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Glass forming ability and mechanical properties of Nb-containing Cu−Zr−Al based bulk metallic glasses

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Abstract: Mechanical properties of $(Cu_{50}Zr_{43}Al_7)_{100-x}Nb_x$ (x=0,1,3,6,9) bulk metallic glasses rods with a diameter of 2.5 mm prepared by suction casting method were studied. The results of uniaxial compression tests at room temperture show that the best mechanical properties of 2.8% and 1.98 GPa for plastic strain and fracture strength, respectively, in the sample with x=3. Microstructure, fracture surface and shear bands of the samples were observed by SEM and XRD methods.

Key words: bulk metallic glass; microstructure; shear bands; mechanical properties

1 Introduction

High strength, large elastic limit, relatively low elastic modulus and high corrosion resistance in some bulk metallic glasses make them excellent candidates for structural materials, but their limited plastic strain and brittle fracture at room temperature restrict their application development [1−4]. Among different bulk metallic glasses, Cu-based and particularly Cu−Zr−Al alloys have received significant attention due to high glass forming ability, relatively high plasticity and low cost [5−7]. Recently, in order to improve the plasticity of BMGs, many attempts have been developed to formation of in situ BMG matrix composites by microalloying process, especially in Zr-, Ti- and Cu-based BMGs [6,8,9]. Propagation of primary shear bands could be impeded by the in situ crystallization. Multiplication of shear bands and their interaction with the second phase cause the improvement of the ductility of BMGs [10−12]. ZHANG and MEN [13] suggested that high plasticity of monolithic BMGs may be attributed to offset increase of free volume and the decrease of viscosity in shear band by the formation of nanocrystallites during the deformation. ECKERT et al [14] reported that increase of mechanical properties in $Cu_{47.5}Zr_{47.5}Al_5$ could be due to intrinsic structural properties of this alloy. LEE et al [15,16] reported that in monolithic Cu−Zr-containing BMGs upon compression, crystallization was induced at localized regions where there is chemical and structural inhomogeneity due to the decrease of activation energy for crystallization. Intermediate transitional metallic atoms such as Fe, Nb, Ti and Co have been used as additives in different bulk metallic glasses, but when their concentration increases to a level of more than 3%, the glass forming ability can be improved [2−4].

In this work, the effects of variation amount of Nb on mechanical and thermal properties in $(Cu_{50}Zr_{43}Al_7)_{100-x}Nb_x$ (x=0,1,3,6,9) bulk metallic glasses were studied.

2 Experimental

Master alloy ingots with composition of $(Cu_{50}Zr_{43}Al_7)_{100-x}Nb_x$ (x=0, 1, 3, 6, 9) were prepared by arc melting the mixtures of high purity Cu, Zr, Al and Nb under a purified argon atmosphere. Due to high melting points of Zr (1852 °C) and Nb (2468 °C), at first step, Zr and Nb were remelted, mixed, and then the other elements were added to this composition and remelted. For more chemical homogeneity of the alloys, each ingot was remelted three times in the arc melter and finally cylindrical rods with 2.5 mm in diameter and 3 centimeter in length were cast in water-cooled copper mold in a high purity argon atmosphere. The structure of rods was analyzed by Philips X-ray diffraction (XRD)

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with Co K_α radiation. The thermal stability of the as-cast rods was performed by NETZSCH differential scanning calorimeter (DSC) at a heating rate of 0.33 K/s. In order to investigate the mechanical properties under compression, the rods with diameter of 2.5 mm and length of 5 mm were tested on Instron testing machine with strain rate of 1×10^{-4} s^{-1} at room temperature. Fracture surface and shear band were examined by scanning electron microscopy (SEM).

3 Results and discussion

The XRD patterns of $(Cu_{50}Zr_{43}Al_7)_{100-x}Nb_x$ (x=0, 1, 3, 6 and 9) alloys are presented in Fig. 1. The samples with x=0 and x=1 show broad scattering peak characterized for glassy state of the alloys. However, for the sample with x=3, the XRD pattern shows a number of peaks corresponding to the precipitation of $Cu_{10}Zr_7$ crystalline phase superimposed on the main broad peak. For the samples with x=6 and x=9, XRD patterns exhibit only a broad peak without any detectable crystalline phase indicating the presence of an amorphous structure.

