

Formation of Zr-Based Bulk Metallic Glasses from Low Purity of Materials by Yttrium Addition

Yong Zhang, Ming Xiang Pan, De Qian Zhao, Ru Ju Wang and Wei Hua Wang*

Institute of Physics & Center for Condensed Matter Physics, Chinese Academy of Science,
Beijing 100080, P.R. China

Zr₅₅Al₁₅Ni₁₀Cu₂₀ bulk metallic glass is formed using low purity materials at a low vacuum with a small amount of yttrium addition. It is found that the glass forming ability, crystallization and melting process of the Zr₅₅Al₁₅Ni₁₀Cu₂₀ alloy are modified with yttrium addition, while the mechanical and elastic properties, such as hardness and Young's Modulus, are not obviously changed. The positive effect of yttrium addition on the glassy formation of the Zr₅₅Al₁₅Ni₁₀Cu₂₀ alloy is clarified.

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1. Introduction

Recently, many bulk metallic glass forming alloys, such as ZrAlNiCu and ZrTiCuNiBe have been developed.^{1,2)} The new types of metallic glasses with excellent glass forming ability (GFA) promise to allow the production of large-scale bulk material by conventional casting processes at a low cooling rate. However, high vacuum (at least 10⁻³ Pa), high purity of constituent elements (the purity of zirconium is at least 99.99 at%, oxygen content should be less than 250 ppm) and high purity of argon gas are necessary for fabrication of the Zr-based bulk metallic glasses (BMGs),³⁾ even traces of oxygen impurities and other impurities, *e.g.*, carbon,⁴⁾ induce the heterogeneous nucleation and reduce the GFA drastically. The strict processing makes the cost of Zr-based BMGs high, and limits its wide application. Previous work shows that proper element addition can greatly improve the GFA of glass forming systems.⁴⁾ A small amount of yttrium addition (2 ~ 8 at%) is effective in the formation of Zr, Al, Ge, Fe and Mg-based metallic glasses.⁵⁻⁸⁾ Inoue and his co-workers⁹⁾ have found two glass transition temperatures as well as two wide supercooled liquid regions in the Zr₃₃Y₂₇Al₁₅Ni₂₅ BMG, and the glass separates into yttrium-rich YAlNi and Zr-rich ZrAlNi glassy phases on heating. In this paper, we present experimental evidences that Zr-based BMG can be prepared with a low purity of zirconium under a low vacuum by introducing a small amount of yttrium into the Zr-Al-Ni-Cu and Zr-Ti-Ni-Cu-Be alloys. The effects of the yttrium addition on the thermal and mechanical properties of the Zr-based BMGs are investigated. The positive effect of the yttrium addition on the glass formation is discussed.

2. Experiments

Ingots with composition of (Zr₅₅Al₁₅Ni₁₀Cu₂₀)_{100-x}Y_x ($x = 0 \sim 10$), (Zr₆₅Al_{7.5}Ni₁₀Cu_{17.5})_{100-x}Y_x ($x = 0 \sim 6$), (Zr₄₁Ti₁₄Cu_{12.5}Ni₁₀Be_{22.5})₉₈Y₂ and Zr₃₄Ti₁₅Cu₁₂Ni₁₁Be₂₈Y₂

were prepared by arc-melting elemental metals in a Ti-gettered argon atmosphere. The ingots were inductively melted in a quartz tube at a low vacuum (1 Pa), and then cast into a water cooled copper mould. All the samples were prepared in the same processing conditions and in the same size of cylindrical shapes with diameter of 5 mm and length of 30 mm. The purity of the zirconium is 99.8 at%, including 1500 ppm of oxygen and other impurities. The purity of other constituent elements is 99.9 at%. The structure of the alloy was identified by a Siemens D5000 X-ray diffractometry with Cu K α radiation, and the thermal properties were measured by Perkin Elmer differential scanning calorimetry (DSC-7) and differential temperature analyzer (DTA-7). The density is measured by Archimedes method. The Vickers hardness (H_V) was measured by micro-hardness-71 with a load of 200 g. Elastic constants were determined by ultrasonic method. The acoustic velocities were measured by using a pulse echo overlap method. The travel time of the ultrasonic waves propagating through the sample with a 10 MHz carrying frequency was measured using a MATEC 6600 ultrasonic system with a measuring sensitive of 0.5 ns.

