In situ Formed $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ Bulk Metallic Glass Composites

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An *in situ* formed $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ bulk metallic glass (BMG) composite was prepared successfully. The ductile Nb-rich crystalline phase with a dendritic structure disperses homogeneously in the BMG matrix. The mean size of the dendritic Nb phase is about 5~10 μm . For Cu-Zr-Ti-Nb glassy ribbons, the additions of Nb element cause the glass transition and crystallization onset temperature to shift to much higher values, and improve the thermal stability of the glassy phase. For the *in situ* formed $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ bulk metallic glass composites, its glass transition temperature and crystallization onset temperature is almost the same as those of the Nb-free $\text{Cu}_{60}\text{Zr}_{25}\text{Ti}_{15}$ BMG, implying that almost all the added Nb element precipitates from the melt upon cooling. The $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ BMG composite also presents a good combination of excellent mechanical properties. The compressive fracture strength and fracture elongation are 2130 MPa and 6.4%, respectively. The increase in elongation results from the homogeneous dispersion of the ductile and dendritic Nb-rich crystalline phase in the BMG matrix.

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1. Introduction

In the past decade, bulk metallic glasses (BMGs) have been comprehensively investigated regarding their composition, glass formation ability (GFA), viscous flow deformation behavior, thermodynamic behavior, mechanical properties as well as fracture features.¹⁻¹²⁾ Due to their excellent mechanical properties, for example, high hardness, high compressive or tensile strength, and high elastic modulus, BMGs have been considered as promising advanced engineering structure materials.^{2-5,9-13)} To further extend the application potentials of the advanced materials, recently, great attention has been paid to prepare BMG composites as an effective way to further improve fracture strength and ductility of BMG alloys.⁹⁻¹⁶⁾ At present, three basic fabrication methods have been employed to realize this aim. The first is to add particles or fiber into BMG matrix, for example, SiC, ZrC, W, and Ta particles, carbon fiber as well as carbon nanotube, and so on;^{5,8,10,14,15)} the second is to form *in situ* BMG composites by introducing some α -phase or β -phase formers or stabilizers, for example, introducing Ta or Mo elements into Zr-based BMG or Ti-based BMG and preparing *in situ* Zr-based or Ti-based BMG composites with the mixed structure of the dendritic β solid solution dispersing in the glassy matrix;^{9,11,12)} The third is to precipitate nanoscale phases from glassy phase by annealing glassy phases above their glass transition temperature.^{17,18)} As one of new BMG systems developed recently, Cu-based BMGs display not only high glass formation ability, but also excellent mechanical properties, for example, high fracture strength and elastic modulus.^{2,19,20)} It is an interesting research work if we can further improve mechanical properties of Cu-based BMG by preparing their composites, especially *in situ* composites. For Cu-Zr-Ti alloys, Nb has a positive heat of mixing with Cu, Zr and Ti element, and its melting point is much higher than the three elements. It means that Nb element dissolved in the liquid melt would separate together upon cooling, and subsequently precipitate from the liquid melt, and solidify in

the form of dendrites or particles. So, it is possible to form *in situ* Cu-based BMG containing the ductile Nb particles in an optimum processing condition. In this paper, we will present our research work firstly about some properties of *in situ* $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ bulk metallic glass composites and the effect of Nb element on microstructure and compressive mechanical properties of the Cu-based BMG alloys. It is useful to develop new bulk metallic glass composites in the future.

2. Experimental Procedure

Multi-component Cu-Zr-Ti and Cu-Zr-Ti-Nb alloy ingots were prepared by arc-melting the mixtures of pure Cu, Zr, Ti and Nb metals in a Ti-gettering argon atmosphere. The purity of metals was over 99.9 mass%. The Cu-based BMG alloys or BMG composites in a cylindrical rod form with a diameter of 1.5~2 mm were produced by copper mold casting. The Cu-based glassy ribbons were prepared by the melt-spinning technique. The glassy phase was identified by X-ray diffraction and thermal stability was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. The microstructure of Cu-based BMG composites was investigated by scanning electron microscopy (SEM). Mechanical properties were measured under a compressive load with an Instron testing machine. The gauge dimension of specimens was 2 mm in diameter and 4 mm in height and the strain rate was 10^{-4} s^{-1} .

