Unusual Glass-Forming Ability of New Zr-Cu-Based Bulk Glassy Alloys Containing an Immiscible Element Pair

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We herein report the unusual glass-forming ability (GFA) of a new series of quinary Zr$_{48}$Cu$_{36-x}$Ni$_x$Ag$_8$Al$_8$ (0 < x ≤ 10 at%) alloys, in which Ni-Ag element pair is an immiscible system with a large positive heat of mixing. Addition of Ni lowers the liquidus temperature of the quaternary Zr$_{48}$Cu$_{36}$Ag$_8$Al$_8$ alloy. By copper mold casting, an as-cast glassy rod with a diameter of 30 mm can be easily obtained for the representative alloy Zr$_{48}$Cu$_2$Ni$_8$Ag$_8$Al$_8$. The possible reasons for the excellent GFA of the new quinary alloys with an immiscible element pair are discussed based on the atomic size distribution, chemical compatibility among the components and atomic structure of glassy alloys.

Keywords: bulk metallic glasses, zirconium-copper-based alloys, glass-forming ability, chemical compatibility

1. Introduction

Bulk metallic glasses (BMGs) have attracted great attention in recent years due to their scientific interests and engineering significance.\textsuperscript{1)} Extensive experimental and theoretical efforts in this area have been made to develop BMG-forming alloys and study their glass-forming ability (GFA). During the past two decades, BMGs have been found in a number of alloy systems, for example, multicomponent Zr-based, Mg-based, La-based, Pd-based and Fe-based alloy systems et al.\textsuperscript{2–6)} The critical sizes for these BMGs range from several micrometers to several centimeters. However, only several BMGs were reported to have a critical diameter of over 25 mm for glass-formation.\textsuperscript{2–6)} The limited dimensions of the BMGs seriously prevent further extension of commercial applications of BMGs. Consequently, much effort has been devoted to develop BMGs with higher GFA.

Recently, we developed a new series of quaternary Cu-Zr-based BMGs with high GFA in Cu$_{42-x}$Zr$_{42+x}$Ag$_8$Al$_8$ (x = 0, 2, 4, 6, 8, 10 at%) alloys.\textsuperscript{7)} In particular, the Zr$_{48}$Cu$_{36}$Ag$_8$Al$_8$ alloy was found to have a large critical diameter of 25 mm for glass-formation.\textsuperscript{8)} As similar for a number of multicomponent bulk glassy alloys,\textsuperscript{1)} we hope to make an optimum alloying to more multicomponent system for the Zr$_{48}$Cu$_{36}$Ag$_8$Al$_8$ alloy to improve its GFA. Previous works showed that Ni addition can significantly increase the GFA of the Zr-Cu-based alloys.\textsuperscript{2,3,7)} Moreover, the atomic size of Ni is nearly equivalent to that of Cu. Accordingly, the Ni addition to replace the Cu might increase the chemical complexity and confuse the Zr$_{48}$Cu$_{36}$Ag$_8$Al$_8$ alloy system, which may lead to higher GFA. Therefore, in recent work, we examined the effect of addition of nickel to replace the copper on the GFA of the quaternary Zr$_{48}$Cu$_{36}$Ag$_8$Al$_8$ alloy. Although the Ni-Ag element pair shows evident immiscibility with large positive heat of mixing, the new quinary Zr$_{48}$Cu$_{36-x}$Ni$_x$Ag$_8$Al$_8$ alloys were found to exhibit very high GFA. The representative Zr$_{48}$Cu$_{36}$Ni$_8$Ag$_8$Al$_8$ alloy can easily form a glassy rod with a diameter of 30 mm using a copper mold casting method. In this paper, we report the glass-forming in this new series of quinary Zr$_{48}$Cu$_{36-x}$Ni$_x$Ag$_8$Al$_8$ (0 < x ≤ 10, in at%) alloys. The possible reasons for the excellent GFA of the new quinary alloys with an immiscible element pair will be discussed.