3. Results and Discussion

Figure 1 is X-ray diffraction (XRD) patterns of the Zr₅₅Al₁₅Ni₁₀Cu₂₀ [Figs. 1(a) and (c)] and the Zr₆₅Al_{7.5}Ni₁₀Cu_{17.5} [Fig. 1(b)] alloys. The alloys of the Zr₅₅Al₁₅Ni₁₀Cu₂₀ [Fig. 1(a)] and the Zr₆₅Al_{7.5}Ni₁₀Cu_{17.5} [Fig. 1(b)] are prepared by using low purity of zirconium and at a low vacuum, Fig. 1(c) shows XRD of the Zr₅₅Al₁₅Ni₁₀Cu₂₀ alloy prepared by using higher purity of zirconium (99.99 at%) and at the same vacuum condition. The figure shows that crystalline compound precipitates in all of the alloys during the cooling process, and almost no amorphous phase is formed in this processing condition for the alloys prepared by using low purity of Zirconium. However, the Zr₅₅Al₁₅Ni₁₀Cu₂₀ alloy using higher purity of Zirconium shows a diffused peak superimposed by some crystalline peaks, indicating the alloy contains more amorphous phase. Other researcher's work has also shown that the fully

*Corresponding author: whw@aphy.iphys.ac.cn

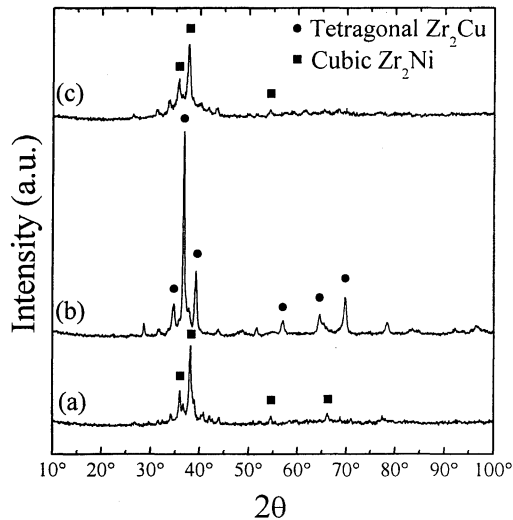


Fig. 1 XRD patterns of the $Zr_{55}Al_{15}Ni_{10}Cu_{20}$ alloy (a), and $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloy (b) prepared by using low purity of Zr at low vacuum, and $Zr_{55}Al_{15}Ni_{10}Cu_{20}$ alloy (c) by using higher purity of Zr at a low vacuum.

ZrAlNiCu BMGs can only be obtained at a high vacuum (at least 10^{-3} Pa), high purity and low oxygen content of constituent elements (the purity of Zr is at least 99.99 at%, oxygen content should be less than 250 ppm).^{3,10-12} Our result confirms that the purity especially the oxygen content of the element has greatly effect on the GFA of the alloy. Cubic Zr_2Ni (Al_2Cu type, space group $Fd\bar{3}m$) is the main precipitation crystalline phase in the $Zr_{55}Al_{15}Ni_{10}Cu_{20}$ alloy. Altounian *et al.*¹¹ also found that oxygen can greatly enhance and stabilize the formation of cubic Zr_2Ni phase in binary Zr-Ni alloy. The main precipitation phase is tetragonal Zr_2Cu ($MoSi_2$ type, space group of $I4/mmm$) in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloy as shown in Fig. 1. Eckert *et al.*¹² found that oxygen induced cubic phases (such as Zr_2Ni) transformed into stable Zr_2Cu compound in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloy during the higher temperature annealing. A. Gebert *et al.*¹⁰ has verified that oxygen triggered nucleation of cubic Zr_2Ni phases which act as heterogeneous nucleation sites for crystallization of other stable phases such as tetragonal Zr_2Cu in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloy. Combining with others results, we conclude that the crystalline precipitation in the ZrAlNiCu alloy results from oxygen contamination introduced from the raw material and low vacuum, the oxygen can be regarded as the main cause for the decrease of the GFA of the glass forming system.

