Nitrogen-doping effect on glass formation and primary phase selection in Cu–Zr–Al alloys

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ABSTRACT

Effects of nitrogen doping on the glass formation and primary precipitate phase in a ternary Cu–Zr–Al alloy were investigated. An optimized doping level of nitrogen ($\sim$1000 appm) can improve the glass-forming ability of $Cu_{49}Zr_{44}Al_7$ alloy. The type of primary phases from ZrCu (B2) to an unknown Zr- and Al-rich crystalline phase with chemical atomic composition of around $Cu_{38}Zr_{49}Al_{13}$ in the bulk glassy matrix is controllable by the micro-adjustment of N concentration, which can be utilized as an effective way to design BMG-based composites with selective second phase particles.

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1. Introduction

Bulk metallic glasses (BMGs) have attracted a great attention due to their novel properties and broad potential applications as structural and functional metallic materials [1–3]. Rigorous fabrication conditions for glass formation influenced by many factors, e.g. purity of raw materials, cooling conditions and operation parameters, limit the practical applications of this kind of metastable alloys. Therefore, it is significant to improve the glass-forming ability (GFA) through a flexible control like adjusting alloy compositions. Many composition design methods, such as pinpointing, minor alloying additions and similar element substitution, have been employed to effectively enhance the GFA [4–12]. The constituent elements adopted in glass-forming systems have almost covered all of conventional metal and metalloid elements. As the most abundant elements in the Earth's atmosphere, nitrogen and oxygen are not easy to be excluded during the purification, melting and machining of metallic materials because of their strong interactions with most of the metal elements at high temperature [13–15]. The effect of this kind of nonmetal elements, e.g. N, O, and H, on the properties of traditional crystalline alloys and inorganic glasses has been intensively studied [15–17]. Mechanical and functional properties of these materials could be significantly influenced by the

ppm-level doping of nonmetal elements. However, the nonmetal elements have rarely been treated as alloying elements in the glass-forming systems [18]. Initially, the nonmetal element of oxygen is generally considered as impurities to severely deteriorate the GFA [19,20] and plasticity [21,22] of BMGs. Recently, it was reported that proper doping of oxygen ($\sim$0.1 at.%) can improve the GFA in some Fe- [23] and Zr-based [24] alloys. The results may give constructive implications that some nonmetal elements with extremely minor addition can be considered as a new group of alloying candidates for the improvement of GFA.

As a unique nonmetal element with plentiful resources and low costs, nitrogen is of importance in the alloying and surface-modification of steels as well as in the adulteration of oxide films, nanowires and carbon nanotubes [15,16,25,26]. However, as we know so far, no work has been performed to explore the roles of nitrogen during glass formation. There exists a high solubility [27] and strong affinity [28] between nitrogen and some main constituents, such as Zr and Ti, in commercial glass-forming systems. Thus an increase in the nitrogen content is basically inevitable during the preparation process of the BMGs, especially for the cost-effective industrial production using the commercial raw materials under low vacuum conditions. Therefore, it is necessary to examine the nitrogen effects on the glass formation of BMGs. In this study, different amounts of nitrogen were introduced into a Cu–Zr–Al ternary alloy with relatively low cost and great potential applications as structural materials [29], and the effect of nitrogen doping on the glass formation and primary precipitate phase was inves-

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Table 1
Nitrogen content, phase constituents, and thermal parameters of $Cu_{49}Zr_{44}Al_7$ alloys with different nitrogen additions.

Nitrogen content (appm)		Phase structure (ϕ5 mm)	T_g (K)	T_x (K)	ΔT_x (K)	T_m (K)	T_l (K)	T_s (K)	ΔT_u (K)	T_{rg}	γ
Nominal	Measured										
0	104	Amorphous + ZrCu (B2)	712	775	63	1147	1176	1145	31	0.605	0.410
1000	1200	Amorphous	710	775	65	1148	1183	1141	42	0.600	0.409
3000	3698	Amorphous + unknown phase	706	773	67	1149	1183	1143	40	0.597	0.409
5000	6237	Amorphous + unknown phase + $Cu_{10}Zr_7$	712	778	66	1148	1181	1144	37	0.603	0.411

tigated. Relevant results and underlying mechanisms related with phase competition and local atomic rearrangement are discussed in detail.

