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73 mm-diameter bulk metallic glass rod by copper mould casting

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To be structural materials, the critical size is always a bottleneck of bulk metallic glasses (BMGs) due to the cooling rate restriction. Here, we report a developed alloy of $\text{Zr}_{46}\text{Cu}_{30.14}\text{Ag}_{8.36}\text{Al}_8\text{Be}_{7.5}$, which can be cast into amorphous rods in 73 mm diameter by copper mould casting. The strong glass forming ability of this alloy is closely related to the Be addition, which not only suppresses the phase separation happening in the as-cast Be-free BMG but also sustains low Gibbs free energy difference for crystallization. This finding will stimulate more interests in developing BMGs and their industrial applications. © 2011 American Institute of Physics. [doi:10.1063/1.3621862]

Bulk metallic glasses (BMGs) are currently on the cutting edge of materials science research. The disordered atomic structure of BMGs results in their remarkable properties.^{1–3} By utilizing viscous flow in the supercooled liquid regime can realize near-net-shape fabrications.⁴ Since the discovery of the quenched Au-Si glassy alloy in 1960,⁵ hunting other alloy systems having high glass-forming ability (GFA) or large critical size, is always concerned by BMG community. In the later of 1980s and the earlier of 1990s several BMG systems, mainly in La-, Mg-, Pd-, and Zr-based, were developed by Inoue's group in Japan and Johnson's group at Caltech, USA.^{1,2} After 2000, significant progress has been made in Cu-,⁶ Fe-,⁷ Ti-,⁸ Y-,⁹ Ca-based BMGs,¹⁰ and also the former Mg- (Ref. 11) and La-based¹² BMGs that were further improved over 20 mm in diameter. The largest critical size of BMG reported was 72 mm in diameter for the Pd-Cu-Ni-P alloy system achieved after a complicate B_2O_3 flux process, while it could only reach 40 mm diameter without fluxing.¹³ Recently, a class of Zr-Cu-Ag-Al BMGs were developed¹⁴ for which the maximum size can be over 20 mm in diameter by copper mould casting. Now a question is raised whether it is possible to enlarge the critical size of these BMGs significantly? It is known that minor alloying can be an effective method to further improve the GFA.¹⁵ In this work, by finely tuning the Cu/Be ratio in a Zr-Cu-Ag-Al-Be alloy system with nominal compositions $\text{Zr}_{46}\text{Cu}_{37.64-x}\text{Ag}_{8.36}\text{Al}_8\text{Be}_x$ ($x = 0\text{--}15$ at. %), the GFA is greatly improved and 73 mm-diameter BMG rod with good properties is prepared by copper mould casting. The amorphous feature is confirmed by x-ray diffraction (XRD) and differential scanning calorimeter (DSC).

Pre-alloyed ingots were prepared by arc melting high purity (>99.9%) Cu, Zr, Ag, and Al with commercial CuBe alloy in a Ti-gettered purified argon atmosphere. 10, 52, and 73 mm diameter rods were produced by copper mould casting under argon atmosphere after ingots were remelted in an Al_2O_3 crucible by induction in a home-made high vacuum

(4×10^{-3} Pa) casting equipment. The pieces of samples were cut down from the transverse cross section in the middle of cylinders with diameters of 10 mm, 52 mm, and 73 mm, respectively. After being carefully polished, x-ray diffraction measurements were performed along two crossed lines passing the central point by an x-ray diffractometer (Philips X'Pert) with Cu-K α radiation. A small slice taken from the central region of the piece was further polished to the weight of about 15 mg and then scanned in a Netzsch DSC 404c at a heating rate of 20 K/min. Small angle x-ray scatterings (SAXS) were performed on the B1 station at DORIS III synchrotron at DESY, Hamburg. Using the same method mentioned in Refs. 12 and 14, the specific heat capacities of the amorphous phase, supercooled liquid phase, and crystalline phase were measured on a Perkin-Elmer Diamond DSC.

