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Electrochemical and chemical corrosion behaviors of the in-situ Zr-based metallic glass matrix composites in chloride-containing solutions

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The $Zr_{58.5}Ti_{14.3}Nb_{5.2}Cu_{6.1}Ni_{4.9}Be_{11}$ metallic glass matrix composites (MGMCs) were prepared by copper mould casting. The corrosion resistance and the pitting susceptibility of Zr-based MGMCs were tested in 1M KCl, 1M NaCl, and 0.5M $CaCl_2$ solutions by potentiodynamic polarization tests and chemical immersion measurements. As a result, the corrosion current density is the smallest, and the pitting potential is the largest in 0.5 M $CaCl_2$ solutions due to the smallest radium of Ca^{2+}, which indicates that the Zr-based MGMCs have better corrosion resistance. On the contrary, the corrosion resistance of Zr-based MGMCs in 0.5M $CaCl_2$ solutions is poor during the immersion tests, which corresponds to the result of roughness. Further investigation of XPS indicates that oxide films are mainly composed of ZrO_2, TiO_2, and Nb_2O_5 formed on the surface of the Zr-based MGMCs. However, the oxide films formed in 0.5M $CaCl_2$ solutions possess the worst protective effect due to the lower contents of ZrO_2, TiO_2, and Nb_2O_5, whereas the oxide films formed in 1M NaCl solutions possess the best protective effect.

1. Introduction

Bulk metallic glasses (BMGs) possess superior mechanical properties at room temperature, such as high strength, large elastic limit, low elastic modulus, excellent corrosion and wear resistance [1–6]. However, low room-temperature plasticity hinders its application as structural engineering materials [7–10]. In order to solve the problem, a large number of *in-situ* metallic glass matrix composites (MGMCs), which combines high-strength glass matrix with ductile crystalline phases, have been developed. By introducing nano-scale and micro-scale secondary phases into the amorphous matrix, the plasticity is greatly improved without obviously deteriorating other mechanical properties [11–17]. Zr-based MGMCs have excellent mechanical properties. For example, $Zr_{58.5}Ti_{14.3}Nb_{5.2}Cu_{6.1}Ni_{4.9}Be_{11}$ MGMCs can work as excellent structural engineering materials due to its high tension fatigue limit and four-point-bending fatigue limit [18].

The world has suffered serious economic losses due to corrosion of various materials in recent years. So the corrosion resistance of materials is very important for the application of engineering materials. Some researchers have studied the corrosion properties of monolithic BMGs, such as Zr, Fe, Ti, and Mg-based BMGs [19–23]. Nevertheless, until now, only a few studies are related to the corrosion properties of MGMCs [24,25]. For BMGs, pitting usually occurs in chloride-containing solutions. It has been reported that Zr-based BMGs and their composites all exhibit passivation behaviors in chloride-free solutions. In contrast, they are very susceptible to chloride-induced pitting corrosion [26]. And, Zr-based MGMCs may be utilized in different chloride-containing environments during actual services. So it is necessary to study the corrosion behavior and corrosion resistance of Zr-based MGMCs in different chloride-containing solutions. But, the corrosion behavior and corrosion resistance of Zr-based MGMCs in different chlorine-containing solutions are seldom studied. In this study, The chemical and electrochemical corrosion, and corrosion resistance of Zr-based MGMCs in three chloride-containing solutions are investigated. By comparing the corrosion behavior and corrosion resistance of Zr-based MGMCs in different chloride-containing environments, We know the service conditions of Zr-based MGMCs in these chloride-

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containing environments, thus reducing the losses caused by corrosion.

2. Experiment

Ingots of nominal composition of $Zr_{58.5}Ti_{14.3}Nb_{5.2}Cu_{6.1}Ni_{4.9}Be_{11}$ were prepared by induction melting of pure Zr, Ti, Nb, Cu, Ni, and Be under purified argon atmosphere. From those ingots, rods with 3 mm diameter and 50 mm length were produced by injection casting into a water cooled Cu mould under argon atmosphere. These rods were cut into 3 mm in diameter and 5 mm in length. Samples were carefully polished with grit SiC papers up to 2000 grade and ultrasonically cleaned before tests. For electrochemical tests, the samples were electrically connected to an isolated copper wire and embedded in the epoxy resin so that only these polished surfaces were exposed.

The corrosion resistance of the present Zr-based MGMCs was evaluated by electrochemical measurements and chemical immersion tests. Electrochemical measurements were conducted in a three-electrode cell using a platinum counter electrode and an Ag/AgCl reference electrode. Potentiodynamic polarization curves were measured at a potential sweep rate of 2.0 mV/s in a potential range from -1.0 to $+1.5$ V after the open circuit potentials (OCP) became almost steady. Once the polarization tests were finished, the corroded samples were immediately taken out, then cleaned in distilled water using ultrasonic treatment, and finally dried in air. These electrolyte solutions include potassium chloride, sodium chloride, and calcium chloride solutions. The measurements were repeated for several times in order to ensure a high reliability of the results. The morphologies of corroded samples were established by a Tescan LYRA 3 XMH scanning-electron microscope (SEM) equipped with energy-dispersive spectra (EDS) after the electrochemical measurements. The chemical immersion tests were conducted in these three chloride-containing solutions. All samples were immersed in these three chloride-containing solutions for 100h. The surface roughness of these samples was measured by a FM-Nanoview 6600 atomic force microscope (AFM) after chemical immersion tests. For further surface analysis, X-photoelectron spectroscopy (XPS) measurements were carried out on the selected samples after immersion tests in three chloride-containing solutions using an ESCALAB 250Xi X-photoelectron spectrometer with monochromatized Al K excitation (hv = 1486.6 eV).

