Hydrogen-induced amorphization of Zr-Cu-Ni-Al alloy

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Abstract: Arc melting was utilized in this study to produce $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloys under mixed atmospheres with various ratios of high-purity hydrogen to argon. The influences of hydrogen addition on the solidification structure and glass-forming ability of $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy were determined by examining microstructures in different parts of the cast ingots. The results showed that different degrees of crystallization structures were obtained in the as-cast button ingots after arc melting in high-purity Ar, and the cross-sectional solidification morphology of arc-melted ingots was found to consist of crystals with varying from the bottom up. By contrast, there were completely amorphous structures in the middle and upper areas of the as-cast button ingots fabricated by adding 10% H_2 to the high-purity Ar atmosphere. A clear solidification interface was found between the crystal and glass in the as-cast button ingots, which indicates that hydrogen addition can enhance the $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy's glass-forming ability. The precise mechanism responsible for this was also investigated.

Key words: Zr-Cu-Ni-Al alloy; melt hydrogenation; solidification structure; hydrogen-induced amorphization

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The limited glass-forming ability (GFA) of metallic glass restricts its application as a structural material. Although many laboratories have reported the development of large-sized (in many cases, centimeter-plus) bulk metallic glasses (BMGs), the actual number of alloys suitable for commercial production is quite low^[1]. It is of considerable practical significance to enhance the GFA of existing BMG-forming alloys. For these alloy systems, the nature and number of components and purity of elements are critical factors in terms of GFA and mechanical properties^[2]. The GFA and properties of BMGs are also quite sensitive to the material's composition. Therefore, minor alloying additions play an important role in the glass formation, thermal stability, and comprehensive properties of BMGs^[3]. Various elements have been employed to change the

GFA; researchers have already explored almost all of the traditional metal and metalloid elements for this purpose. The possible component element additions can be split into three categories: 1) small-atomic-radius metalloid elements such as C, B, or Si, 2) intermediate transition elements such as Fe, Ni, Co, Cu, Mo, Zn, Nb, Ta, and Ti, and 3) elements with large atomic radius such as Zr, Sb, Sn, Sc, Y, La, and Ca^[4-6].

Generally speaking, BMG production requires rather stringent protective conditions. The gas elements are usually discharged during the vacuum process. There have been relatively few studies on the effects of gas element composition on the GFA of BMGs, though a few recent studies have shown that microalloying with oxygen or nitrogen in certain alloy systems can improve the GFA^[7-9]. The results of these studies altogether imply that certain gas elements play an important role in the GFA of BMGs. Hydrogen (which, of course, has the smallest atomic radius of any nonmetal element), may have a particularly notable effect on GFA, but few studies have been conducted to observe said effect.

In this study, hydrogen is regarded as an alloying element for metallic glass. The novelty of the addition method proposed here lies in the fact that hydrogen was introduced via a gas-phase processing route. The GFA is

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strongly dependent on arc-melted master alloys due to structure heredity. Variations in solidification microstructure correspond to different liquid and amorphous structures. The arc-melted master alloy, which represents the first step in the fabrication of metallic glass, is a crucial consideration; we examined the comprehensive casting morphology of arc-melted ingot samples accordingly. The influence of hydrogen on the solidification microstructure and glass formation of $Zr_{55}Cu_{30}Ni_5Al_{10}$ master alloy was analyzed, and the mechanism of hydrogen-induced amorphization was investigated as discussed below.

1 Experimental procedure

The raw materials comprising $Zr_{55}Cu_{30}Ni_5Al_{10}$ (purity>99.9%) were first placed into a water-cooled copper crucible (which had in advance been calibrated to a vacuum state), then passed into mixed atmospheres with different ratios of high-purity hydrogen to argon. The proportion of hydrogen in the atmosphere was adjusted and controlled with a hydrogen analyzer. Figure 1 shows a schematic diagram of the experimental equipment, which included a high-vacuum non-consumable electric arc furnace and JF-2200 multi-component analysis system.

