



## Effect of substituting elements on glass-forming ability of the new $Zr_{48}Cu_{36}Al_8Ag_8$ bulk metallic glass-forming alloy

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### ABSTRACT

The effect of substituting elements on the glass-forming ability (GFA) of the quaternary  $Zr_{48}Cu_{36}Al_8Ag_8$  alloy was investigated by thermal analysis and copper mold casting. Early transition metal Zr is replaced by Ti, Nb and Hf; and late transition metal Cu is substituted with Fe, Au, Pd and Ni. Addition of Ni and Pd was found to improve the GFA of the  $Zr_{48}Cu_{36}Ag_8Al_8$  alloy. Addition of Au to replace Cu or Hf to replace Zr decreases the GFA slightly, while addition of Ti, Nb and Fe significantly degrade GFA. A good consistency between the GFA and the  $T_l$  or  $\gamma$  exists among all the alloys. The possible mechanisms for the improvement or damage to the GFA of the  $Zr_{48}Cu_{36}Al_8Ag_8$  alloy by addition of the substituting elements are interpreted in view of Inoue's three empirical rules and atomic structure of glassy alloys.

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### 1. Introduction

Bulk metallic glasses (BMGs) have been drawing increasing attention in recent years due to their superb properties, such as high strength, high corrosion resistance, etc. [1]. Generally, the alloys with high GFA always belong to the multicomponent alloy systems consisting of more than three constituent elements, which exhibit significantly different atomic size mismatch ratios of over 12% and negative heats of mixing [1]. Following these empirical rules, the researchers have successfully found a number of BMG-forming alloys [1]. However, only a small number of alloys have been reported to show a critical diameter larger than 20 mm. As a result, the engineering commercialization of BMGs as structural materials is hindered by their limited glass-forming ability (GFA). Therefore, extensive experimental and theoretical efforts in this area have been made to develop large size BMGs and study their GFA.

To make BMGs, one must frustrate the process of crystallization. It was also proposed that the more elements involved, the lower the chance that the alloy can select viable crystal structures, and the greater the chance of glass formation [2]. Thus, many researchers tried to add the alloying elements into a base system in order to develop new BMGs with higher GFA. One method for doing so is to add an element into a base alloy without considering the complex nature of element interactions or atomic size, which was usually

used to microalloy BMG-forming alloys [3,4]. Another way is to substitute the constituent element of the base alloy with the elements with the similar atomic size and chemical compatibility as the constituent elements, for example substituting Ti for Zr or Ni for Cu in Zr-based BMGs. As compared with microalloying addition, the later method seems to more effective in developing BMG-forming alloy with high GFA, since several famous BMG-forming alloys were developed based on this consideration [1,5].

Zr–Cu-based BMGs are prospective structural engineering materials because of their high strength and good corrosion resistance as well as low cost. Recently, a new series of quaternary Zr–Cu–Al–Ag alloy system [6,7]. One of representative alloy with a composition of  $Zr_{48}Cu_{36}Ag_8Al_8$  was found to have a large critical diameter of 25 mm for glass formation [8]. Furthermore, with partial substitution of Pd or Ni for Cu, the critical diameters were found to increase from 25 to 30 mm for the  $Zr_{48}Cu_{36}Ag_8Al_8$  alloy [9,10]. Although some explanations have been given [11], the underlying mechanisms and principles of the addition of substituting elements in this alloy are still unclear.

In this work, we systemically examined the effects of the substituting elements on the GFA of the  $Zr_{48}Cu_{36}Al_8Ag_8$  alloy. Early transition metal Zr is replaced by Ti, Nb or Hf; and late transition metal Cu is substituted with Fe, Au, Pd or Ni. All the substituting elements exhibit the similar atomic size and chemical compatibility as the substituted constituent elements. Moreover, the possible mechanisms for the improvement or damage to the GFA of the  $Zr_{48}Cu_{36}Al_8Ag_8$  alloy by addition of the substituting elements are discussed.

