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# Corrosion behavior of Cu<sub>55</sub>Zr<sub>35</sub>Ti<sub>10</sub> metallic glass in the chloride media

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# A R T I C L E I N F O

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## ABSTRACT

 $Cu_{55}Zr_{35}Ti_{10}$  (at. %) ribbon was prepared by melt spinning. Its glassy structure was confirmed by X-ray diffraction (XRD) and differential scanning calorimetry (DSC), respectively. Its corrosion behavior in HCl and NaCl solutions was investigated by electrochemical polarization and immersion measurements. The surfaces before and after corrosion were observed with scanning electron microscope (SEM). The corrosion potential and corrosion resistance of the  $Cu_{55}Zr_{35}Ti_{10}$  metallic glass both decrease with increasing chloride concentration, and are higher in NaCl than in HCl. The current density in anodic curve sharply decreases when the potential reaches up to a value and the chloride concentration is more than 0.5 M in both HCl and NaCl solutions. The different corrosion behavior in HCl and NaCl is also carefully discussed.

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### 1. Introduction

Metallic glasses have acquired significant attention from the scientific and technological viewpoints. They usually show high strength, large elastic strain limit, and excellent wear and corrosion resistances, along with other remarkable engineering properties [1]. Many metallic glasses have been used in practical applications [2,3]. However, the applications of the metallic glasses require high chemical stability in various environments in order to ensure its lifetime. Without high corrosion resistance in the service environments, their favorable mechanical properties cannot be fully exploited. Up to now, many corrosion studies have already been reported for metallic glasses in different corrosive media [4–11].

In order to expand the fields of applications of the metallic glasses, the development of new metallic glasses with better mechanical properties and higher corrosion resistance for lower cost is desirable. Compared with Zr- and Pd-based metallic glasses, Cubased metallic glasses exhibit even higher mechanical properties and lower cost [12,13]. In addition, Cu-based metallic glasses are expected to have applications due to their potential as important catalysts. Molnár et al. [14] investigated activation of amorphous Cu-M (M = Ti, Zr or Hf) alloy powders by being applied as catalyst in the transformation of various alcohols at elevated temperature

(523–573 K). Active, stable and selective catalysts were generated from Cu–Zr and Cu–Hf during the dehydrogenation of 2-propanol to acetone and the transformations of allyl alcohol to form propanal and 1-propanol. Cu–Zr–Ti ternary system is a typical glass forming system firstly explored by Inoue's group [15]. The maximum size for glass formation in this system can be up to 5 mm [13]. In order to apply this type of metallic glass as engineering material, the corrosion behavior of Cu-based metallic glasses, such as Cu–Zr [10,11], Cu–Zr–Ti–(Mo, Ta and Nb) [16], Cu–Zr–Ti–Nb [17], Cu–Hf–Ti–(Mo, Ta and Nb) [18], Cu–Zr–Ti–Ni–(Nb, Cr, Mo and W) [19–22], and Cu–Zr–Al–Y [23] has been carried out.

The chloride ion is one of the common corrosive media. It is important for theory and application by the investigation of the corrosion behavior of the metallic glasses in the chloride medium. Zender et al [24] investigated the corrosion performances of Cu<sub>46</sub>Zr<sub>42</sub>Al<sub>7</sub>Y<sub>5</sub> and Zr<sub>58.5</sub>Cu<sub>15.6</sub>Ni<sub>12.8</sub>Al<sub>10.3</sub>Nb<sub>2.8</sub> bulk metallic glasses in 0.001-0.1 M HCl aqueous solutions. They found that in both cases the corrosion potential changed to more positive potentials and the corrosion current increased with increasing chloride concentration. However, the pitting potential decreased and the usable passive region became smaller with increasing chloride concentration. Recently, Gostin et al [5] have investigated the corrosion behavior of (Fe<sub>44.3</sub>Cr<sub>5</sub>Co<sub>5</sub>Mo<sub>12.8</sub>Mn<sub>11.2</sub>C<sub>15.8</sub>B<sub>5.9</sub>)<sub>98.5</sub>Y<sub>1.5</sub> bulk metallic glass in 0.01-0.6 M NaCl aqueous solutions. They found that the corrosion potential was larger in 0.01 M NaCl aqueous solution than in 0.1 and 0.6 M NaCl aqueous solutions. However, few researchers have carefully investigated the influence of the chloride concentration on the corrosion behavior of



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Cu–Zr–Ti ternary metallic glasses. Thus, it is important for investigating the influence of the chloride concentration on the corrosion property of Cu-based metallic glasses.

