal annealing, the volume fractions of the crystalline phases are determined to be 0, 34, 63, and near 100%. Based on the bio-corrosion voltage and current, as well as the polarization resistance, it is concluded that the fully amorphous alloy exhibits the highest bio-electrochemical resistance. With an increasing degree of partial crystallization, the corrosion resistance becomes progressively degraded. The passive current reveals that the fully amorphous metallic glasses can form a more protective and denser passive film on the metallic glass surface. The formation of reactive nanocrystalline phases in the amorphous matrix would reduce the bio-corrosion resistance.

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1. Introduction

Ideal clinical biomaterials have to satisfy the following conditions: good biocompatibility, non-toxicity, non-allergic responses, non-carcinogenic effects and applicable mechanical properties. Metals, polymers, ceramics, and biopolymers are well-known major types of biomaterials. Polymers and ceramics are widely used in many biomedical applications [1–4], but they are not favorable for load-bearing applications due to their poor strength or fatigue endurance limit [5,6]. On the contrary, the sufficient yield strength and the resistance to cyclic loading make metals suitable for orthopedic load-bearing applications, including dental implants, artificial joint replacement, and bone fixation [5–7]. Notwithstanding that Ti-based and Co-based alloys are popular for metallic implants in early stages, their unsatisfactory wear resistance gives rise to toxic debris after long-term use [8–11].

Because of the outstanding corrosion resistance, high hardness and wear resistance, good biocompatibility and low Young’s modulus, bulk metallic glasses (BMGs), porous metallic glass foams (PMGFs) and thin film metallic glass (TFMG) coating have attracted interest and made them potential candidates for bio-implants [12–16]. The amorphous metallic glasses were the alloys that rapidly quenched from the liquid state to the solid state at a high cooling rate in avoiding the nucleation and growth of the crystalline phases. Thus, there are no structural defects (vacancies, dislocations and grain boundaries) included in the amorphous metallic alloy. Due to the disordered atomic structure and the lack of the periodicity of a crystal, the amorphous metallic glasses own superior mechanical and chemical properties. Hiromoto et al. [17–19] investigated the corrosion behavior of the Zr-based amorphous alloy in the phosphate buffered solution (PBS) and simulated body fluid (SBF). Morrison et al. [20] conducted major studies on the different corrosion behavior between the Zr-based amorphous alloy and various metals (316 stainless steel, CoCrMo, and Ti-6Al–4V) in PBS. In our previous studies, the Zr-based amorphous alloy exhibited good corrosion resistance and electrochemical stability [21]. These results revealed that Zr-based amorphous alloys are high potential materials for biomedical applications. Recently, some studies started to point out the different corrosion behavior of partially amorphous and fully nanocrystalline alloys. For example, Xiang et al. [22] reported that the nanocrystalline phases formed during heat treatment in the Fe47.5Si12B8NbCu4 amorphous alloy can improve corrosion behavior due to the formation of a passive film in a 3.5% NaCl solution. On the other hand, Wu et al. [23] found that the galvanic cell reaction in the nanocrystalline Fe80B18Mo4 alloys would degrade corrosion resistance in a 3.5% NaCl solution. Moreover, the good corrosion behavior of the Zr-based BMGs, in both amorphous and crystalline states, has been demonstrated by Peter et al. [24] when the alloys are exposed in a 0.6 M NaCl solution.

It appears that the formation of different quantities of nanocrystalline phases would affect the corrosion behavior of the amorphous matrix in various corrosive media. But it is still not certain whether the metallic glass alloys in fully amorphous or partially nanocrystalline state would exhibit better bio-corrosion behavior. This can be
an important issue for metallic glass bio-implant application, since all metallic glasses could accidentally induce various amounts of partial nanocrystalline phases within the amorphous matrix, either during fabrication or long-term service. In this work, the electrochemical responses of amorphous and nanocrystalline Zr-based alloys with different crystallinities are investigated in the SBF for establishing the clear profile of their corrosion behavior. The most common model of Zr-based BMGs, Zr53Cu30Ni9Al8, although with 9 at.% Ni, was chosen for this study. This is because this alloy has been extensively studied and the crystallization kinetics and other physical/mechanical properties have been well characterized.