3. Results and Discussion

Figure 1 shows the XRD patterns obtained from the melt-spun $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ glassy ribbon and $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ BMG rods with a diameter of 2 mm. For the melt-spun ribbon, only a single glassy phase was observed from the XRD. This means that the added Nb element has dissolved into the glassy matrix as one of components. The curve of the Nb-containing composite shows a superimposition of broad maximum from the glassy phase and several sharp peaks characteristic for a crystalline phase, suggesting

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Fig. 1 XRD patterns of melt-spun for $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ glassy ribbon (a) and as-cast $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ BMG composite rod with a diameter of 2 mm (b).

Fig. 2 SEM image of the polished cross section of a $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ BMG composite rod.

that a mixture of the glassy phase and some crystalline phases is formed. The position and intensity of the crystalline peaks matches exactly with those of Nb crystalline phase, as shown in Fig. 1. No other phases are detected within the sensitivity limit of XRD. The result indicates that Nb element dissolved in the liquid melt precipitates, and solidifies in the form of crystalline phase. Figure 2 displays SEM image of the polished cross section of the $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ BMG rod. Nb-rich solid solution phase with the dendritic structure disperses homogeneously in the BMG matrix. The dendritic structure has a mean size of about 5~10 μm .

Figure 3 shows DSC traces of the as-cast $\text{Cu}_{60}\text{Zr}_{25}\text{Ti}_{15}$ BMG and $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ BMG composites. The

Fig. 3 DSC traces of as-cast $\text{Cu}_{60}\text{Zr}_{25}\text{Ti}_{15}$ BMG (a) and $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ BMG composite rods (b) with a diameter of 2 mm.

DSC traces show that the composite sample exhibits an endothermic heat characteristic of the glass transition, followed by three main characteristic exothermic heat events, indicating the successive stepwise transformations from supercooled liquid state to crystalline phases. The crystallization behavior is different from that of the $\text{Cu}_{60}\text{Zr}_{25}\text{Ti}_{15}$ BMG. For the Nb-free BMG, three main exothermic heat peaks were also recognized. But, for the DSC of the BMG composite, the position of the second and third peaks shifts to right. This implies that the addition of Nb element affects the crystallization behavior of the glassy phase. However, the thermal stability of both the BMG and the composite is almost the same, namely, the addition of Nb element do not change obviously the thermal stability of the glassy phase. The glass transition temperature, T_g , and the onset temperature, T_x , of the first crystallization peaks of the composite are almost the same as those of the Nb-free BMG. For the as-cast $\text{Cu}_{60}\text{Zr}_{25}\text{Ti}_{15}$ BMG, the glass transition and crystallization onset temperatures are 728 and 774, respectively. The result indicates that most of the Nb element added into BMG precipitates from the melt during cooling, and solidifies as dendritic structure or particle morphology of Nb crystalline phase. This also means that the composition of the glassy matrix in the composites should be close to that of the Nb-free BMG. The composition analysis of EDX shows the similar results. However, the above result is different from that obtained from the glassy ribbons. Figure 4 shows DSC traces of the melt-spun $\text{Cu}_{60}\text{Zr}_{25}\text{Ti}_{15}$ and $(\text{Cu}_{60}\text{Zr}_{25}\text{Ti}_{15})_{93}\text{Nb}_7$ glassy ribbon. The glass transition temperature (T_g) and the onset temperature (T_x) of the crystallization peaks of the $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ glassy alloy shift to much higher temperatures. For the $\text{Cu}_{60}\text{Zr}_{25}\text{Ti}_{15}$ glassy ribbon, the T_g and T_x are 731 and 778, respectively. The supercooled liquid region defined by the difference between T_g and T_x , $\Delta T (= T_x - T_g)$, is 47 K. For the $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ glassy ribbon, T_g and T_x are 737 and 781, respectively. Its ΔT is 44 K. Comparing the Nb-free glassy ribbon with the $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ glassy ribbon, the addition of 7 at% Nb improves the thermal stability of the glassy phase, but reduces slightly its supercooled liquid region. This result is different from that obtained from the $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ BMG composites. The possible

