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Effect of Ag addition on the thermal stability and glass-forming ability of $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ bulk metallic glass

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The thermal stability and glass forming ability (GFA) of $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Ag_x$ (x = 0–10) alloys were studied by X-ray diffraction (XRD), differential scanning calorimetry (DSC) and ultrasonic techniques. We found that the addition of 1 at.% Ag can considerably enhance the GFA as indicated by an increase in the critical glass dimension from 15 mm in the $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ alloy to 20 mm in the $Zr_{34}Ti_{30}Cu_{7.5}Be_{27.5}Ag_1$ alloy. However, with the addition of more Ag the supercooled liquid region (ΔT_x) and γ parameter (defined as $T_x/(T_g+T_l)$) drastically decreased from 155 K and 0.436 to 76 K and 0.363, respectively, resulting in a decrease in the GFA. Additionally, the elastic constant (the ratio of shear modulus to bulk modulus or Poisson's ratio) was also used as a gauge to evaluate the GFA in $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Ag_x$ alloys.

bulk metallic glasses, glass forming ability, thermal stability, elastic properties

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Over the past two decades, bulk metallic glasses (BMGs) have attracted an increasing amount of attention because of their superb properties and potential as new structural materials [1–3]. A considerable number of studies related to the structural relaxation [4–8], fluidity and molding ability [9], corrosion behavior [10,11] and mechanical properties [12–15] of BMGs have been carried out, which contributes to the application of BMGs. However, the potential applications of BMGs are hindered by their limited glass forming ability (GFA). As a result, a great deal of efforts has been put into the development of BMGs and numerous multi-component alloys [16,17] capable of solidifying into bulk glass at relatively low cooling rates have been found in either noble metal Pd-based alloys or Zr-based alloys [18,19].

Minor alloying addition or microalloying technology has proven to be an effective approach in promoting glass formation, enhancing thermal stability and improving the plasticity of BMGs [20–22]. It has been found that microalloying with proper alloying elements can dramatically improve the GFA of various BMGs [23–25]. Previous studies showed that the GFA of Cu-, Mg- and ZrCu-based bulk metallic glasses were significantly enhanced by adding Ag [26–29]. In this work, Ag was also chosen as the doping element in the $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ system, which had a critical diameter of about 15 mm and a wide supercooled liquid region of 165.1 K [30]. To investigate the elastic properties of the resultant ZrTi-based BMGs their acoustic velocities were measured at room temperature by a pulse echo overlap method.

$Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Ag_x$ (x = 0, 1 at.%, 2 at.%, 3 at.%, 5 at.%, 7 at.%, 10 at.%) ingots were prepared by arc melting high purity (⩾99.9 wt.%) constituents under a titanium gettered argon atmosphere. Each ingot was remelted at least four times to ensure chemical homogeneity. Cylindrical alloy rods with diameters of 3, 4, 15 and 20 mm were prepared by injection casting the remelted ingots into a copper mould under an argon atmosphere. The samples were then

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cut into small pieces with a low speed diamond saw and the transverse cross-section of the specimens was examined by X-ray diffraction (XRD) with Cu Kα radiation to examine the structure of the samples. The thermal properties associated with the glass transition, crystallization and melting behavior of the alloys were measured using a Netzsch STA 449C differential scanning calorimeter (DSC) under continuous argon flow at a heating rate of 20 K/min. The acoustic velocities were measured at room temperature by a pulse echo overlap method using a RITEC RAM-5000 ultrasonic system with a measuring sensitivity of 0.5 ns and a carry frequency of 10 MHz at room temperature. The samples used for ultrasonic measurements were 4 mm in diameter and 10 mm in length. The density was measured by the Archimedean principle and the accuracy was within 0.5%. The bulk modulus B, Young's modulus E, shear modulus G and Poisson's ratio v of the BMGs were derived from the acoustic velocities and density [31].

