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Bulk metallic glass formation in Cu–Zr–Ti ternary system

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Abstract

The formation of bulk metallic glasses (BMG) in the Cu-rich Cu–Zr–Ti ternary system is studied by using the '*e*/*a*-variant line criterion'. Three such lines, $(Cu_9Zr_4)_{1-x}Ti_x$, $(Cu_{61.8}Zr_{38.2})_{1-x}Ti_x$ and $(Cu_{56}Zr_{44})_{1-x}Ti_x$, are defined in the Cu–Zr–Ti system by linking three binary compositions Cu_9Zr_4, $Cu_{61.8}Zr_{38.2}$ and $Cu_{56}Zr_{44}$ to the third element Ti. The binary compositions Cu_9Zr_4, $Cu_{61.8}Zr_{38.2}$ and $Cu_{56}Zr_{44}$ correspond to specific Cu–Zr binary clusters. BMGs are obtained by copper mould suction casting method with Ti contents of 7.5–15 at.%, 7.5–12.5 at.% and 5–12 at.%, respectively along the $(Cu_9Zr_4)_{1-x}$ Ti_x, $(Cu_{61.8}Zr_{38.2})_{1-x}Ti_x$ and $(Cu_{56}Zr_{44})_{1-x}Ti_x$ lines. The BMGs on each composition line manifest decreased thermal stabilities and glass forming abilities (GFAs) with increasing Ti contents. The maximum GFA appears at $Cu_{64}Zr_{28.5}Ti_{7.5}$, with characteristic thermal parameters of $T_g = 736$ K, $T_x = 769$ K, $T_g/T_l = 0.627$ and $\gamma = 0.403$, which are all superior to those reported for the known $Cu_{60}Zr_{30}Ti_{10}$ BMG.

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1. Introduction

Compared with Zr-based bulk metallic glasses (BMGs), Cu-based BMGs exhibit even higher mechanical properties and lower cost [1–4]. The Cu–Zr–Ti ternary system is a typical glass forming system first explored by Inoue's group [4]. The optimum composition $Cu_{60}Zr_{30}Ti_{10}$ manifested the highest thermal stability and glass forming ability (GFA), as well as the highest strength among the Cu–Zr–Ti BMGs prepared. However, due to the large composition step of 10 at.%, it is highly possible that the BMG formation composition can be further optimized. For this purpose, a specific criterion to glass-forming compositions is necessary to guide the composition design.

In our previous work, we have proposed and applied a so-called *e*/*a*-variant line criterion for the composition optimization of ternary BMGs in Cu–Zr–Al, Zr–Al–Ni, and Zr–Al–Co [5–7]. This criterion is actually a special straight composition line in a ternary phase diagram, defined by linking a specific binary composition with a high glass forming ability, either near a deep eutectic point or at a binary cluster position, to the third element. The success in the Cu–Zr–Al system encouraged us to investigate the Cu–Zr–Ti system using the same criterion, because Al and Ti are quite similar as far as their atomic sizes are concerned. In the present paper, we will show that the application of the criterion leads to the BMG forming composition optimization.

2. Composition design

The Cu–Zr binary system is a typical glass-forming eutectic system, in which metallic glasses are formed by melt spinning over a broad composition range covering both the Cu-rich and Zr-rich corners. In the study of the Cu-based Cu–Zr–Al glass formation [5], binary Cu–Zr icosahedral clusters Cu_9Zr_4 and Cu_8Zr_5, and capped

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Archimedes anti-prism Cu_6Zr_5 are selected from topological close packing consideration, which are the nearest-neighbor clusters centered by small Cu atom with different coordination numbers in local structures of Cu–Zr phases. While Cu_9Zr_4 does not correspond to any eutectic composition, Cu_8Zr_5 exactly falls on the deepest eutectic composition $Cu_{61.8}Zr_{38.2}$, and Cu_6Zr_5 falls close to the next deepest eutectic composition $Cu_{56}Zr_{44}$. These three specific cluster compositions are used to define the *e*/*a*-variant lines, by linking Cu_9Zr_4, $Cu_{61.8}Zr_{38.2}$ and $Cu_{56}Zr_{44}$ to the third constituent element Ti in Cu–Zr–Ti ternary phase diagram (Fig. 1). The three lines represent respectively the composition series $(Cu_9Zr_4)_{1-x}Ti_x$, $(Cu_{61.8}Zr_{38.2})_{1-x}Ti_x$ and $(Cu_{56}Zr_{44})_{1-x}Ti_x$. In calculating the *e*/*a* values of the Zr-based alloys, conduction electron contributions of 1, 1.5 and 1.5 are respectively assigned to Cu, Zr and Ti [8]. The reported alloy $Cu_{60}Zr_{30}Ti_{10}$ is also considered in the present investigation as the reference sample.