Fig. 4 DSC traces of melt-spun $\text{Cu}_{60}\text{Zr}_{25}\text{Ti}_{15}$ (a) and $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ glassy ribbons (b).

reasons for this difference are due to the compositional variation of the glassy phase. This results from the process that some Nb atoms dissolve into the amorphous matrix during rapid solidification and increase the packing density of the glassy phase. The much more dense packing structure resulting from the different atom sizes improves the thermal stability of the supercooled liquid region, and leads to the increase of T_g and T_x . From the above description, the cooling rate is also one of important factors that affect the precipitation of Nb-rich phase. The ultra-rapid cooling rates obstacle the precipitation of the dendritic Nb phase, and the slow cooling rates are easy to induce the precipitation of intermetallics, and lead to the embrittlement of BMG composites. The optimization of the cooling rates and compositions is important to produce *in situ* Cu-Zr-Ti-Nb BMG composites. This is also confirmed by the microstructure of $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{85}\text{Nb}_{15}$ BMG composites with

Fig. 5 SEM back-scattered image of the polished cross section of a $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ BMG composite rod with a diameter of 3 mm.

Fig. 6 Compressive stress-strain curves of as-cast $\text{Cu}_{60}\text{Zr}_{25}\text{Ti}_{15}$ BMG (a) and $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ BMG composite rod (b).

a diameter of 3 mm, as shown in Fig. 5. The SEM image shows that several phases (gray phase and white phase) disperse randomly in the BMG matrix. From the compositional analysis of EDX, the gray dendrites are the Nb-rich phase and the white dendrites are some (Cu, Zr)-rich phases. The precipitation of (Cu, Zr)-rich intermetallic phases plays a significant effect on mechanical properties of the composites, induces the embrittlement and reduces significantly the plasticity of BMGs.^{11–13)}

Figure 6 shows the compressive stress-strain curves of the as-cast $\text{Cu}_{60}\text{Zr}_{25}\text{Ti}_{15}$ BMG and $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ BMG composites. For the as-cast $\text{Cu}_{60}\text{Zr}_{25}\text{Ti}_{15}$ BMG with a diameter of 2 mm, the compressive fracture strength and compressive fracture strain are 1975 MPa and 1.9%, respectively. $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ BMG composite displays a good combination of high fracture strength and large plastic strain. For the as-cast $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ BMG composites with a diameter of 1.5 mm, the compressive fracture strength and compressive fracture strain (ϵ_f) are 2130 MPa and 6.4%, respectively. Comparing the Nb-free BMG with the $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ BMG composite, the fracture strain improves obviously, and increases from 1.9% for the $\text{Cu}_{60}\text{Zr}_{25}\text{Ti}_{15}$ BMG to 6.4% for the $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ BMG composites. As we know, the plastic deformation of glassy alloys results from the shear deformation behavior of glassy phase under the applying load. The shear deformation behavior leads to the formation of highly localized shear bands and the significant stress intensity in these localized shear bands. Further deformation leads to much more stress intensity and induces the increase in free volume, leading to softening in the localized shear bands. These softening shear bands are large amounts of weak bands in glassy matrix, and induce easily the nucleation and propagation of cracks. Such inhomogeneous deformation yields that the final fracture occurs along the planes of these softened shear bands leading to catastrophic failure of the materials with little overall plastic deformation.^{11–13)} However, for the $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ BMG composite, the mixed structure of the ductile Nb phase with the dendritic morphology dispersing in the BMG matrix is formed. As Nb metal has an excellent ductility at room temperature, it is not surprised that the