2. Experimental procedures

For the fabrication of the Zr53Cu30Ni9Al8 (all in atomic percent) bulk metallic glass, the pure element of Zr (99.9 wt.% purity), Cu (99.999 wt.% purity), Ni (99.9 wt.% purity), and Al (99.99 wt.% purity) were heated to melt and mixed to an alloy ingot by arc melting under an argon atmosphere. Then the well mixed ingot was remelted and suction cast through the water-cooled Cu mold to form the 2 × 5 cm² Zr53Cu30Ni9Al8 amorphous plates with high rapid cooling capability. Then the amorphous plates were sliced to 0.4 × 0.4 cm² for heat treatment and potentiodynamic polarization measurements. Thermal analysis and the carefully controlled preparation of different degrees of partially crystalline Zr2Cu nano-phase in the Zr-based amorphous alloys were carried out by Perkin-Elmer Diamond DSC differential scanning calorimeter (DSC) at constant heating rates of 40 K/min. The Zr53Cu30Ni9Al8 plates were annealed at 713 K for 21, 23 and 40 min under a protective argon atmosphere. After heat treatment, the outer oxidative layers of specimens were polished by P4000-grit abrasive papers and cleaned with acetone and ethanol by sonicator for other measurements. The amorphous nature of the as-cast plate and the phase identification of partially crystalline samples were conducted using Bruker D8 X-ray diffractometry (XRD) with a monochromatic Cu-Kα radiation (λ = 1.5406 Å) and operated at 40 kV and 40 mA. The energy dispersive spectrometry (EDS) associated with JEOL JSM-6330 scanning electron microscopy (SEM) is selected to check whether the compositions of the metallic glasses are mixed homogeneously. The final composition of Zr53Cu30Ni9Al8 is confirmed. In addition, the EDS mapping function of the EDS system was also adopted to verify the uniform atomic distribution.

In this study, SBF Hank’s solution (with a composition of 0.137 M of NaCl, 0.25 mM of KCl, 0.44 mM of KH2PO4, 1.3 mM of CaCl2, 1.0 mM of MgSO4, and 4.2 mM of NaHCO3) was chosen to be the environment of bio-corrosion. The electrochemical behavior and corrosion properties of the fully amorphous and partially crystalline Zr-based alloys in 40 mL SBF (pH: 6.5) at 310 K (37 °C) were studied by potentiodynamic polarization measurements and an AC impedance test which were conducted by the CHI 614D electrochemical workstation in a three-electrode cell. The counter and reference electrodes were platinum wire and Ag/AgCl, and specimens were used as a working electrode with an immersion area of about 16 mm². Before potentiodynamic polarization measurements and the AC impedance test, the specimens were allowed to stabilize in SBF until the open-circuit potential (OCP) changed by no more than 2 mV/5 min. The polarization scan was started from −0.3 V with a scan rate 0.33 mV/s. The corrosion current density (Icorr), corrosion potential (Ecorr) and corrosion rate can be determined by the Tafel extrapolation method from anodic polarization curves. The AC impedance test was carried out with an amplitude of 10 mV in open-circuit potential and the frequency range is 10⁻² to 10⁴ Hz.

