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Effect of minor-addition of Fe on structural and mechanical properties of CuZrAl bulk metallic glass

XU Hong-wei[1,2], DU Yu-lei[1,2], DENG Yu[3]

1. Engineering Research Center of Materials Behavior and Design of Ministry of Education, School of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, China;
2. Jiangsu Institute of Advanced Materials, Danyang 212300, China;
3. National Laboratory of Solid State Microstructures and Center for Materials Analysis, Nanjing University, Nanjing 210093, China

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Abstract: The CuZrAl bulk metallic glass with minor-addition of Fe was prepared by rapid quenching method. The structures were examined by X-ray diffraction (XRD). The effect of Fe on the glass-forming ability was studied by differential scanning calorimetry (DSC). The minor-addition of Fe obviously extends the supercooled liquid region ΔT_x. The plastic strain of the $Cu_{44}Zr_{48}Al_7Fe$ bulk metallic glass is about 1.5%. The microstructures were examined by transmission electron microscopy (TEM). It is found that when 1%−2% Fe (mole fraction) were introduced into the CuZrAl alloy matrix, nanoscale phase separation occurs in the as-prepared $Cu_{44}Zr_{48}Al_7Fe$ bulk metallic glass.
Key words: bulk metallic glass; microstructure; mechanical property; phase separation; Fe addition

1 Introduction

It is well known that bulk metallic glasses(BMGs) exhibit unique mechanical properties, such as high strength and elastic limit, excellent corrosion resistance [1,2], but limited room temperature plasticity [3]. It was reported that the room temperature plasticity of BMGs can be improved by introducing dendritic and spherical bcc crystalline phase [4,5], nano-sized crystalline phase [6] into the amorphous matrix, increasing the Poisson ratio [7] or increasing the amount of free volume in BMGs [8.9]. Phase separation, as a kind of approach for microstructure adjustment, has been discussed in many BMGs systems [10−13], and is likely to be induced in metallic glasses when two elements in the multicomponent alloys have a positive heat of mixing [14,15]. Phase separation in BMGs can be also prepared by heating the amorphous alloys at low temperatures or lowering the cooling rate from melt. This kind of structural heterogeneities leads to generation of multiple shear bands, and obvious improvement of the plasticity. In the present work, $Cu_{44}Zr_{48}Al_7Fe$ BMG was prepared, the effects of Fe on the GFA and plasticity were studied, and the microstructures were examined by TEM.

2 Experimental

Alloy ingots with nominal composition of $Cu_{44}Zr_{48}Al_7Fe$ were prepared from elemental metals (purity >99.9%) by arc-melting under a Ti gettered Ar atmosphere. The alloy ingots were remelted in a fused glass tube under a vacuum level of about 5×10^{-3} Pa and then injection cast with ultrahigh purity argon into a copper mold to prepare cylindrical rods with 100 mm in length and 3 mm in diameter. The samples were remelted into a graphite tube of 3 mm in diameter and then dropping cast into Ga−In alloys. To avoid oxidation, the remelting process of the alloys was carried out at a vacuum of 5×10^{-3} Pa.

X-ray diffraction (XRD) with Cu K_α radiation for phase identification was performed on $Cu_{44}Zr_{48}Al_7Fe$

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Corresponding author: DU Yu-lei; Tel/Fax: +86-25-84315159; E-mail: yldu_njust@mail.njust.edu.cn
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sample via θ−2θ scans. Thermal stability of the $Cu_{44}Zr_{48}Al_7Fe$ sample was examined by differential scanning calorimetry (DSC) at a constant heating rate of 20 K/min in Ar atmosphere using a Netzsch STA 449C device. Specimens for transmission electron microscopy (TEM) were prepared by standard twin-jet electrolytic thinning with a HNO_3−CH_3OH electrolyte (volume ratio 3:1). Microstructure was checked by TEM on a JEM−200CX instrument. Room temperature compression tests were carried out on a WDW−200D machine with the maximum load of 200 kN at an engineering strain rate of 5×10^{-4} s^{-1}. Cross-sectional surfaces of the $Cu_{44}Zr_{48}Al_7Fe$ sample were examined in a S−3400N II scanning electron microscope (SEM).

3 Results and discussion

The X-ray diffraction pattern of the as-cast $Cu_{44}Zr_{48}Al_7Fe$ sample is presented in Fig. 1, which shows broad diffraction maxima characteristic of an amorphous structure. Compared with $Cu_{45}Zr_{48}Al_7$ BMG [18], the formation of a fully amorphous structure was also obtained by introduction of minor amounts of Fe.

