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Ultraviolet light irradiation on pitting corrosion of Cu-based bulk metallic glasses

Jili Wu [a], Xingzhou Li [a], Hongbo Cao [b], Ye Pan [a,*], Yuntian Zhu [c]

[a] School of Materials Science and Engineering, Jiangsu Key Laboratory for Advance Metallic Materials, Southeast University, Nanjing 211189, PR China
[b] GE Global Research, 1 Research Circle, Niskayuna, NY 12309, USA
[c] Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695, USA

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ABSTRACT

We report the observation that UV irradiation substantially improves pitting corrosion resistance of Cu-based bulk metallic glasses. Specifically, two Cu-based bulk metallic glasses in this study showed more stable passive films under UV irradiation than under irradiation-free condition when polarized in 3.5 wt.% NaCl aqueous solution. This finding indicates that Cu-based bulk metallic glasses are promising to serve in high UV irradiation and corrosive environments.

1. Introduction

In the past decades, corrosion behaviors of bulk metallic glasses (BMGs) have been extensively investigated. Generally, BMGs show better corrosion resistance than their crystalline counterparts, because of their ‘perfect’ microstructure, namely the absence of grain boundaries [1,2]. However, BMGs are metastable and often become reactive in electrolytic solutions, due to their high Gibbs free energies [3,4]. Cu-based BMGs enjoy significant cost advantage over Zr- and Pd-based BMGs. Nevertheless, it has been reported that Cu-based BMGs are susceptible to corrosion in acidic and salt solutions, due to the preferential dissolution of the more reactive components, which leaves behind a Cu-enriched and less protective surface layer on the surface [5,6]. The poor corrosion resistance has limited the practical application of Cu-based BMGs as structural materials.

In recent years, extensive effort has been devoted to improving the corrosion resistance of Cu-based BMGs. Qin et al. explored the positive effect of Nb additions on the corrosion behaviors of Cu–Hf–Ti BMGs [5,7]. Wang et al. found that the selective dissolution behavior of Cu–Zr–Al BMGs was strongly influenced by minor Ni additions [8]. Liu et al. demonstrated that the addition of an appropriate amount of Mo can effectively improve corrosion resistance of the Cu–Zr–Ti BMGs in both H_2SO_4 and NaOH solutions [6]. Obviously, these studies are centered on the microalloying effect. Up to date, there are still lacks of understanding on the influence of external factors such as temperature, pressure and irradiation on the corrosion resistance.

It has been reported in previous works that irradiation can have significant influence on the corrosion behavior of metallic alloys. For example, under irradiation with Ultraviolet light (UV), the corrosion potential of TiO_2-coated steel displays a large negative shift [9]. This was attributed to a rapid migration of photoelectrons from the surface to the TiO_2/substrate interface, which prevents the dissolution of Fe element [9]. Another example was that the corrosion rate of pure Zinc and its alloys in fresh water is substantially higher in UV light than in dark condition [10]. To the authors' knowledge, there has been no report on the effects of UV-irradiation on the corrosion behavior of BMGs.

The chemical, physical and mechanical property of BMGs have been widely investigated, among which the pitting corrosion of BMGs has been regarded as an urgent issue to be addressed as soon as possible [11,12]. Studies during the last ten-year have unfortunately discovered that pitting overpotential of BMGs have very little advantage over their crystalline counterparts [13,14]. In the family of Cu-based BMGs, ternary Cu–Zr–Al and Cu–Zr–Ti BMGs are very important members and the overwhelming majority of Cu-based BMGs were descended from these two ternary alloy systems. In

* Corresponding author.
E-mail address: panye@seu.edu.cn (Y. Pan).

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this work, $Cu_{46}Zr_{46}Al_8$ [15] and $Cu_{50.2}Zr_{40.8}Ti_9$ [16] were selected for investigating the irradiation effect on corrosion behavior. We found that Cu-based BMGs have higher resistance to pitting corrosion under UV irradiation. This finding suggests that Cu-based BMGs can potentially serve in high UV irradiation environments.

2. Methods

2.1. Preparation of BMG samples

Ingots with nominal composition of $Cu_{46}Zr_{46}Al_8$ (Al8) and $Cu_{50.2}Zr_{40.8}Ti_9$ (Ti9) were prepared by arc melting a mixture of pure elements (purity $\geq$ 99.99%) in a argon atmosphere that was purified by a Ti-getter. To ensure homogeneity, the ingots were remelted at least four times and then cast into plates with dimensions of $0.15 \times 1 \times 6$ cm^3 by vacuum suction in an arc-melter. The amorphous nature of the as-cast plates was verified by X-ray diffractometry (XRD) (Bruker X-ray diffractometer with a collimated Cu Ka X-ray source).

