Journal of Non-Crystalline Solids xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Enhanced glass-forming ability and mechanical properties of $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10}$ metallic glass by adding Fe

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ARTICLE INFO

Article history:
Received 11 March 2016
Received in revised form 27 April 2016
Accepted 1 May 2016
Available online xxxx

Keywords:
Zr-based
Metallic glass
Fe
GFA
Mechanical property

ABSTRACT

The main objective of the paper is to improve the plasticity and reduce the toxicity of the known $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ alloy. A series of rod samples with diameter of 2 mm $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10-x}Fe_x$ (x = 0, 2, 4, 6, 8, 10) were prepared by injection copper mold casting method. Appropriate addition of Fe can enhance GFA of the base alloy significantly. In addition, compared with the base alloy revealing no plastic deformation, partial substitution of Ni by Fe can also improve the compressive plasticity (ε_p) of alloys effectively. The enhanced plasticity of alloys can be attributed to the positive heat of mixing between Fe and Cu atoms. Alloy with 6% Fe exhibits the relatively good comprehensive properties, as a result of an excellent combination of both good GFA (ΔT_x = 81 K) and remarkable plasticity (ε_p = 6.2%). $Zr_{65}Cu_{17.5}Fe_{10}Al_{7.5}$ metallic glass is environmentally friendly and has large deformation plasticity, making it a promising candidate for engineering applications.

1. Introduction

Zr-based bulk metallic glasses (BMGs) have been attracted much attention in recent years resulting from their superb properties, such as unique mechanical properties, high glass-forming ability (GFA), excellent corrosion resistance and good biocompatibility [1–5]. Metallic glasses can be used in the area of catalyst [6], defence and aerospace, solar energy conversion, biomedical applications, etc.

Zr-Al-Ni-Cu alloy system having high Zr content (above 50%) could be considered as a typical Zr-based system [7]. Alloy additions have historically been an effective metallurgical method for developing new metallic glasses, and play an important role in the properties tailoring [8]. Liu Guang-qiao [9] studied the effect of the minor addition of Fe on glass-forming ability and mechanical properties of $(Zr_{0.55}Al_{0.10}Ni_{0.05}Cu_{0.30})_{100-x}Fe_x$ bulk metallic glasses. The report shows that appropriate Fe addition can improve both GFA and the mechanical properties of the base alloy. $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ alloy is a typical composition of Zr-Al-Ni-Cu alloy system. Scarcely any deformation plasticity of $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ alloy has been reported by Li Chun-yan et al. [10] and Nima Khademian [11]. There is no question that the lack of macroscopic plasticity of BMGs at room temperature restricts their extensive applications [12].

It is well known that element Ni is allergic [13] and possibly carcinogenic for the human body. Because of this problem, currently a series of Ni-free [14–17] Zr-based BMGs in Zr-Cu-Fe-Al system have been fabricated using copper-mold casting technique. Zr-Cu-Fe-Al BMGs are promising candidates for potential biomedical applications due to their combination of exceptional corrosion resistance, good mechanical properties and its high biocompatibility.

Adding little cost effective and green element to decrease Ni content of Zr-based metallic glasses is of great importance. The atomic radius and electro-negativity of Fe are similar to those of Ni, because Fe and Ni belong to the same traditional subgroup in the elemental periodic table. However, Fe is much friendly and cheaper than Ni. Additionally, the effect of substituting only Ni by Fe in Zr-Al-Ni-Cu alloys on GFA and the mechanical properties has not been extensively studied up to now.

In this paper, with the main aim of improving the plasticity and reducing the toxicity of the known $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ alloy, we prepared a series of $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10-x}Fe_x$ (x = 0, 2, 4, 6, 8, 10) metallic glasses by injection copper mold casting method and then studied the effects of Fe addition on GFA and mechanical properties of the $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10}$ alloy.