2. Experimental procedure

Considering the high N solubility of up to ~25 at.% in Zr according to equilibrium Zr–N binary phase diagram [27], a pre-alloy with a nominal composition of $Zr_{92}Al_4N_4$ was prepared by arc-melting a mixture of Zr (99.5 wt.%) with a nitrogen content less than 100 appm (appm: atomic parts per million) and AlN (99 wt.%) in a Ti-gettered high-purity argon atmosphere. The nitrogen content in the prealloy measured by inert gas fusion technique using a LECO-TC436 nitrogen/oxygen analyzer (with the deviation of less than 10%) is 4.1 at.%. The single-Zr(N,Al) solid solution phase was confirmed using a Bruker AXS D8 X-ray diffractometer (XRD) with a Cu target (Cu $K\alpha$, $\lambda = 0.1541$ nm). Furthermore, master alloys of $Cu_{49}Zr_{44}Al_7$ with different nominal amounts of nitrogen additions including 0, 1000, 3000, and 5000 appm were obtained by arc-melting lumps of the $Zr_{92}Al_4N_4$ pre-alloy, pure Cu (99.9 wt.%), Zr (99.5 wt.%), and Al (99.99 wt.%). Each ingot with the nominal chemical compositions of $(Cu_{0.49}Zr_{0.44}Al_{0.07})_{100-x}N_x$ ($x = 0$, 0.1, 0.3 and 0.5) was melted at least five times to ensure the chemical homogeneity. The nitrogen content in the alloys was also measured using the same nitrogen/oxygen analyzer. The master alloys were then remelted in a quartz tube using induction equipment and injected into copper moulds with cylindrical cavities in a diameter of 5 mm. Ribbons with a thickness of ~30 μm and a width of ~1 mm were also prepared by single-roller melt spinning for comparison. The transverse cross sections of the samples were analyzed using the X-ray diffractometer. The microstructure of the as-cast samples was examined by scanning electronic microscopy (SEM) using a CamScan 3400 microscope equipped with an INCA PentaFET × 3 energy dispersive X-ray spectrometer (EDX). The amorphous structure of the bulk samples was further confirmed using a JEM-2100F transmission electron microscope (TEM). Crystallization behaviors of the glassy samples were measured by a NETZSCH 404 C differential scanning calorimeter (DSC) at a heating rate of 0.33 K/s using the melt-spun ribbons. Melting and solidification behaviors of the master alloys were also characterized by the same DSC equipment at a constant rate of 0.33 K/s.

3. Results and discussion

As listed in Table 1, the nitrogen content in the $Cu_{49}Zr_{44}Al_7$ alloy is 104 appm. For the 1000, 3000, and 5000 appm added alloys, the nitrogen concentrations were measured to be 1200, 3698, and 6237 appm, respectively. The matching between the nominal and measured values indicates that nitrogen was introduced into the alloys using the $Zr_{92}Al_4N_4$ pre-alloy.

Fig. 1 shows the XRD patterns of the as-cast 5-mm-diameter rods of $Cu_{49}Zr_{44}Al_7$ alloys with different nitrogen concentrations. The pattern of the sample without nitrogen doping exhibits sharp diffraction peaks identified as ZrCu (B2) phase superimposed on a broad halo, suggesting that this sample consists of amorphous and ZrCu (B2) phases. When the nitrogen addition increased up to 1000 appm in the $Cu_{49}Zr_{44}Al_7$ alloy, the diffraction pattern shows only one main broad amorphous peak with no evidence of the existence of crystalline phase, indicating the improvement of GFA for the alloy with a proper N concentration. For the sample with 3000 appm N addition, indistinctive crystalline peaks from an unknown phase overlap on a broad halo, suggesting the sample is made up of amorphous matrix composite with a minor crystalline phase. It will be discussed later combining with the EDX results. With the further increase in nominal nitrogen content up to 5000 appm, the sample shows strong diffraction peaks characteristic of $Cu_{10}Zr_7$ and the unknown crystalline phase. Therefore, the nitrogen addition with an optimal content of ~1000 appm will

promote the glass formation of the CuZr-based alloy, while excessive nitrogen deteriorates its GFA. It implicates that the nonmetal element of N is not always playing a negative role of increasing the heterogeneous nucleation sites of nitride which will severely decrease the GFA like O [19,20].