Figure 1 shows XRD patterns of the as-cast $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Ag_x$ ($x = 0$, 1 at.%, 2 at.%, 3 at.%, 5 at.%, 7 at.%, 10 at.%) alloys with diameters of 15 and 20 mm. As shown in Figure 1(a), the patterns of the samples that contain 0–3 at.% Ag only contain a broad diffraction hump without any detectable crystalline peaks indicating their amorphous structure. However, for the alloy with 5 at.%, 7at.% and 10 at.% Ag sharp Bragg peaks superimposed over the amorphous maxima were observed implying that the alloys were partially crystallized. The diffraction peaks become more pronounced as Ag increases from 5 at.% to 10 at.%. From Figure 1(b), the best GFA was achieved for $x = 1$, which has a critical diameter of 20 mm. The enhanced GFA can probably be attributed to a denser local atomic packing and smaller differences in the Gibbs free energy between the amorphous and crystalline phases [29]. Therefore, the GFA of the $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Ag_x$ (x=0–10) are $x = 1 > x = 0 > x = 2 > x = 3 > x = 5 > x = 7 > x = 10$.

Figure 2 shows DSC curves for the as-cast $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Ag_x$ ($x = 0$–10) glassy alloys at a heating rate of 20 K/min. These glassy alloys have a distinct glass transition followed by a supercooled liquid region and then an exothermic reaction because of crystallization. The specimens for the DSC measurement were cut from the ϕ3 mm glassy rods. The glass transition temperature (T_g), onset crystallization temperature (T_x), onset melting temperature (T_m), liquidus temperature (T_l) and other thermodynamic parameters of the $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Ag_x$ (x = 0–10) BMGs are listed in Table 1. From these DSC curves and Table 1, the supercooled liquid region (ΔT_x) increases slightly from 153 to 155 K with 1 at.% addition and then steadily decreases to 76 K with an increase in Ag content from 1 at.% to 10 at.%. A large ΔT_x value may indicate that the supercooled liquid can remain stable over a wide temperature range without crystallization and that it has high resistance to the nucleation and growth of crystalline phases. In this study, ΔT_x, the reduced glass transition temperature T_{rg} and the γ parameter were selected as the thermal criteria to evaluate the GFA in the $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Ag_x$ (x=0–10) alloys. The composition dependence of γ, ΔT_x and T_{rg} (shown in the inset) in the $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Ag_x$ BMGs is shown in Figure 3. Combined with the XRD results, we found that ΔT_x and γ proved to be more effective than T_{rg} in evaluating the GFA of the $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Ag_x$ glassy alloys with a variation in the Ag content x from 0 to 10.

Recent work has emphasized the glass transition dependence of elastic properties such as the shear modulus G and the Poisson ratio v, and the elastic criteria is developed by using G/B or the Poisson ratio to judge the GFA [32,33]. The ratio of shear modulus G to bulk modulus B or Poisson's ratio was reported to correlate with the critical cooling rate (R_c) on the basis of experimental observations where glass with high G/B values (or a low Poisson's ratio) roughly correspond to a high GFA for the system [34]. Generally, a small v means that atoms or molecules can hardly rearrange themselves as a result of shear strains without a drastic disturbance in bonding configurations and a large v indicates an easier atomic rearrangement. Therefore, glass-forming systems with relatively low v may exhibit a high GFA.

