

# Formation and mechanical properties of bulk Cu-Ti-Zr-Ni metallic glasses with high glass forming ability

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**Abstract:** Bulk amorphous  $\text{Cu}_{52.5}\text{Ti}_{30}\text{Zr}_{11.5}\text{Ni}_6$  and  $\text{Cu}_{53.1}\text{Ti}_{31.4}\text{Zr}_{9.5}\text{Ni}_6$  alloys with a high glass forming ability can be quenched into single amorphous rods with a diameter of 5 mm, and exhibit a high fracture strength of 2 212 MPa and 2 184 MPa under compressive condition, respectively. The stress—strain curves show nearly 2% elastic strain limit, yet display no appreciable macroscopic plastic deformation prior to the catastrophic fracture due to highly localized shear bands. The present work shows clearly evidence of molten droplets besides well-developed vein patterns typical of bulk metallic glasses on the fracture surface, suggesting that localized melting induced by adiabatic heating may occur during the final failure event.

**Key words:** bulk metallic glass; glass forming ability; mechanical property; adiabatic heating

## 1 Introduction

In recent years, Cu-based bulk metallic glasses (BMGs) have drawn increasing attention, due to their ultrahigh strength, comparatively larger plastic elongation and good glass forming ability(GFA), especially the lower material cost compared with other BMGs based on, for example, Zr and Ti. Several research groups have developed different Cu-based BMG systems, including Cu-(Zr, Hf)-Ti[1], Cu-(Zr, Hf)-Al[2],  $(\text{Cu}_{50}\text{Zr}_{50})_{100-x}\text{Al}_x$ [3] and Cu-Ti-Zr-Ni[4], etc. Appropriate minor alloying additions, such as Be[5], Y[6], Sn[7] or Si[8], may effectively increase the glass forming ability(GFA) and enhance the thermal stability. Among them, bulk glassy alloy  $\text{Cu}_{47}\text{Ti}_{34}\text{Zr}_{11}\text{Ni}_8$  has been successfully fabricated by injection copper mold casting with the maximum sample thickness of 4 mm[4].  $\text{Cu}_{47}\text{Ti}_{34}\text{Zr}_{11}\text{Ni}_8$  amorphous strips with 2 mm in thickness can be successively rolled at room temperature down to 0.15 mm in thickness without cracking. This demonstrates the ductile behavior of the amorphous materials when the deformation occurs under a confined geometry. Moreover, substitution of only 2%Ni (mole fraction, the same below) with Sn in  $\text{Cu}_{47}\text{Ti}_{33}\text{Zr}_{11}\text{Ni}_8\text{Si}_1$

alloy increases its maximum diameter for glass formation from 4 mm to 6 mm[9]. Thus, quaternary Cu-Ti-Zr-Ni system is believed to be an excellent glass former when the compositions are further optimized, and a promising base composition for creating other Cu-based BMGs. In this paper, we investigated the effect of the compositional optimization on the GFA, thermal and mechanical properties of Cu-Ti-Zr-Ni system.

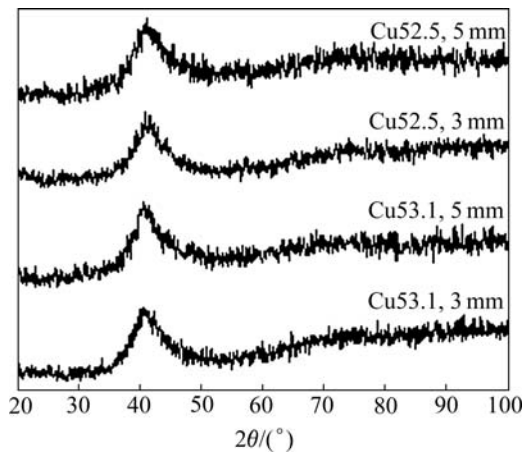
## 2 Experimental

The alloy ingots were prepared by arc melting the mixtures of pure Cu, Ti, Zr, Ni with a purity of more than 99.9% in argon atmosphere. The ingots were re-melted three times to ensure chemical homogeneity. Bulk cylindrical samples with diameters of 3 and 5 mm and a length of 40 mm were prepared by re-melting the prealloyed ingots on the top of a copper mold, and then dropping the molten liquid into the copper mold by their own gravity. The amorphism of the as-cast sample was identified by X-ray diffractometry (XRD) with Cu  $K_\alpha$  radiation. The thermal stability associated with glass transition was evaluated by differential scanning calorimetry (Perkin-Elmer, DSC7) at a heating rate of 0.67 K/s. Solidus and liquidus temperature were deter-