3. Results

3.1. Electrochemical corrosion behavior

The surface morphology and elemental distribution in as-cast $Zr_{58.5}Ti_{14.3}Nb_{5.2}Cu_{6.1}Ni_{4.9}Be_{11}$ MGMCs are studied by SEM and EDS. The SEM morphology of the sample surface is shown in Fig. 1(a). The crystalline dendrites are uniformly distributed in the amorphous matrix. The elemental distributions are depicted in Fig. 1(b). The content of Zr in crystalline dendrites and amorphous matrix is highest. The content of Zr, Ti, and Nb in dendrites is higher than that in the amorphous matrix, while Cu and Ni are mainly distributed in the amorphous matrix. With respect to Be element, in-situ dendrites in MGMCs was reported to be Be free, and it is found that Be almost totally dissolves in the amorphous matrix [27].

This study focuses on the corrosion resistance behavior of Zr-based MGMCs in three chloride-containing solutions. To this end, the potentiodynamic polarization measurements of Zr-based MGMCs are conducted in 1 M NaCl, 1 M KCl, and 0.5 M $CaCl_2$ solutions at room temperature. The obtained potentiodynamic polarization curves are illustrated in Fig. 2. Similar potentiodynamic polarization curves are displayed in these three chloride-containing solutions. The cathodic polarization curves show similar trends. With the increase of the applied potential, the current density decreases in these three solutions. At the stage of anodic polarization curves, the current density is increased with the increase of the applied potential. Particularly, when the applied potential reaches a critical value, i.e., -0.262 V, -0.098 V, and 0.265 V in 1 M KCl, 1 M NaCl, and 0.5 M $CaCl_2$ solutions, respectively. The current density rapidly increases in three chloride-containing solutions. It is the pitting corrosion. As can be seen from Fig. 2, the pitting potential in $CaCl_2$ solutions is larger than that in NaCl

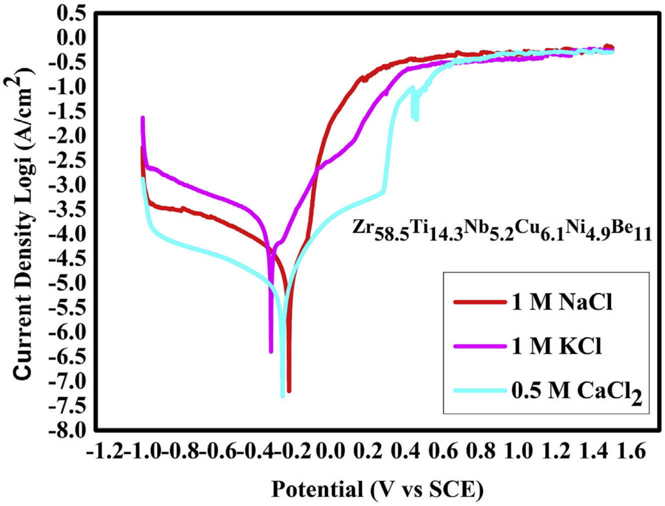

Fig. 2. Potentiodynamic polarization curves of Zr-based MGMCs in different chloride-containing solutions.

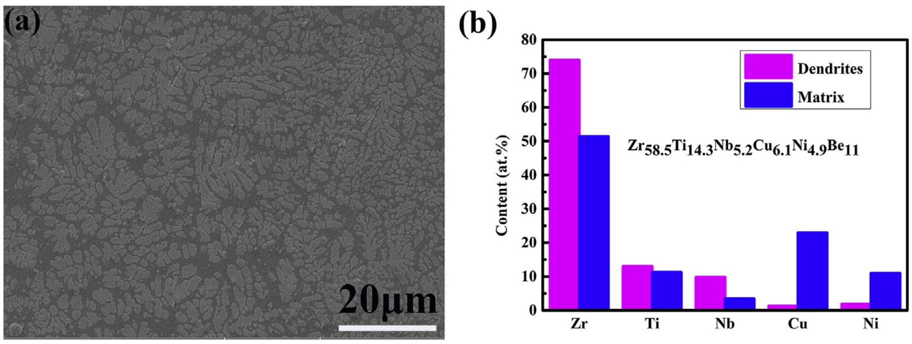

Fig. 1. (a) The microstructure of the present Zr-based composites, (b) and the elements content in dendrites and glass matrix.