Fig. 1(a) shows the XRD patterns for the prepared samples in 10 mm diameter with Be content increasing from 0 to 15 at. %. It displays only broad diffraction maxima without appearance of sharp Bragg peaks, representing the feature of an amorphous structure. In order to estimate the GFA of this series of BMGs, the parameters of T_{rg} (T_g/T_l) (Ref. 16) and γ (Ref. 17) defined as $T_x/(T_g + T_l)$ are calculated by using the characteristic temperatures measured by DSC, where T_g is the glass transition temperature, T_x the onset temperature of crystallization, and T_l the liquidus temperature. As shown in Fig. 1(b), the variation trends of T_{rg} and γ are not exactly consistent with each other within the whole composition range. The high T_{rg} values (>0.635) appear when Be content is less than 7.5%, whereas large γ values (>0.44) locate in the range of Be content about 6–12%. However, the experimental results demonstrate that the critical size is less than 52 mm in diameter for a 10% Be-bearing alloy and less than 35 mm for a Be-free alloy. Good glass formers are located in the range of 5–8% of Be. Fig. 1(c) presents the image of a $\text{Zr}_{46}\text{Cu}_{30.14}\text{Ag}_{8.36}\text{Al}_8\text{Be}_{7.5}$ BMG cylinder of 73 mm in diameter and 85 mm in length by simple copper mould casting. This alloy has smooth outer surface and good metallic luster. Figs. 1(d) and 1(e) show XRD patterns and DSC traces for the samples taken from the 73 mm, 52 mm, and 10 mm-diameter cylinders prepared by copper mould casting. XRD patterns display only

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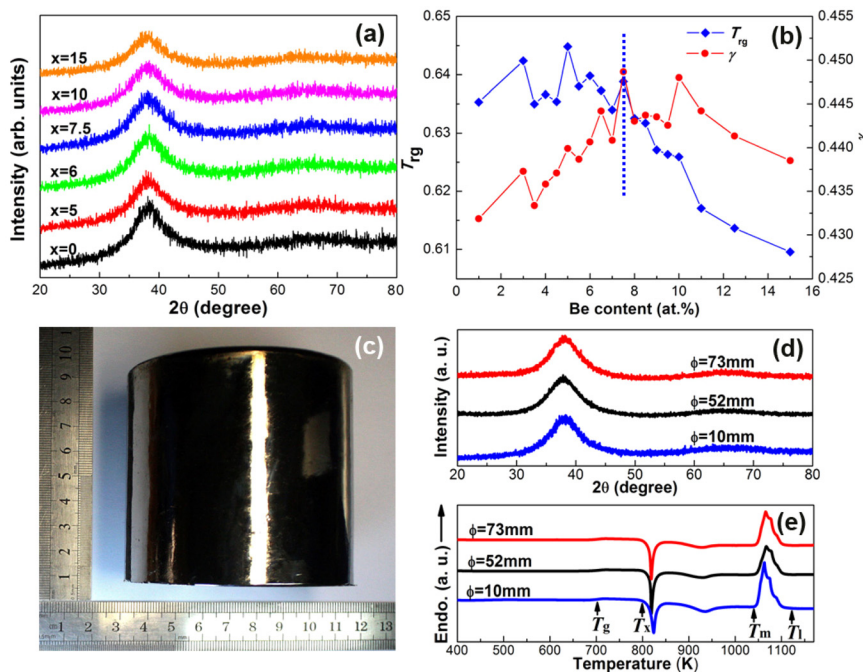


FIG. 1. (Color online) (a) XRD patterns for the prepared samples in 10 mm diameter with Be content increasing from 0 to 15 at. %. (b) Variation of T_g and γ changing with Be content. (c) Image of a $\text{Zr}_{46}\text{Cu}_{30.14}\text{Ag}_{8.36}\text{Al}_8\text{Be}_{7.5}$ BMG cylinder of 73 mm in diameter and 85 mm in length by simple copper mould casting. (d) and (e) XRD patterns and DSC curves for the samples taken from the central region in the middle transverse cross section of the cylinders with diameters of 73 mm, 52 mm, and 10 mm prepared by copper mould casting, respectively.

broad diffraction of an amorphous structure. DSC traces for three samples, measured at a heating rate of 20 K/min, exhibit almost the same exothermic enthalpies for crystallization.

The major thermal and mechanical parameters for this series of BMGs changing with Be content are listed in Table I. The density of amorphous rods decreases almost linearly with increasing Be content. The mechanical properties like Vickers hardness, elastic modulus E , and shear modulus G increase with Be content while the Poisson's ratio ν shows an opposite trend in variation, decreasing from 0.366 to 0.351. Although the Poisson's ratio is closely related to mechanical properties of BMG materials,¹⁸ we found that the compressive fracture strengths of $x = 5, 6, 7.5$, and 10% BMGs are almost the same of about 2.1 GPa, and plastic strain $< 0.5\%$, without distinguished difference. If using the S parameter ($S = \Delta T / (T_f - T_g)$) (Ref. 19) to judge the thermo-plasticity of these BMGs, it shows that the formability could be significantly enhanced from 0.170 for the Be-free BMG to 0.377 for the 10% Be-bearing BMG.

