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Corrosion resistance of Cu–Zr–Al–Y and Zr–Cu–Ni–Al–Nb bulk metallic glasses

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Abstract

Electrochemical tests of amorphous $Cu_{46}Zr_{42}Al_7Y_5$ in comparison to amorphous $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ (Vit106a) were conducted by potentiodynamic polarization at room temperature in 0.001–0.1 M $NaCl_{aq}$ (pH 8). The influence of corrosion on the surface topography was studied by X-ray diffraction and SEM. Electrochemical measurements indicate a good corrosion resistance of both bulk metallic glasses in NaCl solutions with low molarity at pH 8 due to the formation of protective oxide films. However, at high NaCl molarity the Cu–Zr–Al–Y glass shows no passive layer and is very susceptible to pitting corrosion. The mechanisms of the formation of the oxide films as well as the nucleation and growth of pitting were clarified by associating microstructural investigations with the results of electrochemical measurements.

Keywords: Bulk metallic glasses; Corrosion; Electrochemical reactions

1. Introduction

Many efforts were attempted to develop bulk metallic glasses in different alloy systems: in the early 90s Peker and Johnson [1] as well as Inoue [2] developed Zr based bulk metallic glasses which were due to their excellent mechanical properties, i.e. high elastic limit and strength, of high interest, e.g. for golf clubs or penetrators [3]. Bulk metallic glasses based on late transition metals, e.g. Fe, Co, Ni, Cu, have many potential advantages such as higher elastic limit and strength in comparison to those based on early transition metals. Recently, Xu et al. [4] reported about quaternary Cu based alloys, $Cu_{46}Zr_{47-x}Al_7Y_x$ ($0 < x < 10$), which possess unusually high glass forming ability. For any application, however, the corrosion resistance of these glasses has to be adequate.

The corrosion of metallic alloys is strongly influenced by alloying elements as well as by the microstructure. In general, the amorphous structure is known to improve the corrosion resistance of an alloy, which can be explained with respect to the lack of defects like dislocations or grain boundaries, the optimized composition (not available as a single crystalline phase) and the chemical homogeneity of the metallic glass.

First investigations of the corrosion behavior of bulk amorphous $Zr_{55}Cu_{30}Ni_5Al_{10}$ showed the rapidly formation of passivating surface layers in 0.1 M Na_2SO_4 (pH 2–8) and 0.1 M NaOH (pH 13) solutions which are stable in a wide pH and potential range [5]. Later investigation regarding the passivation behavior of bulk amorphous $Zr_{55}Cu_{30}Ni_5Al_{10}$ compared to the crystalline counterpart and zirconium in weakly alkaline sulphate solutions revealed that the barrier effect of anodic films grown on the amorphous alloy were slightly lower than on zirconium. Anodic layers on the surface of Zr–Cu–Ni–Al consist apparently of a mixture of simple oxides or complex oxidic compounds of all alloying elements [6]. The influence of additional alloying elements such as Ti, Cr, Nb or Ta were studied to improve the corrosion resistance of amorphous Zr–Al–Ni–Cu alloys in HCl as well as NaCl solutions [7]. The addition of Nb and Ta exhibited rather low corrosion rates below 0.1 mm/year after immersion for 64 h; the largest effect of additional elements on the corrosion resistance can be obtained for Nb followed by Ta, Ti and Cr [8].

First investigations on the influence of microstructure on the corrosion of amorphous and crystalline Cu–Zr alloys in 1N NaCl, 1N HCl and 1N H_2SO_4 [9,10] revealed only minor differences in the corrosion behavior. Recently good corrosion resistance was reported of bulk $Cu_{50}Zr_{40}Al_5Nb_5$ metallic glass in comparison to Cu–Zr–Al alloys in 1 M HCl and 3 mass% NaCl [11]. It was assumed that the addition of 5% Nb to $Cu_{55}Zr_{40}Al_5$

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leads to depletion of Cu in the surface film, but increases Zr and Nb; thus leading to the formation of a Zr(Nb)-rich protective surface film. The aim of this paper is to present results on the pitting corrosion of bulk $Cu_{46}Zr_{42}Al_7Y_5$ in comparison to $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ metallic glasses and to clarify the corrosion mechanisms.

