

Unusual Glass-Forming Ability of Bulk Amorphous Alloys Based on Ordinary Metal Copper

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We report the unusual glass-forming ability (GFA) of a family of Cu-based alloys, $\text{Cu}_{46}\text{Zr}_{47-x}\text{Al}_7\text{Y}_x$ ($0 < x \leq 10$, in at. %), and investigate the origin of this unique property. By an injection mold casting method, these alloys can be readily solidified into amorphous structures with the smallest dimension ranging from 4 mm up to 1 cm without detectable crystallinity. Such superior GFA is found primarily due to the alloying effect of Y, which lowers the alloy liquidus temperature and brings the composition closer to a quaternary eutectic. Other beneficial factors including appropriate atomic-size mismatch and large negative heat of mixing among constituent elements are also discussed.

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Bulk amorphous alloys (also known as BMGs: bulk metallic glasses) have been drawing increasing attention in recent years due to their scientific and engineering significance [1,2]. A great deal of effort in this area has been devoted to developing BMGs in different alloy systems. BMGs based on certain late transition metals (e.g., Fe, Co, Ni, Cu) have many potential advantages over those based on early transition metals. These include even higher strength and elastic moduli, and lower materials cost, to name a few, which are highly preferable for a broad application of BMGs as engineering materials. Nevertheless, these ordinary-late-transition-metal-based BMGs generally have quite limited glass-forming ability (GFA). Their favored single-amorphous-phase structures get compromised and undesired first-order phase transitions start to intervene once their casting thickness (or diameter) exceeds a critical value ~ 5 mm (or lower) [3–11]. In contrast, this critical value of thickness for many early-transition-metal-based BMGs to sustain their fully glassy structures can reach as high as several centimeters [12–15].

Very recently, BMGs have surprisingly been found in the binary Cu-Zr system by several groups [10,11,16,17], among which $\text{Cu}_{46}\text{Zr}_{54}$ has a critical casting thickness up to 2 mm, highest within its local compositional vicinity [16]. The discovery of these binary BMGs strongly suggests that even higher GFA may be achievable in Cu-based alloys by appropriately introducing additional alloying elements. As a matter of fact, Inoue *et al.* reported earlier [18] that the critical casting thickness of certain ternary Cu-based alloys in a Cu-Zr-Al system is ~ 3 mm. Following the “confusion principle” proposed by Greer [19], we further examined the effects of other alloying elements on the GFA of a preselected ternary alloy $\text{Cu}_{46}\text{Zr}_{47}\text{Al}_7$ (“matrix alloy” in the following context). In this Letter, we report a series of quaternary Cu-based alloys, $\text{Cu}_{46}\text{Zr}_{47-x}\text{Al}_7\text{Y}_x$ ($0 < x \leq 10$, in at. %), which possess unusually high GFA. The amorphous structure of a representative alloy $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$ can be readily obtained even when the casting diameter exceeds 1 cm.

The possible mechanisms involved in the achievement of this unusual GFA will be discussed.

The alloy ingots of nominal compositions $\text{Cu}_{46}\text{Zr}_{47-x}\text{Al}_7\text{Y}_x$ ($0 \leq x \leq 10$) were prepared by arc melting mixtures of ultrasonically cleansed Cu, Zr (crystal bar), Al, and Y pieces having a purity of 99.99+%, 99.5%, 99.99+%, and 99.9%, respectively, in a Ti-gettered high-purity argon atmosphere. Each ingot was melted at least three times in the arc melter in order to obtain chemical homogeneity. The ingots were then remelted under high vacuum in a quartz tube using an induction heating coil and injected through a ~ 0.5 –1 mm (inner diameter) nozzle into copper molds using high-purity argon at a pressure of ~ 3 –5 atm. The copper molds have internal cylindrical cavities of diameters ranging from 2 to 14 mm. The transverse cross sections of the as-cast samples were analyzed with the x-ray diffraction (XRD) method using a $\text{Cu-K}\alpha$ source. A Perkin-Elmer DSC7 (differential scanning calorimeter) was utilized for both isothermal and constant heating rate ($dT/dt = 0.33$ K/s) scanning, aimed at confirming the amorphous structures and studying the glass transition and crystallization behaviors of these alloys, respectively. The melting behaviors of the alloys were analyzed with a Setaram DSC 2000K high temperature calorimeter at a heating rate of 0.33 K/s to investigate the mechanisms underlying the glass formation in this system.