Fig. 1: Schematic diagram of experimental equipment

During the melting process, a minute quantity of hydrogen was broken up into the atomic level and forced into the alloy by a high-temperature electric arc while a certain amount of hydrogen was retained after repetitive melting, where therefore the residual hydrogen in the alloy was proportional to the percentage of hydrogen in the mixed atmosphere. As hydrogen content was gradually increased in the mixed atmosphere, the quantity of hydrogen introduced into the alloy likewise gradually increased. Accordingly, the properties of atmospheric elements in which the alloy was prepared were used here to indicate the hydrogen content of the $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy: namely Ar (excluding hydrogen) and Ar+10% H_2 , in which the content in the mixed atmosphere was 100%. The changes in the alloy microstructure before and after melt hydrogenation were observed by scanning electron microscopy back scattered electron (SEM-BSE) on a FEI Quanta 200FEG and by optical microscopy on an Olympus GX71. The hydrogen and oxygen concentrations were obtained from the LECO-ROH600 oxygen/hydrogen analyzer with infrared radiation detection. Each sample was measured in three replications to obtain average oxygen and hydrogen concentrations. The accuracy of oxygen and hydrogen concentration is 0.025 wppm and 0.05 wppm, respectively. The structures of the as-cast alloys were identified by a Rigaku D/max-rB X-ray diffractometer (XRD) using Cu $K\alpha$ radiation.

2 Results and discussion

Figure 2(a) shows an outer view of the $Zr_{55}Cu_{30}Ni_5Al_{10}$ master alloy and Fig. 2(b) shows a corresponding cross-sectional diagram. As shown in Fig. 2(a), the surface of the solidified alloy fabricated in Ar+10% H_2 is smooth, metallic, and mirror-like, while the alloy prepared under Ar is rougher and smokier (not shown). The ingots present a button-like appearance, so the samples are referred to here as “button ingots”.

The button ingot was used for the master alloy before the preparation and melt hydrogenation of BMGs. The metallic luster of the button ingot reflects the degree of vitrification in

Fig. 2: (a) Morphology and (b) cross section of schematic of $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy ingots

the master alloy, which is associated with GFA. High metallic luster indicates that the solidified surface is composed of glass phase, while a smoky surface indicates that the solidified surface is crystallized due to low glass-forming ability. As stated by Yan et al.^[10], GFA strongly depends on the structure of the original master alloy buttons – microstructure characteristics are a critical factor in the first step of BMG fabrication. Accordingly, we observed the changes in solidification morphology and structure at different areas in the master alloy buttons before and after melt hydrogenation to elucidate the effect of hydrogen addition on the GFA of $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ alloys. To ensure experiment repeatability, the weight of button ingots used in the experiment was controlled to 20 g and the processing parameters (e.g., current, melting time) were kept constant. The samples were cut by wire electrical discharge machining, then the positions of the button ingots were observed as shown in Fig. 2(b).

Figure 3 shows the solidification morphology of the button ingot prepared under the high-purity argon atmosphere. As shown in Fig. 3(a), the solidification structures exhibit obvious stratification from the bottom of the ingot to the top, denoted as regions A, B, and C. Amplification of these regions are shown in Fig. 3(b)-(d). There were fine equiaxial microstructures near the bottom of the water-cooled copper crucible, shown as

region A in Fig. 3(a) and in Fig. 3(b). It is worth noting that the cooling rate of this location was the fastest in the ingot, where the microstructures did not form a typical amorphous structure. According to Inoue et al.'s research^[11], this was as a result of the ohmic contact during solidification leading to crystallization.

Coarse dendrites were formed in region B, as shown in Fig. 3(c). During the button ingot solidification process, the heat flux was roughly top-down, leading to the directional growth of dendrites marked by the arrow in Fig. 3(a). The coarse dendrites did not grow throughout the entire sample. A blurry interface can be seen in Fig. 3(a).

Moreover, it worth noticing that a morphological transition from the dendrites to fine equiaxed grains was also observed. At the upper part of the button ingot, marked as Region C in Fig. 3(a), fine equiaxed grains were dispersed in the amorphous matrix as shown in Fig. 3(d). This suggests that glass formation in the upper part of the button ingot is closely related to its own GFA. However, at the near-top side of the ingot, coarse grains were found embedded in the fine equiaxed grains, as shown in Fig. 3(d), which may be as a result of the grain growth of the fine microstructures neighboring to the copper crucible due to a recrystallization process with lower rate of cooling.