Figure 2 is the XRD patterns of $[Zr_{55}Al_{15}Ni_{10}Cu_{20}]_{100-x}Y_x$ ($x = 0.5, 1, 2, 4, 6$ at%) alloys. The figure shows that 0.5 at% of yttrium addition suppresses the precipitation of cubic Zr_2Ni Laves phase, but some AlNiY crystalline peaks can be observed superimposing on the amorphous diffused scattering peak. With adding increase of yttrium from 1 at% to 2 at%, the crystalline peaks become fewer and weaker. When the amount of yttrium reaches 4 at%, almost no crystalline diffraction peaks are observed, and fully metallic glass is formed within the XRD detection limit. With more yttrium addition (>6 at%), crystalline AlNiY phase precipitates. Therefore, a proper yttrium addition can greatly im-

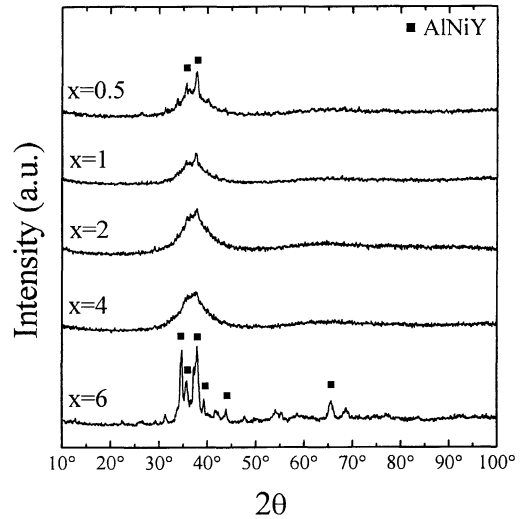


Fig. 2 XRD patterns of the $[Zr_{55}Al_{15}Ni_{10}Cu_{20}]_{100-x}Y_x$ alloys.

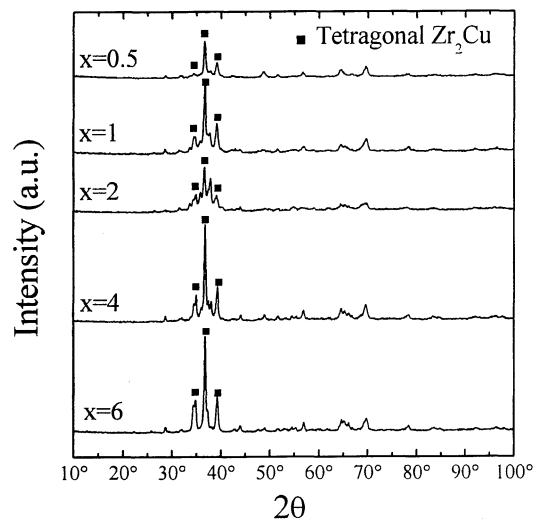


Fig. 3 XRD patterns of the $[Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}]_{100-x}Y_x$ alloys.

prove the GFA of the $Zr_{55}Al_{15}Ni_{10}Cu_{20}$ alloy, and the yttrium adding can suppress the precipitation of the cubic Zr_2Ni Laves phase. Too little (less than 2 at%) or too much (more than 6 at%) of yttrium addition leads to the precipitation of yttrium crystalline phase. For the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloy, however, yttrium addition cannot suppress the formation of the Zr_2Cu Laves phase as shown in Fig. 3. Fully metallic glass can not be obtained for the alloy with yttrium addition in the same processing condition.

The effect of yttrium addition on the $Zr_{55}Al_{15}Ni_{10}Cu_{20}$ alloy is also confirmed by DTA and DSC measurements. Figure 4(a) is the DTA curves of $[Zr_{55}Al_{15}Ni_{10}Cu_{20}]_{100-x}Y_x$ alloys with a heating rate of 0.33 K/s. No exothermic peak is observed for the alloy with $x = 0$, meaning no amorphous phase formed in the $Zr_{55}Al_{15}Ni_{10}Cu_{20}$ alloy without yttrium addition. With 0.5 to 4 at% yttrium addition, an exothermic peak is observed, XRD result indicates the crystallization occurs when annealing the sample at the reaction temperature. The result confirms the existence of amorphous phase in the alloy. For the alloys with 2 to 4 at% yttrium addi-