Figure 1(a) shows the pictures of three as-cast samples, S1, S2, and S3, of a representative alloy, $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$, having diameters of 10, 12, and 14 mm, respectively. Their as-cast surfaces all appear smooth and lustrous. No apparent volume reductions can be recognized on their surfaces, indicating that there was no drastic crystallization during the formation of these samples. The XRD patterns of S1, S2, and S3 are presented in Fig. 1(b). It can be seen that the pattern of S1 consists of only a series of broad diffraction maxima without any detectable sharp Bragg peaks, indicating that this 10 mm diameter sample is mostly amorphous. Moreover, the 12 mm (S2) and 14 mm (S3) samples, even though

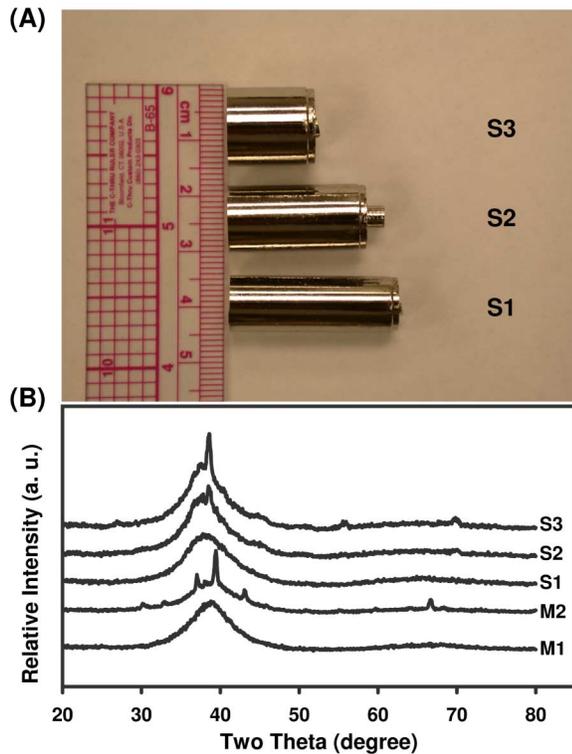


FIG. 1 (color online). (a) Pictures of three cast samples of $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$, with different diameters: S1, 10 mm; S2, 12 mm; S3, 14 mm. (b) XRD patterns obtained from 10 mm (S1), 12 mm (S2), and 14 mm (S3) diameter rods of $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$ and from 3 mm (M1) and 4 mm (M2) diameter rods of the matrix alloy $\text{Cu}_{46}\text{Zr}_{47}\text{Al}_7$.

partially crystallized, still possess very large amorphous fractions judging from the broad diffraction background on their XRD patterns. This implies that the growth of the crystalline phase(s) in the supercooled liquid is quite sluggish even when the sample size exceeds the critical value (~ 10 mm) for the formation of a fully amorphous structure by $\sim 40\%$. For a comparison, Fig. 1(b) also presents the XRD patterns of 3 mm (M1) and 4 mm (M2) diameter rods of the matrix alloy $\text{Cu}_{46}\text{Zr}_{47}\text{Al}_7$, from which it can be seen that the critical casting diameter of the matrix alloy is only ~ 3 mm, in agreement with the report in Ref. [18].

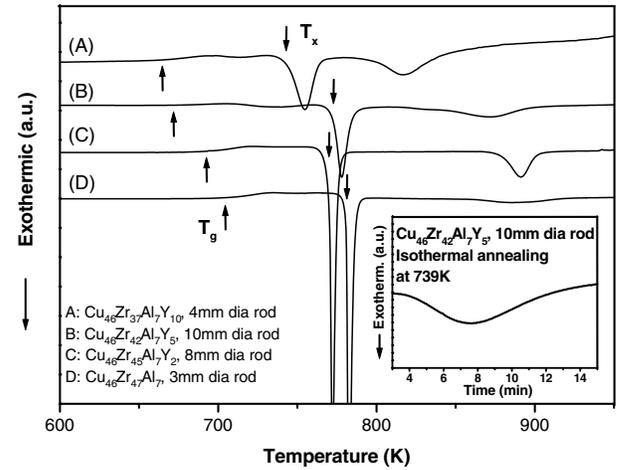


FIG. 2. DSC scans of selected alloys at a constant heating rate of 0.33 K/s. The upward arrows refer to the glass transition temperatures and the downward arrows refer to the onset of the first crystallization events. The inset at the lower right corner is the isothermal DSC profile of the 10 mm diameter rod of $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$ at a constant temperature of 739 K.

It was pointed out by Chen and Spaepen [20] that isothermal calorimetric profiles can distinguish truly amorphous materials from “microcrystalline” materials that exhibit similarly broad diffraction halos. Truly amorphous materials exhibit exothermic peaks during isothermal scan, while microcrystalline materials release monotonically decaying heat flow signals. Hence, isothermal scanning was performed on the present alloys. The inset in Fig. 2 presents the isothermal DSC profile of the 10 mm diameter as-cast sample of $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$ maintained at a constant temperature 739 K. The apparent exothermic peak characteristic of a nucleation-and-growth process confirms the as-cast glassy structure of this alloy as concluded from its XRD pattern. Other as-cast alloys which are shown to be amorphous by XRD also exhibit the same character. The isothermal DSC scanning was also performed at different temperatures for each alloy. More detailed results on this will be reported elsewhere.