In the Be-free Zr-Cu-Ag-Al BMG, phase separation happens by forming Cu-enriched and Ag-enriched zones.²⁰ However, with 7.5% Be substituting for Cu, the phase separation disappears. Fig. 2(a) shows the total intensity of SAXS patterns at the energy of 8954 eV near the Cu K edge for the as-cast $\text{Zr}_{46}\text{Cu}_{37.64}\text{Ag}_{8.36}\text{Al}_8$ and $\text{Zr}_{46}\text{Cu}_{30.14}\text{Ag}_{8.36}\text{Al}_8\text{Be}_{7.5}$ BMGs. The $I(q)$ of the as-cast Be-free sample

is high and also a correlation peak appears at the q range of about $0.02\text{--}0.1 \text{ \AA}^{-1}$, indicating that an inhomogeneous microstructure exists. In contrast, there is almost a power law relationship ($I(q) \propto q^{-2.56}$) between $I(q)$ and q within the whole scattering range ($0.006\text{--}0.1 \text{ \AA}^{-1}$) for the as-cast $\text{Zr}_{46}\text{Cu}_{30.14}\text{Ag}_{8.36}\text{Al}_8\text{Be}_{7.5}$ BMG. The reduced scattering intensity and absence of the broad hump in the high q range suggests that Be addition could restrict the phase separation. Moreover, for different selected local regions ($30 \text{ nm} \times 30 \text{ nm} \times 70 \text{ nm}$), the concentration depth profiles measured by three-dimensional atom probe (3DAP) show no obvious composition fluctuations in the as-cast $\text{Zr}_{46}\text{Cu}_{30.14}\text{Ag}_{8.36}\text{Al}_8\text{Be}_{7.5}$ BMG (Fig. 2(b)), well consistent with above SAXS results.

By introducing Be into the Zr-Cu-Ag-Al system, the GFA is significantly improved. More Be addition could make the atomic packing denser, which seems good for glass formation. However, the optimized Be contents are only from 5 to 8% in the present case. In principle, a glass formation is determined by both thermodynamic and kinetic factors. It was demonstrated that the low difference in Gibbs free energy between the supercooled liquid state and the crystalline plays a crucial role in the strong GFA for La- and Zr-Cu-based BMGs.^{12,14} Fig. 3(a) shows the C_p curve and the fitting functions for a $\text{Zr}_{46}\text{Cu}_{30.14}\text{Ag}_{8.36}\text{Al}_8\text{Be}_{7.5}$ BMG sample. To compare the driving force of crystallization for

TABLE I. Thermal, mechanical properties and density and thermoplastic parameters of $\text{Zr}_{46}\text{Cu}_{37.64-x}\text{Ag}_{8.36}\text{Al}_8\text{Be}_x$ BMGs, $x = 0\text{--}15$ at. %.

Be (at. %)	T_g (K)	T_x (K)	T_l (K)	ΔT_x (K)	T_{rg}	γ	ρ (g/cm ³)	H_v	E (GPa)	G (GPa)	ν	S
0	703	775	1126	72	0.642	0.424	7.229	543	91.5	33.5	0.366	0.170
3	707	790	1100	83	0.642	0.437	-	551	92.5	33.9	0.364	0.269
5	707	793	1096	86	0.645	0.440	7.037	559	95.1	35.0	0.359	0.278
6	706	797	1103	91	0.640	0.441	6.979	563	96.0	35.3	0.358	0.298
7.5	705	811	1103	106	0.639	0.449	6.933	571	96.3	35.4	0.358	0.364
10	703	818	1123	115	0.626	0.448	6.827	577	97.1	35.8	0.355	0.377
12.5	701	814	1143	113	0.614	0.441	-	584	98.7	36.5	0.352	0.342
15	700	811	1149	111	0.610	0.439	6.617	581	100.0	37.0	0.351	0.327