The microstructures of the specimens were further analyzed by SEM and the images are shown in Fig. 2. For the as-cast 5-mm-diameter sample without nitrogen addition, the primary phase embedded in the amorphous matrix is spherical with typical diameters between 50 and 150 μm, and sometimes the grains overlap each other, as shown in Fig. 2(a). The crystalline phase is absent in the 1000 appm-doped specimen and no sharp contrast is visible across the whole section in Fig. 2(b). The fully amorphous nature of the 1000 appm-doped bulk sample is further confirmed by the homogeneous contrast in the high-resolution TEM image and the broad halo ring in the selected area diffraction pattern, as shown in Fig. 2(d). For the alloy with 3000 appm nitrogen addition, a distinguishable dendritic primary phase with smaller grain sizes of 2–20 μm are distributed in the glassy matrix compared to the ZrCu (B2) phase in the as-cast $Cu_{49}Zr_{44}Al_7$ alloy. This unknown-structure phase was identified to be a Zr- and Al-rich CuZrAl phase by EDX of which the chemical atomic composition consists of 37.8 ± 1.8 at.% Cu, 49.2 ± 1.6 at.% Zr and 13.0 ± 0.4 at.% Al. Combining with the XRD, SEM and EDX results, it indicates that an appropriate content of nitrogen destabilizes the initial ZrCu (B2) phase thus enhances the glass formation, while excessive nitrogen induces the formation of a new Zr- and Al-rich primary phase and diminishes the GFA. Recently, it is worth noting that the tensile ductility with high yield strength of 1.3~1.6 GPa can be obtained in CuZr-based bulk metallic glass composites [30–32]. The successful introduction of ductile shape-memory B2 phase in metallic glass matrix is a key factor. Our results can provide the useful information about phase selection during solidification process affected by the doping of nonmetal element of N for this kind of CuZr-based glassy composites.
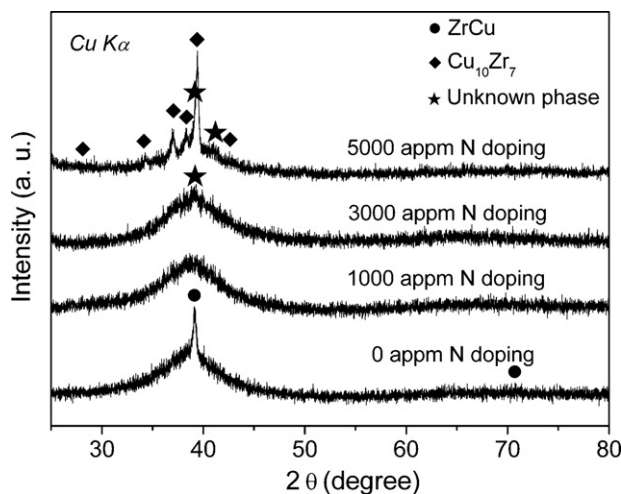

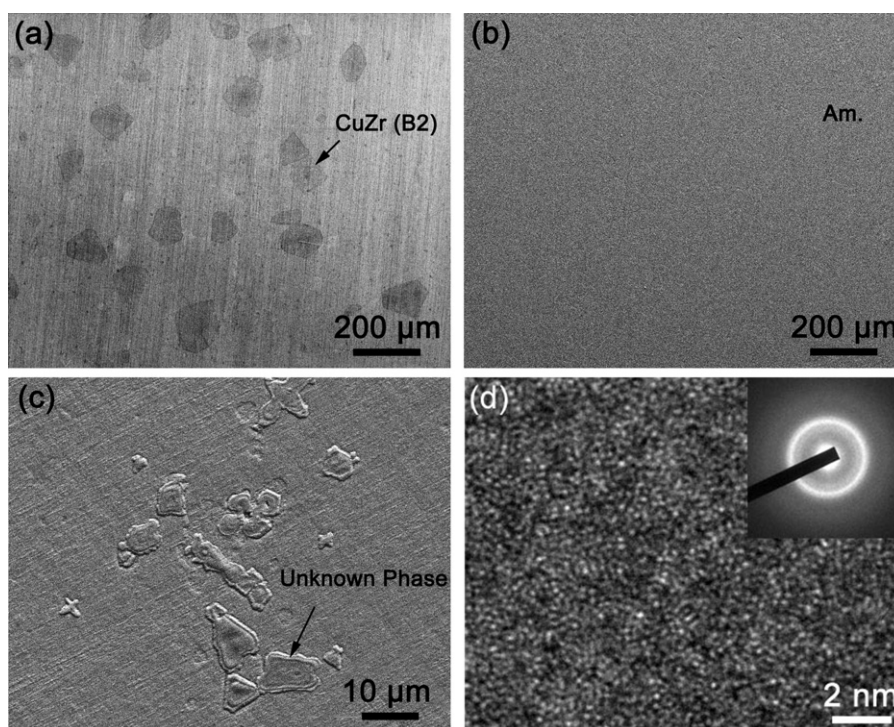**Fig. 1.** XRD patterns of the as-cast 5-mm-diameter rods of $Cu_{49}Zr_{44}Al_7$ alloys with different nitrogen additions.

