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A CuZr-based bulk metallic glass composite with excellent mechanical properties by optimizing microstructure

Song-Shan Jiang[a,b], Yong-Jiang Huang[a,*], Fu-Fa Wu[b,**], Peng Xue[a], Jian-Fei Sun[a]

[a] School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China
[b] School of Materials Science and Engineering, Liaoning University of Technology, Jinzhou 121001, China

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ABSTRACT

The dependence of microstructure and mechanical properties on alloy composition of a series of $Cu_{48}Zr_{48-x}Al_4Nb_x$ (x = 0, 0.3, 0.8, 1.2, 1.5, 2.0 at.%) bulk metallic glass composites (BMGCs) was studied in detail. It was found that the doping element Nb exerts a crucial role on the mechanical properties of the studied BMGCs. By adjusting Nb content, a BMGC possessing an excellent combination of high strength (~1.3 GPa) and significant tensile plasticity (~8%) was obtained. Such superior mechanical performance can be attributed to the formation of multiple shear bands and the deformation-induced martensitic transformation from a cubic primitive B2 phase to a monoclinic B19′ phase.

1. Introduction

Bulk metallic glasses (BMGs) have attracted considerable attention due to their unique properties, such as high strength, high elastic limit, and excellent wear resistance [1–5]. However, the plastic deformation of BMGs is highly localized within narrow shear bands of ~20 nm thick under quasi-static uniaxial loading at room temperature, which results in rapid propagation of shear bands and thus catastrophic failure [6, 7]. Limited plasticity severely hinders the industrial applications of BMGs as engineering materials [8–14]. To address this issue, extensive interests have focused on the exploration of ductile bulk metallic glass composites (BMGCs) due to their favorable effect on the improvement of ductility [15–21]. So far, BMGCs fabricated mainly by *ex-situ* and *in-situ* methods have been explored in various alloy systems [7, 22–30], in which most exhibit remarkable ductility under compression [22, 27, 28] and some even possess large tensile plasticity [29, 30]. However, the lack of work-hardening mechanism for these BMGCs often involves unstable deformation with the occurrence of work-softening once yielding. In order to overcome the shortcoming, the concept of transformation-induced plasticity (TRIP) has been proposed into the BMGCs [10, 14, 31]. According to the TRIP effect, B2 phase reinforced CuZr based and TiCuNi based BMGCs have been achieved, undergoing martensitic transformation during deformation, which possess enhanced toughness and obvious work-hardening properties [10, 16, 32, 33]. For CuZr-based BMGCs, tuning the morphology, volume fraction and distribution of second phase precipitating from the glassy matrix by introducing minor elements can effectively favor the formation of multiple shear bands, which significantly stabilizes their plastic deformation [34–37]. Meanwhile, the microstructure and mechanical properties can also be optimized by tailoring stacking fault energy through addition of minor elements [38]. B2 phase reinforced CuZr-based BMGCs possess excellent plasticity and high strength. A question arises here: can we further improve their mechanical properties? Due to a positive mixing enthalpy with Cu and Zr, Nb element plays an important role in promoting the precipitation of crystals and inhibiting their coarsening for CuZr-based BMGCs [28, 39, 40]. Meanwhile, minor Nb addition can improve tensile plasticity and work-hardening capability of B2 phase reinforced BMGCs by tailoring stacking fault energy [38]. Therefore, to accelerate the precipitation of single B2 phase, modify the microstructure and thus enhance the tensile properties of B2 phase reinforced CuZr-based BMGCs, Nb is selected as the doping element to replace Zr element in the CuZrAl alloy system. The effect of Nb addition on the microstructure and mechanical properties of $Cu_{48}Zr_{48}Al_4$ alloys was studied. The results indicated that a BMGC with a combination of high strength, significant tensile plasticity and strong work-hardening capability can be achieved by finely tuning the Nb content. Also, morphology and distribution of B2 phase play important roles on the mechanical properties of the studied BMGCs.

2. Experimental detail

Alloy ingots with nominal compositions of $Cu_{48}Zr_{48-x}Al_4Nb_x$

* Corresponding author.
** Corresponding author.
E-mail addresses: yjhuang@hit.edu.cn (Y.-J. Huang), ffwooxy@163.com (F.-F. Wu).