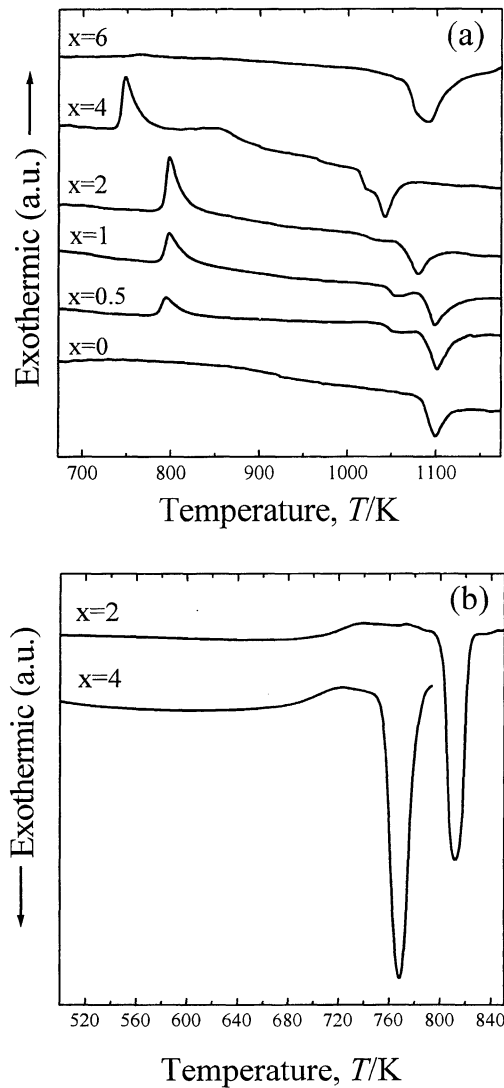


Fig. 4 DTA curves of the $[\text{Zr}_{55}\text{Al}_{15}\text{Ni}_{10}\text{Cu}_{20}]_{100-x}\text{Y}_x$ alloys with a heating rate of 0.33 K/s (a), and DSC curves of $[\text{Zr}_{55}\text{Al}_{15}\text{Ni}_{10}\text{Cu}_{20}]_{98}\text{Y}_2$ and $[\text{Zr}_{55}\text{Al}_{15}\text{Ni}_{10}\text{Cu}_{20}]_{96}\text{Y}_4$ alloys with a heating rate of 0.67 K/s.

tion, the DTA traces exhibit distinct exothermic peaks (XRD verifies the crystallization reaction at the temperature), confirming that much more fraction of amorphous phase was formed in the alloys. With 6 at% yttrium addition, there is no exothermic reaction occurring, meaning that there is no amorphous phase formed in the alloy. This result is in a good agreement with the XRD results shown in Fig. 1 and Fig. 2. Figure 4(a) also shows that the melting temperature, T_m , decreases with increasing yttrium addition, more yttrium addition results in higher T_m . XRD and DTA results indicate that a small and proper amount of yttrium addition can suppress Laves phase formation and greatly increase the GFA of the $\text{Zr}_{55}\text{Al}_{15}\text{Ni}_{10}\text{Cu}_{20}$ alloy. Figure 4(b) is the DSC curves of $[\text{Zr}_{55}\text{Al}_{15}\text{Ni}_{10}\text{Cu}_{20}]_{98}\text{Y}_2$ and $[\text{Zr}_{55}\text{Al}_{15}\text{Ni}_{10}\text{Cu}_{20}]_{96}\text{Y}_4$ alloys with a heating rate of 0.67 K/s. Both of them exhibit distinct glass transition process and broaden supercooled liquid region [SLR, defined by the temperature difference between onset crystallization temperature (T_x) and glass transition temperature (T_g), $\Delta T = T_x - T_g$]. The T_g , T_x and ΔT of $[\text{Zr}_{55}\text{Al}_{15}\text{Ni}_{10}\text{Cu}_{20}]_{98}\text{Y}_2$ alloy are larger than that of