dendritic Nb-rich phase with the means size of about $5\sim 10\mu\text{m}$ dispersing in the BMG matrix acts as an important role in the fracture behavior of the composites and has a significant effect on shear deformation of the glassy phase. This is confirmed by large amounts of the softening regions and shear bands observed from the fracture surface. Figure 7 shows SEM images of fracture surface and shear bands for the as-cast $\text{Cu}_{60}\text{Zr}_{25}\text{Ti}_{15}$ BMG and $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ composite. Under a uniaxial compressive loading, the fracture surface of the Nb-free BMG presents typical fracture characteristics of the glassy alloys. The well-developed vein-like patterns and shear bands were observed clearly, as shown in Figs. 7(a)(b). Shear bands are completely parallel to the shear stress direction, and also consistent with the direction of fracture surface (the shear plane). But, the fracture feature of the $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ BMG composite changes significantly, as shown in Figs. 7(c)(d). The fracture of the composites occurs in a shear mode. Vein patterns originating from shear deformation of the glassy phase are still observed.

The mixing structure of the dendrite and the softening glass matrix can be found throughout the fracture surface. The large incompatibility of yield strength and elastic modulus induces the formation of the mixing structure. This also implies that the dispersion of the ductile dendrite in the BMG matrix induces strong deformation. Further SEM observation shows that a large number of shear bands distributes randomly on the specimen surface, as shown in Fig. 7(d). For BMGs, shear bands are completely parallel to the shear stress direction (shown in Fig. 7(b)). But, for the present composite, large amounts of the secondary shear bands are branched. These secondary shear bands have no fixed propagating direction. The random distribution of the secondary shear bands suggests that the homogeneous dispersion of the Nb-rich dendrites in the BMG matrix has significant effect on shear deformation behavior. During the propagation of a main shear band, it is natural that the forefront of this main shear bands meets the μm -scale dendrite Nb-rich phase. As the Nb-rich phase has crystalline

Fig. 7 SEM images of fracture surface and shear bands for the compressive $\text{Cu}_{60}\text{Zr}_{25}\text{Ti}_{15}$ BMG (a–b) and $(\text{Cu}_{0.6}\text{Zr}_{0.25}\text{Ti}_{0.15})_{93}\text{Nb}_7$ BMG composite (c–d) subjected to compressive test.

structure and excellent ductility, shear bands that originate from the shear deformation of the glassy phase under the loading are almost impossible to cross through the μm -scale and ductile Nb crystalline phase, and have to change their propagating direction under continuing compressive loading, and induce the formation of the secondary shear bands. By the same mechanism, the secondary shear bands still branch and form the third shear bands, then fourth, fifth, and so like. The formation of large amounts of the branching shear bands causes the increase significantly in deformation, and further improves greatly the plasticity of the materials.

4. Summary

In situ formed $(\text{Cu}_{60}\text{Zr}_{25}\text{Ti}_{15})_{93}\text{Nb}_7$ bulk metallic glass (BMG) composites were prepared successfully. The ductile Nb-rich phase with a dendritic structure disperses homogeneously in the BMG matrix. The mean size of the Nb-rich dendrite is about $5\sim 10\ \mu\text{m}$. For the *in situ* formed $(\text{Cu}_{60}\text{Zr}_{25}\text{Ti}_{15})_{93}\text{Nb}_7$ bulk metallic glass composites, the compressive fracture strength and fracture strain (ε_f) are 2130 MPa and 6.4%, respectively. The dispersion of the ductile Nb dendrite obstacles the propagation of main shear bands, induces the formation of the secondary shear bands. This is the reason for the increase in elongation of the *in situ* Cu-based BMG composites with the mixed structure of the ductile Nb-rich dendrite dispersing in the BMG matrix.

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