Binary Cu-Zr Bulk Metallic Glasses *

TANG Mei-Bo(汤美波), ZHAO De-Qian(赵德乾), PAN Ming-Xiang(潘明祥), WANG Wei-Hua(汪卫华)**
Institute of Physics, Chinese Academy of Sciences, Beijing 100080

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We report that bulk metallic glasses (BMGs) can be produced up to 2 mm by a copper mold casting in Cu_xZr_{1-x} binary alloy with a wide glass forming composition range ($45 < x < 60$ at.%). We find that the formation mechanism for the binary Cu-Zr binary BMG-forming alloy is obviously different from that of intensively studied multicomponent BMGs. Our results demonstrate that the criteria of the multicomponent alloys with composition near deep eutectic and strong liquid behaviour are no longer the major concern for designing BMGs.

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The key criteria for the bulk metallic glass (BMG) formation include:[1,2] (1) multi-component alloys of three or more elements with alloy composition, (2) more than 12% atomic radius mismatch between elements, (3) negative heat of mixing between the main elements, (4) using an alloy composition close to a deep eutectic forms a liquid stable at low temperatures. One of the general guiding principles to designing alloys that form BMGs is to pick multicomponent elements with dramatic differences in size, which leads to an increasing complexity and an increasing size of the crystal unit cell to reduce the energetic advantage of forming an ordered structure of longer-range periodicity than atomic interactions.[2] The complicated structure with atomic configuration corresponding to a higher degree of the dense random packed structure leads to high viscous of the supercooled liquid state and slow crystallization. The effect of multicomponents on BMG formation is concluded as "confuse principal."[3] Because binary alloys have simply chemical compositions, binary metallic glasses were thought to be obtained only by rapid quenching with a cooling rate as high as 10^6 K/s.[1–3] In this study, we find that CuZr binary alloy can be readily cast into fully glassy rods up to 2 mm in diameter by a conventional Cu-mold casting method. Our results show that the formation mechanism and the criteria for the binary BMG are obviously different from those of multicomponent BMGs. In the multicomponent BMGs, near deep eutectic composition and strong liquid empirical criteria are not essential for BMG formation in some binary BMG forming alloys.

Ingot of CuZr alloy was prepared by melting 99.9% (at.%) pure Cu and Zr in an arc-melting furnace under argon atmosphere. The rod samples were produced by suction of the melt into a copper mold to obtain 50-mm-long cylindrical rod in different diameters. The preparation process is the same as that of the multicomponent BMGs.[1,2] The amorphous sample was characterized by x-ray diffraction (XRD) using a MAC M03 XHF diffractometer with Cu K_α radiation and by differential scanning calorimeter (DSC) measurements. The DSC measurement was carried out in a Perkin Elmer DSC-7. The melting was measured by a Perkin Elmer DTA-7 at heating rate 10 K/min.

The XRD patterns of as-cast $Cu_{50}Zr_{50}$ alloys with different diameters are shown in Fig. 1. The alloy with the diameter of 2 mm exhibits a broad diffraction maxima characteristic of amorphous structures. When the diameter is larger than 3 mm, the alloy shows some crystalline peaks. With the increasing diameter, the peaks are more obvious. The crystalline peaks are mainly corresponding to the $Cu_{51}Zr_{14}$ crystal structure and some unknown crystal structures (as shown in Fig. 1). This demonstrates that the binary CuZr alloy rod with a diameter up to 2 mm is full amorphous phase with the detectable limitation of the XRD. To our knowledge, the $Cu_{50}Zr_{50}$ alloy is the best and most simple binary glass forming alloy. The critical cooling rate for the quenched alloys were estimated by[4] dR/dt (K/s)$= 10/R^2$ (cm), where R is the typical dimension of the formed amorphous alloy. For the $Cu_{50}Zr_{50}$ BMG, the estimated critical cooling rate is about 250 K/s.