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**Table 1**Thermal data and the critical diameters ( $d_c$ ) of the  $Zr_{48-x}M_xCu_{36}Al_8Ag_8$  ( $M=Ti, Hf$  and  $Nb$ ;  $x=0, 2, 4, 6$ ) and  $Zr_{48}Cu_{36-x}N_xAl_8Ag_8$  ( $N=Fe$  and  $Au$ ;  $x=0, 2, 4, 6$ ) alloys.

	$T_g$ (K)	$T_x$ (K)	$T_l$ (K)	$\Delta T_x$ (K)	$T_{rg}$	$\gamma$	$d_c$ (mm)
$Zr_{48}Cu_{36}Al_8Ag_8$	690	791	1143	101	0.604	0.432	25
Ti2	696	750	1145	54	0.608	0.407	10
Ti4	700	738	1181	38	0.593	0.392	<10
Ti6	704	731	1212	27	0.581	0.381	<5
Hf2	692	794	1147	102	0.603	0.432	20–25
Hf4	694	795	1155	101	0.601	0.430	20
Hf6	695	796	1187	101	0.585	0.423	15
Nb2	707	765	1150	58	0.614	0.412	10
Nb4	709	759	1209	50	0.586	0.395	<10
Nb6	715	755	1218	40	0.587	0.390	<5
Fe2	705	806	1169	101	0.603	0.430	10
Fe4	706	799	1213	93	0.582	0.416	<10
Fe6	708	797	1238	89	0.571	0.409	<5
Au2	705	799	1153	94	0.611	0.430	20
Au4	713	806	1153	93	0.618	0.432	20
Au6	723	813	1159	90	0.624	0.432	15
Pd2	699	794	1140	95	0.613	0.432	30
Pd4	705	795	1153	90	0.611	0.427	25
Pd6	709	796	1155	87	0.614	0.427	20
Ni2	687	797	1131	110	0.607	0.438	25
Ni4	693	788	1129	95	0.614	0.432	30
Ni6	695	779	1131	84	0.614	0.426	25

## 2. Experimental methods

Multicomponent alloy ingots with nominal compositions of  $Zr_{48-x}M_xCu_{36}Al_8Ag_8$  ( $M=Ti, Hf$  and  $Nb$ ;  $x=0, 2, 4, 6$ ) and  $Zr_{48}Cu_{36-x}N_xAl_8Ag_8$  ( $N=Fe, Ni, Pd$  and  $Au$ ;  $x=0, 2, 4, 6$ ) were prepared by arc melting mixtures of elements with high purity 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 atmosphere. The copper molds have internal cylindrical cavities of diameters ranging from 10 to 30 mm. Ribbon samples with a cross-section of  $0.02\text{ mm} \times 1.2\text{ mm}$  were prepared by melt spinning. The structure of the as-cast samples and mater ingots 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  $0.67\text{ K/s}$ . The liquidus temperature was examined by differential thermal analysis (DTA) at a heating rate of  $0.33\text{ K/s}$ . This is an express method which let us roughly estimate the liquidus temperature  $T_l$  value. The upper offset temperature (after the endothermic peak) has been used as a relative  $T_l$  value. The authors understand that this is rather imprecise method to determine  $T_l$  and this value depends on the machine used. However, for one group of alloys in a single set of experiments it seems to be acceptable for express determination of  $T_l$  for many alloys which otherwise will be a very time consuming procedure. Sometimes researchers prefer to use peak temperature of the endothermic peak as  $T_l$ . However, in some alloys the endothermic peak consists of two peaks—high and low-temperature one.

