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A Ti–Zr–Be–Fe–Cu bulk metallic glass with superior glass-forming ability and high specific strength

P. Gong, X. Wang, Y. Shao, N. Chen, X. Liu, K.F. Yao*

School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

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ABSTRACT

It has been found that alloying with Cu element could significantly enhance the glass-forming ability (GFA) of Ti–Zr–Be–Fe alloy. As a result, a series of centimeter-scale $(Ti_{41}Zr_{25}Be_{28}Fe_6)_{100-x}Cu_x$ (x = 0–20 at.%) bulk metallic glasses (BMGs) have been developed. Especially for those with x = 7–13 at.% Cu content, the critical size is larger than 20 mm. Among these Ti-based BMGs, $(Ti_{41}Zr_{25}Be_{28}Fe_6)_{91}Cu_9$ (also noted as $Ti_{37.31}Zr_{22.75}Be_{25.48}Fe_{5.46}Cu_9$) glassy alloy exhibits superior GFA with a critical size larger than 32 mm, which is the largest size of Ti-based BMGs ever reported so far. The enhancement of the GFA is suggested to arise from the Cu addition-induced decrease in both the liquidus temperature and the Gibbs energy difference between the undercooled liquid and the crystalline phases of Ti–Zr–Be–Fe alloy. In addition to its superior GFA, the lightweight $(Ti_{41}Zr_{25}Be_{28}Fe_6)_{91}Cu_9$ alloy also exhibits a remarkable high specific strength of 3.7×10^5 N m kg^{-1} and an apparent plastic strain of 1.2%.

1. Introduction

Because of the disordered atomic structure, bulk metallic glasses (BMGs) possess unique properties, such as high strength, large elastic limits, excellent corrosion resistance, etc. [1]. However, their wide application as structural materials remains a great challenge due to the limited glass-forming ability (GFA). With the tremendous efforts made by the scientists in this field, substantial progress has been made in producing centimeter-scale BMGs in different metal-based alloys [2–7]. For example, the world's biggest BMG with a diameter of 80 mm and a length of 85 mm has been obtained in $Pd_{42.5}Cu_{30}Ni_{7.5}P_{20}$ alloy by water quenching [2], while Zr–Cu–Ag–Al–Be glassy alloy [3] with a diameter of 73 mm and Mg–Cu–Ag–Gd [4] with 27 mm have been successfully prepared respectively. According to the reported results, only a handful of BMGs possess high GFA with a critical size larger than 30 mm. As a typical representative of light-metal based amorphous alloys, Ti-based BMGs are very attractive due to their high specific strength [8]. Unfortunately, the GFA of Ti-based BMGs is relatively low compared with other bulk glassy alloy systems so that there are few Ti-based BMGs with critical size larger than 10 mm in spite of years of research attention [9–12]. Until recently, a TiZr-based BMG with a maximum size of over 50 mm has been reported by Tang et al. [13]. High Zr content in this alloy, however, dramatically increases its density and thus reduces its specific strength compared to those high Ti containing BMGs [14,15]. Driven by the desire to further lower the cost and enhance the specific strength, developing new Ti-based BMGs with excellent GFA is thus meaningful.

Alloying method has been widely adopted to improve GFA and mechanical properties of BMGs [16]. Using this strategy with different elements based on a ternary $Ti_{41}Zr_{25}Be_{34}$ alloy [14], we have developed a series of lightweight Ti-based quaternary and quinary BMGs [17–20]. Among these newly developed glassy alloys, some of Ti–Zr–Be–Fe alloys can be cast into glassy rods with critical diameters up to centimeter scale owing to a significantly beneficial alloying effect of Fe on the GFA of the $Ti_{41}Zr_{25}Be_{34}$ matrix alloy [18,20]. Given that Cu plays a crucial role in drastically improving the GFA of Pd–Ni–P and TiZr-based amorphous alloys [2,13], Cu was selected as an alloying element with the aim of further improving GFA of $Ti_{41}Zr_{25}Be_{28}Fe_6$ glassy alloy in the present study. By optimizing the composition in Ti–Zr–Be–Fe–Cu system with nominal compositions $(Ti_{41}Zr_{25}Be_{28}Fe_6)_{100-x}Cu_x$ (x = 0–20 at.%), 32 mm-diameter fully glassy $(Ti_{41}Zr_{25}Be_{28}Fe_6)_{91}Cu_9$ rods were obtained by copper mold casting. The origin of the superior GFA of $(Ti_{41}Zr_{25}Be_{28}Fe_6)_{91}Cu_9$ glassy alloy was investigated in terms of thermodynamics and kinetics considerations. Mechanical properties of $(Ti_{41}Zr_{25}Be_{28}Fe_6)_{91}Cu_9$ glassy alloy were also investigated.