2. Experimental

$Cu_{46}Zr_{42}Al_7Y_5$ and $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ ingots were prepared by arc melting in a Ti-gettered argon atmosphere. Bulk $Cu_{46}Zr_{42}Al_7Y_5$ and $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ (Vit106a) metallic glasses with a thickness of 2 mm and a rectangular shape (about 5 mm × 15 mm) were produced at Caltech by casting in a copper mold. Details of the experimental procedure are described elsewhere [4].

The potentiondymamic curves were obtained using a FAS1 potentiostat (Gamry Instruments) with a voltage scan rate of 0.1 mV/s. All the potential values are reported with respect to the reference electrode ($E_{Hg/HgO}$ versus SCE). The electrochemical tests using the d.c. (potentiodynamic polarization) technique was carried out in deaerated, not stirred 0.001–0.1 M $NaCl_{aq}$ electrolytes (pH 8, 298 K) to study the pitting corrosion of $Cu_{46}Zr_{42}Al_7Y_5$ and $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$. For all measurements a three electrode electrochemical cell was used with an Hg/HgO reference electrode and a platinum counter electrode. The samples were embedded in a thermoplastic resin to provide electrical isolation. Sample surfaces were ground up to 1200 grid with wet SiC-emery paper.

The microstructure before and after corrosion was studied by X-ray diffraction (Cu Kα radiation), optical microscopy and scanning electron microscopy (SEM + EDS, Hitachi S-4500).

3. Results and discussion

Figs. 1 and 2 show potentiodynamic polarization scans obtained for $Cu_{46}Zr_{42}Al_7Y_5$ (Fig. 1) and $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ (Fig. 2) bulk metallic glasses in 0.001–0.1 M HCl_{aq} (pH 8). In both cases the corrosion potential changes to more positive potentials with increasing chloride concentration. This change in the corrosion potential depending from the chloride concentration can be explained by the Nernst equation which considers the concentrations of the oxidized and reduced component. $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ exhibits a more negative corrosion potential than $Cu_{46}Zr_{42}Al_7Y_5$. From the thermodynamic point of view $Cu_{46}Zr_{42}Al_7Y_5$ seems to be more noble than $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$. Investigating the kinetics in more detail it was observed that the corrosion current (see Figs. 1 and 2) and therefore the corrosion rate is higher for $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ than for $Cu_{46}Zr_{42}Al_7Y_5$ specially for low chloride concentration. In 0.001 M $NaCl_{aq}$ corrosion rates of 4.7×10^{-7} m/a were obtained for $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ and of 2.7×10^{-7} m/a for $Cu_{46}Zr_{42}Al_7Y_5$. Corrosion rates of 10^{-6} m/a were observed for both alloys in 0.01 M $NaCl_{aq}$. For both glasses the corrosion current increases with increasing chloride concentration.

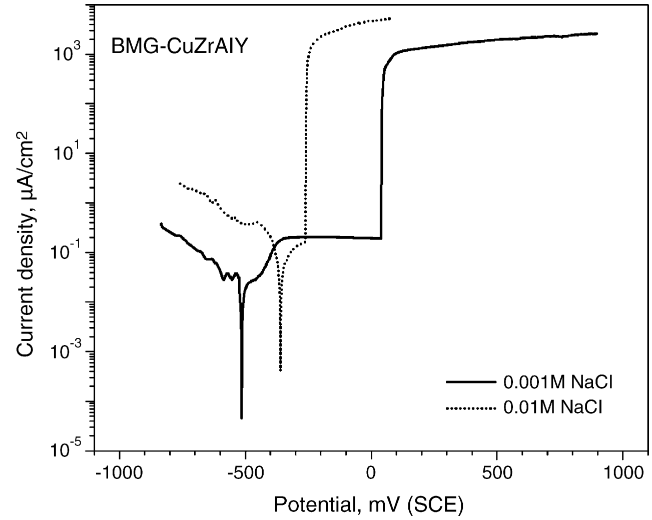

Fig. 1. Potentiodynamic polarization of $Cu_{46}Zr_{42}Al_7Y_5$ metallic glass in 0.001 M and 0.01 M NaCl solution (pH 8, 298 K, 0.1 mV/s).

