A abrasive and corrosive behaviors of Cu-Zr-Al-Ag-Nb bulk metallic glasses

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Abstract. The present work investigated effects of Nb (1-5 at.%) on CuZrAlAg bulk metallic glasses. The addition of Nb did not change the amorphous structure but affected the thermal behaviors significantly. The corrosion resistances of the BMGs with addition of 5 at% Nb in 0.5 N H₂SO₄ solutions was the best among the samples. Pin-on-disk measurements showed that the hardest sample, viz. the one with 3 at% Nb exhibited the best wear resistance. Mechanical properties were also investigated using a nanoindentation technique. It was found that the addition of Nb may improved corrosion resistance and wear resistance of the Cu-based BMG, but not in a simple and systematic manner.

1. Introduction

Recently, bulk metallic glasses (BMGs) with critical dimension up to several centimeters were successfully synthesized [1]. These glass forming compositions are not only limited to noble metals-based alloys such as Pd, Pt, but can also be found in Zr- and Cu-based alloys. Apart from the high hardness and mechanical strength, BMG are also expected to exhibit good environmental or surface properties, such as corrosion-resistance [2], wear properties [3], etc., due to their isotropy and homogeneity. This family of materials is therefore promising candidates for many engineering applications [4]. Cu-Zr-Al-Ag alloys were recently developed BMGs with large critical dimensions of more than 30 mm and relatively low materials cost [5]. In this paper, corrosive behaviours and wear

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properties of CuZrAlAg BMG were investigated. Minor content of Nb was added to examine the effects of Nb on the corrosive, abrasive and mechanical properties of BMG.

2. Experimental

Cu-based alloys with nominal composition of $(\text{Cu}_{42}\text{Zr}_{42}\text{Al}_{8}\text{Ag}_{8})_{100-x}\text{Nb}_x$ (x=0-5) were prepared by arc melting the mixtures of pure Cu (99.99 wt.%), Zr (99.9 wt.%), Al (99.99 wt.%), Ag (99.99 wt.%) and Nb (99.9 wt.%) metals in a Ti-gettered argon atmosphere. BMG rods with 3mm diameters were then prepared by suction casting into a water-cooling copper mold. The amorphous structure was confirmed with a Siemens D500 diffractometer using CuK$_\alpha$ ($\lambda=0.1542\text{nm}$) radiation. DSC measurements were performed under a purified nitrogen atmosphere in a Perkin Elmer DSC 7 at a constant heating rate of 20K/min. Corrosion behavior of the glassy alloys was evaluated by electrochemical measurements. Corrosion test samples were first mechanically polished in cyclohexane with silicon carbide paper up to No. 1200 and degreased in acetone. The sample were then dried in air and further exposed to air for 24 h for consistent surface conditions. Electrochemical measurements were conducted with 0.5 N H$_2$SO$_4$ aqueous solution as electrolyte in a three-electrode cell using graphite as counter electrode and saturated calomel as reference electrode (SCE, U(SHE) = 241 mV). The potentiodynamic polarization curves were measured with an EG&G Instruments VersaStatTM II using a sweep rate of 50 mV/min. The cell was open to air at 298 K and measurement started after the immersion of the samples for one hour so that the open-circuit potentials of the samples became stable. Abrasive wear tests were conducted using pin-on-disc equipment (WAZAU model TRM 5000) in air at room temperature. The sliding velocity employed was 0.5m/s. The SiC abrasive paper was replaced after every 100m of sliding distance. Mechanical tests were performed using a Nanoinstigator XP with a pyramid-shaped Berkovich-type diamond indenter.

