International Journal of Minerals, Metallurgy and Materials

International Journal of Minerals, Metallurgy and Materials

Volume 14 | Issue 7 Article 7

June 2007

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Recommended Citation

Fu Junying, Men Hua, Pang Shujie, Ma Chaoli, Zhang Tao. Formation and thermal stability of Cu-Zr-Al-Er bulk metallic glasses with high glass-forming ability, *Int. J. Miner. Metall. Mater.*, 14 (2007), No. 7, Article 7, p. 36-38.

Journal of University of Science and Technology Beijing
Volume 14, Supplement 1, June 2007, Page 36

Formation and thermal stability of Cu-Zr-Al-Er bulk metallic glasses with high glass-forming ability

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(Received 2006-06-12)

Abstract: The formation and thermal stabilities of $Cu_{46.25}Zr_{46.25-x}Al_{7.5}Er_x$ (x=0 to 8) bulk metallic glasses (BMGs) were investigated. The addition of a small amount of Er (2at%) for replacing Zr effectively improves the glass-forming ability of $Cu_{46.25}Zr_{46.25}Al_{7.5}$ alloy, and the glassy rod with a diameter of at least 12 mm can be formed. The glass transition temperature (T_g), temperature interval of supercooled liquid region ΔT_x ($=T_x-T_g$), and reduced glass transition temperature T_{rg} ($=T_g/T_l$) of $Cu_{46.25}Zr_{44.25}Al_{7.5}Er_2$ glassy alloy are 699 K, 62 K and 0.607, respectively.

Key words: Cu-based alloy; bulk metallic glass; glass-forming ability; glass transition temperature; Erbium

[This work was financially supported by the National Natural Science Foundation of China (No.50225103, 50471001, and 50631010).]

1. Introduction

Cu-based bulk metallic glasses (BMGs) generally exhibit good mechanical properties, such as relatively high strength and good ductility. Due to the combination of good mechanical properties and low material cost, the Cu-based BMGs show potential application as structural materials. A great deal of Cu-based BMGs have been developed, such as $Cu_{47}Ti_{33}Zr_8Ni_{11}Si_1$, $Cu_{43}Zr_{43}Al_7Ag_7$, $Cu_{46}Zr_{42}Al_7Y_5$, and $Cu_{44.25}Ag_{14.75}Zr_{36}Ti_5$ [1-3], for which the maximum diameters are 7-10 mm. Recently, it was proposed that the glass-forming ability (GFA) of the alloys can be strongly enhanced by small addition of alloying elements. For example, the GFA of the Fe-, Zr- or Cu-based alloys was reported to be remarkably enhanced by the addition of a small amount of Er or Y, *etc.* [4-7].

$Cu_{50}Zr_{50}$ alloy shows a good GFA [8] and the BMG with a diameter of 2 mm can be formed by copper mold casting. The glass formation of $(Cu_{0.5}Zr_{0.5})_{100-x}Al_x$ alloys was investigated and it was found that the x=7.5 alloy is the best glass former in this system and a glassy rod with a diameter of 7 mm can be produced by copper mold casting [9]. The composition of the x=7.5 alloy is very close to the ternary eutectic $Zr_{48}Cu_{45}Al_7$, which has a slightly larger critical diameter of 8 mm for glass formation [9]. In this study, the effect of substituting of a small amount of Er for Zr on the GFA of $(Cu_{0.5}Zr_{0.5})_{92.5}Al_{7.5}$ alloy was investigated. This paper intends to present the formation and thermal stability of $Cu_{46.25}Zr_{44.25}Al_{7.5}Er_2$ BMG with a diameter up to 12 mm. The origin for the glass formation of the Cu-Zr-Al-Er alloys is also discussed.

2. Experimental procedure

The alloy ingots with nominal compositions of $Cu_{46.25}Zr_{46.25-x}Al_{7.5}Er_x$ (x=0 to 8) were prepared by arc melting the mixtures of pure elements Cu, Zr, Al and Er under a purified argon atmosphere. Cylindrical rods of 1 to 15 mm in diameter were obtained by copper mold casting and ribbons with a cross section of 0.02 mm×2 mm were prepared by melt spinning. The structure of the specimens examined by X-ray diffraction (XRD) with Cu K_α radiation. Thermal stability associated with glass transition and crystallization of the glassy alloys was investigated by differential scanning calorimetry (DSC) at a heating rate of 0.333 K/s.