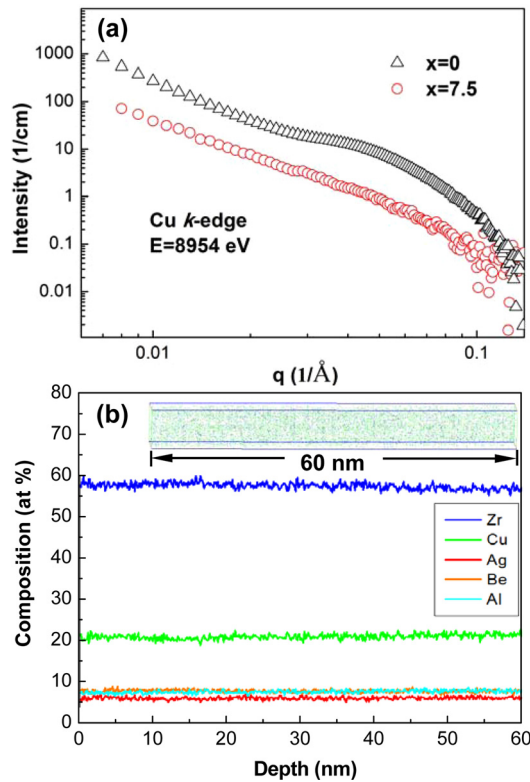


FIG. 2. (Color online) (a) Total SAXS at the energy of 8954 eV near the Cu K edge for the as-cast $\text{Zr}_{46}\text{Cu}_{37.64}\text{Ag}_{8.36}\text{Al}_8$ ($x=0$) and the as-cast $\text{Zr}_{46}\text{Cu}_{30.14}\text{Ag}_{8.36}\text{Al}_8\text{Be}_{7.5}$ ($x=7.5$) BMGs. (b) Composition depth profiles in 60 nm depth measured by 3DAP, showing non-existence of phase separation in the $x=7.5$ BMG.

different alloys, the excess Gibbs free-energy differences as a function of temperature normalized to the melting point of the corresponding alloy are plotted in Fig. 3(b). It is surprising to find that the $\text{Zr}_{46}\text{Cu}_{37.64}\text{Ag}_{8.36}\text{Al}_8$ BMG with $x=0$ exhibits the lowest difference in Gibbs free energy, which means it would have the strongest GFA in this series of BMGs from the thermodynamic aspect of view. But, this is inconsistent with the above experimental results. The existence of phase separation in this BMG could be more favourable for crystallization kinetically. However, the $\Delta G_{l-s}(T)$ values for Be-bearing BMGs decrease with Be content almost in the order of $x=7.5 < x=5 < x=6 < x=10$, and are comparable with that of Vit 1,²¹ a well-known BMG with Be containing. Accordingly, the critical size can reach 73 mm for the BMG with $x=7.5$, less than 52 mm for the BMG with $x=10$, and almost locates in between for the BMGs with $x=5$ and $x=6$, respectively. Thus, the change in Gibbs free-energy differences of Be-bearing BMGs is almost in agreement with the magnitudes of their critical sizes. More investigations are still needed to uncover the origin of high GFA in this developed system.

In summary, a series of Zr-Cu-Ag-Al-Be BMGs with strong GFA has been developed. The critical size of glassy rods can be up to 73 mm in diameter prepared by direct copper mould casting. The enhanced GFA is due to the Be addition that not only hinders the phase separation but also sustains the relatively low difference in Gibbs free-energy for crystallization. We expect that this discovery will stimulate more interests in developing BMGs and their industrial applications.

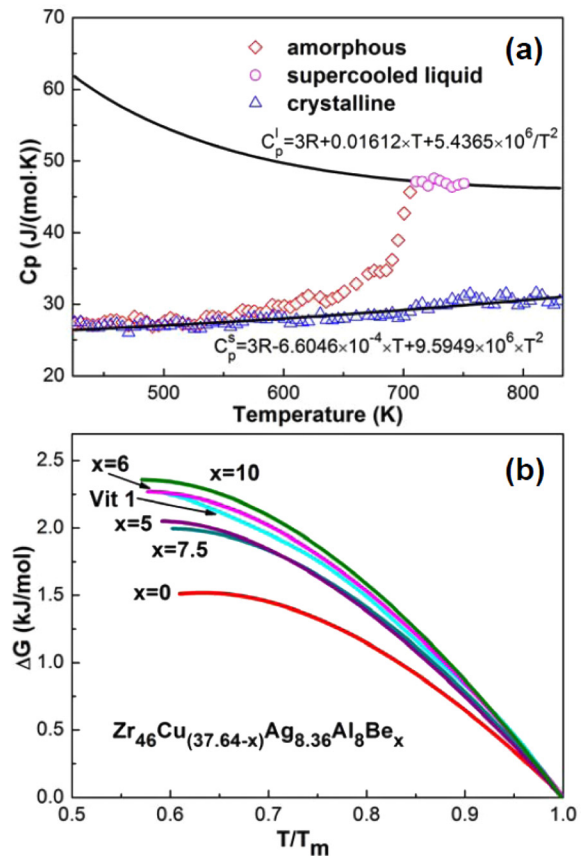


FIG. 3. (Color online) (a) The C_p curve and the fitting functions for a $\text{Zr}_{46}\text{Cu}_{30.14}\text{Ag}_{8.36}\text{Al}_8\text{Be}_{7.5}$ BMG sample. (b) Difference in Gibbs free-energy as a function of temperature normalized to the melting point of the corresponding alloy.

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