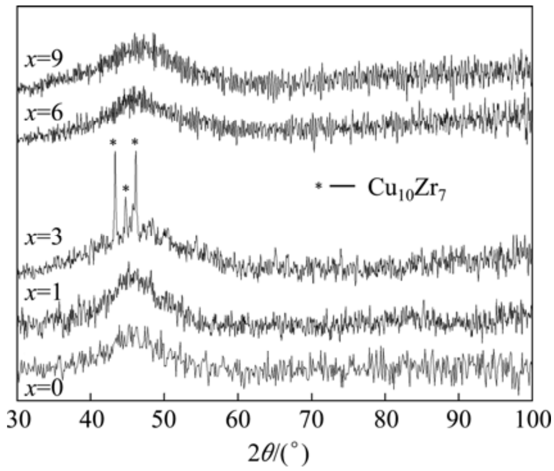

Fig. 1 XRD patterns for $(Cu_{50}Zr_{43}Al_7)_{100-x}Nb_x$($x$=0, 1, 3, 6, 9) bulk metallic glasses

Figure 2 shows the DSC curves of the as-cast specimens. The obtained data from DSC experiment are summarized in Table 1. As can be seen, the variation of ΔT with the Nb content of the samples confirms the XRD results. Although the solidification rate for all the specimens is constant, glass forming ability decreases (GFA) up to adding 3% Nb, and then improves with more than 3% Nb.

The reason of thermal stability improvement in single-stage crystallization during reheating is the increase of the difficulty in atomic rearrangements [3]. Initially, the decrease of thermal stability up to 3% Nb is

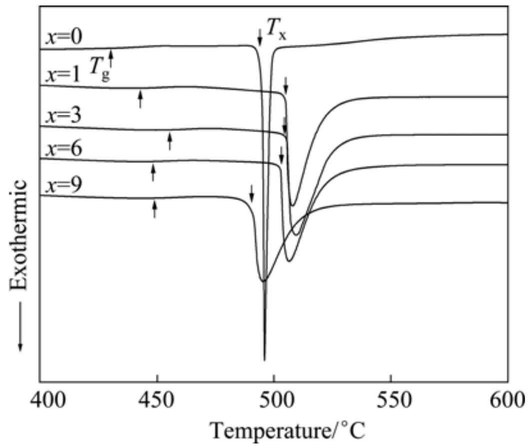

Fig. 2 DSC traces with heating rate of 20 K/min for $(Cu_{50}Zr_{43}Al_7)_{100-x}Nb_x$($x$=0,1,3,6,9) bulk metallic glasses

Table 1 Glass transition temperature (T_g), onset crystallization temperature (T_x) and extension of supercooled liquid region (ΔT) for $(Cu_{50}Zr_{43}Al_7)_{100-x}Nb_x$($x$=0, 1, 3, 6, 9) bulk metallic glasses

Sample	T_g/°C	T_x/°C	ΔT/°C
$Cu_{50}Zr_{43}Al_7$	430	494	64
$(Cu_{50}Zr_{43}Al_7)_{99}Nb_1$	443	505	62
$(Cu_{50}Zr_{43}Al_7)_{97}Nb_3$	455	505	50
$(Cu_{50}Zr_{43}Al_7)_{94}Nb_6$	448	503	55
$(Cu_{50}Zr_{43}Al_7)_{91}Nb_9$	449	490	41

due to high solubility of it in the melt and a decrease of packing density. So, based on the Hume−Rothery and Inoue's empirical rules, because of the marginal atomic size mismatch of Nb with Zr (approximately 4% different atomic radii) and the high tendency of solid-solution formation, adding 3% Nb with intermediate atomic size causes a decrease of GFA.

However, the addition of more than 6% Nb to the alloy system partially suppresses the nucleation and growth process, probably due to the falling of the alloy's composition into a deep eutectic region in phase diagram.

The engineering stress—strain curves of $(Cu_{50}Zr_{43}Al_7)_{100-x}Nb_x$ (x=0, 1, 3, 6, 9) under compression are shown in Fig. 3. The obtained data from the compression tests are summarized in Table 2.

As-cast $Cu_{50}Zr_{43}Al_7$ and $(Cu_{50}Zr_{43}Al_7)_{99}Nb_1$ specimens show the plasticity (ε_p) of less than 1% and fracture strength (σ_f) of 1589 MPa and 1656 MPa, respectively. Most of monolithic BMGs exhibit brittle compressive behavior at room temperature because the required energy for deformation plastic is more than that for crack. Since the glass transition temperature (T_g) indicates the degree of bounding force among constituent elements [10], it can be correlated with the highest strength obtained with x=3.

