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Co substituted Zr-Cu-Al-Ni metallic glasses with enhanced glass-forming ability and high plasticity

Yu Zhang[a], Min Zhou[a], Xiangyu Zhao[a,b,*], Liqun Ma[a]

[a] College of Materials Science and Engineering, Nanjing Tech University, Xinmofan Road 5, Nanjing 210009, China
[b] Jiangsu Collaborative Innovation Center for Advanced Inorganic Functional Composites, Nanjing Tech University, Xinmofan Road 5, Nanjing 210009, China

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ABSTRACT

Zr-based bulk metallic glasses have been considered as promising engineering materials. However, their widespread application is limited by their contrasting properties of glass-forming ability (GFA) and plasticity. Herein, the effects of Ni substitution by Co on the GFA and plasticity of the representative Zr-based metallic glass of $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10}$ were investigated. A series of $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10-x}Co_x$ (x = 0, 2, 4, 6, 7, 8, 10) rod samples with 2 mm in diameter were prepared by injection copper mold casting method. Amorphous structure was successfully achieved when the Co content is less than 8 at.%. Importantly, the Co addition contributed to significant enhancements in both GFA and plasticity of the amorphous $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10-x}Co_x$ (x = 0, 2, 4, 6, 7) alloys. The as-prepared $Zr_{65}Cu_{17.5}Al_{7.5}Ni_8Co_2$ amorphous alloy shows the best and attractive performance with a supercooled liquid region width of 80 K and a compressive plasticity of 7.4%, which are much higher than 50 K and 0.2% of the pristine $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10}$ amorphous alloy, demonstrating that the Co substituted Zr-Al-Ni-Cu metallic glass has the potential to be used for engineering applications.

1. Introduction

Bulk metallic glasses (BMGs) are expected to be used as engineering materials due to their combinative properties of high strength, large elastic elongation and good corrosion resistance [1–4]. During the last two decades, a number of BMG-forming alloys such as Mg-, Cu-, Fe-, and Ti-based alloys [4] have been developed by a conventional copper mold casting method. However, they typically exhibit little plastic strain due to the limited plastic flow and the lack of work hardening [5], and thus are prone to catastrophic failure at room temperature. Among various types of BMGs, Zr-based BMGs with high Zr contents (62.5–70%) have been considered to be important candidates for structural applications due to their desirable plastic deformation and fracture toughness [6–9]. Nevertheless, it should be noted that it was hard to get a balance between superior GFA and high plasticity. For instance, the increase in the Zr content could lead to a decrease in the GFA of the Zr-based BMGs [9]. The approach of elemental addition in the Zr-based BMGs has been well carried out to improve the comprehensive performance of the BMGs [10,11]. Li et al. [12] have studied the effects of Cu, Fe and Co addition on the GFA and mechanical properties of the ternary Zr-Al-Ni BMGs. It was found that the addition of Cu could significantly improve the plasticity of the ternary Zr-Al-Ni BMGs. Further work by Zhou el al [13] showed that the addition of Fe is also beneficial to improve both the GFA and mechanical properties in a quaternary Zr-Cu-Al-Ni alloy. Actually, among these elemental substitutions, Co shows similar atomic radius and electro-negativity with Ni as they are in the same traditional subgroup in the elemental periodic table. Moreover, Co has a large negative heat of mixing with the constituent elements of Zr and Al, and furthermore, the heat of mixing is positive for the Co-Cu system (6 kJ/mol) [14]. It is possible that Ni substitution by Co in the Zr-Cu-Al-Ni alloy system may develop new metallic glasses with unique mechanical properties in conjunction with good GFA.

In this work, the elemental substitution in the representative Zr-based metallic glass of quaternary $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ has been performed, contributing to the formation of a series of new $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10-x}Co_x$ (x = 0, 2, 4, 6, 7) metallic glasses by the injection copper-mold casting method. The effects of Co addition on the GFA and mechanical properties of $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10}$ alloy were investigated.

