



Effect of atomic mobility on the electrochemical properties of a $Zr_{58}Nb_3Cu_{16}Ni_{13}Al_{10}$ bulk metallic glass

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ABSTRACT

The corrosion behaviour of bulk metallic glasses is greatly related to their microstructures. The microstructures in bulk metallic glasses of the same chemical composition are represented to a certain extent by their atomic mobility. Evolution of the microstructure and mechanical properties of $Zr_{58}Nb_3Cu_{16}Ni_{13}Al_{10}$ bulk metallic glass after annealing were studied with X-ray diffraction, dynamic mechanical analysis and Vickers hardness tests. Polarization curve, open circuit potential, electrochemical impedance spectroscopy and Mott-Schottky analysis were performed to investigate the effect of atomic mobility on the corrosion behaviour in 1 mol/L de-aerated H_2SO_4 at 333 K. Dynamic mechanical analysis indicated that the atomic mobility of $Zr_{58}Nb_3Cu_{16}Ni_{13}Al_{10}$ bulk metallic glass was reduced by structural relaxation and crystallization. All electrochemical measurements showed that the passivation ability decreased and the corrosion resistance of $Zr_{58}Nb_3Cu_{16}Ni_{13}Al_{10}$ bulk metallic glass deteriorated as the annealing temperature increased. Mott-Schottky analysis revealed that the defect concentration in the passive films increased and the flat-band potential shifted to a negative potential with a decrease in the atomic mobility. X-ray photoelectron spectroscopy results proved that the main chemical compositions of the passive films were ZrO_2 , Al_2O_3 and Nb_2O_5 . The formation of a passive film was suppressed because the atomic mobility of strong passivating elements (Zr, Al and Nb) decreased. In addition, the precipitation of crystals (Zr_2Cu and $Cu_{10}Zr_7$) accelerated the corrosion of the bulk metallic glass in H_2SO_4 .

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1. Introduction

Metallic glasses with long-range disordered amorphous structures at the atomic scale can be prepared by various methods (rapid-quenching, physical vapor deposition etc.) in which atomic configurations might display topological short-range ordering (TSRO) or chemical short-range ordering (CSRO) [1]. In many cases, the bulk metallic glasses exhibited excellent corrosion resistance due to their chemical homogeneity and the lack of conventional defects in crystalline solids, i.e., grain boundaries, dislocations and secondary phases [2–4].

It is well documented that bulk metallic glasses show high energy (i.e., they are conventionally unstable) but are

thermodynamically metastable. However, the crystalline alloys exist in lower energy wells corresponding to an equilibrium state. Thus, the atoms in bulk metallic glasses are more electrochemically active than those in crystalline alloys [5]. When bulk metallic glass is annealed below the glass transition temperature T_g , leading to transformation of the structure towards a more relaxed (close to equilibrium) state, this bulk metallic glass is structurally relaxed [6]. Structural relaxation would induce structural rearrangement and shift to a more stable state, thereby leading to various changes in its mechanical and chemical properties [7].

Mechanical and physical properties of metallic glasses are closely associated with their atomic mobility. The atomic mobility of metallic glass is described by some physical models, e.g., free-volume model, quasi-point defects model and potential energy landscape [8]. Free-volume theory is generally used to interpret the structural relaxation, and the free volume in metallic glasses is annihilated during the structural relaxation process [9–11].

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Consequently, the mobility of atoms in bulk metallic glasses is reduced after structural relaxation [12–14]. Hence, their properties are modified. The densities of Pd₄₀Ni₄₀P₂₀ and Pd_{42.5}Cu₃₀Ni_{7.5}P₂₀ bulk metallic glass increased as the free volume decreases [9,11]. A decrease in free volume also led to the deterioration in plasticity of Zr₆₅Cu_{17.5}Al_{7.5}Fe₁₀ bulk metallic glass [15].

Modifications in the free volume also affect the corrosion properties of bulk metallic glasses. Liu et al. [16] reported that the corrosion resistance of Ni₅₅Nb₂₀Ti₁₀Zr₈Co₇ metallic glass was improved by decreasing the free volume. Tailleart et al. [17] found that a reduction in free volume could increase the bond cleavage energy, resulting in better corrosion resistance for Al₈₇Co₇Ce₆ amorphous alloys after relaxation. The corrosion resistance of Cu₅₀Zr₅₀ amorphous alloy was improved due to the reduced free volume [18]. Jayaraj et al. [5] also found that the passivation behaviour of the Zr₄₈Cu₃₆Ag₈Al₈ bulk metallic glass was significantly improved in 1 mol/L H₂SO₄ due to a reduction in the free volume. They suggested that, in a high-energy metastable state, Zr₄₈Cu₃₆Ag₈Al₈ metallic glass contained a relatively large free volume and exhibited poor passivation due to the active dissolution of Cu. The fully crystallized Zr₆₀Cu₂₀Al₁₀Fe₅Ti₅ [19] alloy showed better corrosion resistance compared with its amorphous alloy in Hank's solution, and the enhanced corrosion resistance was attributed to the reduction in free volume, which reduced the energy wells and the electrochemical activity restricting the removal of atoms during dissolution. In contrast, Wang et al. [20] reported that decreased free volume had a detrimental effect on the corrosion resistance of Zr₅₆Al₁₆Co₂₈ bulk metallic glass after heat treatment. Obviously, the corrosion resistance of bulk metallic glasses highly depends on their free volume; that is, the atomic mobility of bulk metallic glasses significantly affects their corrosion properties. However, how the atomic mobility affects the corrosion resistance of bulk metallic glass is still under debate according to discussions in previous literature, as mentioned above.