Figure 2 shows the DSC and DTA traces at the heating rate 10 K/min, which exhibit the glass transition, the crystallization and melting process of the $Cu_{50}Zr_{50}$ alloy, respectively. The DSC trace of the alloy in Fig. 2 shows an obvious endothermic characteristic before crystallization demonstrating a distinct glass transition with the onset at $T_g = 670$ K. Following the glass transition, the alloy exhibits obvious two exothermic heat release events associated with the transformations from undercooled liquid state to the equilibrium crystalline intermetallic phases. The first crystalline temperature T_{x1} and the undercooled liquid region $\Delta T (\Delta T = T_{x1} - T_g)$ are 717 K and 47 K, respectively. The distinct glass transition and

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** Email: To whom correspondence should be addressed. Email: whw@aphy.iphy.ac.cn

sharp crystallization event further confirm the glassy structure and highly glass forming ability of the binary Cu-Zr alloy.[1,2] The complex melting process of the $Cu_{50}Zr_{50}$ alloy shown by the DTA trace in the inset of Fig. 2 is deviated far from the eutectic point. The melting temperature T_m and liquid temperature T_l for the alloy are about 1010 K and 1219 K, respectively. The reduced glass transition temperature $T_{rg}(= T_g/T_m)$, which is a critical parameter in determining the GFA of an alloy, is about 0.66, demonstrating the excellent glass forming ability of the alloy.[5] With a small addition, for example, 1–5 at.% Al, $(Cu_{50}Zr_{50})$-Al ternary amorphous rods can be produced up to 5 mm at least, further confirming the excellent glass forming ability of the $Cu_{50}Zr_{50}$ alloy.

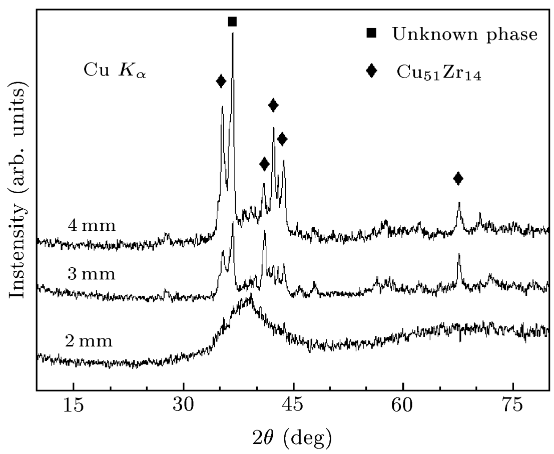

Fig. 1. X-ray diffraction patters of the $Cu_{50}Zr_{50}$ alloy with different diameters of 2 mm, 3 mm, and 4 mm.

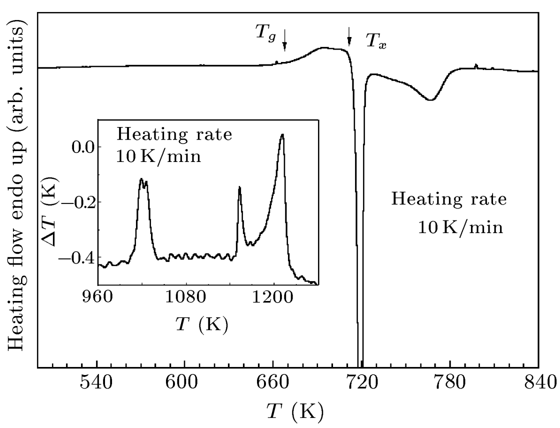

Fig. 2. DSC trace at heating rate 10 K/min of the $Cu_{50}Zr_{50}$ BMG. Inset: DTA trace at heating rate 10 K/min.