2. Experimental

Zr-based alloy ingots with nominal compositions of $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10-x}Co_x$ (x = 0, 2, 4, 6, 7, 8, 10) were prepared by arc melting a mixture of pure Zr (99.99 wt%), Cu (99.9 wt%), Al

* Corresponding author at: College of Materials Science and Engineering, Nanjing Tech University, Xinmofan Road 5, Nanjing 210009, China.
E-mail address: xiangyu.zhao@njtech.edu.cn (X. Zhao).

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(99.9 wt%), Ni (99.9 wt%) and Co (99.9 wt%) in an argon atmosphere. The pure titanium was melted previously to absorb oxygen atoms in the furnace. In order to obtain a homogeneous composition, the master alloys were remelted at least four times. Seven $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10-x}Co_x$ (x = 0, 2, 4, 6, 7, 8, 10) rod samples with 2 mm in diameter were prepared by the injection copper mold casting method under high-purity argon atmosphere.

The structure of the as-cast $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10-x}Co_x$ (x = 0, 2, 4, 6, 7, 8, 10) alloys was examined by XRD with CuK_α radiation (Dmax/RBRigaku). Thermal properties of the alloys were studied by different scanning calorimetry (DSC, NETZSCH DSC 204) under a continuous argon flow at a heating rate of 20 K/min. The glass transition temperature (T_g), the onset crystallization temperature (T_x) and the liquidus temperature (T_l) of the metallic glasses were determined with an accuracy of ± 1 K. Compression tests were carried out using a domestic WDW-100D test machine with a load strain rate of $5 \times 10^{-4} s^{-1}$ at room temperature. The cylindrical alloy rods for compressive tests were 2 mm in diameter and 4 mm in length. In order to ensure that the results are reproducible and reliable, at least five samples were measured for mechanical testing. The fracture morphologies and lateral view of alloys after compression were observed by SEM (Philips Quanta 200).

3. Results and discussion

3.1. Structural and thermal stability characterization

Fig. 1 shows the XRD patterns of the as-cast $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10-x}Co_x$ (x = 0, 2, 4, 6, 7, 8, 10) alloys with 2 mm in diameter. The as-cast alloys with a Co content < 7 at.% exhibit a broad diffraction peak around 2θ = 36°, which is an important feature of the amorphous structure. There are no other detectable crystalline peaks within the detection limit of the XRD measurement, indicating that these samples are mostly amorphous. The increase of Co content to 7 at.% in the as-cast alloy also results in the formation of a broad diffraction peak and thus an amorphous structure. Note that this broad peak slightly shifts to a lower position as compared with those peaks of the as-cast alloys with a Co content < 7 at.%. This may be ascribed to the change of the amorphous structure at a high Co content. When the Co content was further increased from 8 to 10 at.%, some sharp diffraction peaks in the XRD patterns were formed, demonstrating that these two alloys have a composite structure consisting of both the crystalline and amorphous phases. The crystalline phases can be indexed and assigned to the $CoZr_2$ phase (PDF card no. 44-1309), $CuZr_2$ phase (PDF card no. 18-466), Al_3Zr phase (PDF card no. 65-674), ZrCu phase (PDF card no. 49-1483) and Zr_2Cu phase (PDF card no. 65-2647) in the as-cast $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10-x}Co_x$ (x = 8 and 10) alloys.