* Corresponding author. Tel.: +86 10 62772292; fax: +86 10 62770190.
E-mail addresses: gongpan126@gmail.com (P. Gong), kfyao@tsinghua.edu.cn (K.F. Yao).

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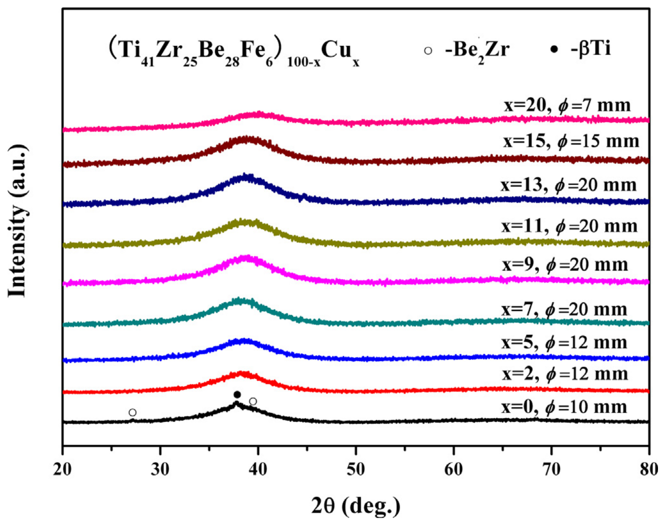

Fig. 1. (a) XRD patterns of $(Ti_{41}Zr_{25}Be_{28}Fe_6)_{100-x}Cu_x$ alloy rods (x = 0–20 at.%) with different diameters prepared by copper mold suction casting.

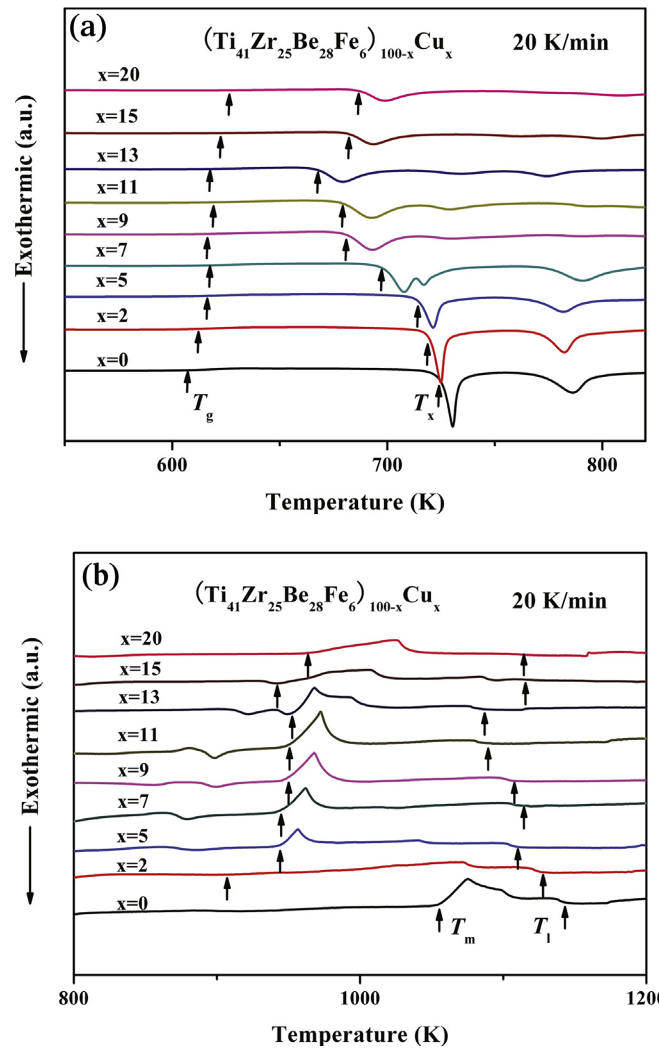

Fig. 2. (a) DSC traces of $(Ti_{41}Zr_{25}Be_{28}Fe_6)_{100-x}Cu_x$ (x = 0–20 at.%) glassy alloys with the ϕ2 mm rods at a heating rate of 20 K/min. (b) DSC scans of the alloys in (a) near their melting temperatures.