Longitudinal and transverse velocities were determined

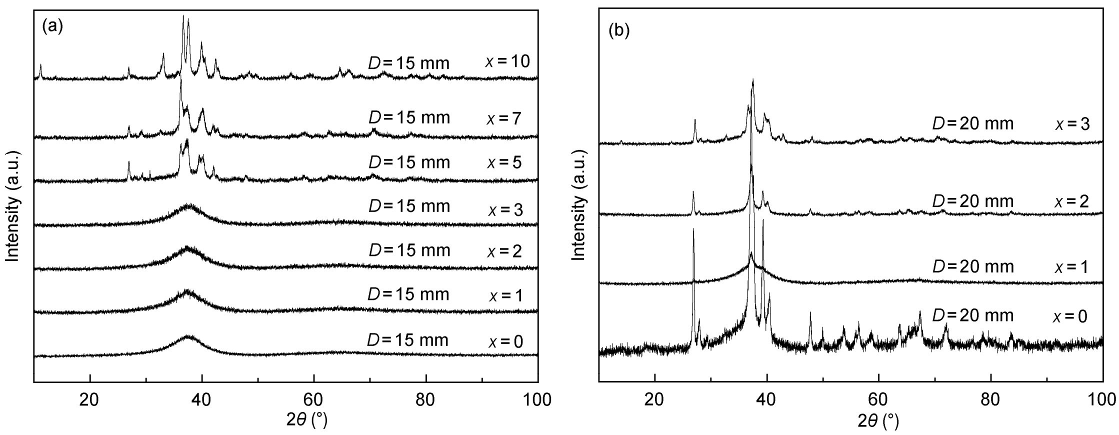

Figure 1 XRD patterns of the as-cast $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Ag_x$ alloys with different diameters.

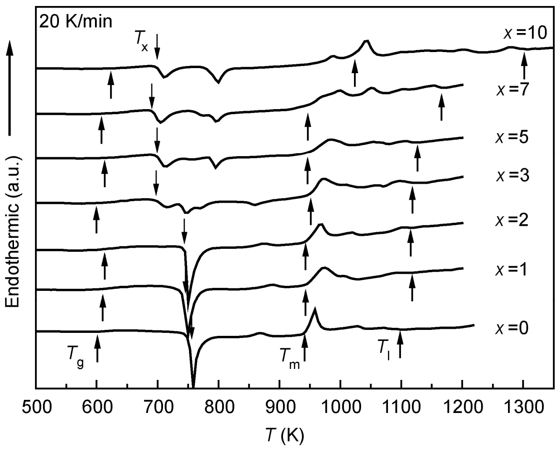

Figure 2 DSC curves of the as-cast $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Ag_x$ (x=0, 1, 2, 3, 5, 7 and 10) glassy alloys with a heating rate of 20 K/min.

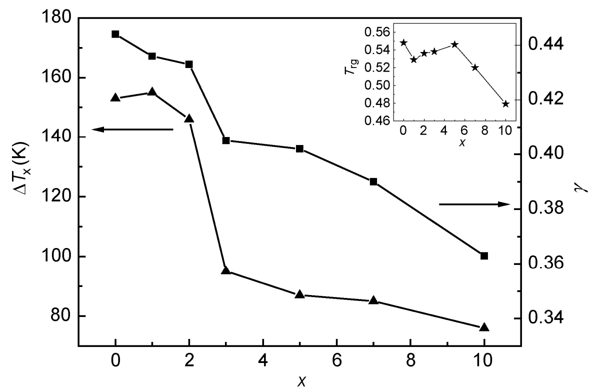

Figure 3 Composition dependence of γ, ΔT_x and T_{rg} (shown in the inset) in the $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Ag_x$ BMGs.

Table 1 Thermodynamic parameters of the $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Ag_x$ bulk glassy alloys[a)]

Samples	T_g (K)	T_x (K)	T_m (K)	T_l (K)	ΔT_x (K)	T_{rg}	γ	D_{max} (mm)
$x = 0$	601	754	940	1097	153	0.548	0.444	$15 < D_{max} < 20$
$x = 1$	591	746	944	1119	155	0.529	0.436	$D_{max} = 20$
$x = 2$	597	743	944	1115	146	0.536	0.433	$15 < D_{max} < 20$
$x = 3$	601	696	951	1118	95	0.538	0.405	$15 < D_{max} < 20$
$x = 5$	611	698	946	1127	87	0.546	0.402	$D_{max} < 15$
$x = 7$	607	692	945	1167	85	0.520	0.390	$D_{max} < 15$
$x = 10$	623	699	1023	1301	76	0.479	0.363	$D_{max} < 15$

a) D_{max} denotes the critical glass dimensions used in this study.