Figure 4 shows the XRD patterns taken from several areas

Fig. 3: Solidification structures of $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_5\text{Al}_{10}$ alloy ingots prepared under high-purity Ar: (a) Region near crucible wall, (b) Region A magnification, (c) Region B magnification, (d) near-top side above Region C

Fig. 4: XRD patterns taken from several areas corresponding to Regions A, B and C in arc-melted $Zr_{55}Cu_{30}Ni_5Al_{10}$ ingot

corresponding to A, B and C in the arc-melted $Zr_{55}Cu_{30}Ni_5Al_{10}$ ingot. All curves exhibit Bragg peaks corresponding to CuZr and $Cu_{10}Zr_7$ overlapped on the broad halo peak. This indicates that the sample was partially amorphous. XRD analysis indicates that regions A, B and C were roughly composed of CuZr and $Cu_{10}Zr_7$ phases.

The solidification structures of $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy prepared under Ar+10% H_2 atmosphere are shown in Fig. 5. The microstructures near the bottom of the crucible characterized by tiny crystals are displayed in Fig. 5(a). The tiny dendrite structures denoted “B” generated in a directional growth

trend similar to the crystals mentioned above. A single, large area without contrast was observed in the upper part of the sample, marked as Region C in Fig. 5(b), representing typical amorphous microstructure. There was also a distinct glass-crystal interface, as shown in Fig. 5(b). The glass phases formed after the crystalline phases grew from the bottom of the ingot, showing that a transition is closely related to a high GFA.

The formation of glassy phase in arc-melted ingots may require certain preparation conditions in order to restrict active thermal convection in the molten alloy. Figures 5(c) and 5(d) show the amorphous area under different levels of magnification, where it is difficult to find any remaining crystal phase. In effect, the $Zr_{55}Cu_{30}Ni_5Al_{10}$ button ingots prepared under Ar+10% H_2 atmosphere showed featureless, amorphous microstructure, likely due to the addition of hydrogen. Figure 6 shows the XRD patterns taken from several areas corresponding to Regions A, B, and C in the $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy ingots prepared under 10% H_2 +Ar. The former two curves exhibit Bragg peaks corresponding to CuZr and $Cu_{10}Zr_7$ on the broad halo peak, which indicates that these samples were partially amorphous. XRD analysis indicates that regions A was composed of CuZr and $Cu_{10}Zr_7$ phases, and region B was composed of $Cu_{10}Zr_7$. Note that XRD analysis indicates that region C is completely amorphous in accordance with the solidification structures shown in Fig. 5(c-d), which further suggests that hydrogen addition increased the glass-forming ability.

Fig. 5: Solidification structures of $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy ingots prepared under 10% H_2 +Ar atmospheres: (a) Regions near crucible wall, (b) magnification of Region B, (c) and (d) showing Region C from Fig. 5(b)

By comparing the solidification structures of $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy button ingots prepared under various controllable atmospheres, we confirmed that the microstructures in the rapidly cooled area near the water-cooled copper crucible featured tiny crystals regardless of preparation conditions (high-purity Ar or Ar+10% H_2) as shown in Figs. 3(a) and 5(a). The formation of small crystals was inevitable due to ohmic-contact-induced nucleation^[11], as mentioned above. In the middle and lower parts of the button ingots in both experimental groups, dendritic crystals formed in a specific growth direction; the crystals formed under Ar+10% H_2 atmosphere were denser and more uniform in orientation than the others. It is worth noting that at the upper parts of the button ingots, solidification structures prepared under pure Ar showed fine equiaxed grains while those prepared under Ar+10% H_2 showed a typical amorphous morphology. To this effect, the addition of hydrogen inhibited the production of crystal phase in the $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloys to a certain extent, thus enhancing their GFA.

Fig. 6: XRD patterns taken from several area corresponding to A, B and C in $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy ingots prepared under 10% H_2 +Ar atmospheres

Based on the solidification morphology and structure of arc-melted $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloys, a schematic diagram of structure change with hydrogen addition was drawn as shown in Fig. 7. The cross-sectional solidification morphology of arc-melted $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloys has three distinct regions, i.e., Regions A, B, and C. Regions A and B are located at the bottom of the button, which directly contacts the water-cooled copper crucible during the experiment. In both cases, the arc-melted $Zr_{55}Cu_{30}Ni_5Al_{10}$ was composed of typical layered structures due to element fluctuation. In the middle and upper parts of the button ingot, the solidification morphology and structure changed dramatically upon hydrogen addition. A morphological transition from crystalline phase to glass phase was observed, as shown in Fig. 7(b). The transition is related to the alloy's GFA, so it is reasonable to conclude that hydrogen addition promotes the formation of an amorphous alloy.