The glass formation range in the Cu_xZr_{100-x} alloy has been studied for $20 \le x \le 80$ at.%. The glass-forming range of the Cu_xZr_{100-x} binary BMG (the diameter of the rod sample is larger than or equal to 1 mm) is about $45 < x < 60$ at.%. The $Cu_{50}Zr_{50}$ alloy is the best composition to form binary BMG in the alloy. When the composition is over the glass-forming range, the CuZr and $Cu_{10}Zr_7$ crystalline phases precipitate in the amorphous matrix. The composition range is similar to that of the CuZr metallic glasses obtained by rapid quenching[6] and the mechanical alloying methods.[7]

To understand the glass forming ability, the liquid behaviour of the Cu-Zr alloy was investigated in terms of Angell's fragility concept.[8] Figure 3 shows the DSC traces at different heating rates of ϕ from 5 to 120 K/min. The T_g value of the BMG shifts to higher temperature with the increasing heating rate. The relationship of T_g versus the heating rate ϕ was fitted with the Vogel-Fulcher (VF) equation:[9]

$$\ln\phi = \ln B - D^* T_g^0/(T_g - T_g^0), \qquad (1)$$

where B is a constant, T_g^0 is the hypothetical kinetic instability point, which is the Vogel-Fulcher temperature and D^* is the strength parameter which can be used to describe how closely the system obeys the Arrhenius law.[8] The fitting shown in the inset of Fig. 3 demonstrates that the relationship of T_g versus $\ln\phi$ fits the VFT equation well. T_g^0 is then calculated to be 651 K. The value of D^* is evaluated to be 0.15. From the VFT fitting, the fragility parameter m can be written as[10]

$$m = (D^*/\ln 10) * (T_g^0/T_g) * (1 - T_g^0/T_g)^{-2}. \qquad (2)$$

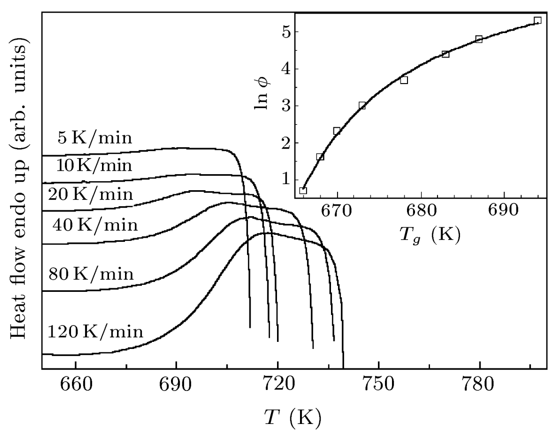

Fig. 3. DSC traces at different heating rates ϕ (5, 10, 20, 40, 80, 120 K/min) of the $Cu_{50}Zr_{50}$ BMG. Inset: the dependence of T_g on the heating rate ϕ from the VFT equation.

The m value of the Cu-Zr BMG evaluated at a heating rate of 20 K/min is 62. The large value of m, which is much greater than that of multicomponent BMGs, classifies the Cu-Zr system into a fragile category according to Angell's classification.[9] Whereas their values of m normally range from 30–40[11−13] for the multicomponent BMGs, such as Zr-base BMGs

($m = 34$–39),[11] La-($m = 32$),[11] Fe-($m = 34$–37),[12] Mg-($m = 41$),[11] Pr-($m = 31$),[13] and Pd-based ($m = 41$)[11] BMGs (all of these m values are evaluated at 20 K/min). Thus, the multicomponent BMGs are strong glasses being less sensitive to the temperature changes and more stable than fragile liquids.[8] Even though there is no direct connection between the value of m and the glass forming ability of an alloy,[14] the small value of m is considered to be one of empirical rules for designing the bulk metallic glass formers, whose metastable-equilibrium supercooled liquid is fairly stable.

The general guiding principles for designing alloys that form BMGs were to pick multicomponent elements with large differences in size and strong liquid behaviour and to use a closely deep eutectic composition,[1−3] but the $Cu_{50}Zr_{50}$ alloy with highly glass forming ability has only two transition metal components and deviates the deep eutectic point with fragile liquid properties. Our experimental results demonstrate that the $Cu_{50}Zr_{50}$ binary BMG can be produced easily up to the diameter 2 mm, and the fragility parameter m shows that the alloy is fragile glass. Our results indicate that the criteria of the multicomponent alloys with composition near deep eutectic are no longer the major concern for designing BMG-forming alloys. The binary BMG is important for studying some underlying physical issues in condensed matter physics and materials sciences.

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