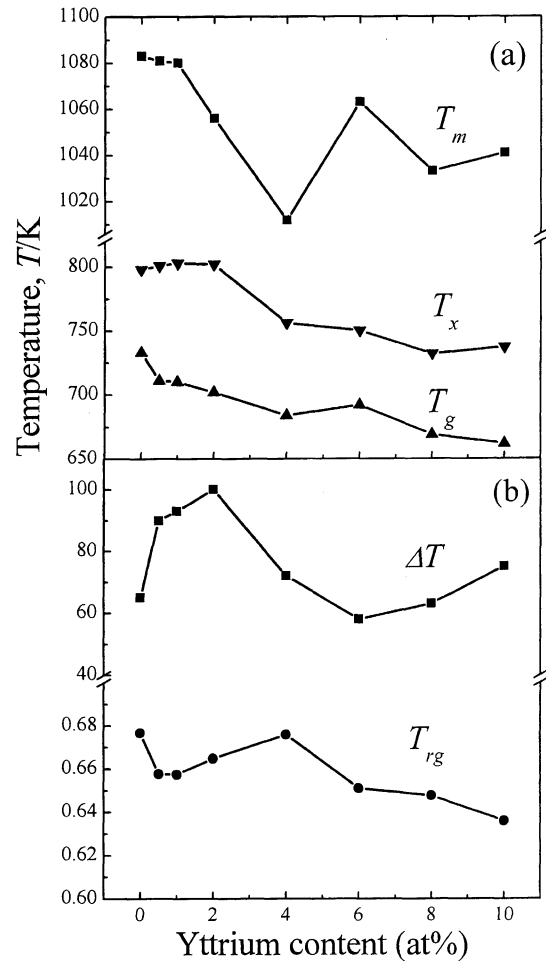


Fig. 5 T_m , T_x and T_g changes with yttrium addition x for $[\text{Zr}_{55}\text{Al}_{15}\text{Ni}_{10}\text{Cu}_{20}]_{100-x}\text{Y}_x$ alloys (a), ΔT and T_{rg} changes with x of $[\text{Zr}_{55}\text{Al}_{15}\text{Ni}_{10}\text{Cu}_{20}]_{100-x}\text{Y}_x$ alloys (b).

$[\text{Zr}_{55}\text{Al}_{15}\text{Ni}_{10}\text{Cu}_{20}]_{96}\text{Y}_4$ alloy.

To investigate the effect of yttrium on the thermal properties of the $\text{Zr}_{55}\text{Al}_{15}\text{Ni}_{10}\text{Cu}_{20}$ alloys, $[\text{Zr}_{55}\text{Al}_{15}\text{Ni}_{10}\text{Cu}_{20}]_{100-x}\text{Y}_x$ alloys in a sheet of 0.5 mm thick were prepared by casting the liquid alloys with the same purity and vacuum conditions mentioned above into a wedge-shaped copper mould, fully amorphous phase can be obtained for the alloys with $x = 0$ to 10. The values of T_g , T_x and T_m determined by DSC with a heating rate of 0.33 K/s are plotted in Fig. 5(a). The figure shows that T_x does not change with the yttrium addition obviously up to $x = 2$, and then decreases slowly with more yttrium addition. The T_g decreases slowly with the yttrium addition. The T_m exhibits a minimum at $x = 4$. The ΔT and the reduced glass transition temperature T_{rg} ($T_{rg} = T_g/T_m$) which can represent the GFA of an alloy¹⁾ are plotted in Fig. 5(b). For the Y bearing alloys, the ΔT reaches a maximum at $x = 2$, and T_{rg} reaches a maximum at $x = 4$. It is known that, the larger the ΔT and T_{rg} , the easier the formation of amorphous and the smaller the critical cooling rate.¹⁾ The thermal analysis results further confirm that the GFA of the $\text{Zr}_{55}\text{Al}_{15}\text{Ni}_{10}\text{Cu}_{20}$ alloy with low purity components is improved with 2 ~ 4 at% yttrium addition.

Yttrium has also been introduced in the ZrTiCuNiBe glass forming alloys with low purity of the components,

Table 1 The properties of the Zr-based BMGs with yttrium addition.