Thermal properties of these new glassy alloys, including the glass transition temperature (T_g) and the onset

TABLE I. A list of representative alloys and selected properties.

Alloy composition (in at. %)	Critical casting diameter (mm)	T_g (K)	T_x (K)	T_l (K)	$\Delta T = T_x - T_g$ (K)	$T_{rg} = T_g/T_l$	$\gamma = T_x/(T_g + T_l)^a$
$\text{Cu}_{46}\text{Zr}_{54}^b$	2	696	746	1201	50	0.58	0.393
$\text{Cu}_{46}\text{Zr}_{47}\text{Al}_7$	3	705	781	1163	76	0.61	0.418
$\text{Cu}_{46}\text{Zr}_{45}\text{Al}_7\text{Y}_2$	8	693	770	1143	77	0.61	0.419
$\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$	10	672	772	1113	100	0.60	0.432
$\text{Cu}_{46}\text{Zr}_{37}\text{Al}_7\text{Y}_{10}$	4	665	743	1118	78	0.59	0.417

^a γ was defined in Refs. [21,22].

^bThese data were taken from Ref. [16].

temperature of the first crystallization event (T_x), were measured with DSC at a constant heating rate of 0.33 K/s. The characteristic data are listed in Table I and the complete DSC signals are shown in Fig. 2. Upon heating, these amorphous alloys all exhibit a clear endothermic glass transition followed by a series of exothermic events characteristic of crystallization. As Y content increases, the exothermic peaks tend to be broadened, indicating a possible slow-down in the kinetics of crystal nucleation and growth.

As can be seen from Table I, the GFA of the current alloy system strongly depends on the Y content. Without Y, the matrix alloy can be cast only into fully amorphous samples of a diameter no larger than ~ 3 mm. The additions of 2% and 5% Y significantly increase the critical casting diameter to ~ 8 and ~ 10 mm, respectively. When more Y is added, the critical casting diameter is reduced, dropping down to ~ 4 mm at a Y content of 10%. To our knowledge, the best (in terms of GFA) alloy in this series, $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$, may be the only Cu-based alloy discovered so far that can retain its mostly amorphous structure when the minimum dimension exceeds 1 cm.

To understand the above dependence of GFA on the Y content and investigate the mechanisms underlying the unusually high GFA of $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$, the melting behaviors of these alloys were studied through high temperature calorimetric scanning. The signals are exhibited in Fig. 3, where the liquidus temperatures (defined by the offset temperature of an entire melting process) T_l are marked with arrows, whose values are included in Table I. It can be seen that Y content significantly affects T_l and the melting behaviors of these alloys. The ternary matrix alloy $\text{Cu}_{46}\text{Zr}_{47}\text{Al}_7$ has a rather high $T_l \sim 1163$ K, although it is quite close to a ternary eutectic composition as indicated by the nearly single-event feature of its

melting process (the ternary eutectic is located around $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ according to Ref. [23]). When 2% Y is added, the quaternary alloy $\text{Cu}_{46}\text{Zr}_{45}\text{Al}_7\text{Y}_2$ shows a lower $T_l \sim 1143$ K but multiple exothermic events, which indicate that this alloy is quite far from any quaternary eutectic composition. With 5% Y, the alloy $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$ shows an even lower $T_l \sim 1113$ K and a simpler melting process consisting of one major exothermic event characteristic of a quaternary eutectic reaction, followed by a minor secondary event corresponding to the melting of a less-concentrated primary crystal. When Y content is further increased, the T_l tends to become higher, reaching ~ 1118 K at 10% Y, and multiple events appear again during its melting process. It is apparent that the alloy $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$, which has the highest GFA, is the closest to a nearby quaternary eutectic among this present alloy series.

Considering together $\text{Cu}_{46}\text{Zr}_{54}$, $\text{Cu}_{46}\text{Zr}_{47}\text{Al}_7$, and the present $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$, we find that all three of these bulk glass formers are associated with the eutectic compositions in their individual systems, binary, ternary, and quaternary, respectively. As the dimension of the alloy system (i.e., the number of components) increases, the eutectic temperature is continuously lowered, and the GFA of the alloys is improved as evidenced by the increased critical casting thickness using the same copper mold casting method (refer to Table I). This agrees very well with the confusion principle proposed in Ref. [19] and the previous observation that high GFA often occurs around deep eutectics [24]. Therefore, it is clear that the unusual GFA of the present quaternary alloy series, especially the alloy $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$, comes in large part from the alloying effect of Y, which lowers the liquidus temperature of the matrix alloy and brings the composition to a deeper eutectic.

