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The corrosion behavior of *in-situ* Zr-based metallic glass matrix composites in different corrosive media

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ABSTRACT

The corrosion behavior of $Zr_{58.5}Ti_{14.3}Nb_{5.2}Cu_{6.1}Ni_{4.9}Be_{11.0}$ metallic glass matrix composites (MGMCs) in different corrosive media, including 1 M NaCl, 1 M HCl, 0.5 M H_2SO_4, and 1 M NaOH solutions, was studied. The electrochemical characteristics of the composites were investigated by potentiodynamic-polarization measurements. The results show that the corrosion resistance in NaOH solution is the poorest in terms of the corrosion potential (E_{corr}) and corrosion current density (i_{corr}). For comparison, the chemical immersion tests were conducted. The corroded surface morphologies after electrochemical and immersion measurements both show that the amorphous matrix and crystalline dendrites exhibit different corrosion behaviors. The possible interpretation of the observed morphology evolution was proposed. The effect of a very base metallic element of beryllium on the corrosion dynamic process has been emphasized.

1. Introduction

The successful development of bulk metallic glasses (BMGs) triggered a great deal of research enthusiasm on the pursuit of the new-generation structural engineering materials in recent years [1–3]. BMGs exhibited high strength, large elastic limits, and excellent corrosion resistance [4–9], showing great application potentials. However, extensive applications of BMGs are seriously hindered by their poor macroscopic ductility. To circumvent this obstacle, recently, a series of *in-situ* metallic glass matrix composites (MGMCs), which combines the high-strength glass matrix with ductile crystalline phases, have been developed [10–14]. The crystalline phases distributed in the glassy matrix stabilize the shear localization and leads to significant improvement in both the compressive plasticity and tensile ductility [15–17].

Up to now, the corrosion behavior of Zr-based BMGs in different aqueous, hydrothermal, and dry high-temperature environments has been studied in detail [18–22]. Excellent passivation behavior in halide-free solutions at room temperature were found on these Zr-based BMGs, which was attributed to the properties of their valve metal components, e.g., Zr, Al, and Ti [23]. However, the investigation of *in-situ* Zr-based MGMCs is mainly focused on the glass-forming ability, structural and mechanical properties. Very few attentions have been paid to the fundamental chemical and environmental stability for *in-situ* Zr-based MGMCs, which is also a crucial factor for their applications. Only a few studies have been devoted on the corrosion resistance of the *in-situ* Zr-based MGMCs in chloride-containing solutions [24,25]. The complexity of corrosion resistance behavior of *in-situ* Zr-based MGMCs revealed by these studies grants the further investigation on this topic. Therefore, in this study, the corrosion properties of $Zr_{58.5}Ti_{14.3}Nb_{5.2}Cu_{6.1}Ni_{4.9}Be_{11.0}$ MGMCs were studied in different media by means of potentiodynamic-polarization and chemical immersion measurements.

2. Experimental

Master ingots of the atomic nominal composition (at.%) of $Zr_{58.5}Ti_{14.3}Nb_{5.2}Cu_{6.1}Ni_{4.9}$ $Be_{11.0}$ alloys were prepared by arc melting a mixture of Zr, Ti, Nb, Cu, Ni, and Be elements with purities greater than 99.9% (wt.%) in a Ti-gettered high-purity argon

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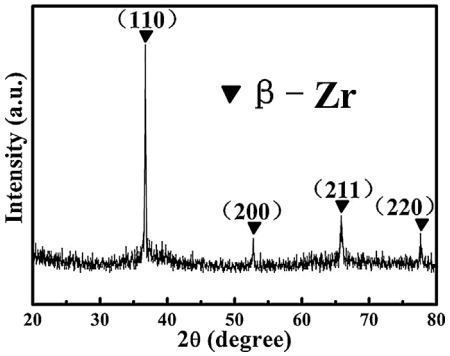

Fig. 1. XRD pattern of the $Zr_{58.5}Ti_{14.3}Nb_{5.2}Cu_{6.1}Ni_{4.9}Be_{11.0}$ MGMCs.

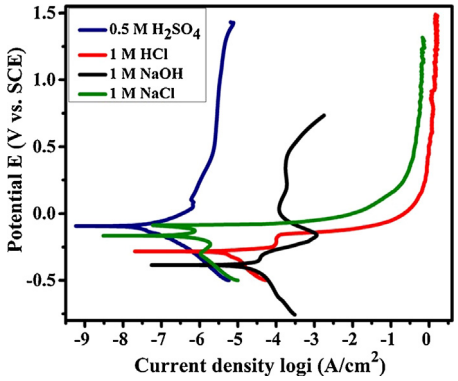

Fig. 3. Potentiodynamic-polarization curves of the $Zr_{58.5}Ti_{14.3}Nb_{5.2}Cu_{6.1}Ni_{4.9}Be_{11.0}$ MGMCs in different solutions.

atmosphere. Then, by copper mould casting, cylinder-shaped samples with a diameter of 5 mm and a length of 70 mm were obtained. The casted ingots were, then, cut into small size samples using a low-speed precision-cutting machine for further corrosion experiments. All the samples were prudentially ground with SiC grit papers (up to grit No. 1200), then, polished by an electropolishing machine to diminish the effects of the surface composition on the corrosion and anodic polarization behavior, and ultrasonically cleaned with distilled water, ethanol, dried in air, and embedded in epoxy resin before the electrochemical and surface analytical tests.