Fig. 2a shows the DSC curves of the as-cast $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10-x}Co_x$ (x = 0, 2, 4, 6, 7) alloys at a heating rate of 20 K/min. The transition temperature (T_g), onset temperature of crystallization (T_x) and liquidus temperature (T_l) are marked by arrows. These values are listed in Table 1. The T_g position was determined by the intersection of two tangents on each DSC curve, as illustrated in Fig. 2b. All the five amorphous samples exhibit a small endothermic event, which is characteristic of glass transition, followed by a broad subcooled liquid region, as well as the exothermic peaks due to the crystallization reactions, and the different melting endothermic peaks. The pristine $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10}$ alloy appears a two-stage crystallization. The Co addition with a content of 2–6 at.% did not change this crystallization. It is clear that the alloys with 0–6 at.% Co show two-stage endothermic reactions in the temperature range from 1100 to 1200 K, suggesting that these alloy systems have a non-eutectic composition [15]. Interestingly, a single endothermic peak associated with the melting process of the glassy alloy with 7 at.% Co was observed, suggesting that the formation of an eutectic composition. This is consistent with the XRD result in Fig. 1 that the amorphous composition is changed by the addition of 7 at.% Co. The supercooled liquid region width ($\Delta T_x = T_x - T_g$), the reduced glass transition temperature ($T_{rg} = T_g/T_l$), and the parameter $\gamma = T_x / (T_g + T_l)$ are important indicators of the GFA of metallic glasses, and are also summarized in Table 1. The $Zr_{65}Cu_{17.5}Al_{7.5}Ni_8Co_2$ alloy shows the lowest liquidus temperature (about 1161 K), indicating that this alloy possesses the highest glass forming ability according to the deep eutectic theory of Turnbull [14]. ΔT_x exhibits an obvious increase from only 57 K for the base alloy to 80 K for the alloy with 2 at.% Co, and then decreases with the increase of Co content. Furthermore, T_{rg} exhibits a slight change with the increase of Co addition and parameter γ follows the similar trend as ΔT_x. On the basis of the results of ΔT_x and γ, part of Ni substitution by Co is beneficial to enhance the GFA of the $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10}$ alloy and the best GFA in the as-cast $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10-x}Co_x$ was obtained when the Co content is 2 at.%.

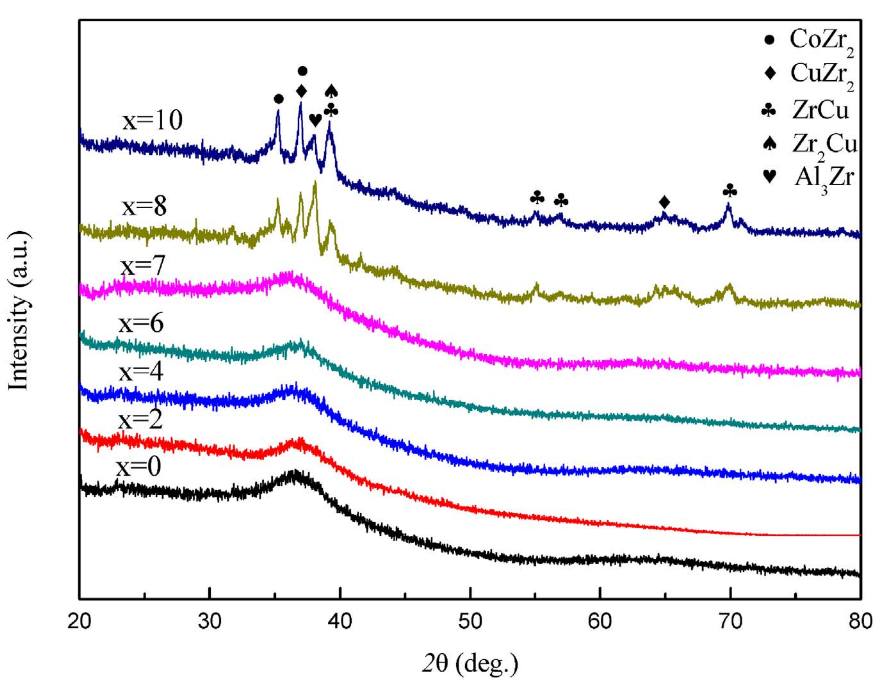

Fig. 1. XRD patterns of the as-cast $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10-x}Co_x$ (x = 0, 2, 4, 6, 7, 8, 10) alloys.