2. Experimental methods

The alloy ingots with nominal compositions of $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10-x}Fe_x$ (x = 0, 2, 4, 6, 8, 10) were prepared by arc melting of the mixture of pure Zr, Al, Ni, Cu and Fe with a purity above 99.9% in a purified argon atmosphere. The pure titanium was melted prior to the preparation of the master alloys to absorb oxygen atoms in the furnace. The master alloys were remelted four times in order to obtain a homogeneous composition. Six alloy rods with diameter of 2 mm were fabricated by injection copper

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http://dx.doi.org/10.1016/j.jnoncrysol.2016.05.004
0022-3093/

mold casting method under high-purity argon atmosphere and ribbon samples were prepared by melt spinning.

The amorphous structure of the samples was characterized by XRD with CuK$_\alpha$ radiation (Dmax/RBRigaku, diffraction range from 20° to 80°). Phase transformations were studied on a 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 performed at room temperature on a domestic WDW-100D test machine at the loading strain rate of 5×10^{-4} s^{-1} using cylindrical rods with the diameter of 2 mm and a height of 4 mm. At least three samples for mechanical testing were measured to ensure that the results are reproducible and statistically meaningful. The fracture surfaces after compression were observed by SEM (Philips Quanta 200).

3. Results

3.1. Structural analysis

Fig. 1 shows XRD patterns of the as-cast $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10-x}Fe_x$ (x = 0, 2, 4, 6, 8, 10) alloys with a diameter of 2 mm. All of the XRD patterns reveal a broad peak around $2\theta = 36°$, which is the characteristic of the amorphous structure. No other detectable crystalline peaks can be identified within the detection limit of the XRD measurement (Fig. 1). This indicates that all the alloys examined in this study are mostly amorphous, even when Ni is totally (x = 10) substituted by Fe. In other words, $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10-x}Fe_x$ (x = 0, 2, 4, 6, 8, 10) alloys possess an excellent GFA which is important to form metallic glasses.

3.2. GFA

Fig. 2 shows DSC curves of $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10-x}Fe_x$ (x = 0, 2, 4, 6, 8, 10) glassy alloy ribbons at the heating rate of 20 K/min. The glass transition temperature (T_g), onset temperature of crystallization (T_x) and liquidus temperature (T_l) are marked by arrows in the DSC curves, and are listed in Table 1. All ribbon samples exhibit a small endothermic peak corresponding to the glass transition followed by a wide supercooled liquid region, as well as exothermic reactions associated with the crystallization, and the distinct melting endothermic peaks. Without addition of Fe, the ribbon appears two-stage crystallization. Moreover, we can see that ribbons with 0–4% Fe appear two-stage melting phenomenon, indicating that the alloy systems are off-eutectic compositions [7]. Whereas, as Fe content surpasses 6%, the melting behavior of glassy alloys changes from two peaks to a single one, suggesting that appropriate addition of Fe drives the alloy system to eutectic compositions.

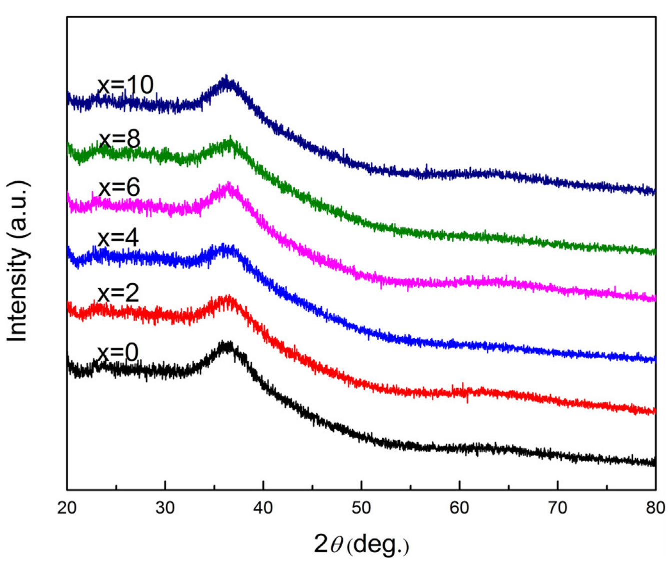

Fig. 1. XRD patterns of as-cast $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10-x}Fe_x$ (x = 0, 2, 4, 6, 8, 10) alloys.