Fig. 2. SEM images of the as-cast 5-mm-diameter rods of $Cu_{49}Zr_{44}Al_7$ alloys with nominal (a) 0, (b) 1000, and (c) 3000 appm nitrogen additions. (d) High-resolution TEM image of the 1000 appm-doped bulk sample. The selected area diffraction pattern (SADP) is shown in the inset.

Thermal stabilities of the fully glassy ribbons with different nitrogen concentrations were studied by DSC. The thermal parameters, including the glass transition temperature (T_g), the onset crystallization temperature (T_x), and the supercooled liquid region before crystallization ΔT_x ($\Delta T_x = T_x - T_g$), are listed in Table 1. The samples show similar glass transition and crystallization behaviors, as shown in Fig. 3(a), indicating that the thermal stability of the fully glassy alloy is not significantly influenced by the nitrogen addition. The crystallized samples all exhibit apparent endothermic heat events at $\sim$990 K which corresponds to the eutectoid reaction from low temperature equilibrium phases to ZrCu (B2) phase [27]. As the DSC traces of the amorphous ribbons do not imply a change in the crystallization behavior, the unknown phase in the 3000 appm N-doped alloy is supposed to precipitate only from the melt. To understand the above dependence of GFA on the nitrogen content and explore the mechanisms underlying the enhanced glass formation, melting and solidification behaviors of the alloys were investigated by DSC at a constant rate of 0.33 K/s. Fig. 3(b) shows typical DSC curves of the samples at heating and cooling processes. The melting temperatures (T_m) are nearly the same for the four alloys, but the liquidus temperatures (T_l) and the onset solidification temperatures (T_s) vary significantly as a function of the nitrogen content, as listed in Table 1. The reduced glass transition temperature ($T_{rg} = T_g/T_l$) [33] and the γ parameter ($\gamma = T_x/(T_g + T_l)$) [34] of these alloys were also calculated and listed in Table 1. It can be seen that the glass-forming criteria, including ΔT_x [5], T_{rg} and γ, cannot give appropriate indications of the GFA in the present N-doped alloys. The undercooling degree (ΔT_u) between T_l and T_s is calculated to be about 31, 42, 40 and 37 K for the alloys with nominal N concentration of 0, 1000, 3000 and 5000 appm, respectively. The proper N doping can enlarge ΔT_u of the alloy resulting in a higher GFA. Similar results have been reported in other glass-forming system, like LaCe- and Fe-based BMGs [11,23]. The results suggest that optimized amount of nitrogen suppresses the formation of the competing crystalline phase and slows down its precipitation during the solidification process, thus increases the GFA of the alloy. With further increased nitrogen contents, however, ΔT_u decreases gradually probably due to the emergence of the new primary phase.