2. Experimental Methods

Multicomponent alloy ingots with nominal compositions of Zr$_{48}$Cu$_{36-x}$Ni$_x$Ag$_8$Al$_8$ (x = 0, 2, 4, 6, 8, 10) were prepared by arc melting mixtures of Zr, Cu, Ni, Al and Ag with a purity of 99.5%, 99.99%, 99.99%, 99.99% and 99.99%, respectively, in a high purity argon atmosphere. Each ingot was melted four times in the arc melter to avoid the chemical heterogeneity. The ingots were remelted in a copper hearth using an arc furnace and then poured into copper molds under a high purity argon temperature. The copper molds have internal cylindrical cavities of diameters ranging from 20 to 30 mm. Ribbon samples with a cross section of 0.02 × 1.2 mm$^2$ were prepared by melt spinning. The structure of the as-cast samples was examined by X-ray diffraction (XRD) using Cu-K$\alpha$ source. Thermal stability associated with glass transition and crystallization was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K s$^{-1}$. The melting behavior was examined by differential thermal analysis (DTA) at a heating rate of 0.33 K s$^{-1}$.

3. Results

Figure 1(a) shows a Zr$_{48}$Cu$_{32}$Ni$_4$Ag$_8$Al$_8$ master ingot with a weight of 20 gram prepared by arc-melting mixtures of the elements. The surface of the ingot exhibits mirror-like luster. XRD and optical examinations revealed that the master ingot is composed of more than 95% glassy phase and a 1-mm layer of crystallites at the bottom, indicating that the growth of the crystalline phases in the supercooled liquid is quite sluggish. Figure 1(b) shows the outer shape of an as-cast Zr$_{48}$Cu$_{32}$Ni$_4$Ag$_8$Al$_8$ alloy rod with a diameter of 30 mm. The sample exhibits good metallic luster and no distinct concave can be recognized on its surface, indicating the absence of evident crystallization during the preparation of the bulk sample. Figure 2(a) shows the XRD patterns of

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the as-cast bulk rods with a diameter of 30 mm for the Zr$_{48}$Cu$_{36}$/Co$_x$Ni$_x$Ag$_8$Al$_8$ ($x = 0, 2, 4, 6$) alloys. The detected region for XRD examination was the central part of the cross-section of the bulk samples. It can be seen that the pattern of the Zr$_{48}$Cu$_{32}$/Ni$_4$Ag$_8$Al$_8$ rod consists of only a series of broad diffraction maxima without any detectable sharp Bragg peaks, indicating that this 30-mm diameter sample is mostly amorphous. For comparison, the CuZr phase precipitated from the other alloy rods. However, it can be found that the other alloy rods, even though the partially crystallized, still possess very large amorphous fractions judging from the broad diffraction background on their XRD patterns. We also found that the critical diameter ($d_c$) for the Zr$_{48}$Cu$_{36}$/Ni$_4$Ag$_8$Al$_8$ alloy with rather high content of Ni is near 20 mm (see the Table 1). These results imply that the Zr$_{48}$Cu$_{36}$/Ni$_4$Ag$_8$Al$_8$ alloy system exhibits unusual high GFA. The DSC analysis was also carried out to confirm the formation of a single glassy phase in the central region of the 30-mm Zr$_{48}$Cu$_{32}$/Ni$_4$Ag$_8$Al$_8$ rod. Figure 2(b) shows the DSC curve of the Zr$_{48}$Cu$_{33}$/Ni$_4$Ag$_8$Al$_8$ rod with a diameter of 30 mm in comparison with that of the melt-spin glassy alloy ribbon. The sample for DSC measurement was taken from the central region of the 30-mm rod. Consistent with the ribbon sample, the bulk sample exhibits a sequent transition of an endothermic reaction due to glass transition and an exothermic peak due to crystallization on the DSC profile, demonstrating the as-cast glassy structure of this sample as concluded from its XRD pattern.