mined by using differential thermal analysis (Perkin-Elmer, DTA7) at a heating rate of 0.33 K/s. Mechanical properties under compressive condition were measured with an Instron-type testing machine. The gauge dimension was 3 mm in diameter and 6 mm in length, and the initial strain rate was  $5.0 \times 10^{-4} \text{ s}^{-1}$ . Fracture surface was examined by scanning electron microscopy (SEM).

### 3 Results and discussion

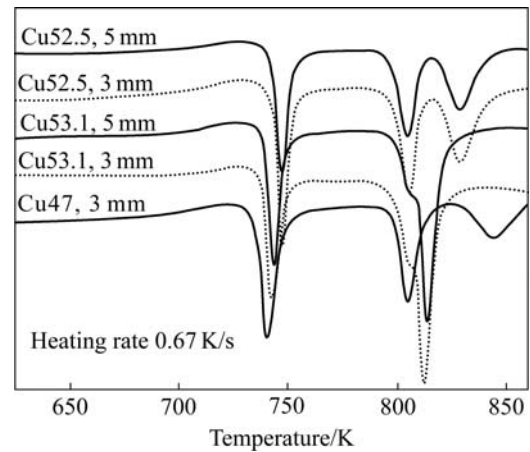
Previous experimental results show that there exists a wide glass forming range in Cu-Ti-Zr-Ni system, in which various compositions can be quenched into single amorphous structure with a diameter of 3 mm[10]. In particular,  $\text{Cu}_{52.5}\text{Ti}_{30}\text{Zr}_{11.5}\text{Ni}_6$  and  $\text{Cu}_{53.1}\text{Ti}_{31.4}\text{Zr}_{9.5}\text{Ni}_6$  alloys show superior GFA compared with  $\text{Cu}_{47}\text{Ti}_{34}\text{Zr}_{11}\text{Ni}_8$ , and can be cast into fully glassy rods up to 5 mm (hereafter referred to as alloys Cu52.5, Cu53.1 and Cu47, respectively). Fig.1 shows the X-ray diffraction patterns of Cu52.5 and Cu53.1 alloys with diameters of 3 mm and 5 mm. Each sample exhibits a broad, symmetric halo around  $41^\circ$ , which is a typical single amorphous phase.



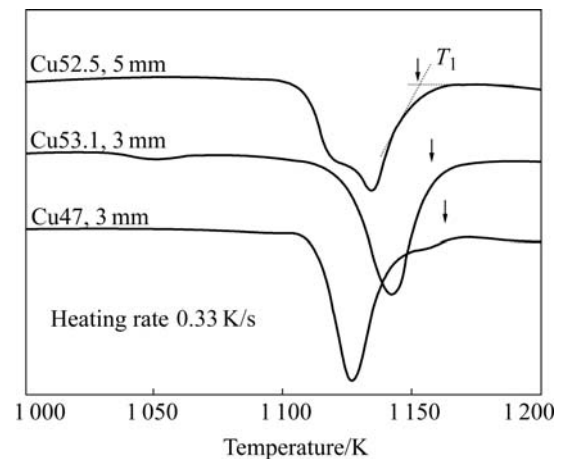
**Fig.1** XRD patterns of bulk Cu52.5 and Cu53.1 amorphous alloys with diameters of 3 mm and 5 mm

Fig.2 shows the DSC curves of the as-cast glassy alloys. The DSC traces exhibit distinct glass transition followed by a supercooled liquid region, and then exothermic reaction characteristic of the crystallization. We have confirmed that  $T_g$ ,  $T_{x1}$  and heat of crystallization  $\Delta H$  for the 5 mm rods of Cu52.5 and Cu53.1 are nearly the same as those for the corresponding 3 mm rod. Since reduced glass transition temperature  $T_{rg}$  based on  $T_g/T_1$  is a critical parameter in evaluating the GFA of an alloy,  $T_{rg}$  is used to gauge the GFA of Cu-Ti-Zr-Ni system. Fig.3 shows the DTA curves of the glassy alloys with a diameter of 3 mm, in which the liquidus temperature  $T_1$