2.2. Electrochemical experiments and characterization

Electrochemical experiments were carried out in a glass cell with BMG working electrode, platinum counter electrode and saturated calomel reference electrode (SCE) in a 3.5 wt.% NaCl aqueous solution (prepared from reagent grade chemical and deionized water) in air at room temperature. Prior to testing, the solution was deaerated by bubbling purified nitrogen gas for at least 20 min to eliminate the effect of dissolved oxygen. All potentials reported here are relative to the SCE electrode hereafter. Potentiodynamic polarization curves were measured at a potential sweep rate of 0.01 V/s under UV light irradiation (source: 16 W UV lamp, wavelength 365 nm). Each test was started from a potential of −0.5 V. The stop potentials for Al8 and Ti9 are −0.275 and −0.225 V, respectively. All electrochemical tests were conducted after immersing the samples for 1800 s, when the open-circuit potential (OCP) became almost steady (variation within ±5 mV in a time interval of 200 s). All test specimens were cut from the as-cast plates and then cold-mounted in epoxy. Prior to the electrochemical tests, the exposed surface of each specimen was mechanically ground with SiC abrasive paper up to 1500 grit and polished to mirror surface with diamond paste (0.5 μm particle size), degreased in ethanol and dried in air. After the electrochemical tests the samples were further examined by scanning electron microscopy (SEM) (Philips XL30 ESEM) to investigate the microstructure on the surface of electrochemically treated samples. For comparison, the electrochemical experiments were also performed without UV irradiation, namely irradiation-free condition.

3. Results

Fig. 1 shows the XRD patterns of as-cast Al8 and Ti9 BMGs. Both as-cast alloys are characterized by a broad hump within the diffraction angle 2θ in the range of 30–50° and without any obvious crystalline peaks. It verifies that the as-cast alloys are of amorphous structure, namely, monolithic glass.

The cyclic polarization curves of as-cast Al8 and Ti9 BMGs are shown in Fig. 2. For the electrochemical tests under irradiation-free condition, it is clear that both Al8 and Ti9 BMGs samples exhibited a cathodic current density decrease to a minimum value at the corrosion potential (E_{corr}) with increasing potential. The cathodic current density corresponds to hydrogen formation. The specimens retained their passivity up to the pitting potential (E_{pit}), at which the current density suddenly increased due to the initiation of pitting corrosion. Furthermore, a current hysteresis loop can be

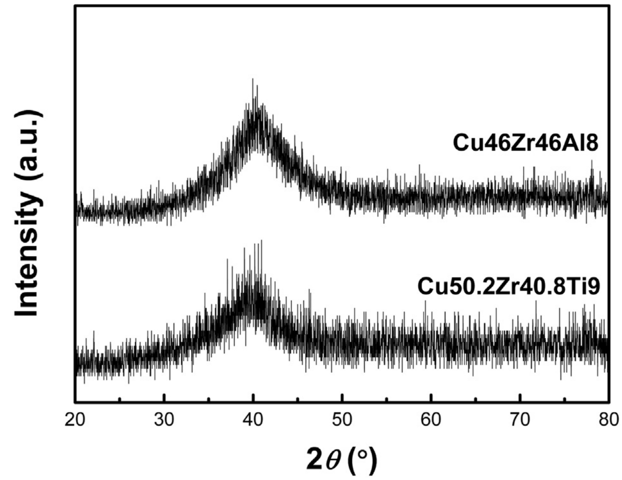

Fig. 1. XRD patterns of as-cast Al8 and Ti9 alloys verifying their amorphous nature.

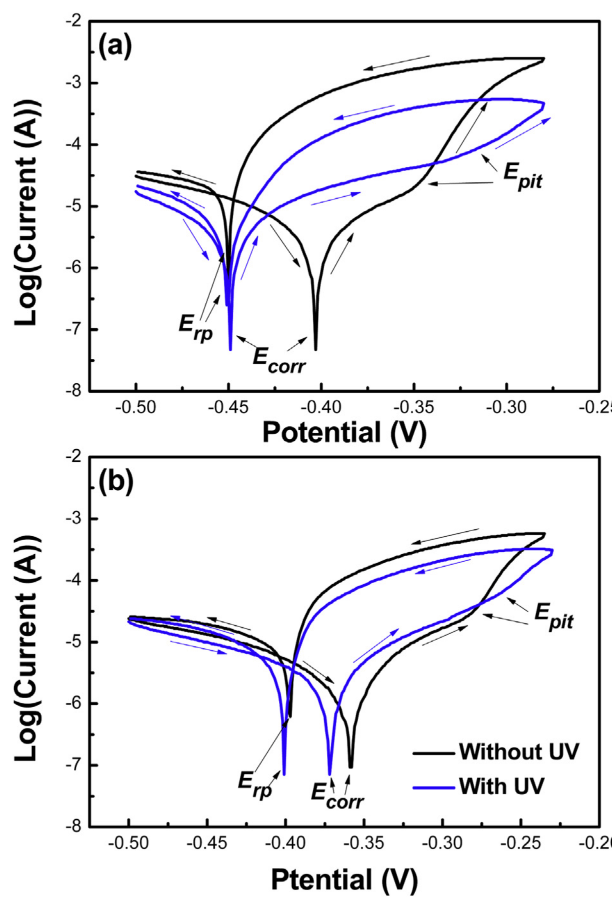

Fig. 2. The cyclic polarization curves of as-cast (a) Al8 and (b) Ti9 BMGs with UV irradiation and without UV irradiation.

evidently observed. This loop determines the repassivation potential (E_{rp}) of each specimen, at which the current density returns to passive value. As shown in Fig. 2, the E_{rp} is significantly lower than E_{corr} for both Al8 and Ti9 BMGs, which indicates that both BMGs are susceptible to pitting corrosion on their surfaces [14].

For the electrochemical tests under UV irradiation, positive hysteresis loops for both Al8 and Ti9 BMGs in cyclic polarization curves also appeared. It is worthy noting that the current density in