3. Results and discussion

The amorphous states of the $(\text{Cu}_{42}\text{Zr}_{42}\text{Al}_{8}\text{Ag}_{8})_{100-x}\text{Nb}_x$ (x=0-5) alloys were confirmed by XRD, the results of which are shown in Fig. 1. All diffraction patterns exhibit the characteristic broad peak for an amorphous structure only without crystalline peak. Fig.2 shows the continuous heating DSC traces of $(\text{Cu}_{42}\text{Zr}_{42}\text{Al}_{8}\text{Ag}_{8})_{100-x}\text{Nb}_x$ (x=0-5) BMGs at a heating rate of 20 K/min. Related thermal data were listed in table 1. Addition of 1-3 at.% Nb led to slightly increasing glass transition temperature $(T_g)$, while the $T_g$ of sample containing 5 at.% Nb was reduced significantly compared with the original one. Crystallization temperatures $(T_x)$ of all Nb-containing samples decreased. The changes of $\Delta T=T_x-T_g$ were shown in Table 1.

The polarization curves of these glassy alloys in 0.5 N H$_2$SO$_4$ solutions were shown in Fig. 3. The glassy alloys did not exhibit systematic changes in corrosion potential and passive current density with Nb content. The passive current density increased from approximately 1 A/m$^2$ to near 10$^2$A/m$^2$ at first,
but then decreased to $10^{-2}$ A/m$^2$ with 5 at.% Nb addition. In general, the lower passive current density, the easier is the formation of the protective passive film. Therefore, the addition of 3-5 at% of Nb is demonstrated to enhance the corrosion resistance.

![Figure 1. XRD patterns of BMG rods with 3 mm diameters.](image1)

![Figure 2. Continuous heating DSC traces of (Cu$_{42}$Zr$_{42}$Al$_8$Ag)$_{100-x}$Nb$_x$ BMG.](image2)

| x  | $T_g$ (K) | $T_x$ (K) | $\Delta T$ (K) | D (g·cm$^{-3}$) | H (GPa) | G (GPa) |
|----|-----------|-----------|----------------|----------------|--------|--------|
| 0  | 726       | 779       | 53             | 7.225          | 6.81   | 112.7  |
| 1  | 729       | 778       | 49             | 7.225          | 6.68   | 110.9  |
| 2  | 730       | 767       | 37             | 7.185          | 7.09   | 110.8  |
| 3  | 729       | 771       | 42             | 7.247          | 7.14   | 114.1  |
| 4  | 721       | 764       | 43             | 7.247          | 6.74   | 107.4  |
| 5  | 719       | 768       | 49             | 7.256          | 6.75   | 109.8  |

Nanoindentation tests were performed four times on each sample, and the average values of hardness (H) and elastic modulus (G) are listed in Table 1. The addition of Nb did not always increase the hardness of alloys. Only the 3 at.% Nb BMG showed larger hardness and modulus than the original one. The density (D) used to evaluate the volume loss in abrasive tests was measured using Archimedes’ law and the data are given in Table 1. The wear resistance of the samples can be simply defined as the reciprocal of wear volume loss [6]. It is reasonable to think that the hardest 3 at.% Nb sample should show the best wear resistance while the softest 1 at.% Nb sample the worst, as shown in Fig.4. However, wear resistance was not always in proportional to hardness in this investigation. For samples containing 0, 4, 5 at.% Nb, the differences of hardness are negligible compared with those of their wear resistance. Abrasive wear involves several mechanisms such as plowing, microcutting and...
microcracking that are damage modes to the sample surface and result in material removal. The discrepancies can arise from the different dominant wear mechanisms in different samples.

Figure 3. Polarization curves of 3 mm diameter alloy rods in 0.5 N H₂SO₄ solutions.

Figure 4. Volume loss of BMG rods (Cu₄₂Zr₄₂Al₈Ag₈)₁₀₀₋ₓNbₓ after 200 m sliding in abrasive wear test.

4. Summary
Corrosive, mechanical and abrasive properties of (Cu₄₂Zr₄₂Al₈Ag₈)₁₀₀₋ₓNbₓ (x=0-5) BMGs were investigated. (Cu₄₂Zr₄₂Al₈Ag₈)₉₅Nb₅ BMG showed the best corrosion resistance with a passive current density of 10⁻²A/m⁻² in 0.5 N H₂SO₄ solutions. The (Cu₄₂Zr₄₂Al₈Ag₈)₉₇Nb₃ BMG exhibited the best wear resistance and highest hardness of 7.14 GPa with an elastic modulus of 114 GPa.

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