is defined by the offset temperature of an entire melting process. It is clearly seen that  $T_1$  shows a minimum value of 1 150 K for  $\text{Cu}_{52.5}\text{Ti}_{30}\text{Zr}_{11.5}\text{Ni}_6$ . Table 1 summarizes the characteristic thermal data of the Cu52.5, Cu53.1 and Cu47. As can be seen from Table 1 that the GFA has a close relation with  $T_{rg}$ . Generally,  $T_g$  does not vary with composition as rapidly as  $T_1$  for most of BMGs[11]. A higher  $T_{rg}$ , as in the case for Cu52.5 and Cu53.1, implies that the alloy is close to the nearby deep eutectics, demonstrating the better GFA of the alloys. The enhanced GFA may essentially derive from the content optimization of the constituent elements. A small increase of Cu content decreases the liquidus temperature, which is consistent with the thermodynamic assessment



**Fig.2** DSC traces of bulk Cu52.5, Cu53.1 and Cu47 amorphous alloys



**Fig.3** DTA traces of bulk Cu52.5, Cu53.1 and Cu47 amorphous alloys with diameter of 3 mm

**Table 1** Characteristic thermal data of as-cast amorphous alloys with diameter of 3 mm

Alloy	$T_g/\text{K}$	$T_x/\text{K}$	$\Delta T_x/\text{K}$	$T_1/\text{K}$	$T_g/T_1$
Cu52.5	694	746	52	1 150	0.603
Cu53.1	693	738	45	1 159	0.598
Cu47	683	734	51	1 168	0.585

of the Cu-Ti-Zr system[12], apparently leading to the higher  $T_{rg}$  and thus better GFA. Previous research reveals that the addition of 5% or more Ni to Cu-Zr-Ti system induces primary precipitation of the equilibrium  $(\text{Cu,Ni})_{10}(\text{Zr,Ti})_7$ [13]. The content of Ni is also reduced in the present study from 8% to 6% aiming to suppress the formation of  $(\text{Cu,Ni})_{10}(\text{Zr,Ti})_7$  intermetallics.

Fig.4 shows the compressive stress—strain curves of the as-cast bulk amorphous Cu52.5 and Cu53.1 rods with diameter of 3 mm. The glassy alloys exhibit high fracture strength ( $\sigma_{c,f}$ ) of 2 212 MPa and 2 184 MPa, elastic modulus ( $E$ ) of 112 GPa and 106 GPa, and fracture elongation ( $\varepsilon_{c,f}$ ) including elastic elongation of 2.1% and 2.2% for the Cu52.5 and Cu53.1, respectively. Compared with Cu53.1 alloy, the Cu52.5 alloy contains higher Zr content that has high attractive bonding interaction with Cu element. The negative heat of mixing between Cu and Zr is  $-23$  kJ/mol, much larger than that of Cu and Ti ( $-9$  kJ/mol)[1]. The Cu52.5 alloy may have favorable bonding force among the constituent elements. Thus, the Cu52.5 alloy shows enhanced compressive fracture strength and relatively higher elastic modulus. The fracture occurs along nearly the maximum shear plane that is declined by about  $42^\circ$  to the direction of applied load. It can be seen that the bulk amorphous Cu52.5 alloy exhibits appreciable yield behavior and plastic elongation, yet Cu53.1 alloy shows an instant and catastrophic failure, when reaching the maximum loads. However, the fracture surfaces both consist of well developed vein pattern typical of Zr-based bulk glassy alloys with good ductility, as shown in Fig.5(b) for the Cu52.5 alloy. The vein pattern morphology is commonly attributed to local change in viscosity near planes of maximum shear stress. When the crack propagates along the fracture plane, an adiabatic heating occurs in highly localized shear bands. Local adiabatic heating in the

shear bands is thought to significantly reduce the glass viscosity by several orders of magnitude. The temperature increase is somewhat proofed by the flash of light when the compressed specimen crashes. Present work shows clearly evidence of resolidified droplets on the fracture surface, as shown in Fig.5(c), strongly suggesting that localized melting have occurred during the final rupture.