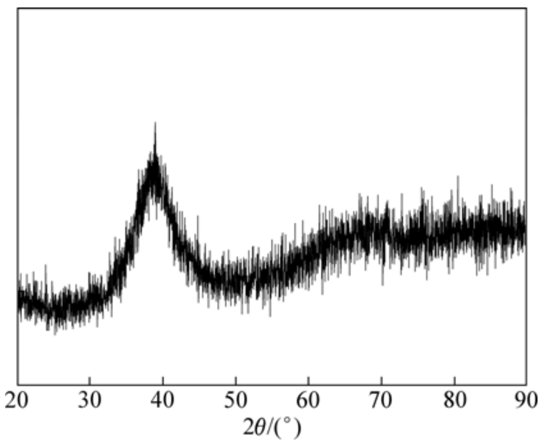

Fig. 1 XRD pattern of as-cast $Cu_{44}Zr_{48}Al_7Fe$ bulk metallic glass

Figure 2 displays the DSC trace obtained from the as-cast $Cu_{44}Zr_{48}Al_7Fe$ rod. During heating, the sample exhibits a distinct endothermic peak due to glass transition, followed by a super-cooled liquid region, and then a sharp exothermic peak as a result of crystallization. The glass transition temperature of the as-cast $Cu_{44}Zr_{48}Al_7Fe$ sample (defined as the onset temperature of the endothermic DSC event) is 717 K. The onset temperature of crystallization T_x of the as-cast $Cu_{44}Zr_{48}Al_7Fe$ sample is 790 K. Apparently, the addition of 1% Fe (mole fraction) increases the width of the super-cooled liquid region ($\Delta T=T_x-T_g$) from 61 to 73 K, indicating that the addition of Fe can enhance the glass forming ability of $Cu_{45}Zr_{48}Al_7$.

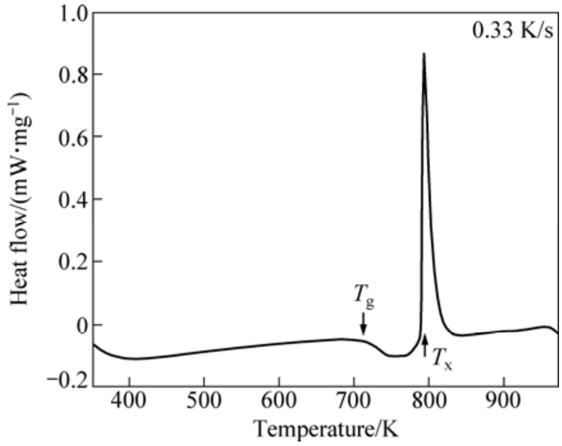

Fig. 2 DSC trace of as-cast $Cu_{44}Zr_{48}Al_7Fe$ bulk metallic glass

The room temperature engineering stress—strain curve of the as-cast $Cu_{44}Zr_{48}Al_7Fe$ rod with 6 mm in length and 3 mm in diameter is illustrated in Fig. 3. The elastic strain (ε_y), plastic strain (ε_p), ultimate compression strain (ε_f) and yielding compression stress (σ_y) are summarized in Table 1. Compared with $Cu_{45}Zr_{48}Al_7$ BMG [18], the ultimate yielding compression stress of $Cu_{44}Zr_{48}Al_7Fe$ BMG slightly decreases from 1892 to 1870 MPa. However, the plastic strain increases remarkably from 0 to about 1.5%. Also from Fig. 3, we can note that the $Cu_{44}Zr_{48}Al_7Fe$ BMG exhibits an obvious work hardening-like behavior. In previous work, this phenomenon has been presented, which is mostly attributed to the phase separation.

The fracture surface of specimen after deformation was investigated by SEM, as shown in Fig. 4. It can be

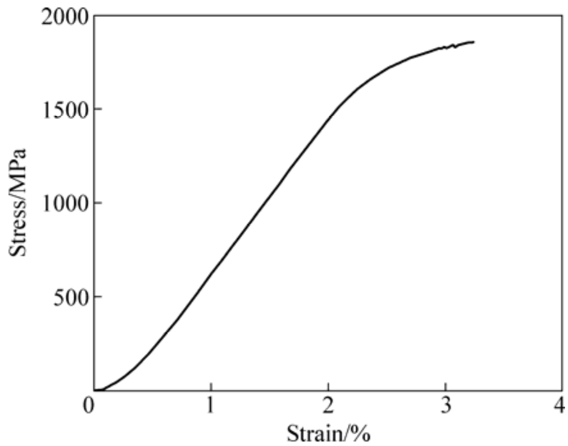

Fig. 3 Compressive stress — strain curve of as-cast $Cu_{44}Zr_{48}Al_7Fe$ bulk metallic glass at room temperature

Table 1 Mechanical properties of as-cast $Cu_{44}Zr_{48}Al_7Fe$ bulk metallic glass