Different explanations have been attempted to understand the correlation between high GFA and deep eutectics [1,2,24]. Generally, these explanations fall into two categories: thermodynamics and kinetics. From a thermodynamic point of view, a deep eutectic means that the liquid state is energetically favored over ordered solid state in a large temperature range above the eutectic temperature, either through the stabilization of the liquid or through the destabilization of the ordered solid(s); and below the eutectic temperature, the energy difference between these two states (i.e., the driving force for crystal nucleation and growth) is relatively small, compared with the case of noneutectic; thus, it becomes easier to quench the liquid to an amorphous state before a detectable fraction of ordered crystals can be formed. From a kinetic angle, around eutectics, there are multiple ordered phases competing with each other, especially in multicomponent systems, and the crystallization of the liquid requires simultaneous rearrangement of different species of atoms, which significantly limits the kinetics of the process and thus promotes glass formation.

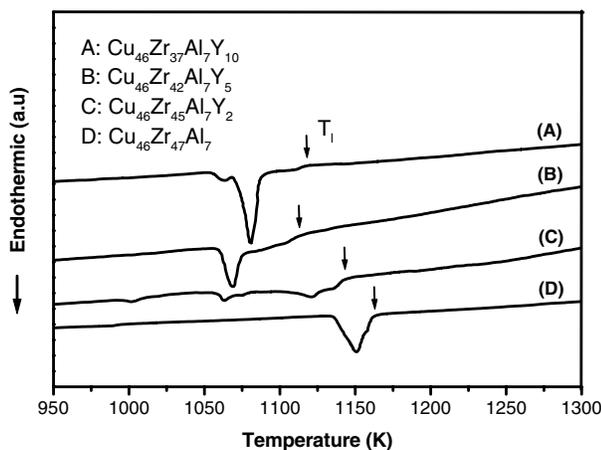


FIG. 3. Melting behaviors of selected alloys measured at a heating rate of 0.33 K/s. The arrows refer to the liquidus temperatures.

Computer simulations [25], topological studies [26,27], and empirical rules drawn from experimental results [2] have all shown that certain atomic-size mismatch and efficient atomic packing may enhance GFA of a system. In Ref. [27] (Table I), a set of preferred values R^* for the ratio (R) of the solute atom radius to the solvent atom radius is presented, at which the local packing efficiency (defined in terms of a coordination number) assumes its maximum 1. In the present system, the atomic radii of the component atoms are Y, 1.74 Å; Zr, 1.58 Å; Al, 1.43 Å; and Cu, 1.27 Å, respectively [28]. Therefore, $R_{\text{Zr/Cu}} = 1.244$, $R_{\text{Al/Cu}} = 1.126$, $R_{\text{Y/Cu}} = 1.37$. Comparing these values with the critical values listed in Table I of Ref. [27], good agreement can be found between $R_{\text{Zr/Cu}}$ and R_{17}^* (1.248), $R_{\text{Al/Cu}}$ and R_{15}^* (1.116), $R_{\text{Y/Cu}}$ and R_{19}^* (1.373). Therefore, the present combination of atomic sizes can produce an efficiently packed local structure, which is often associated with low energy and high viscosity of liquids. It is noteworthy that a simple calculation using the measured density data of these alloys (to be published elsewhere) shows that the global packing efficiency (defined by the ratio of the sum of all atomic volumes to the total volume concerned) of all the present alloys is ~ 0.75 – 0.76 , even larger than the 0.74 of fcc crystals [29]. This further confirms that the present system is highly efficiently packed.

Another factor that may benefit GFA has been reported to be large negative heat of mixing (HM) among the constituent elements [2]. In the present system, this criterion is also satisfied since the HM values of Y-Al, Y-Cu, and Zr-Cu are -31 , -22 , and -23 kJ/mol, respectively [30]. These large negative values of HM enhance the interactions among the components and promote chemical short range ordering in liquids, which can improve the local packing efficiency and restrain long range diffusion of atoms.

To summarize, we have reported the unusual GFA of a series of quaternary Cu-based alloys: $\text{Cu}_{46}\text{Zr}_{47-x}\text{Al}_7\text{Y}_x$ ($0 < x \leq 10$). By injection mold casting, the amorphous structure of a representative alloy $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$ can be readily obtained with a diameter larger than 1 cm. The superior GFA of these alloys originates primarily from the alloying effect of Y, which lowers the liquidus temperature of the matrix alloy $\text{Cu}_{46}\text{Zr}_{47}\text{Al}_7$ and brings it closer to a quaternary eutectic. Other factors including appropriate atomic-size mismatch and large negative heat of mixing among constituent elements may have also benefited the GFA of present alloys.

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Note added.—After submitting this manuscript, we learned that centimeter level bulk metallic glasses had been reported in Fe-based alloy systems very recently, by Lu *et al.* [31] and Ponnambalam *et al.* [32].

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