3. Results and discussion

X-ray diffraction patterns of the as-cast $Cu_{46.25}Zr_{46.25-x}Al_{7.5}Er_x$ (x=0, 2, 4, and 6) rods with different diameters of 7-15 mm are shown in Fig. 1. For

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the base alloy $Cu_{46.25}Zr_{46.25}Al_{7.5}$, the XRD pattern of 7 mm in diameter exhibits a broad diffraction maximum which is characteristic of a monolithic amorphous phase, however sharp crystalline peaks are recognized on the XRD pattern of the 8-mm diameter sample. This indicates that the critical diameter for glass formation of the base alloy is 7 mm. For the x=2 and 4 alloys, there are no crystalline peaks discernible except for the main amorphous halos on the XRD patterns taken from the 12-mm diameter samples, demonstrating that these samples consist of a glassy structure. A mixed crystalline and amorphous microstructure is formed for the rods with d=15 mm of both of the alloys, as depicted by the XRD patterns which show sharp diffraction patterns superimposed on the diffuse halo. It seems that the x=2 alloy rod has larger volume fraction of glassy phase than that of the x=4 alloy. The GFA is dramatically degraded with a further increase of Er content, and the x=6 alloy rod with d=9 mm is partially crystallized, judged from the XRD pattern shown in Fig. 1. Fig. 2 shows the DSC curves of the x=2 alloy rods with diameters of 9 and 12 mm, and the data of the as-quenched ribbon is also included for comparison. The as-cast rods and as-quenched ribbon exhibit almost identical values of T_g, T_x, and heat of crystallization, further confirming that the rod with d=12 mm is fully glassy.

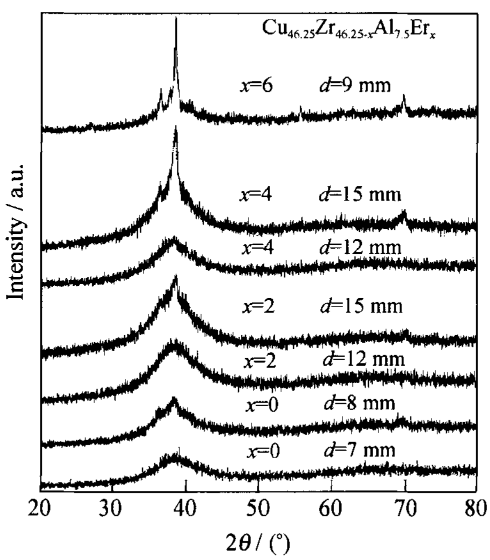

Fig. 1. XRD patterns of $Cu_{46.25}Zr_{46.25-x}Al_{7.5}Er_x$ (x=0, 2, 4, and 6) alloy rods with various diameters (d denotes the diameters of rods).

Therefore, the x=2 alloy is the best glassy former in the $Cu_{46.25}Zr_{46.25-x}Al_{7.5}Er_x$ alloys. The diameter for glass formation of the $Cu_{46.25}Zr_{44.25}Al_{7.5}Er_2$ alloy is between 12 and 15 mm, indicating it is one of the best glass formers in the Cu-based BMGs up to date.

Fig. 3 depicts the DSC traces taken from the melt-spun $Cu_{46.25}Zr_{46.25-x}Al_{7.5}Er_x$ (x=0, 2, 4, and 6) glassy ribbons, which typically shows a clear endothermic inflection characteristic of glass transition at temperatures ranging from 671 to 710 K, followed by one or more pronounced exothermic peaks corresponding to crystallization events. The values of glass transition temperature (T_g), crystallization temperature (T_x) and temperature interval of supercooled liquid region ΔT_x ($=T_x-T_g$) are listed in Table 1. With the increase in Er content, T_g and T_x decrease simultaneously. The x=0 and 2 glassy alloys show ΔT_x of about 63 K, and it rapidly decreases to about 33 K for the x=4 alloy.

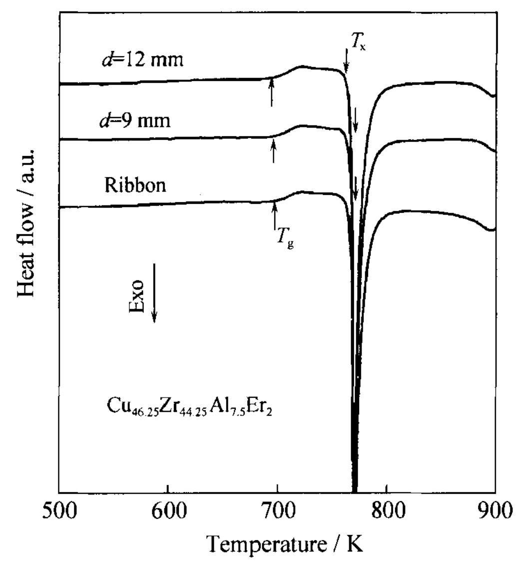

Fig. 2. DSC curves of as-quenched ribbon and as-cast rods with d=9 and 12 mm for $Cu_{46.25}Zr_{44.25}Al_{7.5}Er_2$ alloy.