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($x = 0$, 0.3, 0.8, 1.2, 1.5, 2.0 at.%) were prepared by arc melting a mixture of constituent elements with purity higher than 99.9% in a Ti-gettered argon atmosphere. The ingots were re-melted at least four times in order to guarantee the compositional homogeneity, followed by drop casting the molten alloy into a copper mold. Cylinder rods of 3 mm in diameter and ~40 mm in length were then produced. The microstructure of the as-cast rods was characterized by X-ray diffraction (XRD) using a Rigaku D/max 2200 diffractometer with Cu Kα radiation, a Leica DM 4000M optical microscope (OM) and a JEM-2100 transmission electron microscopy (TEM). The crystalline volume fraction of the as-cast rods was quantitatively calculated by an Image-Pro Plus 6.0 software. The dog-bone shaped tensile samples with a cross section of $1 \times 1\ mm^2$ and a gauge length of 2 mm were electric discharging machined from the as-cast samples. The room temperature tensile tests were carried out by a CMT5305 testing machine at an initial strain rate of $6 \times 10^{-4}\ s^{-1}$. In order to ensure reproducibility, each test was repeated at least five times. The fracture features of tensile samples were examined by scanning electron microscopy (SEM) in a Helios Nanolab 600i instrument.

3. Results and discussion

3.1. Composition–microstructure relationship

Fig. 1 shows the XRD patterns obtained from the as-cast $Cu_{48}Zr_{48-x}Al_4Nb_x$ ($x = 0$, 0.3, 0.8, 1.2, 1.5, 2.0 at.%) rods with 3 mm in diameter. The XRD spectrum for the $Cu_{48}Zr_{48}Al_4$ alloy exhibits a sharp Bragg peak superimposed on a broad halo ($2\theta = 38°$), corresponding to a mixture of precipitated crystal and amorphous matrix. The crystalline phase is characterized as CuZr phase with a body-centered cubic (*bcc*) structure (*i.e.*, the B2 phase), consistent with the previous report [11]. For the 0.3% Nb sample, the intensity of crystalline peaks increases, indicating the increase in the volume fraction of B2 phase. With further increasing Nb content ($x = 0.8$–1.5), the intensity of the B2 phase decreases in comparison to that of the Nb-free alloy, showing the inhibition on the precipitation of the crystal. However, beside the peak at $2\theta = 38°$, there exists a sharp peak at the position of $2\theta = 56.7°$ for $Cu_{48}Zr_{46.5}Al_4Nb_{1.5}$ alloy, which may result from the preferential orientation of B2 phase. Contrarily, for the 2.0% Nb sample, the broad halo almost disappears and crystalline phases dominate the whole structure of the cast sample. Furthermore, there is another crystalline phase (Al_2Zr) precipitating from the glassy matrix.

Fig. 2 shows the OM images obtained from the cross sections of the as-cast $Cu_{48}Zr_{48-x}Al_4Nb_x$ ($0 \le x \le 2.0$) alloy samples. For the Nb-free sample (Fig. 2(a)), round B2 phases with sizes ranging 30–120 μm and homogeneous distribution are embedded in the glassy matrix. The 0.3% Nb alloy displays a significant increase of crystalline volume fraction. In addition, most grains coarsen and agglomerate each other to form patch-like framework (Fig. 2(b)). For 0.8% Nb-added sample, round B2 phases reappear and distribute homogeneously in the glassy matrix. With further increasing the Nb content, the amount of crystalline phases for $Cu_{48}Zr_{48-x}Al_4Nb_x$ ($x = 1.2$ and 1.5) alloys decreases (Fig. 2(d)–(e)), indicating an improvement of the glass forming ability (GFA) for these alloys. For the 2.0% Nb sample, crystalline phases connecting with each other come into prominence and only small area of glassy matrix exists at the edge of the sample. The above microstructural observations show that, at the same cooling rate (casting diameter), Nb content has a strong effect on the morphology, distribution and volume fraction of crystalline phases for the current BMGCs, and single round B2 CuZr phase can be achieved by fine adjusting the Nb content.