3. Results and discussion

The thermal properties of specimens have to be determined for confirming the amorphous structures and ideal annealing temperature. The DSC curves of Zr53Cu30Ni9Al8 amorphous alloys reveal obvious glass transition (Tg) and crystallization (Tx) temperatures, as shown in Fig. 1. which means that the structure of as-cast specimens are amorphous and the Tg and Tx are 693 K and 768 K, respectively. The proper annealing temperatures were between Tg and Tx to avoid the formation of too pronounced phases which will cause complex electrochemical analysis. Fig. 2a shows the DSC scanning curve of the as-cast and annealed specimen to different time periods, the crystallinities of the annealed specimens can be calculated from the enthalpy release (ΔH) of the annealed specimens by DSC analysis program. The ΔH

![Fig. 1. DSC curve of as-cast Zr53Cu30Ni9Al8 metallic glasses.](image)

![Fig. 2. (a) DSC curves and (b) XRD patterns of as-cast Zr53Cu30Ni9Al8 and its partial crystalline alloys.](image)
of the as-cast and annealed specimens for 21, 23, and 40 min are 59.62, 39.25, and 22.29, respectively. The volume fractions of the crystallinities are determined to be 0, 34, and 63, respectively. The XRD patterns of as-cast and annealed specimens. The crystallization peaks reveal the formation of predominant Zr2Cu and minor Zr2Ni phases. For longer annealing time, Zr2Cu appears as the major phase, due to the high atomic percentage of the copper. Based on our previous studies, the Zr2Cu nanocrystal size and volume fraction increase with increasing heat treatment time. The representative bio-corrosion potential versus immersion time for the as-cast and the specimen annealed for 21 min is first studied by the open circuit potential curve (also called the OCP or E-t curve), as shown in Fig. 3. The open circuit potential of as-cast and annealed specimen is stabilized over immersion time, indicating the formation of an oxidative passive layer for all alloys after a 5400 s immersion in Hank's solution. Because the open circuit potential is equal to corrosion potential approximately, the as-cast specimen possesses lower corrosion activity (at about −0.380 V), 23 min (at about −0.300 V), and 40 min (at about −0.436 V), due to the higher stabilized open circuit potential, as compared in Table 1. Hence, the OCP curves reveal that the bio-corrosion activity increases with an increasing annealing time period. There are many important corrosion parameters of as-cast and annealed specimens that can be determined by potentiodynamic polarization measurement, as shown in Fig. 4. The corrosion potential (Ecorr) is used to evaluate driving force for bio-corrosion, and the system with a higher Ecorr means it needs more energy to start a corrosion reaction. The average Ecorr of the as-cast, partially (annealed for 21 min and 23 min), and fully (annealed for 40 min) crystalline specimens are about −0.214, −0.333, −0.391, and −0.423 V, respectively (Table 1). Hence, the OCP curves reveal that the bio-corrosion activity increases with an increasing annealing time period.

The corrosion current density (Icorr) is another important parameter for determining the activity of corrosion reaction. The average Icorr is determined to be about 0.06 × 10−5 A for the as-cast specimen and about 0.198 × 10−5, 0.433 × 10−5 A for the specimens annealed for 21 to 40 min. The much higher Icorr values of the annealed specimens again stand for the greater degree of electrochemical activity as compared with the as-cast specimen. The induced corrosion current of the fully crystallized sample is almost 20 times that of the fully amorphous one, directly indicating that the bio-corrosion reaction is significantly more severe in the crystallized samples. Both the above Ecorr and Icorr data consistently indicate that the fully amorphous metallic glass would exhibit the strongest bio-electrochemical resistance. With an increasing degree of partial crystallization, the sample corrosion resistance becomes progressively degraded.

In the SBF, the higher ionic strength of chloride makes serious pitting reaction on amorphous materials. The pitting potential (Epit) is an index to determine whether the chloride-induced pitting occurred from the sudden signal rise of polarization curve, as defined in Fig. 4. For the as-cast specimen, the pitting reaction is seen to start from a high potential at 0.035 V, as listed in Table 1. The Epit of partially and fully crystalline specimens all lie in a much lower potential range from −0.037 to −0.060 V; Epit seems to be slightly lower with an increasing crystalline volume fraction. But overall, the difference of Epit is not significant (only 0.095 V from +0.035 to −0.060 V), suggesting that both the amorphous and crystalline materials cannot avoid pitting reaction in SBF when the applied potential reaches this level.