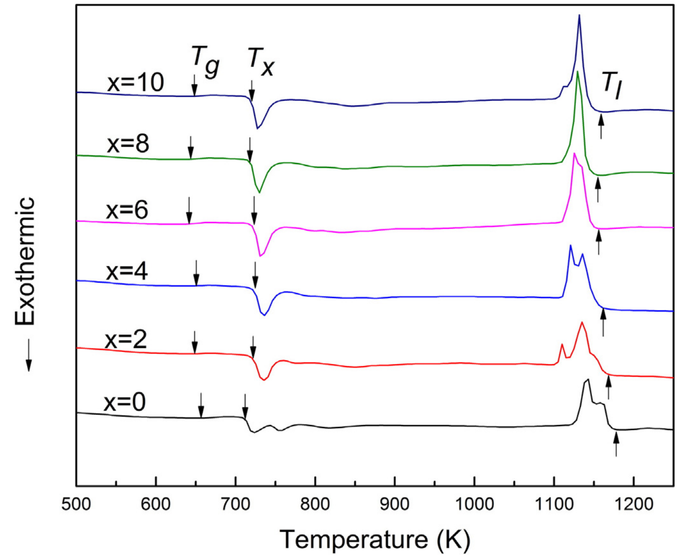

Fig. 2. DSC curves of $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10-x}Fe_x$ (x = 0, 2, 4, 6, 8, 10) glassy alloy ribbons at a heating rate of 20 K/min.

ΔT_x ($= T_x - T_g$), T_{rg} ($= T_g / T_l$) as well as γ ($= T_x / (T_g + T_l)$) values are usually taken as indicators of the GFA of glassy alloys [18], which are useful in choosing appropriate alloys that could be easily formed into glasses. The ΔT_x, T_{rg} and γ values of glassy ribbons are also summarized in Table 1. From Table 1, it is seen that, with the increase of Fe content, ΔT_x exhibits an obvious increase first from only 55 K for the base alloy to 81 K for the alloy with 6% Fe, then a decrease with the increase of Fe content to 72 K for the alloy with 10% Fe. It is obvious that the Fe addition could increase ΔT_x of base alloy effectively. Parameter γ follows the similar trend as ΔT_x – Fe content. Besides, T_{rg} has a slight change with the increase of Fe content. According to ΔT_x, T_{rg} and γ values, we can conclude that adding appropriate amount of Fe can effectively enhance the GFA of the base alloy.

3.3. Mechanical properties

As we know, mechanical properties, especially the strength and plasticity, are very important for structural materials. Fig. 3 displays typical compressive stress-strain curves at room temperature of as-cast $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10-x}Fe_x$ (x = 0, 2, 4, 6, 8, 10) alloy rods under uniaxial compression. The important mechanical properties, including compressive fracture strength (σ_f) and ε_p measured from each curve, are listed in Table 2. Again, the average of the σ_f and ε_p were calculated based on several measurements with the standard deviation as the error.

It is seen that all alloys exhibit an initial elastic strain around 2.3%, followed by a distinct substantial plastic deformation consisting of jerky serrated flow, and then fracture. The σ_f of the base alloy is around

Table 1
GFA parameters of $Zr_{65}Cu_{17.5}Al_{7.5}Ni_{10-x}Fe_x$ (x = 0, 2, 4, 6, 8, 10) alloys.

Alloy	T_g/K	T_x/K	T_l/K	ΔT_x/K	T_{rg}	γ
x = 0	657	712	1178	55	0.558	0.388
x = 2	649	722	1168	73	0.556	0.397
x = 4	651	724	1162	73	0.560	0.399
x = 6	642	723	1156	81	0.555	0.402
x = 8	644	718	1155	74	0.558	0.399
x = 10	648	720	1159	72	0.559	0.398

Please cite this article as: M. Zhou, et al., Enhanced glass-forming ability and mechanical properties of Zr65Cu17.5Al7.5Ni10 metallic glass by adding Fe, J. Non-Cryst. Solids (2016), http://dx.doi.org/10.1016/j.jnoncrysol.2016.05.004