In order to investigate the reason for the high GFA of the new quinary alloys, the thermal stability and melting
behavior of the Zr_{48}Cu_{36-x}Ni_{x}Ag_{8}Al_{8} glassy alloys were examined by DSC and DTA. Figure 3 shows the DSC curves of the melt-spun Zr_{48}Cu_{36-x}Ni_{x}Ag_{8}Al_{8} glassy samples. All the samples exhibit a clear glass transition to a supercooled liquid state and then crystallization. The glass transition temperature \( T_g \) and the onset temperature of crystallization \( T_c \) are marked with arrows in Fig. 3. The \( T_g \) monotonously increases from 683 to 692 K with increasing the Ni content. On the contrary, the \( T_c \) increases from 791 to 799 K with adding of 2% Ni, and then decreases from 788 to 768 K as the content of Ni increases from 4 to 10%. Thus, the Zr_{48}Cu_{34}Ni_{2}Ag_{8}Al_{8} has a very large supercooled liquid region \( \Delta T_g \) \( (\Delta T_g = T_c - T_g) \) of 116 K. Figure 4 shows the DTA curves of the Zr_{48}Cu_{36-x}Ni_{x}Ag_{8}Al_{8} alloys, in which the liquidus temperature \( T_l \) is marked with arrows. As the Ni content increases, the \( T_l \) decreases from 1143 to 1129 K in the range from 0 to 4 at% Ni, and then increases with further increasing Ni content. It is worth noting that the Zr_{48}Cu_{32}Ni_{4}Ag_{8}Al_{8} alloy has the lowest \( T_l \) in the alloy series of Zr_{48}Cu_{36-x}Ni_{x}Ag_{8}Al_{8}, which is consistent with the highest GFA of the alloy. Based on the thermal data obtained by DSC and DTA, three well-known criteria for GFA, i.e., the temperature interval of the supercooled liquid region \( \Delta T_g \), the reduced glass transition temperature \( T_{gR} \) \( (T_{gR} = T_g / T_i) \) and \( \gamma \) \( (\gamma = T_s / (T_g + T_i)) \) are listed in Table 1. However, we cannot see a strong correlation for the GFA (or \( d_i \)) with \( \Delta T_g \), \( T_{gR} \) or \( \gamma \) for the Zr_{48}Cu_{36-x}Ni_{x}Ag_{8}Al_{8} alloys.

4. Discussion

The alloys with high GFA always belong to the multi-component alloy systems consisting of more than three elements which exhibit significantly different atomic size mismatch ratios of over 12% and negative heats of mixing. \(^1\) The atomic structure of metallic glasses is characterized not only by randomness but also by short range order (SRO), medium range order (MRO) and efficient atomic packing around both solute and solvent atoms. \(^10\) To understand the unusual high GFA of the present quinary alloys, the atomic size distribution, chemical compatibility among the components and atomic structure of glassy alloys must be taken into account together. The optimal atomic size ratio \( R \) between solute and solvent atoms is crucial for efficient atomic packing and potential energy minimization in both liquid and glassy state. \(^10\) In the present system, the atomic radius of the solvent atom Zr \( (r_Zr) \) is 0.158 nm; for the atom radii of the solute atoms, \( r_{Cu} = 0.128 \) nm, \( r_{Ag} = 0.144 \) nm, \( r_{Al} = 0.143 \) nm, \( r_{Ni} = 0.124 \) nm, respectively. Therefore, \( R_{Cu/Zr} = 0.81 \), \( R_{Ag/Zr} = 0.91 \), \( R_{Al/Zr} = 0.90 \), \( R_{Ni/Zr} = 0.78 \). From an efficient packing point of view, the icosahedral type clusters could be the preferred SRO in metallic glass when R is close to 0.85. \(^12\) This is because the R~0.85 is energetically most favored in forming icosahedral clusters. Computer simulations have shown that the atomic size ratio \( R \) is close to 0.85, the potential energy of icosahedral cluster approaches minimum in metallic glasses. \(^13\) Therefore, the present combination of atomic sizes can produce an efficiently packed local structure. In the meantime, it is seen that the heats of mixing are negative for Zr-Ni, Zr-Cu, Zr-Al, Zr-Ag, Ni-Al, and Cu-Al pairs. \(^15\) The negative heats of mixing would 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. \(^16\) Based on the above discussion, it is concluded that the addition of Ni to replace Cu should cause denser packing in the liquid state and lead to higher viscosity and lower atomic mobility due to the chemical complexity and compatibility. This may be the reason for the increase of GFA as the compositions changed from the quaternary Zr_{38}Cu_{36}Al_{8}Ag_{8} to the quinary Zr_{48}Cu_{32}Ni_{4}Al_{8}Ag_{8} alloy.