Presuming that the stored elastic strain energy completely converts to the adiabatic heating at the moment of fracture, we can estimate the width of the total shear-band region that experiences the localized melting. The total elastic strain energy ( $E_e$ ) stored in the gauge section prior to fracture is estimated from the following equation[14]:

$$E_e = (1/2)\sigma_c \varepsilon_c A l_g \quad (1)$$

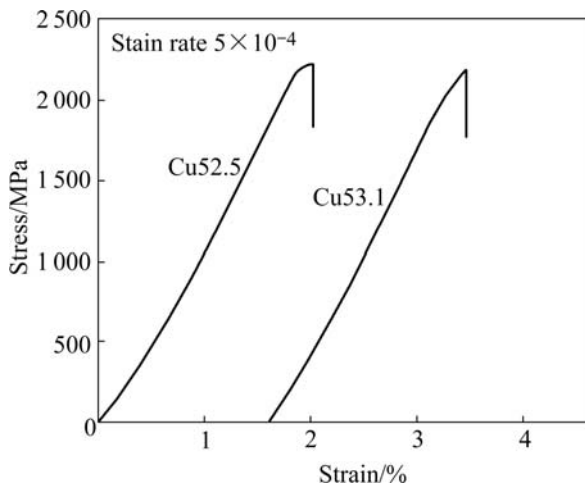
where  $\sigma_c$  is the fracture strength,  $\varepsilon_c$  is the elastic strain fractured,  $A$  is the cross-section area of the gauge, and  $l_g$  is the gauge length.

The energy  $E_r$  required for the shear-band region to be adiabatically heated to melting temperature, is referred from the following equation[14]:

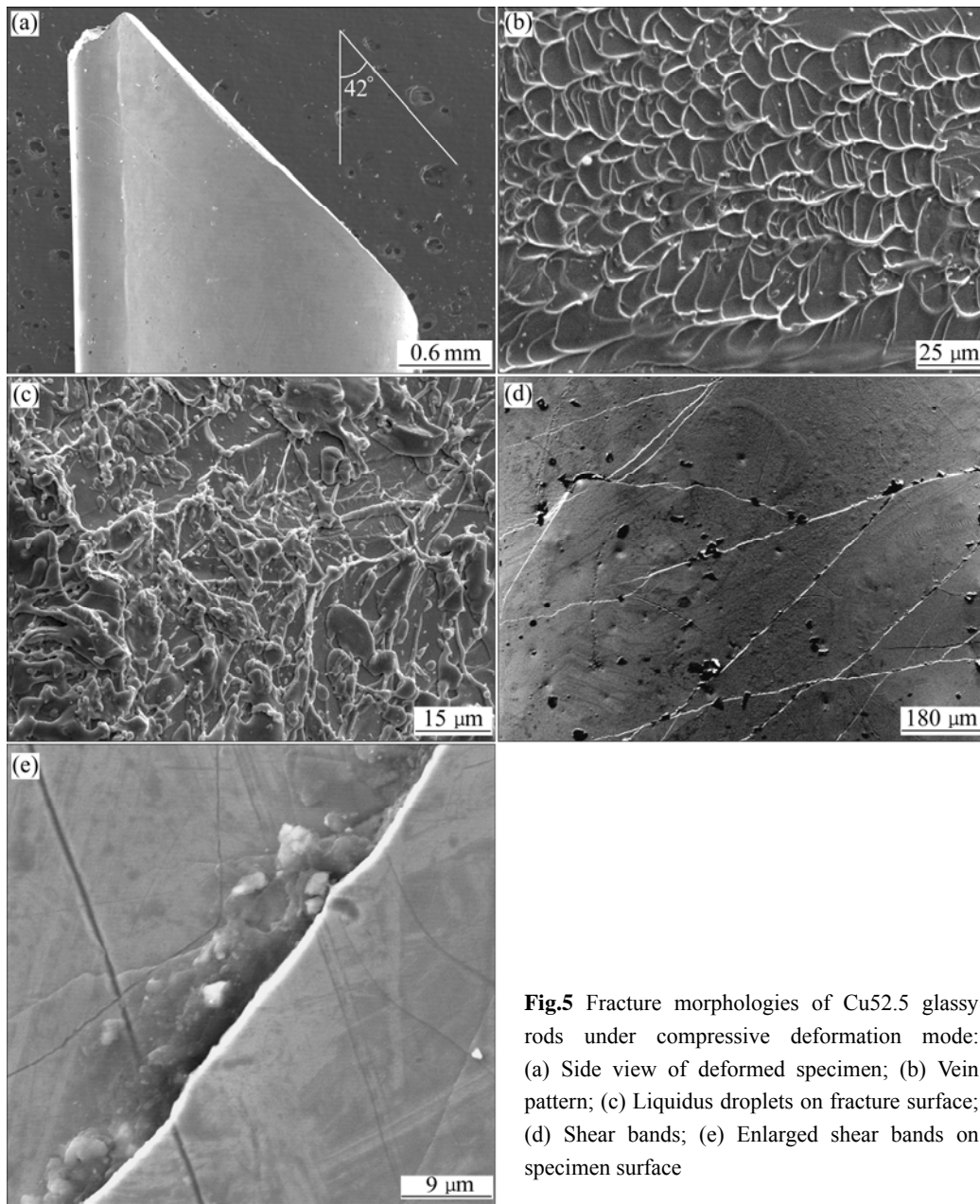
$$E_r = (1/M)c_p \Delta T (A/\sin\theta) l_s \quad (2)$$