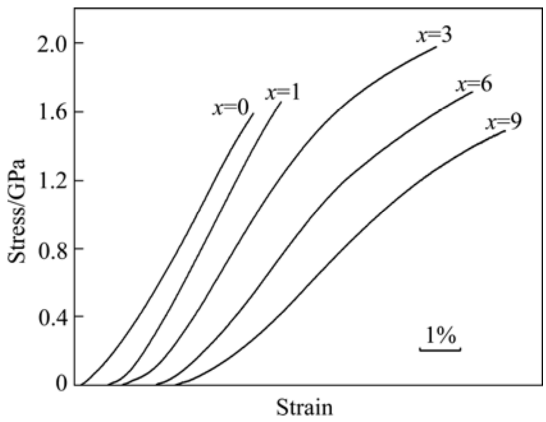

Fig. 3 Compression stress—strain curves of $(Cu_{50}Zr_{43}Al_7)_{100-x}$-$Nb_x$ (x=0, 1, 3, 6, 9) bulk metallic glasses

Table 2 Mechanical properties of $(Cu_{50}Zr_{43}Al_7)_{100-x}Nb_x$ (x=0, 1, 3, 6, 9) bulk metallic glasses

Sample	σ_f/MPa	ε_p/%
$Cu_{50}Zr_{43}Al_7$	1589	0.75
$(Cu_{50}Zr_{43}Al_7)_{99}Nb_1$	1656	0.94
$(Cu_{50}Zr_{43}Al_7)_{97}Nb_3$	1979	2.8
$(Cu_{50}Zr_{43}Al_7)_{94}Nb_6$	1717	2.8
$(Cu_{50}Zr_{43}Al_7)_{91}Nb_9$	1486	2.38

For all the samples, shear fractures happened at the angle closed to 45° are shown in Fig. 4. The vein-like pattern on the fracture surface of $Cu_{50}Zr_{43}Al_7$ alloy and the river-like pattern with few branches on the fracture surface of $(Cu_{50}Zr_{43}Al_7)_{99}Nb_1$ are seen in Figs. 4(a) and