2. Experimental procedure

The master ingots with nominal compositions of $(Ti_{41}Zr_{25}Be_{28}Fe_6)_{100-x}Cu_x$ (x = 0–20 at.%) were prepared by arc-melting the mixtures of pure Ti, Zr, Be, Fe, and Cu (>99.4 mass%) in a Ti-gettered high purity argon atmosphere. To achieve chemical homogeneity, each ingot was remelted for at least 4 times. From these ingots, smaller samples (diameter ≤20 mm) were prepared by copper mold suction casting, while rods with diameters of 32 and 50 mm were obtained by copper mold tilt-pour casting method. The structure of the as-cast samples was examined by X-ray diffraction (XRD, Rigaku D/max/RB, Cu $K\alpha$ radiation) and scanning electron microscopy (SEM, QUANTA 200 FEG). Thermal analyses were carried out by differential scanning calorimetry (DSC, Netzsch STA 409 CD) under the protection of high purity Ar gas at a heating rate of 20 K/min. Cylindrical specimens ($\phi 2 \times 4$ mm) were cut from the middle part of as-cast ϕ2 mm rod and used for room temperature compression tests on a WDW-50 testing machine at a strain rate of 4×10^{-4} s^{-1}.

3. Results and discussion

Fig. 1 shows the XRD patterns of as-cast $(Ti_{41}Zr_{25}Be_{28}Fe_6)_{100-x}Cu_x$ (x = 0–20 at.%) rods with various diameters. According to our previous research, ϕ8 mm fully glassy $Ti_{41}Zr_{25}Be_{28}Fe_6$ rod can be easily prepared by copper mold suction casting [18]. When the sample diameter further increases to 10 mm, some weak crystalline peaks can be noticed on an otherwise amorphous background, indicating the critical size (D_{max}) of $Ti_{41}Zr_{25}Be_{28}Fe_6$ alloy is no more than 10 mm. With addition of 2–5 at.% Cu, the GFA of the resulting alloys has been effectively improved and the D_{max} of the glassy rods increases to 12 mm. Further increase of Cu content to 7–13 at.% will enhance the GFA more significantly. Fully glassy rods with at least 20 mm in diameter can be prepared in this wide composition range. However, the GFA degrades as Cu addition is over 15 at.%. The D_{max} of $(Ti_{41}Zr_{25}Be_{28}Fe_6)_{80}Cu_{20}$ is only 7 mm, even smaller than that of Cu-free alloy.

Fig. 2 displays the DSC curves for 2-mm-diameter as-cast $(Ti_{41}Zr_{25}Be_{28}Fe_6)_{100-x}Cu_x$ (x = 0–20 at.%) alloy rods at a heating

Table 1
The critical diameters (D_{max}) and thermal parameters of $(Ti_{41}Zr_{25}Be_{28}Fe_6)_{100-x}Cu_x$ (x = 0, 2, 5, 7, 9, 11, 13, 15, 20 at.%) BMGs with a measuring error less than ±2 K for temperature.

Composition	T_g (K)	T_x (K)	ΔT_x (K)	T_m (K)	T_l (K)	T_{rg}	γ	D_{max} (mm)
$Ti_{41}Zr_{25}Be_{28}Fe_6$	608	725	117	1055	1143	0.532	0.414	8 < D_{max} < 10
$(Ti_{41}Zr_{25}Be_{28}Fe_6)_{98}Cu_2$	613	720	107	907	1128	0.534	0.414	12
$(Ti_{41}Zr_{25}Be_{28}Fe_6)_{95}Cu_5$	617	714	97	944	1110	0.556	0.413	12
$(Ti_{41}Zr_{25}Be_{28}Fe_6)_{93}Cu_7$	617	698	81	946	1114	0.554	0.403	>20
$(Ti_{41}Zr_{25}Be_{28}Fe_6)_{91}Cu_9$	616	681	65	950	1108	0.556	0.395	>20
$(Ti_{41}Zr_{25}Be_{28}Fe_6)_{89}Cu_{11}$	619	679	60	952	1089	0.568	0.398	>20
$(Ti_{41}Zr_{25}Be_{28}Fe_6)_{87}Cu_{13}$	617	668	51	954	1086	0.568	0.392	>20
$(Ti_{41}Zr_{25}Be_{28}Fe_6)_{85}Cu_{15}$	622	682	60	946	1116	0.557	0.392	15
$(Ti_{41}Zr_{25}Be_{28}Fe_6)_{80}Cu_{20}$	627	687	60	965	1114	0.562	0.395	7