In the present work, the corrosion behavior of  $Cu_{55}Zr_{35}Ti_{10}$  metallic glass is investigated in HCl and NaCl aqueous solutions with different chloride concentration.

#### 2. Experimental procedures

Cu<sub>55</sub>Zr<sub>35</sub>Ti<sub>10</sub> (at. %) ternary alloy ingots were prepared from the mixture of pure metals by arc melting in an argon atmosphere. Ribbon samples with a thickness of 50 µm and a width of 2.5 mm were prepared by melt spinning at the wheel speed of 30 ms<sup>-1</sup>. The glassy structure was confirmed by X-ray diffraction (XRD) using Cu K<sub>α</sub> radiation and differential scanning calorimetry (DSC) at a heating rate of 30 K min<sup>-1</sup>, respectively.

Corrosion behavior of the glassy alloy was investigated by electrochemical polarization and weight loss measurements, respectively. Prior to electrochemical polarization and weight loss measurements, the specimens were degreased in acetone, washed in distilled water and dried in air. Electrolytes were NaCl and HCl aqueous solutions whose concentrations were 0.005, 0.01, 0.5, and 1 M, respectively, which were prepared from reagent grade chemicals and deionized water. Electrochemical measurements were conducted using a three-electrode cell with a platinum foil as a counter electrode. The reference electrode was a standard saturated calomel electrode (SCE). Potentiodynamic polarization curves were measured with an IM6ex instrument at a potential sweep rate of 0.05 mV s<sup>-1</sup> from -0.6 V to 1.0 V. The cell was open to air at room temperature and measurement started after the immersion of the samples for 20 min so that the open-circuit potentials of the samples became almost stable. The working electrode was exposed only to an area of 0.05–0.08 cm<sup>2</sup> while the rest of the specimen was embedded in a thermoplastic resin to provide electrical isolation. All potentials given in this article are referred to the SCE electrode. The corrosion rates were estimated from the weight loss after immersion at room temperature for 30 days. The surfaces of the samples before and after corrosion were observed with a SIRION scanning electron microscope (SEM) and compositional analysis was performed using electron dispersive spectroscopy (EDS).

### 3. Results

The glassy structure of Cu<sub>55</sub>Zr<sub>35</sub>Ti<sub>10</sub> alloy ribbon was confirmed by XRD, the result of which is shown in Fig. 1. The diffraction pattern exhibits the characteristic broad peak for a glassy structure without any distinct crystalline peaks within the sensitivity limit of XRD measurement. In order to further examine its glassy structure, the DSC was conducted. The inset in Fig. 1 displays the DSC curve in the mode of isochronal heating with a rate of 30 K min<sup>-1</sup> for the melt-spun ribbon. An endothermic signal associated with the glass transition and exothermic signals due to crystallization reactions are observed. The glass transition temperature  $T_{\rm g}$  and onset crystallization temperature T<sub>x</sub> are 675.3 and 729.3 K, respectively. Thus the undercooled liquid region (defined as the interval between  $T_{g}$ and  $T_x$ ) is 54.0 K. It also manifests four crystallization peaks, indicating its complex crystallization procedure. Therefore, the XRD and DSC results indicate the glassy structure of the melt-spun Cu<sub>55</sub>Zr<sub>35</sub>Ti<sub>10</sub> ribbon.

The corrosion behavior of the Cu<sub>55</sub>Zr<sub>35</sub>Ti<sub>10</sub> metallic glass ribbon was examined by potentiodynamic polarization measurement. Fig. 2 shows the anodic and cathodic polarization curves in NaCl and HCl aqueous solutions open to air at room temperature, respectively. In both cases, the Cu<sub>55</sub>Zr<sub>35</sub>Ti<sub>10</sub> metallic glass exhibits the active dissolution state in the whole anodic region in 0.005 and

**Fig. 1.** X-ray diffraction pattern for Cu<sub>55</sub>Zr<sub>35</sub>Ti<sub>10</sub> glassy alloy: the inset displays DSC curve of Cu<sub>55</sub>Zr<sub>35</sub>Ti<sub>10</sub> glassy alloy at heating rate of 30 K min<sup>-1</sup>.

0.01 M chloride-containing solutions. When the chloride concentration exceeds 0.5 M, a sharp decrease of the current density similar to the passivation appears at the potential of 579 mV vs. SCE in 0.5 M HCl, 484 mV vs. SCE in 1 M HCl, 748 mV vs. SCE in 0.5 M



Fig. 2. The polarization curves in aqueous solutions containing different chloride concentration open to air at room temperature: (a) for HCl, and (b) for NaCl.

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