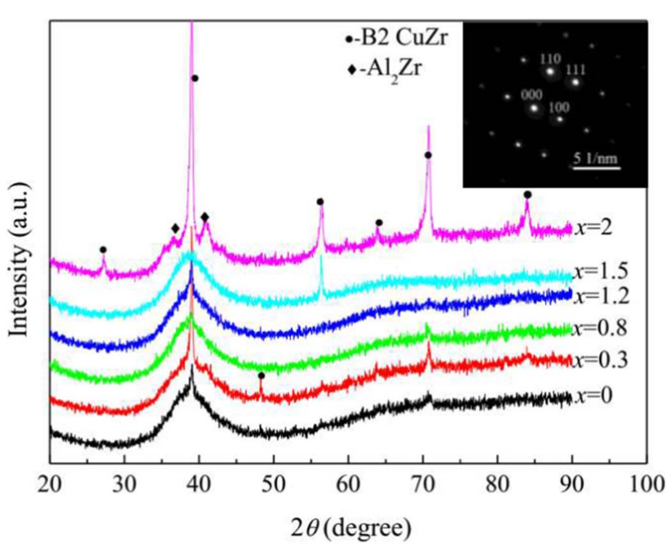

Fig. 1. XRD pattterns of as-cast $Cu_{48}Zr_{48-x}Al_4Nb_x$ ($0 \le x \le 2.0$) alloys with a diameter of 3 mm, with inset showing the selected area electron diffraction pattern of B2 CuZr phase.

3.2. Mechanical properties

In order to study the mechanical properties of the current BMGCs with different Nb content, tensile tests were conducted on the dog-bone-shaped samples machined from the as-cast rods with 3 mm diameter. As shown in Fig. 3, the tensile mechanical properties of the samples strongly depend on both their microstructures and the different crystalline volume fraction. The characteristic deformation parameters are summarized in Table 1. As can be seen, the alloys exhibit a yield strength ranging 416–1727 MPa and a plastic strain of 0.1%–16.7%. The $Cu_{48}Zr_{48}Al_4$ alloy exhibits ~2% plastic strain with a tensile strength of 1060 ± 15 MPa. With increasing the volume fraction of crystalline phases, the $Cu_{48}Zr_{47.7}Al_4Nb_{0.3}$ alloy shows relatively large plasticity but low yield strength. As the Nb content increases, the high yield strength of 1332 ± 18 MPa and a significant plasticity of 7.8 ± 0.2% can be obtained in the alloy containing 0.8% Nb with homogeneous distribution of B2 particles embedded in the glassy matrix. In contrast, the Nb-free sample, possessing similar morphology and distribution of crystalline phases, exhibits lower strength and plastic strain. It should be attributed to the decrease in the stacking fault energy of the B2 phase in the 0.8% Nb-added sample, which can promote phase transformation and hence improve the tensile plasticity and work-hardening capability [38]. Furthermore, for the 1.2% and 1.5% Nb samples, brittle fracture occurs without remarkable yielding. The lack of plasticity should result from heterogeneous distribution of crystalline phase [11]. While the $Cu_{48}Zr_{46}Al_4Nb_2$ alloy displays the nature of crystalline materials with relatively low strength due to the high crystalline volume fraction of ~80%. There is brittle Al_2Zr phase precipitating from the glassy matrix (Fig. 1), which results in the poor tensile plasticity of $Cu_{48}Zr_{46}Al_4Nb_2$ alloy. Hence, the morphology, distribution and volume fraction of B2 CuZr phase play important roles in tensile deformation of the current BMGCs. Furthermore, as mentioned in previous literatures [40, 41], the deformability of BMGCs is closely related to the normalized strain hardening rate K $\left(K = \frac{d\sigma}{\sigma_y d\varepsilon}\right)$. Here, K values of all alloys are calculated and also listed in Table 1. If K is ≥ 1, the stable plastic deformation of BMGCs can be achieved under tension [41]. As shown in Table 1, all the alloys except brittle failure samples ($x = 1.2$ and 1.5) exhibit strong strain hardening ability and stable deformability. Thus, a BMGC ($x = 0.8$) with single B2 CuZr phase exhibiting optimal tensile properties has been achieved by tuning Nb addition.

3.3. Mechanisms of enhanced deformability

To understand the intrinsic mechanisms of the current CuZr based BMGCs with enhanced mechanical properties, a comparative analysis