Given the above results, the frustration of crystallization may account for the enhanced glass formation by proper nitrogen additions in the present alloy [3]. The change in the primary phase can be explained by the phase selection theory [6], which points that the primary phase in the as-cast samples with an appropriate size would shift from one to another as a function of the alloy composition. Therefore, the effect of nitrogen on the GFA of the CuZr-based alloys is similar to that of any other alloying elements in the BMG systems. The GFA can be severely influenced by the nitrogen concentration on the order of $\sim$1000 appm. Such a high elemental content sensitivity of the GFA might be attributed to two reasons: one is the small atomic radius of nitrogen (0.056 nm) [35]; the other is the strong interactions between nitrogen and the basic elements of the alloy, as reflected by the large positive or negative heat of mixing between N–Cu (71 kJ/mol), N–Zr ($-$78 kJ/mol), and N–Al (63 kJ/mol) binary pairs [28]. Because of the significant mismatch of atomic size between nitrogen and other main constituent elements, proper nitrogen dissolution can generate a wider atomic size distribution and produce a more efficient cluster packing structure, which is often associated with a higher viscosity and lower atomic diffusivity, thus the nucleation and growth of the crystalline phases can be suppressed and as a result the GFA could be improved [1,35]. Furthermore, because of the large negative heat of mixing between Zr–N and large positive one between Cu–N and Al–N [26], minor nitrogen doping may generate new atomic pairs with strong affinity and change the local atom arrangements significantly [36]. The new cluster structure might restrict the diffusion of Zr and increase the multiplicity and stability of the chemical and topological short-range orderings. The phenomena of the phase selection for primary crystallization and the variation of undercooling degree during solidification affected by N doping in the $Cu_{49}Zr_{44}Al_7$ alloy can be attributed to this kind of atomic
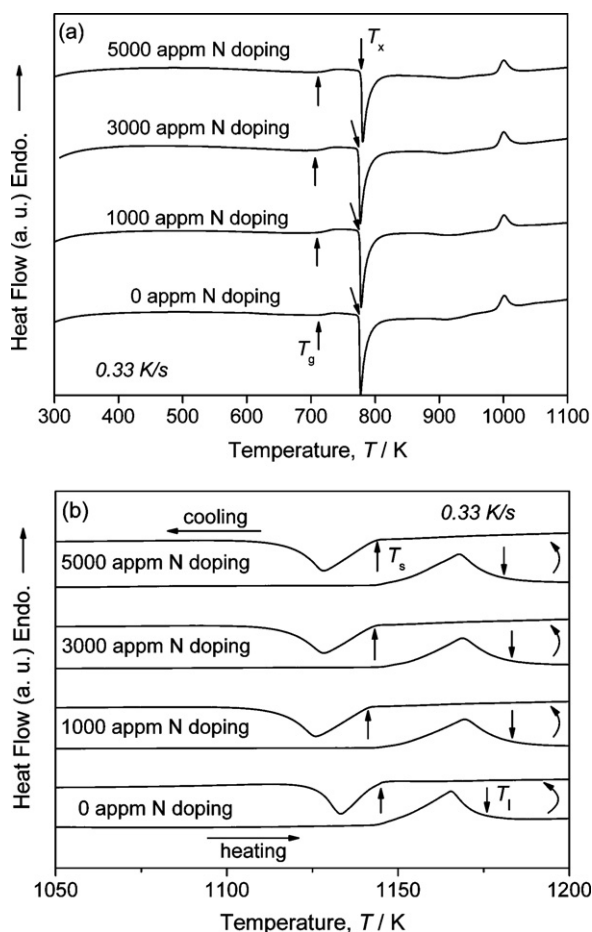
Fig. 3. (a) DSC curves of crystallization behavior for the amorphous ribbons, and (b) melting and solidification behaviors for master alloys of $Cu_{49}Zr_{44}Al_7$ alloys with different nominal nitrogen contents measured at a constant heating and cooling rate of 0.33 K/s.

rearrangement. Consequently, nitrogen, maybe as well as other nonmetal elements like O, S, and H, can be treated as one new group of alloying elements to improve the GFA in glass-forming systems. Because the GFA is extremely sensitive to the nitrogen content, the reported best glass formers obtained under laboratory conditions may be not reproducible in the industrial production under low vacuum or other nitrogen-containing conditions. The dependence of optimal composition on nitrogen concentration should be anticipated and utilized purposely in the designing and manufacturing of Zr- and Ti-based BMGs with low-grade materials and low processing costs. On the other hand, the study of primary phase selection influenced by N doping is also significant for the design of BMG-based composites with selective second phase particles like ZrCu (B2) [30,31].

4. Conclusions

Different nominal amounts of nitrogen from 0 to 5000 appm were introduced into a ternary $Cu_{49}Zr_{44}Al_7$ alloy. The effects of nitrogen content on the glass formation of the CuZr-based alloys were evaluated. The GFA of $Cu_{49}Zr_{44}Al_7$ was enhanced by proper additions of nitrogen of 1000 appm due to the destabilization of the initial primary phase and the suppression of crystallization during solidification process, while excessive nitrogen deteriorated the GFA. The primary crystallization phase in glassy matrix is selected from ZrCu (B2) to an unknown phase with the increase of doping

content of N. The results indicate that the nonmetal element of N can be treated as an alloying element in CuZr-based alloy system to improve the GFA, and, furthermore, the adjustment of trace concentration of N can be employed as an effective way in the designing of BMG-based composites with selective second phase particles.

Acknowledgements

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