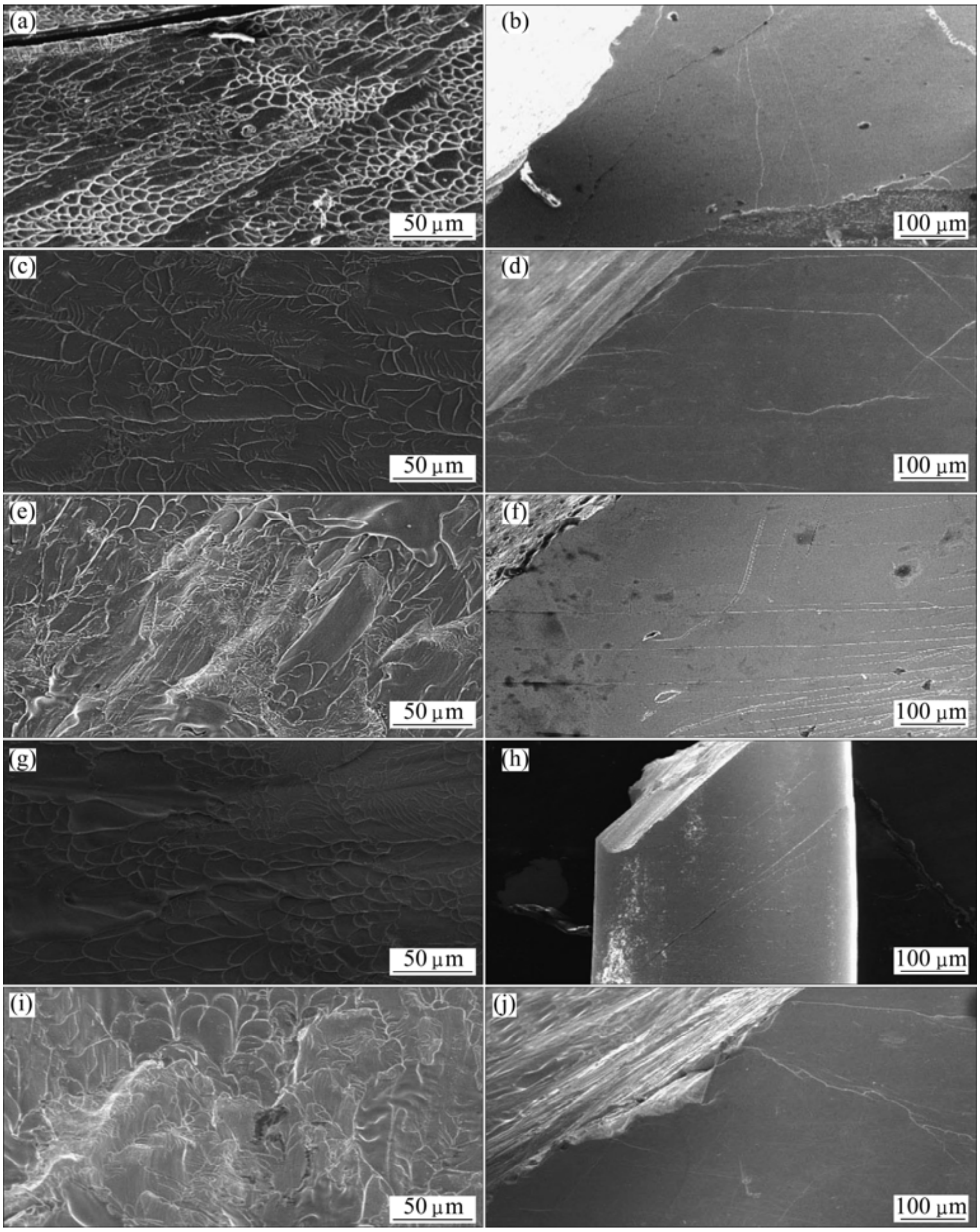

Fig. 4 SEM images of fracture surfaces and side surfaces of $(Cu_{50}Zr_{43}Al_7)_{100-x}Nb_x$ (x=0, 1, 3, 6, 9) bulk metallic glasses: (a, b) x=0; (c, d) x=1; (e, f): x=3; (g, h) x=6; (i, j) x=9

(c), respectively. On the fracture surface of these alloys a few shear bands parallel to the final fracture plane are visible (Figs. 4 (b) and (d)). Rapid propagation of single shear bands leads to catastrophic failure in monolithic BMGs.

Among these BMGs, $(Cu_{50}Zr_{43}Al_7)_{97}Nb_3$ alloy exhibits the most compressive strength and high plastic strain, which is attributed to precipitation of $Cu_{10}Zr_7$ crystalline phase in the amorphous matrix. In the BMG matrix in situ composites, crystalline phases act as nucleation sites of multiple shear bands due to different elastic properties of crystalline phase and BMG matrix and concentration stress at interface between these two phases [10]. Interaction and intersection of shear bands enhance the strength and strain of the sample. Multiplication of shear bands relaxes a part of strain localization in the main shear band and transfers plastic strain in a smaller quantity to other shear bands and global strain occurs in the sample [17,18].

Figure 4(f) shows the side surface of this alloy containing many shear bands accompanied with several cracks along vertical direction with respect to compression axis. The fracture surface of this alloy displays a mixture of vein-like pattern, river-like pattern and some molten liquid as indicated in Fig. 4(e).

It seems that during the compressive test due to excessive local temperature rise within the shear cracks, the alloy melts and the molten liquid with high pressure come out from the inside of shear cracks. Viscose molten liquid hinders propagation of shear cracks and leading to the formation of secondary and multiple shear bands [9].

$(Cu_{50}Zr_{43}Al_7)_{94}Nb_6$ and $(Cu_{50}Zr_{43}Al_7)_{91}Nb_9$ alloys are fully amorphous, but their mechanical behaviors are ductile. This change in mechanical behavior with the increase of Nb content can be attributed to either the improvement of the inherent properties of bulk metallic glasses by adding Nb [14] or deformation-induced nanocrystallization occurring in heterogeneous sites formed by the addition of Nb [15,16]. Fracture surfaces of these two alloys also include vein-like pattern, river-like pattern and molten liquid as shown in Figs. 4 (g) and (i).

4 Conclusions

1) The supercooled liquid region as well as the glass forming ability of the BMGs decreases with the increase of Nb content up to 3% then it interestingly increases with the further increase of Nb content.

2) The addition of 3% Nb results in the formation of $Cu_{10}Zr_7$ crystalline phase, leading to introducing an in-situ BMG composite.

3) $(Cu_{50}Zr_{43}Al_7)_{94}Nb_3$ BMG composite exhibits a combination of the maximum strength of 1979 MPa and total plastic strain of about 3%.

4) The plasticity is improved by the addition of Nb in a limited composition range, due to the shear band interaction with the crystalline phase, leading to their multiplication, branching, and inhibition of their rapid propagation.

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含 Nb 的 Cu−Zr−Al 基大块金属玻璃的玻璃形成能力和力学性能

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摘　要：研究了由真空吸铸法制备的直径为 2.5 mm 的$(Cu_{50}Zr_{43}Al_7)_{100-x}Nb_x$ (x=0, 1, 3, 6, 9)大块金属玻璃棒的力学性能。在温室条件下进行的单轴压缩试验结果表明，当 x=3 时样品具有最佳的力学性能(塑性应变和断裂强度分别为 2.8%和 1.98 GPa)。采用扫描电镜(SEM)和 X 射线衍射(XRD)方法观察样品的微观结构、断裂面和剪切带。

关键词：大块金属玻璃；微观结构；剪切带；力学性能

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