and the elastic constants of interest were calculated. Table 2 summarizes the longitudinal, transverse ultrasonic velocities, the calculated elastic moduli, Poisson's ratio v and the *G*/*B* value of the $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Ag_x$ BMGs as the Ag content x was varied from 0 to 10. To examine the validity of *G*/*B* in evaluating the GFA of the $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Ag_x$ glass-forming alloys the dependence of ΔT_x and γ on *G/B* was determined, as shown in Figure 4. The *G/B* value is basically scales inversely with γ or ΔT_x, that is, the glassy alloys with a higher GFA have a lower *G/B* in the $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Ag_x$ alloys. This appears to contrast with previous observations for various other glass forming metallic alloys where systems with a high GFA roughly retain a high *G*/*B*. In recent work [35], we studied the effect of Al addition on the GFA of $Zr_{35}Ti_{30}Cu_{7.5}Be_{27.5}$ alloys and the *G*/*B* value also correlated inversely with GFA. Therefore, the discrepancy between the *G*/*B* value and γ (or ΔT_x) in judging the GFA in our work indicates that the explanation of the GFA requires a more comprehensive consideration.

In conclusion, the glass forming ability of $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Ag_x$ (x = 0–10) bulk metallic glasses was studied using calorimetric and elastic moduli measurements. A $Zr_{34}Ti_{30}Cu_{7.5}Be_{27.5}Ag_1$ BMG with a critical diameter of 20 mm was successfully prepared. The thermodynamic parameter ΔT_x

Table 2 Density (ρ), longitudinal and transverse ultrasonic velocity (V_L, V_S), elastic moduli (E, G and B), Poisson's ratio (v) and *G*/*B* of the $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Ag_x$ glassy alloys

Samples	ρ (g/cm^3)	V_L (km/s)	V_S (km/s)	G (GPa)	B (GPa)	E (GPa)	v	G/B
$x = 0$	5.329	5.172	2.545	34.5	96.5	92.5	0.340	0.358
$x = 1$	5.402	5.250	2.493	33.6	104.1	90.9	0.354	0.322
$x = 2$	5.454	5.399	2.493	33.9	113.8	92.5	0.365	0.297
$x = 3$	5.483	5.304	2.567	36.1	106.0	97.4	0.347	0.341
$x = 5$	5.579	5.119	2.597	37.6	96.0	99.8	0.327	0.392
$x = 7$	5.672	5.079	2.584	37.9	95.8	100.4	0.325	0.395
$x = 10$	5.791	5.170	2.616	39.6	101.9	105.2	0.328	0.389

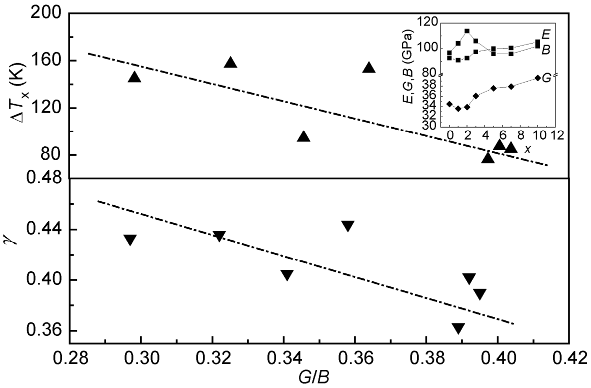

Figure 4 Dependence of the supercooled liquid region ΔT_x and γ on the ratio of the shear modulus to the bulk modulus (*G/B*) in $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Ag_x$ bulk metallic glasses. Composition dependence of *G*, *B* and *E* is plotted in the inset.

and the γ parameter are more effective than the *G*/*B* value for an evaluation of the GFA of $Zr_{35-x}Ti_{30}Cu_{7.5}Be_{27.5}Ag_x$ (x=0–10) glass forming alloys.

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