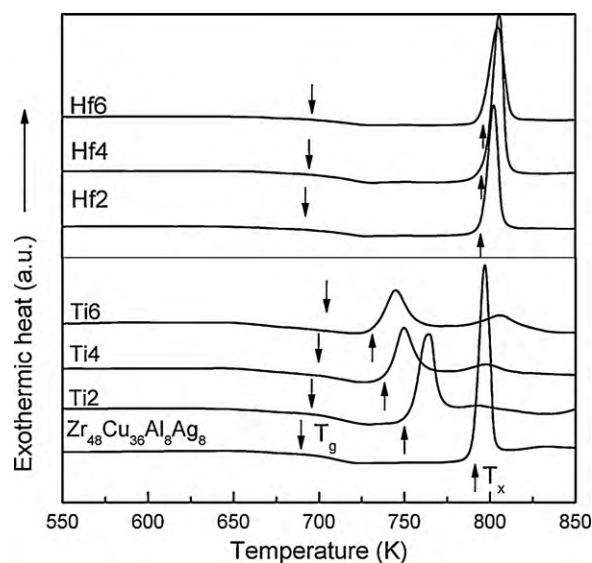
## 3. Results and discussion

### 3.1. Substitution of Ti, Hf and Nb for Zr

Thermal properties of these glassy alloys, including the glass transition temperature ( $T_g$ ) and the onset temperature of the first crystallization event ( $T_x$ ) were measured with DSC. The value of  $T_g$  is determined by analyzing the temperature dependence of heat flow.  $T_g$  is the temperature corresponding to the intersection of two tangents at the start of the corresponding endotherm in DSC curve. The characteristic data are listed in Table 1 and the DSC curves of the representative alloys with addition of Ti or Hf are shown in Fig. 1. The glassy samples exhibit a clear endothermic heat event due to the glass transition, followed by a supercooled liquid region and then exothermic transformations from the supercooled liquid to equilibrium crystalline phases. The  $T_g$  and  $T_x$  are marked with arrows in Fig. 1. One can see that the addition of Ti to replace of Zr increases the  $T_g$  and significantly decreases the  $T_x$ . As a result, the supercooled liquid region  $\Delta T_x$  ( $\Delta T_x = T_x - T_g$ ) decreases from 101 K for the base alloy to 27 K for the alloy with addition of 6 at.% Ti. The alloys with addition of Nb show the similar thermal properties as

the alloys with addition of Ti. As listed in Table 1, addition of Nb seriously decreases the  $\Delta T_x$ . It is worth noting that substitution of Hf for Zr does not obviously affect the thermal stability of the base alloy. As listed in Table 1, the value of  $\Delta T_x$  of the alloys containing Hf is the same as the base alloy. Fig. 2 shows the DTA curves of the  $Zr_{48-x}M_xCu_{36}Al_8Ag_8$  ( $M=Ti, \text{ and } Hf$ ;  $x=0, 2, 4, 6$ ) alloy, where the liquidus temperature  $T_l$  is marked with arrows, which corresponds to the intersection of two tangents at the end of the corresponding endotherm in DTA curve (The data for addition of Nb is also listed in Table 1). It is seen that addition of the early transition substituting elements increases the liquidus temperature  $T_l$ , especially in case of addition of Ti or Nb. As listed in Table 1, addition of 6 at.% Ti or Nb increases  $T_l$  from 1143 to 1212 K or 1218 K.

The GFA of the alloys was evaluated by microstructure of master ingot and copper mold casting. The bulk samples with the same size were prepared twice. In order to reduce materials cost, the copper molds with diameters ranging from 5 to 30 mm in 5 mm step were used to evaluate the critical diameter. Previous work showed that the ingot of the base alloy prepared by arc furnace exhibits an amor-



**Fig. 1.** DSC curves of the  $Zr_{48-x}M_xCu_{36}Al_8Ag_8$  ( $M=Ti, Hf$  and  $Nb$ ;  $x=0, 2, 4, 6$ ) glassy ribbon samples.