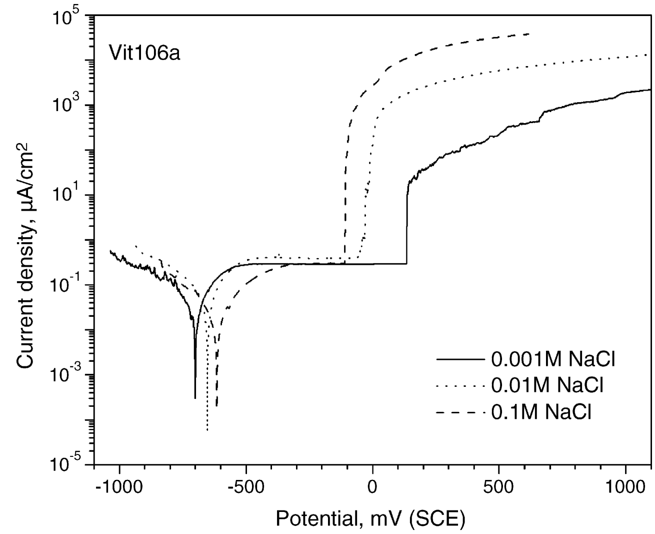

Fig. 2. Potentiodynamic polarization of $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ metallic glass in 0.001 M and 0.01 M NaCl solution (pH 8, 298 K, 0.1 mV/s).

Since both driving force (corrosion-tendency) and kinetic (corrosion-rate) considerations are crucial in determining the extent of corrosion of a metal surface, a key factor controlling the rate is the existence of the phenomenon of passivity for certain metals and alloys. Very low values in the range of 10^{-7} A/cm^2 for the passive current were observed which indicate a very good passivation behavior for both alloys at higher potentials and pH 8 and are comparable with the passive currents from stainless steel under similar conditions.

The initiation of a pit occurs when electrochemical or chemical breakdown exposes a small local site on a metal surface to damaging species such as chloride ions. As expected the pitting potential decreases with increasing chloride concentration for both alloys. The usable passive region becomes smaller with increasing chloride concentration. Amorphous $Cu_{46}Zr_{42}Al_7Y_5$ exhibits no passive region in 0.01 M $NaCl_{aq}$ and is therefore very susceptible for pitting corrosion. Qin et al. [11] investigated the influence of Nb on Cu–Zr–Al metallic glasses and reported corrosion rates of 10^{-4} m/a for $Cu_{55}Zr_{40}Al_5$ and 10^{-5} m/a for $Cu_{50}Zr_{40}Al_5Nb_5$ in 0.5 M $NaCl_{aq}$ and no passive region during polarization.

Microstructural investigation (Fig. 3) of the surface of $Cu_{46}Zr_{42}Al_7Y_5$ after polarization in 0.01 M NaCl solution (pH 8) revealed pits as well as corrosion products all over the sam-

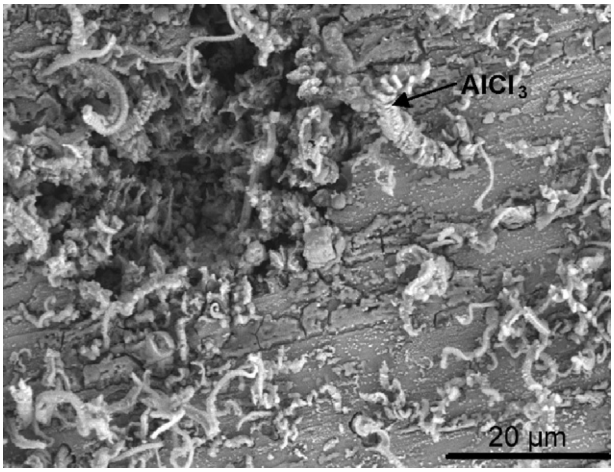

Fig. 3. SEM of $Cu_{46}Zr_{42}Al_7Y_5$ metallic glass after polarization in 0.01 M NaCl solution (pH 8, 298 K, 0.1 mV/s).