The passive region (ΔE = Epit − Ecorr) is a region for the formation of the oxidative film during anodic polarization. Although the crystalline materials appear to possess a slightly wider region (about 0.1 V in Table 1) for the formation of the passive film, the Epit levels of crystallized samples were all low. Thus ΔE does not act as a solid indication for protection capability of the oxidation film. The passivation current density, i-pass, has to be considered. The fully amorphous material possesses a much lower passive current density (about 10−7 A in Table 1) than the crystalline materials (about 10−6 A in Table 1), meaning that a more protective and dense passive film has formed on the surface of the fully amorphous specimen in SBF [30]. The partial and

Table 1
Bio-corrosion properties of the as-cast and annealed Zr53Cu30Ni9Al8 metallic glasses in Hank’s solution. All specimens are tested two to three times to ensure reproducibility.

<table>
<thead>
<tr>
<th></th>
<th>Icorr (10−9 A/cm²)</th>
<th>Ecorr (V)</th>
<th>Epit (V)</th>
<th>ΔE = Epit − Ecorr (V)</th>
<th>i-pass (10−6 A/cm²)</th>
<th>Rp (106 Ω cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-cast</td>
<td>0.006 ± 0.001</td>
<td>−0.214 ± 0.043</td>
<td>0.035 ± 0.008</td>
<td>0.250 ± 0.044</td>
<td>0.040 ± 0.001</td>
<td>0.62 ± 0.40</td>
</tr>
<tr>
<td>21 min</td>
<td>0.198 ± 0.015</td>
<td>−0.333 ± 0.034</td>
<td>−0.037 ± 0.028</td>
<td>0.396 ± 0.003</td>
<td>0.987 ± 0.176</td>
<td>0.21 ± 0.02</td>
</tr>
<tr>
<td>23 min</td>
<td>0.433 ± 0.020</td>
<td>−0.391 ± 0.001</td>
<td>−0.045 ± 0.053</td>
<td>0.349 ± 0.051</td>
<td>3.480 ± 0.283</td>
<td>0.06 ± 0.02</td>
</tr>
<tr>
<td>40 min</td>
<td>1.134 ± 0.392</td>
<td>−0.423 ± 0.017</td>
<td>−0.060 ± 0.012</td>
<td>0.363 ± 0.025</td>
<td>10.823 ± 9.405</td>
<td>0.04 ± 0.01</td>
</tr>
</tbody>
</table>
fully crystalline specimens are more sensitive and prone to the chloride-induce pitting reaction. Based on the above results, both the \( E_{\text{corr}} \) and \( I_{\text{pass}} \) data again consistently indicate that the fully amorphous metallic glass is inherent with the strongest bio-electrochemical resistance.

Finally, a common electrochemical impedance method is adopted to ensure the above findings. It utilizes the so-called Nyquist plot [15] to illustrate the electrochemical impedance spectra (EIS) for evaluating the polarization resistance (\( R_p \)). The equivalent circuit model for the Nyquist plots is shown in Fig. 5. The impedance of constant phase element (CPE) is defined as \( Z_{\text{CPE}} = 1 / Q(\omega)^n \), where \( \omega \) is angular frequency, \( Q \) is pre-factor of CPE, and \( n \) is its exponent with the range \( 0 \leq n \leq 1 \). In an AC circuit, the impedance \( Z \) is more appropriate to represent the system’s entire resistance. From Euler’s relations, we know that \( Z = Z_0(\cos \theta + j \sin \theta) \). Hence, the impedance can be described by the real and imaginary part (\( Z = Z' + jZ'' \)), and the Nyquist plot is often represented by \( Z' \) versus \( Z'' \).

The relation between \( R_p \) and \( Z \) is given by [31]:

\[
Z = R_s + \frac{R_p \left( 1 + R_p Q_0^n \cos(\frac{\pi n}{2}) \right)}{1 + 2R_p Q_0^n \cos(\frac{\pi n}{2}) + \left( R_p Q_0^n \right)^2} + j \frac{-R_p Q_0^n \sin(\frac{\pi n}{2})}{1 + 2R_p Q_0^n \cos(\frac{\pi n}{2}) + \left( R_p Q_0^n \right)^2},
\]

where \( R_s \) is electrolyte resistance.