where  $M$  is the molar volume,  $c_p$  is the specific heat capacity and  $l_s$  is the width of total shear-band region.

Since all plastic deformation is highly localized in the shear bands, it is reasonable to assume that the elastic energy is entirely dissipated in the shear band region. Since  $c_p$  for Cu52.5 (or Cu53.1) BMG is not known,  $c_p = 45$  J/(mol·K) for Cu47 BMG[15] is used for calculation in Eqn.(2). By taking  $\sigma_c = 2\,212$  MPa,  $\varepsilon_c = 0.021$ ,  $\Delta T = 850$  K,  $\theta = 42^\circ$ , and the molar volume of  $8.47 \times 10^{-6}$  m<sup>3</sup>/mol, the  $l_s$  is estimated to be  $20.6 \mu\text{m}$  from the Eqns.(1) and (2). The average width of shear bands is roughly  $5\text{--}8 \mu\text{m}$  (Fig.5(e)), then we may estimate that a total of  $3\text{--}4$  shear bands are heated adiabatically to  $\Delta T = 850$  K through the conversion of the elastic strain energy. Known that not the whole fracture surface is heated to melting temperature, it's consistent with the feature that several primary shear bands with ejected molten droplets are observed on the specimen surface adjacent to the fracture section, as shown in Fig.5(d) and Fig.5(e). The small value of  $l_s$  also reveals that flow is extremely inhomogeneous in the bulk Cu52.5 and Cu53.1 metallic glasses. This is also illustrated by the stress—strain curves as shown in Fig.4 that displays no macroscopic plastic deformation prior to catastrophic fracture. Recent work reveals that small amount addition of Al to some Cu-based amorphous alloys can significantly improve the GFA[3] and room temperature deformability[16]. An investigation on the effects of minor alloying addition on



**Fig.4** Compressive stress—strain curves for bulk Cu52.5 and Cu53.1 glassy rods



**Fig.5** Fracture morphologies of Cu52.5 glassy rods under compressive deformation mode: (a) Side view of deformed specimen; (b) Vein pattern; (c) Liquidus droplets on fracture surface; (d) Shear bands; (e) Enlarged shear bands on specimen surface

the GFA and mechanical properties of Cu52.5 and Cu53.1 alloys is currently in progress.

#### 4 Conclusions

1) New  $\text{Cu}_{52.5}\text{Ti}_{30}\text{Zr}_{11.5}\text{Ni}_6$  and  $\text{Cu}_{53.1}\text{Ti}_{31.4}\text{Zr}_{9.5}\text{Ni}_6$  alloys can be quenched into fully glassy rods up to 5 mm in diameter by the copper mold casting method. The glass forming ability has a close correlation with the  $T_{\text{rg}}$  in Cu-Ti-Zr-Ni system.

2) Under compressive condition, the glassy alloys exhibit high fracture strength of 2 212 MPa and 2 184 MPa, and fracture elongation including elastic elongation of 2.1% and 2.2% for the Cu52.5 and Cu53.1, respectively. Macroscopic plastic deformation is hardly

appreciable prior to the catastrophic fracture, though high elastic strain limit (nearly 2%) is reached during the fracture process. This is attributed to highly localized deformation, accompanied by the adiabatic heating that may induce a temperature surge even beyond the melting temperature.

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