In this work, bulk Zr₅₈Nb₃Cu₁₆Ni₁₃Al₁₀ metallic glasses were employed to shed light on the effect of structural relaxation and crystallization on the electrochemical properties. We tried to determine the relationship between the atomic mobility and the corrosion resistance of bulk metallic glasses. Different amorphous states of this bulk metallic glass and its crystalline counterparts were obtained by annealing at different temperatures.

2. Experimental

Master alloys with the composition Zr₅₈Nb₃Cu₁₆Ni₁₃Al₁₀ (at.%) were prepared in melting equipment in a Ti-gettered argon atmosphere. Cylindrical samples with a diameter of 3 mm were made using a copper mould suction casting method. The thermal property of the metallic glass was evaluated by differential scanning calorimetry (DSC) using a Perkin Elmer Diamond DSC with continuous heating at a heating rate of 20 K/min under a protective argon atmosphere. Structural relaxation and crystallization were performed using a Quartz tube furnace (BEQ BTF-1200C) under argon at different temperatures (523 K, 673 K, 773 K and 873 K) for 6 h, and the corresponding alloys were labelled Zr-523 K, Zr-673 K, Zr-773 K and Zr-873 K respectively.

The amorphous features of the Zr₅₈Nb₃Cu₁₆Ni₁₃Al₁₀ bulk metallic glasses and microstructures of the crystalline alloys were determined by X-ray diffraction (XRD) experiments using an X'Pert PRO MPD diffractometer with Cu K α radiation (1.54 Å). The crystallinity of the partially crystallized alloy was calculated from the ratio of the area of all crystalline peaks to the total area of all peaks including the non-crystalline fraction using MDI Jade 6 software employing the deconvolution method. Then, the Vickers hardness test was measured using an HVS-1000 hardness tester with a

typical diamond indenter to confirm the variation in the mechanical properties. At least five points on each sample were selected for the Vickers hardness test, which was conducted using a load of 200 g for 20 s at each point.

Dynamic mechanical analysis (DMA) experiments were carried out by a TA DMA Q800 under sinusoidal stress with a fixed frequency of 1 Hz during continuous heating with a constant heating rate of 5 K/min from room temperature to 873 K. The size of the rectangular alloy samples for DMA measurements was 30 mm (length) \times 3 mm (width) \times 1 mm (thickness). All experiments were performed under a protective argon atmosphere to avoid oxidation. Before the DMA measurements, all samples were annealed at different temperatures, as introduced before.

The cylindrical samples were connected by copper wire, and the non-working area was sealed with epoxy resin leaving a working area of 0.07 cm². They were polished using 500 to 5000 waterproof abrasive papers to produce a mirrored and repeatable surface and then were cleaned by acetone, ethanol and de-ionized water. A 1 mol/L H₂SO₄ solution was used as the electrolyte, which was de-aerated continuously by nitrogen bubbling during the measurements. The experimental temperature was set to 333 K and controlled by a thermostat water bath.

The corrosion properties of as-cast Zr₅₈Nb₃Cu₁₆Ni₁₃Al₁₀ bulk metallic glass and the annealed alloys were evaluated by electrochemical measurements (conducted by a CHI660e electrochemical workstation) using a three-electrode cell with a Zr₅₈Nb₃Cu₁₆Ni₁₃Al₁₀ working electrode, a saturated mercurous sulfate electrode (MSE, E_{MSE} = 0.652 V_{SHE}), and a platinum counter electrode. Prior to the electrochemical measurements, cathodic polarization at -1.5 V/MSE was performed to clean the surface of the alloys. The potentiodynamic polarization curves were obtained from -0.2 V (vs. open-circuit potential) to 1.5 V (vs. MSE) with a scan rate of 0.5 mV/s after immersion for 3 h. Open-circuit potential (OCP) tests and electrochemical impedance spectroscopy (EIS) were also conducted. The EIS measurement was first conducted after 2 h and 6 h of immersion and in a frequency range of 100 kHz to 10 mHz at 12 points per decade with a sinusoidal potential perturbation of \pm 10 mV/MSE under OCP. In addition, to obtain further information about the passivation property of the different samples, alloys were potentiostatically polarized at 0.6 V/MSE for 6 h before the EIS measurements were conducted. X-ray photoelectron spectroscopy (XPS) analysis was performed to characterize the chemical compositions of passive films formed on the surface of the as-cast Zr-based bulk metallic glass and the annealed Zr-based alloys after potentiostatic polarization at 0.6 V/MSE for 6 h in 1 mol/L H₂SO₄ at 333 K. XPS (XSAM 800) with a monochromatic Al K α X-ray source (h ν = 1486.6 eV) was used. To analyse the semiconductor properties of the passive films, Mott-Schottky curves were performed by sweeping in the positive direction at a frequency of 1000 Hz with an amplitude signal of 10 mV/MSE and a potential range from the OCP to 1.1 V/MSE. Prior to the Mott-Schottky curves measurements, the samples were immersed in 1 mol/L H₂SO₄ at 333 K for 6 h.

3. Results

3.1. Thermal properties and microstructures of Zr₅₈Nb₃Cu₁₆Ni₁₃Al₁₀ alloys

Fig. 1 shows the DSC curve of the as-cast Zr₅₈Nb₃Cu₁₆Ni₁₃Al₁₀ bulk metallic glass with a heating rate of 20 K/min. The as-cast Zr₅₈Nb₃Cu₁₆Ni₁₃Al₁₀ bulk metallic glass displays a pronounced glass transition region before the primary crystallization behaviour. The glass transition temperature (T_g), onset crystallization temperature (T_x), crystallization temperature (T_c) and super-cooled liquid region ($\Delta T = T_x - T_g$) are 685 K, 760 K, 779 K and 75 K,

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