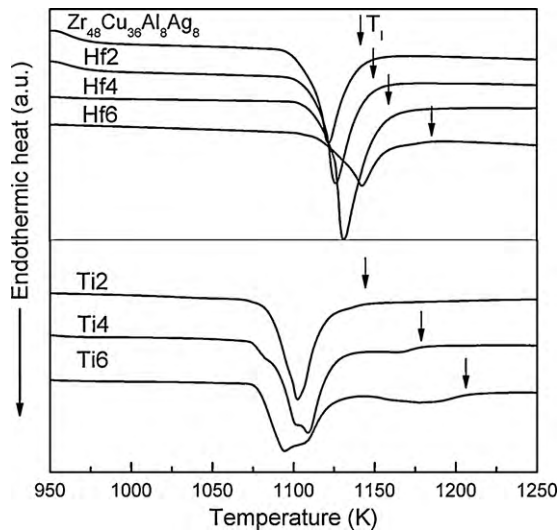


Fig. 2. DTA curves of the  $Zr_{48-x}M_xCu_{36}Al_8Ag_8$  ( $M = Ti, Hf$  and  $Nb$ ;  $x = 0, 2, 4, 6$ ) alloys.

phous structure [8,12]. Similar to the base alloy, the master ingots of the alloys with addition of Hf show an amorphous structure. However, the volume of glassy phase in ingots is lower than that of the base alloy, indicating that addition of Hf slightly decreases the GFA of the base alloy. Based on the results of copper mold casting, the critical diameter ( $d_c$ ) was found to range from 20 to 25 mm for the alloys with addition of 2–4 at.% Hf. In case of addition of Ti or Nb, no any amorphous phase was found in ingots. Even if with 4 at.% addition, the bulk glassy rod with a diameter of 10 mm cannot be formed by copper mold casting. This indicates that the GFA was significantly deteriorated by addition of Ti or Nb to replace Zr.

### 3.2. Substitution of Fe or Au for Cu (see Refs. [9,10] for substitution of Ni or Pd for Cu)

Fig. 3 shows the DSC curves of  $Zr_{48}Cu_{36-x}N_xAl_8Ag_8$  ( $N = Fe$  and  $Au$ ;  $x = 0, 2, 4, 6$ ) glassy ribbon samples. It is seen that addition of Au or Fe increases the  $T_g$  and  $T_x$ . However, the  $\Delta T_x$  decreases with

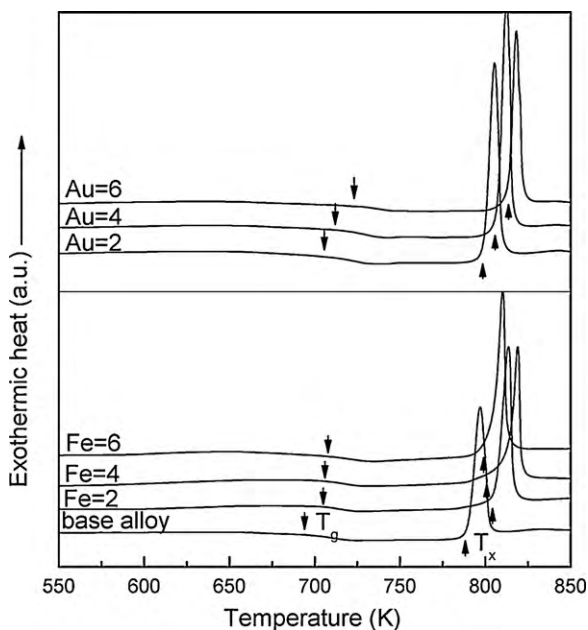


Fig. 3. DSC curves of  $Zr_{48}Cu_{36-x}N_xAl_8Ag_8$  ( $N = Fe$  and  $Au$ ;  $x = 0, 2, 4, 6$ ) glassy ribbon samples.