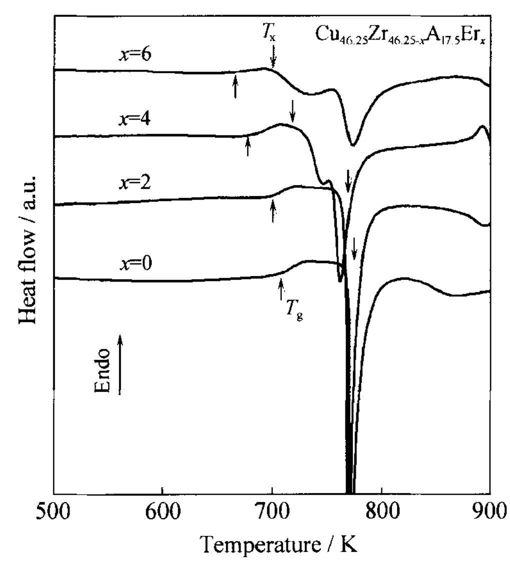

Fig. 3. DSC curves of melt-spun $Cu_{46.25}Zr_{46.25-x}Al_{7.5}Er_x$ (x=0, 2, 4 and 6) glassy ribbons at a heating rate of 0.333 K/s.

The melting behavior of $Cu_{46.25}Zr_{46.25-x}Al_{7.5}Er_x$ (x=0, 2, 4, and 6) alloys are shown in Fig. 4. For the base alloy, a single major melting peak can be observed on the DSC trace in addition to a minor endothermic peak at lower temperature, which may correspond to a solid-state transformation of $Cu_{10}Zr_7$ and $CuZr_2$ phases to an intermediate compound CuZr [10]. The DSC traces of the Er-containing alloys exhibit overlapped multiple melting peaks, indicating that they are off-eutectic compositions. With the increase in Er content, the liquidus temperature (T_l) decreases continuously from 1183 K for x=0 to 1124 K for x=6. The values of the liquidus temperature (T_l), reduced glass transition temperature T_{rg} (=T_g/T_l), and γ (=$T_x/(T_g+T_l)$) are listed in Table 1 as well. The present glassy alloys show close values of T_{rg} (0.597-0.607) and γ (0.391-0.412).

For the Cu-Zr-Al-Er system, the atomic diameter of Er is the largest, the large atomic size probably limits the solubility of Er in the competing crystalline phases. The precipitation of the competing crystalline phases may involve redistribution of Er in the undercooled liquid. The requirement of Er diffusion could cause sluggish crystallization kinetics of the undercooled liquid on cooling for the x=2 alloy. As a consequence, the addition of 2at% Er for replacing Zr effectively improves the GFA of the base alloy. With the increase in Er content in the undercooled liquid, the Er-rich phase probably precipitates firstly on cooling, which can further trigger the crystallization of the remaining undercooled liquid and therefore leads to the degradation of the GFA. By substituting different rear-earth (RE) elements for Zr in $Cu_{46.25}Zr_{46.25}Al_{7.5}$ alloy, however, the alloys exhibit varied GFA, and the effect of RE on the GFA will be published elsewhere. The variation of GFA probably stems from the difference in electronic configuration among RE elements [11].

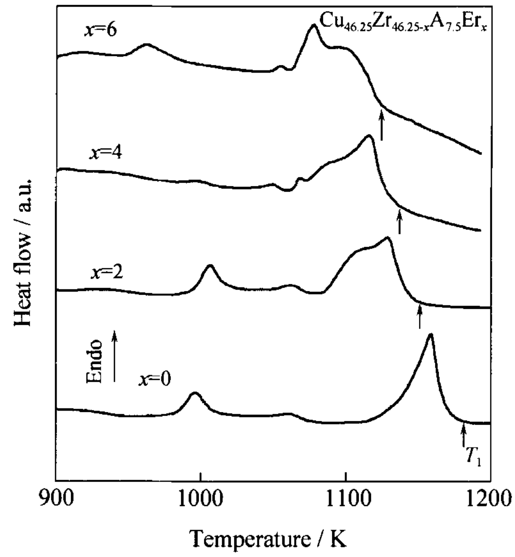

Fig. 4. Melting behaviors of $Cu_{46.25}Zr_{46.25-x}Al_{7.5}Er_x$ (x=0, 2, 4, and 6) alloys at a heating rate of 0.333 K/s.

Table 1. Thermal stabilities and representative GFA parameters for $Cu_{46.25}Zr_{46.25-x}Al_{7.5}Er_x$ (x=0, 2, 4, and 6) glassy alloys

x	T_g / K	T_x / K	ΔT_x / K	T_l / K	T_{rg}	γ	d_{max} / mm
0	710	773	63	1183	0.600	0.408	7
2	698	762	64	1150	0.607	0.412	12-15
4	682	715	33	1137	0.600	0.393	12-15
6	671	701	30	1124	0.597	0.391	<9

4. Conclusions

$Cu_{46.25}Zr_{46.25-x}Al_{7.5}Er_x$ (x=0 to 8) BMGs with high GFA were formed by copper mold casting. The critical diameter for glass formation increases from 7 mm for the x=0 alloy to at least 12 mm for the x=2 one, and then decreases to less than 9 mm at x=6. T_g, T_x and T_l decrease simultaneously with an increase in Er content, and the glassy alloys exhibit close values of T_{rg} and γ.

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