3. Experimental procedure

Ingots of the $(Cu_9Zr_4)_{1-x}Ti_x$, $(Cu_{61.8}Zr_{38.2})_{1-x}Ti_x$ and $(Cu_{56}Zr_{44})_{1-x}Ti_x$ alloys were prepared by using arc melting under argon atmosphere. The purities of elements are 99.99 wt% for Cu, 99.9 wt% for Zr and 99.99 wt% for Ti, respectively. Alloy rods with a diameter of 3 mm were prepared by means of copper mould suction casting. The weight loss is less than 0.1% after the whole preparation process. The reference alloy $Cu_{60}Zr_{30}Ti_{10}$ [4] was also prepared under the same conditions. Structural identification of these alloys was carried out by means of X-ray diffractometry (XRD) on the bottom of the rods using Cu K_α radiation ($\lambda = 0.15406$ nm). Differential Scanning Calorimetry (DSC) and Differential thermal analysis (DTA) were employed to study the thermodynamic behaviors of the BMGs obtained along the *e*/*a*-variant lines. The thermal analysis experiments were carried out on a Mettler DSC822^e and a Mettler TGA/SDTA851^e at a heating rate of 0.33 K/s.

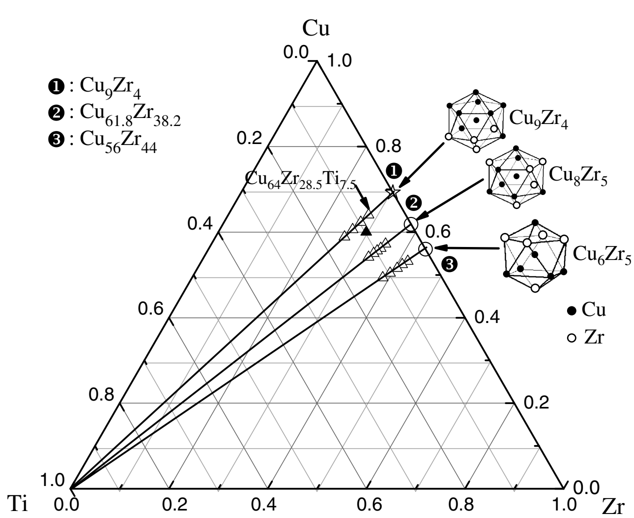

Fig. 1. Composition chart of the Cu–Zr–Ti system. Three '*e*/*a*-variant' composition lines and the corresponding binary atomic clusters are marked. The open triangles represent the BMG-forming compositions in our ϕ3 rods, the filled triangle the reported composition as the reference, the open circles the deep Zr–Cu eutectic points, and the open pentacle the icosahedral cluster composition.

4. Results

XRD results show that BMGs are formed within a range of Ti content from 7.5 to 15 at.% (an *e*/*a* range of 1.180–1.206) along the $(Cu_9Zr_4)_{1-x}Ti_x$ line, from 7.5 to 12.5 at.% (an *e*/*a* range of 1.214–1.23) along the $(Cu_{61.8}Zr_{38.2})_{1-x}Ti_x$ line, and from 5 to 12 at.% (an *e*/*a* range of 1.234–1.254) along the $(Cu_{56}Zr_{44})_{1-x}Ti_x$ line, as shown in Fig. 1. The *e*/*a* values do not vary much in the three glass forming ranges and can be regarded as being constant.

The DSC and DTA traces of these three series of BMGs are shown in Figs. 2–4. Those of the reported BMG $Cu_{60}Zr_{30}Ti_{10}$ are also included in Fig. 2. Obvious glass transitions are manifested in the DSC traces, followed by several crystallization exothermic peaks. At an elevated temperature, endothermic peaks appear in the DTA traces, indicating the melting process. The glass transition temperature (T_g), the onset temperature of crystallization (T_x), the onset temperature of melting (T_m) and the offset melting point (T_l) of these BMGs are all shown in Table 1.

5. Discussion

The characteristic thermodynamic temperatures of these three serial BMGs are all very sensitive to composition. On every composition line, T_g and T_x decrease monotonically with increasing Ti content, making ΔT_x a decreasing tendency. The variations of T_l of these three series BMGs are similar to those of T_g and T_x, while T_m does not vary much. As a result, the melting region becomes narrow as Ti increases, but the melting is always a multi-peak process. The characteristic temperatures of the reference BMG $Cu_{60}Zr_{30}Ti_{10}$ are also listed in Table 1. They agree fairly well with the reported values [4] and the small discrepancies may be due to the different heating rates used in the thermal analyses, 0.33 K/s in the present case and 0.67 K/s in Ref. [4].

The thermal stability of a metallic glass is evaluated generally by T_g or T_x. The higher the T_g and T_x, the higher the thermal stability of the metallic glass. T_g and T_x of these three serial BMGs decrease monotonously with increasing Ti content, which indicates the thermal stability is weakening. Among the three alloy series, the T_g and T_x values of the $(Cu_9Zr_4)_{1-x}Ti_x$ BMGs are distinctively higher than those of the $(Cu_{61.8}Zr_{38.2})_{1-x}Ti_x$ and $(Cu_{56}Zr_{44})_{1-x}Ti_x$ BMGs. This shows that the thermal stability of the $(Cu_9Zr_4)_{1-x}Ti_x$ BMGs are the highest among the three series. The $Cu_{64}Zr_{28.5}Ti_{7.5}$ BMG of this series has the largest thermal stability, and its characteristic temperatures are $T_g = 736$ K, $T_x = 769$ K.