Alloy	ε_y/%	ε_p/%	ε_f/%	σ_y/MPa
$Cu_{44}Zr_{48}Al_7Fe$	1.8	1.5	3.3	1870

seen that the fracture surface is dominated by typical vein-like patterns, which is indicative of the ductile fracture in BMGs. This is the common feature of BMGs, which is attributed to local softening of melting inside the shear band induced by the instantaneous release of high elastic energy. Therefore, the addition of Fe influences the fracture behavior of CuZrAl BMGs. The $Cu_{44}Zr_{48}Al_7Fe$ BMG will be more ductile than $Cu_{45}Zr_{48}Al_7$ BMG. In addition, the $Cu_{44}Zr_{48}Al_7Fe$ BMG exhibits a special fracture morphology with big vein-like patterns containing large amount of small-sized vien-like patterns. To understand the special ductile fracture behavior, TEM was carried out to clarify its microstructure. As shown in Fig. 5, the selected-area diffraction pattern expresses halo diffraction intensity, which is the typical characteristic of an amorphous phases, indicating that the as-cast $Cu_{44}Zr_{48}Al_7Fe$ alloy is fully amorphous. Moreover, the bright-field TEM image clearly manifests the presence of two different amorphous phases, with brighter and darker contrasts. This means that amorphous phase separation does occur in $Cu_{44}Zr_{48}Al_7Fe$ system. It is indicated that this phenomenon could be due to the positive heat of mixing of Cu−Fe (13 kJ/mol). The difference between these phases is Fe-rich phase or Cu-rich phase, what's more, Fe-rich phase is harder than Cu-rich phase. During the compression process, the preferentially activated soft shear band meets a block with a higher critical shear stress, and the soft shear band will be hindered. A new preferential shear band will be produced, which leads to plasticity enhancement during loading.

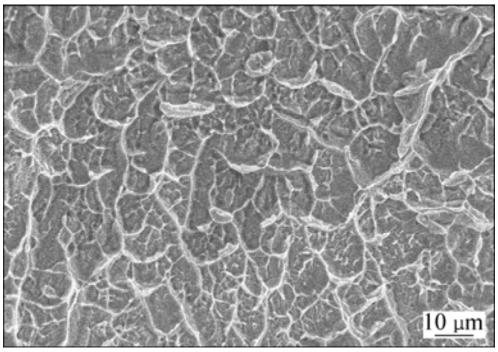

Fig. 4 SEM image for fracture surface of as-cast $Cu_{44}Zr_{48}Al_7Fe$ bulk metallic glass

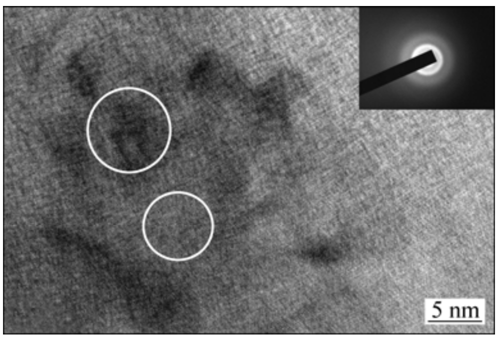

Fig. 5 TEM image with inset of selected-area diffraction pattern for as-cast $Cu_{44}Zr_{48}Al_7Fe$ bulk metallic glass

4 Conclusions

1) An as-cast $Cu_{44}Zr_{48}Al_7Fe$ bulk metallic glass is fully amorphous with phase separation between Cu-rich phase and Fe-rich phase. TEM shows that phase separation occurs in the $Cu_{44}Zr_{48}Al_7Fe$ bulk metallic glass. The addition of Fe increases the width of the super-cooled liquid region and improves the glass forming ability of $Cu_{45}Zr_{48}Al_7$ bulk metallic glass.

2) The phase separation is responsible for the enhancement of plasticity. The plastic strain of the $Cu_{44}Zr_{48}Al_7Fe$ bulk metallic glass is about 1.5%. Mechanism of plasticity suggests that phase separation in bulk metallic glass by minor-addition of Fe can obviously enhance its plasticity.

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微量添加 Fe 元素对 CuZrAl 块体金属玻璃的结构和力学性能的影响

许宏伟[1,2]，杜宇雷[1,2]，邓 昱[3]

1. 南京理工大学 材料科学与工程学院，材料评价与设计教育部工程研究中心，南京 210094；
2. 江苏省(丹阳)高性能合金材料研究院，丹阳 212300；
3. 南京大学 固态微结构国家重点实验室和现代分析中心，南京 210093

摘 要：使用水淬法制备含微量 Fe 元素的 CuZrAl 块体金属玻璃。使用 X 射线衍射(XRD)检测其结构；采用 DSC 研究 Fe 元素的添加对块体金属玻璃热稳定性的影响，微量添加 Fe 元素显著拓宽了过冷液相区。$Cu_{44}Zr_{48}Al_7Fe$ 块体金属玻璃的塑性应变约为 1.5%。使用透射电子显微镜(TEM)观察其微观结构，结果发现，添加 1%~2%Fe(摩尔分数)的 CuZrAl 合金中出现了相分离的富 CuZr 非晶相。

关键词：块体金属玻璃；微观结构；力学性能；相分离；Fe 添加

(Edited by LI Xiang-qun)