Fig. 7: Schematic diagram of structure change: (a) without hydrogen addition and (b) with proper hydrogen addition

To better understand the increase in GFA, hydrogen and oxygen contents were measured with a LECO-ROH600 oxygen/hydrogen analyzer. When the $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloys were prepared under Ar + (0, 10)% H_2 , the hydrogen concentrations in the alloys were measured to be 20 and 210 wppm, respectively, and the oxygen contents were 320 and 250 wppm, respectively. The hydrogen content of $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy fabricated in Ar + 10% H_2 was about 10 times greater than that of $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy fabricated in pure Ar. The oxygen concentrations of $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloys prepared under mixed hydrogen and argon only slightly decreased. The thermal conductivity of hydrogen is 10 times greater than that of argon, so we suspect that the difference in GFA glass formation may have originated from the difference in the cooling rate. In a similar study, Granata et al.^[12, 13] investigated Zr-based metallic glasses prepared under helium (which possesses the similar thermal conductivity as hydrogen), but observed quite different effects on glass-forming ability and plasticity. Apparently, the cooling rate is not the major factor. We can assume, therefore, that hydrogen addition is a major factor in GFA.

Inoue et al.^[14] established three empirical rules for effective GFA: 1) there must be more than three constituent elements, 2) the atomic radius difference of the main principal components must be greater than 12%, and 3) there must be large negative heat of the mixture among the main principal components. When the amorphous alloy system satisfies these three rules, it will have high atomic random coordination density, higher neighboring atom coordination than that of crystal, very uniform atom coordination concentration in the long range, and other favorable qualities; in short, the alloy system will possess high GFA.

In this study, the atomic radius of components of $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloys possess the following characteristics^[15]: 0.162 nm atomic radius of Zr, 0.128 nm atomic radius of Cu, 0.125 nm atomic radius of Ni, 0.143 nm atomic radius of Al, and 0.037 nm atomic radius of H. Accordingly, hydrogen addition is directly related to intensified atomic size mismatch, which more effectively produces atomic layer stacking structure, creates larger melt viscosity, and reduces atom diffusion. The nucleation and growth of the crystal phase in the solidification process were thus suppressed upon hydrogen addition, which enhanced the alloy's GFA. The added hydrogen atoms also affect heat during mixing with other components^[15]. The heat of mixing Zr with H is about $-69 \text{ KJ}\cdot\text{mol}^{-1}$, Cu with H is about $-6 \text{ KJ}\cdot\text{mol}^{-1}$, Ni with H is about $-23 \text{ KJ}\cdot\text{mol}^{-1}$, and Al with H is about $-8 \text{ KJ}\cdot\text{mol}^{-1}$, therefore, after adding hydrogen, the heat in the alloy due to mixing was negative – this caused new atom pairs to form and altered the local atomic structure. The new generation of atom pairs hindered atomic diffusion, improving the chemical and topological short-range order, as well as improving the stability of the liquid phase. Once the content of hydrogen in the alloy reached a certain value, the formation of primary phases was inhibited and the alloy composition became more eutectic, thus allowing glass to form very easily.

3 Conclusions

The influence of hydrogen addition on the solidification structure and GFA of $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloys was studied by examining microstructures in different parts of cast ingot samples. Main conclusions can be summarized as follows:

(1) Various degrees of crystallization structures were obtained in the as-cast button ingots after arc melting in high-purity Ar atmosphere, and the cross-sectional solidification morphology of arc-melted ingots consisted of crystals with different morphologies from the bottom up.

(2) By observing the microstructures at different positions in the button ingots, we found that the structure of $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloys fabricated under Ar+10% H_2 atmosphere presents typical amorphous morphology at the upper region of the ingot, while this morphology cannot be produced when pure Ar is used as protective gas.

(3) The GFA of the sample alloys improved due to the addition of hydrogen during fabrication. The mechanism of said

improvement is mainly associated with the increase in atomic mismatch between the components and the negative heat of mixture.

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