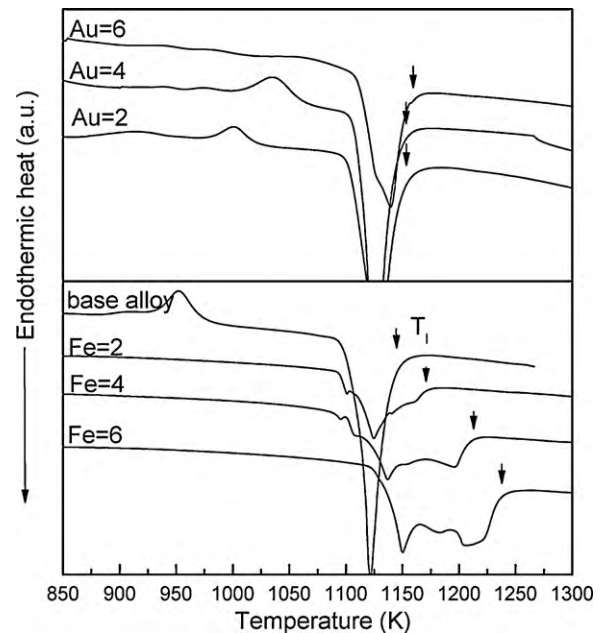


Fig. 4. DTA curves of  $Zr_{48}Cu_{36-x}N_xAl_8Ag_8$  ( $N = Fe$  and  $Au$ ;  $x = 0, 2, 4, 6$ ) alloys.

addition of Au or Fe, as listed in Table 1. Fig. 4 shows the DTA curves of  $Zr_{48}Cu_{36-x}N_xAl_8Ag_8$  ( $N = Fe$  and  $Au$ ;  $x = 0, 2, 4, 6$ ) alloys. As shown in Fig. 4, addition of Au increases the  $T_g$  slightly, while addition of Fe significantly increases the  $T_g$ .

Although the master ingots of the alloys with addition of Au to replace Cu show amorphous structure, the GFA of the based alloy does not improved by addition of Au, which is very similar to addition of Hf. The  $d_c$  was found to range from 20 to 25 mm for the alloys with addition of 2–4 at.% Au. For addition of Fe, the GFA was seriously degraded. Even if with 4 at.% addition, the bulk glassy rod with a diameter of 10 mm cannot be formed by copper mold casting, which is very similar to addition of Ti or Nb.

## 4. Discussion

Based on the above results and previous works [9,10], one can see that the GFA of the base alloy is significantly affected by different substituting element. Addition of Ni or Pd increases the  $d_c$  up to 30 mm; addition of Au or Hf decreases the GFA slightly, but addition of Ti, Nb or Fe seriously decreases the  $d_c$  less than 10 mm. In order to understand the effect of substituting elements, two well-known criteria for GFA, i.e., the reduced glass transition temperature  $T_{rg}$  ( $T_{rg} = T_g/T_l$ ) and ( $\gamma = T_x/(T_g + T_l)$ ) [13] are also listed in Table 1. Fig. 5 shows the variation of the  $d_c$ ,  $T_{rg}$ ,  $\gamma$  and  $T_l$  with content of substituting elements. We cannot see a strong correlation for the  $d_c$  with  $T_{rg}$ , for example, addition of 2 at.% Nb or Au decreases the GFA, but increases the value of  $T_{rg}$ . It seems that a good consistency between the  $d_c$  and the  $\gamma$  or  $T_l$  exists among all the alloys. The substituting elements that improve the GFA decrease the  $T_l$  or increases the  $\gamma$ , whereas the elements that degrade the GFA increase the  $T_l$  or decreases the  $\gamma$ . It is therefore clear that the effective substituting element is the one that can bring the base alloy to a deeper liquidus temperature and increase the  $\gamma$ .

Based on a number of BMG-forming alloys developed in Inoue group, Prof. Inoue proposed a simple three empirical rules for achieving high GFA as follows: (1) multicomponent system consisting of more than three elements, (2) significantly difference in atomic size ratios above about 12% among the main constituent elements, and (3) negative heats of mixing among their elements [1]. From thermodynamic and kinetics points of view, the alloy