The fitted data are presented as the Nyquist plot in Fig. 6 for the four specimens. In the Nyquist plot, the larger diameter of the semi-circle represents a higher corrosion resistance [15]. It is clear that the as-cast specimen owns the highest corrosion resistance. The \( R_p \) reading is \( 6.82 \times 10^5 \) \( \Omega \) for the as-cast specimen, \( 0.21 \times 10^5 \) and \( 0.06 \times 10^5 \) for the partially crystalline 21 and 23 min ones, and \( 0.04 \times 10^5 \) for the fully crystalline 40 min sample. The \( R_p \) reading of the fully amorphous MG is 170 times higher than that of the fully crystallized sample, exhibiting significant corrosion resistance in SBF.

As for the underlying reasons for the lower bio-corrosion resistance in the crystallized specimens, it is believed to be caused by the structure and composition of the precipitated phases. Because Cu and Ni is both nobler than Zr [30,32], the dominant Zr2Cu and minor Zr2Ni nanocrystalline phases will induce serious galvanic corrosion. With increasing annealing time, the size and quantity of the reactive Zr2Cu and minor Zr2Ni nanocrystals both increase. Preferential electrochemical reaction would undergo more and more intensely around the precipitated phases. With increasing annealing time and thus an increasing crystallite volume fraction, the bio-corrosion becomes more severe. Hence, in comparison with the fully amorphous and fully crystallized specimens, the starting corrosion potential \( E_{\text{corr}} \) in the crystallized specimens would become lower (from around \(-0.2 \) to \(-0.4 \) V), the measured corrosion current \( I_{\text{corr}} \) would become higher (from \( 6 \times 10^{-8} \) A/cm\(^2 \) to \( 1 \times 10^{-5} \) A/cm\(^2 \)), the passivation current density \( I_{\text{pass}} \) would become higher (from \( 10^{-7} \) A/cm\(^2 \) to \( 10^{-4} \) A/cm\(^2 \)), and the polarization resistance \( R_p \) would become lower (from around \( 7 \times 10^4 \) \( \Omega \) cm\(^2 \) to \( 4 \times 10^3 \) \( \Omega \) cm\(^2 \)).

4. Conclusions

Metallic glasses have recently been considered to be applied for bio-applications. It is always inevitable that some metallic glasses would possess a certain degree of nano-sized crystalline phases. It is critical in application and of interest in scientific understanding whether the fully amorphous or the partially crystallized alloys would exhibit better bio-corrosion resistance in body fluid.

In this study, through controlled thermal annealing, the Zr-based metallic glasses with the crystalline phase volume fractions (predominantly Zr2Cu plus minor Zr2Ni) of 0, 34, 63, and near 100% are prepared. Based on the bio-corrosion voltage and current, as well as the polarization resistance, it is concluded that the fully amorphous alloy exhibits the highest bio-electrochemical resistance. With increasing annealing time and thus an increasing degree of partial crystallization, the corrosion resistance becomes progressively degraded. In comparison with the fully amorphous and fully crystallized specimens, the starting corrosion potential \( E_{\text{corr}} \) in the crystallized specimens would become lower (by 0.2 V), the measured corrosion current \( I_{\text{corr}} \) would become higher (by almost three orders of magnitude from \( 10^{-4} \) to \( 10^{-1} \) A/cm\(^2 \)), and the polarization resistance \( R_p \) would become lower (by two orders of magnitude from \( 10^3 \) to \( 10^1 \) \( \Omega \) cm\(^2 \)).

Preferential electrochemical reaction would undergo more and more intensely around the precipitated phases. The fully amorphous metallic glasses can form a more protective and denser passive film on the metallic glass surface. The formation of reactive nanocrystalline phases, which themselves would induce serious galvanic corrosion, in the amorphous matrix would reduce the bio-corrosion resistance.

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References