However, it is noted that Ni-Ag element pair is an immiscible system with a large positive heat of mixing \( (\Delta H_m = 15 \text{ KJ/mol}) \). \(^15\) Addition of the solute elements with positive heats of mixing between solute additions and host elements or alloy components was considered to degrade the GFA or lead to limited GFA enhancement, since repulsive chemical interaction can result in segregation of the component atoms and increase the potential energy of a system. \(^17\) Thus, our present results are clearly inconsistent with this rule. This is most likely because of the absence of the direct solute-solute contacts or solute-solute avoidance. \(^12\)

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Fig. 3 DSC curves of the melt-spun Zr_{48}Cu_{36-x}Ni_{x}Ag_{8}Al_{8} (x = 0, 2, 4, 6, 8, 10) glassy alloys. The upward arrows refer to the glass transition temperatures and downward arrows refer to the onset of the first crystallization events.

Fig. 4 Melting behaviors of the Zr_{48}Cu_{36-x}Ni_{x}Ag_{8}Al_{8} (x = 0, 2, 4, 6, 8, 10) alloy at a heating rate of 0.33 Ks\(^{-1}\). The arrows refer to the liquidus temperatures.
According to Sheng’s work,\textsuperscript{12} a net-work-type arrangement of the solute atoms should take form for the Zr\textsubscript{48}Cu\textsubscript{36−x}Ni\textsubscript{x}Ag\textsubscript{8}Al\textsubscript{8} alloys due to high solute concentration of Cu. It is imaged that to replace Cu with topological equivalent but chemically distinct Ni might cause a much more confused net structure with a lower potential energy, which corresponds to higher GFA of the quinary Zr\textsubscript{48}Cu\textsubscript{36−x}Ni\textsubscript{x}Ag\textsubscript{8}Al\textsubscript{8} alloys. On the other hand, there should be little or no Ni-Ag atomic pair correlation in the solute net structure. Otherwise, the potential energy of the alloy system would be increased,\textsuperscript{17} which would be deleterious to GFA. Therefore, Ni-Ag avoidance should exist in the quinary Zr\textsubscript{48}Cu\textsubscript{36−x}Ni\textsubscript{x}Ag\textsubscript{8}Al\textsubscript{8} glassy alloys. And then, the contacted elements can still satisfy the negative heats of mixing among the constituent elements. In comparison with addition of Ni, we also examined the effect of addition of topological equivalent Fe to replace Cu on GFA of the quaternary Zr\textsubscript{48}Cu\textsubscript{36}Ag\textsubscript{8}Al\textsubscript{8} alloy, since Fe exhibits immiscibility with not only Ag but also Cu. We found that addition of Fe significantly increases the liquidus temperature and seriously decreases the GFA of the quaternary Zr\textsubscript{48}Cu\textsubscript{36}Ag\textsubscript{8}Al\textsubscript{8} alloy,\textsuperscript{19} Based on the above discussion, this observation is not surprising because the occurrence of Fe-Cu contact could not be avoided in the network-type arrangement of the solute Cu.

5. Conclusion

We have reported the unusual GFA of a series of quinary Zr\textsubscript{48}Cu\textsubscript{36−x}Ni\textsubscript{x}Ag\textsubscript{8}Al\textsubscript{8} (0 < x ≤ 10) alloys, in which Ni-Ag element pair is an immiscible system with a large positive heat of mixing. By copper mold casting, an as-cast glassy rod with a diameter of 30 mm can be easily obtained for the representative alloy Zr\textsubscript{48}Cu\textsubscript{32}Ni\textsubscript{4}Ag\textsubscript{8}Al\textsubscript{8}. The superior GFA of the quinary Zr\textsubscript{48}Cu\textsubscript{32}Ni\textsubscript{4}Ag\textsubscript{8}Al\textsubscript{8} alloy is related to a lower liquidus temperature as compared with the matrix Zr\textsubscript{48}Cu\textsubscript{36}Ag\textsubscript{8}Al\textsubscript{8} alloy. The increase of the GFA by Ni addition may be due to the chemical complexity and compatibility, which can cause denser packing in the liquid state and lead to higher viscosity and lower atomic mobility. Ni-Ag avoidance should be responsible for non-reduction of GFA of the quinary Zr\textsubscript{48}Cu\textsubscript{36−x}Ni\textsubscript{x}Ag\textsubscript{8}Al\textsubscript{8} alloys. The results provide a new view to the choice of elements for designing a BMG-former. Moreover, the finding of the new bulk glassy alloy with the extremely high GFA is promising the future extension of application fields of bulk glassy alloys.

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