The microstructure of Zr-based MGMCs was examined by X-ray diffraction (XRD) with Cu Kα radiation (D-8 Bruker AXS). A Tescan LYRA 3 XMH scan electron microscopy (SEM) coupled with energy-dispersive spectrum (EDS) was employed to obtain the morphology and elemental distribution. The electrochemical characteristics of the samples were investigated by potentiodynamic-polarization methods with a potential sweep rate of 0.5 mV/s in a three-electrode cell. All reported potentials in this study were referred to the saturated calomel electrode (SCE). A CS350 electrochemical measurement system was employed to conduct all electrochemical measurements. Electrochemical-impedance-spectroscopy (EIS) measurements were conducted in the frequency range from 10^{-2} to 10^5 Hz. The electrolytes are 1 M NaCl, 1 M HCl, 0.5 M H_2SO_4, and 1 M NaOH solutions. The corrosion current density (i_{corr}) was measured from the intersection of anodic and cathodic polarization curves (Tafel slope methods). All measurements were conducted at least three times to ensure the repeatability.

3. Results and discussion

3.1. Microstructure characterization

Fig. 1 exhibits a typical X-ray diffraction (XRD) pattern of in-*situ* $Zr_{58.5}Ti_{14.3}Nb_{5.2}Cu_{6.1}Ni_{4.9}Be_{11.0}$ MGMCs. As can be seen from Fig. 1, four sharp crystalline peaks are superimposed on a broad diffuse diffraction peak, indicating a composite containing both amorphous and crystalline phases. The careful evaluation of the XRD pattern reveals that the four sharp scattering peaks correspond to body-centered-cubic (bcc) β-Zr solid solution [26]. There are no other phases that can be detected from the diffraction pattern of composites.

The surface morphology and elemental distribution of as-polished in-*situ* $Zr_{58.5}Ti_{14.3}Nb_{5.2}Cu_{6.1}Ni_{4.9}Be_{11.0}$ MGMCs samples are studied by SEM and EDS. The SEM image of typical sample surface and the corresponding EDS analysis results are showed in Fig. 2. As can be seen from Fig. 2(a), the crystalline dendrites are evenly distributed in the otherwise featureless amorphous matrix. The elemental distributions obtained from EDS are illustrated in bar chart, as shown in Fig. 2(b). For the sake of comparison, elemental distribution both in dendrite and glass matrix is illustrated together. As demonstrated in Fig. 2(b), the elemental distribution discrepancy between dendrite and matrix is negligible except for Zr and O. Zr content in amorphous matrix is higher than that in the crystalline dendrite. The high concentration of oxygen (more than 25%) strongly suggests the presence of oxide on the surface. Note that the element Be is beyond the EDS capacity and cannot be detected.

3.2. Electrochemical corrosion behavior

The potentiodynamic-polarization measurements of in-situ Zr-based MGMCs are conducted at room temperature within a wide pH value range. The anodic and cathodic polarization curves are shown in Fig. 3. As indicated from the blue line (H_2SO_4) in Fig. 3, when the applied potential is higher than 0.1 V_{SCE}, (where V_{SCE} is the potential related to the saturated calomel electrode potential), the current stop increasing with further increase of potential. Even without the appearance of an obvious active dissolution regime,

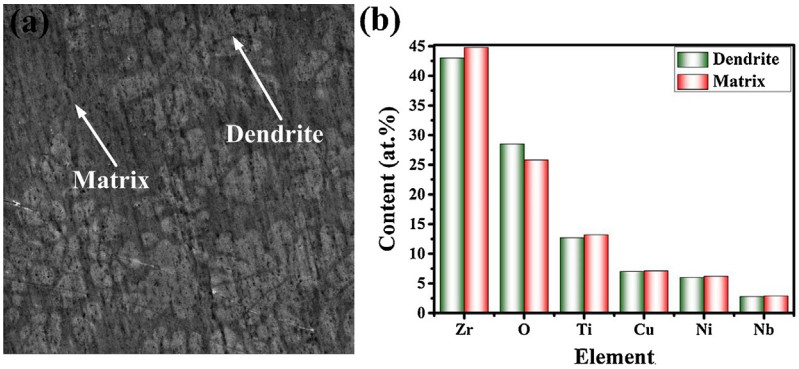

Fig. 2. The SEM image and EDS results on the as-polished the $Zr_{58.5}Ti_{14.3}Nb_{5.2}Cu_{6.1}Ni_{4.9}Be_{11.0}$ MGMCs.