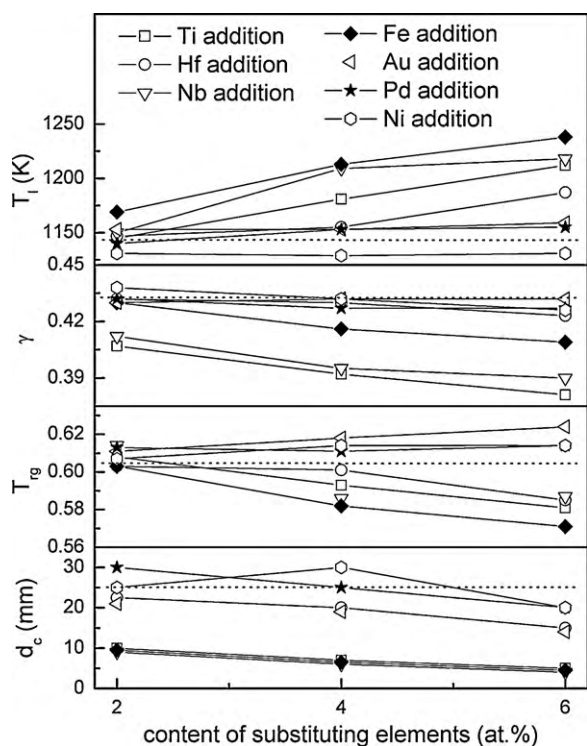


Fig. 5. Critical diameter ( $d_c$ ),  $T_g$ ,  $\gamma$  and  $T_l$  as a function of content of substituting elements. (The dot lines correspond to the values of the base alloy.)

satisfying the three empirical rules is closely related with the high-stabilized supercooled liquid with low potential energy [1], which generally results in high GFA. In the present work, the substituting element belongs to the same or neighboring family of the constituent elements in the periodic table. This indicates that the substituting elements show the similar atomic size and chemical compatibility as the main constituent elements. As a result, the new alloys developed by adding the substituting elements would conform to the three empirical rules as the base alloy, for example addition of Pd shows the similar effects as the Ni on topology of local atomic packing and chemical compatibility. This could be the main reason for the higher GFA of the quinary alloys caused by substitution of Ni or Pd for Cu.

However, due to the complex interaction among the constituent elements, some substituting elements sometimes lead to the opposite side, for example, addition of Fe, Ti or Nb seriously degrades the GFA of the base alloy. It is worth noting that the elements that degrade the GFA increase the  $T_l$ . Therefore, the negative side on GFA should be due to the increase of potential energy of the liquid state of the alloy, which is closely linked with the local atomic

structure of glassy phase. Recent work [14] reported that the atomic structure of metallic glasses consisted of a number of geometrically distinct polyhedron types with statistical frequencies, and certain polyhedra, which shows efficient atomic packing and low potential energy, appear with high frequencies. Consequently, it is assumed that the decrease of the GFA should be attributed to formation of much more polyhedral with high potential energy by addition of the substituting elements; for example, the immiscibility between Fe and Cu or Ag may seriously increase the potential energy of system. If the substituting elements do not distinctly change the atomic structure of the base alloy, the new alloys should show the similar GFA as the base alloy. This may be the reason for that addition of Au or Hf does not significantly change GFA of the base alloy. Unfortunately, a correlation between GFA and atomic structure has not been established up to now, since the true atomic structure of the glassy alloy is unknown. Therefore, to establish such correlation is a challenging but indispensable work for understanding the origination of GFA and designing new BMG-formers.

## 5. Conclusions

The GFA of  $Zr_{48}Cu_{36}Ag_8Al_8$  alloy is significantly affected by addition of substituting elements. Substitution of Ni or Pd for Cu improves the GFA of the  $Zr_{48}Cu_{36}Ag_8Al_8$  alloy; addition of Au to replace Cu or Hf to replace Zr does not distinctly change the GFA, while addition of Ti, Nb to replace Zr or Fe to replace Cu significantly degrade GFA. A good consistency between the GFA and the  $T_l$  and  $\gamma$  exists among all the alloys. The substituting elements that improve the GFA decrease the  $T_l$  and increases the value of  $\gamma$ , whereas the elements that degrade the GFA increase the  $T_l$  and decreases the value of  $\gamma$ . To locate a lower eutectic point with large  $\gamma$  is an effective way to develop a BMG-forming alloy with higher GFA.

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