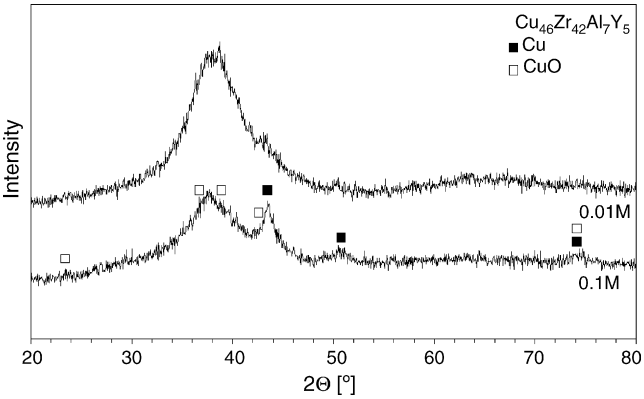

Fig. 4. X-ray diffraction of $Cu_{46}Zr_{42}Al_7Y_5$ metallic glass after polarization in 0.01 M NaCl solution (pH 8, 298 K, 0.1 mV/s).

ple surface after polarization up to $-0.26\ V_{(SCE)}$. EDS studies of the surface as well as of the corrosion products (obtained by collecting those products from the surface) indicate a very complex corrosion mechanism initiated by chlorides which leads to corrosion products where all elements such as Cu, Zr, Al, (Y) as well as Cl are involved in. The X-ray study of $Cu_{46}Zr_{42}Al_7Y_5$ after polarization up to $-0.26\ V_{(SCE)}$ in 0.01 M and 0.1 M $NaCl_{aq}$ (pH 8) (see Fig. 4) reveals still an amorphous microstructure and additional crystalline peaks which can be determined as Cu and CuO. The loss of intensity for the sample after corrosion in 0.1 M $NaCl_{aq}$ can be explained by a thicker passivation layer.

It is well known from Cu–Al alloys that the addition of only a small amount of Al leads to galvanic corrosion due to the combination of a noble element such as Cu (+0.35 V) and a base element such as Al (−1.66 V). In addition compositional heterogeneities between, e.g. Cu and Al in the amorphous matrix will support the nucleation of pits. Since Cu is known to form a protective passive layer of CuO in chloride solutions at pH 8 [12] the formation of $AlCl_3$ as well as Cu or CuCl as an additional corrosion product can be assumed during pitting. The large amount of Zr which was observed by EDS of $Cu_{46}Zr_{42}Al_7Y_5$ after corrosion might be attributed to the formation of an amorphous ZrO_2 layer. Earlier corrosion studies of $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ [13] showed the formation of an amorphous ZrO_2 layer. Corrosion investigations of $Cu_{50}Zr_{40}Al_5Nb_5$ in 0.5 M $NaCl_{aq}$ [11] indicate the depletion of Cu in the surface film and increases Zr and Nb; leading to the formation of a Zr(Nb)-rich protective surface film. Further TEM investigations of the passive layer are underway and should give more details also about the precipitation of Cu and the influence of Y on the formation of the passive layer. However the formation of CuO and ZrO_2 leads to a large cathodic surface area in comparison to the small anodic area in the pit; this results in the corrosion reaction observed in the amorphous $Cu_{46}Zr_{42}Al_7Y_5$.

4. Conclusion

Electrochemical tests of $Cu_{46}Zr_{42}Al_7Y_5$ in comparison to $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ (Vit106a) bulk metallic glasses indicate a good corrosion resistance in $NaCl_{aq}$ with low molarity at pH 8 due to the formation of protective oxide films. Corrosion rates in the range of 10^{-7} m/a to 10^{-6} m/a were observed dependent on the chloride concentration. The Cu–Zr–Al–Y glass, however, shows no passive layer at higher $NaCl_{aq}$ molarity (0.01 M) and is very susceptible to pitting corrosion. It is assumed that the corrosion mechanism of $Cu_{46}Zr_{42}Al_7Y_5$ metallic glass consists of passivation of Zr and Cu and galvanic corrosion coupled with pitting corrosion.

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