Composition	ρ (kg/m ³)	H_V (GPa)	G (GPa)	μ	K (GPa)	E (GPa)	θ_D (K)
Zr ₄₁ Ti ₁₄ Cu _{12.5} Ni ₁₀ Be _{22.5}	6.13×10^3	5.97	37.4	0.35	114.1	101.2	328
[Zr ₄₁ Ti ₁₄ Cu _{12.5} Ni ₁₀ Be _{22.5}] ₉₈ Y ₂	5.86×10^3	6.76	40.3	0.34	109.0	107.6	337
Zr ₃₄ Ti ₁₅ Cu ₁₀ Ni ₁₁ Be ₂₈ Y ₂	5.78×10^3	6.07	41.0	0.34	113.9	109.8	352
Zr ₅₅ Al ₁₅ Ni ₁₀ Cu ₂₀	6.51×10^3	5.20				90	
[Zr ₅₅ Al ₁₅ Ni ₁₀ Cu ₂₀] ₉₈ Y ₂	6.56×10^3	6.49	33.8	0.36	110.6	92.1	286
[Zr ₅₅ Al ₁₅ Ni ₁₀ Cu ₂₀] ₉₆ Y ₄	6.44×10^3	5.93	31.5	0.36	104.8	86.0	275

fully amorphous alloys with nomination composition of [Zr₄₁Ti₁₄Cu_{12.5}Ni₁₀Be_{22.5}]₉₈Y₂ and Zr₃₄Ti₁₅Cu₁₀Ni₁₁Be₂₈Y₂ were obtained. Figure 6 shows the DTA curves of the alloys with a heating rate of 0.33 K/s. The DTA shows that yttrium addition can also greatly modify the crystallization process of the ZrTiCuNiBe alloy. The crystallization process changes from a multistep crystallization process of ZrTiCuNiBe BMG²⁾ to a single exothermic peak. The DTA curves also show that the yttrium bearing alloys have a single endothermic peak meaning a single-step melting process. The low melting temperature (about 960 K) and single melting process facilitates the improvement of GFA. These results indicate that a small amount of yttrium addition can also modify the GFA and the crystallization process of ZrTiCuNiBe alloy.

Elastic properties, such as Young's modulus E , shear modulus G , bulk modulus K , Debye temperature θ_D and Poisson ratio μ measured by ultrasonic method, and Vicker's hardness H_V , of the Zr-based BMG with yttrium addition are listed in Table 1. The elastic constants measured by ultrasonic method are very close to the results obtained by other measurements.^{13,14)} As shown in Table 1, the yttrium addition does not significantly change the H_V and elastic properties of the Zr-based alloys.

The limiting factor to the glass formation of the Zr₅₅Al₁₅Ni₁₀Cu₂₀ alloy is the precipitation of crystalline

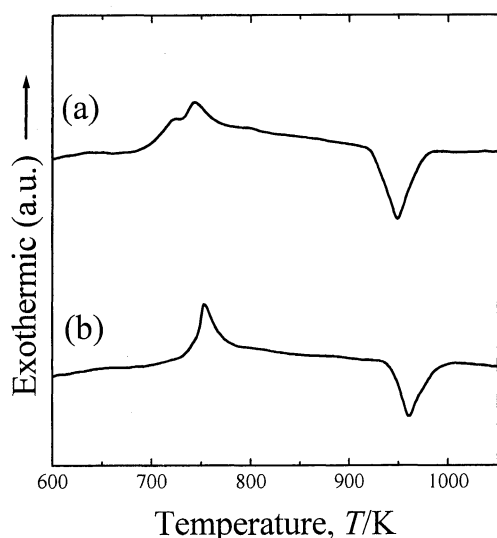


Fig. 6 DTA curves of the Zr₃₄Ti₁₅Cu₁₀Ni₁₁Be₂₈Y₂ (a), and [Zr₄₁Ti₁₄Cu_{12.5}Ni₁₀Be_{22.5}]₉₈Y₂ alloys (b) with a heating rate of 0.33 K/s.

Zr₂Ni phase during cooling, and for the Zr₆₅Al_{7.5}Ni₁₀Cu_{17.5} alloy, it is the crystalline Zr₂Cu. Since the crystalline Zr₂Ni and zirconium oxide are similar in crystalline structure,¹¹⁾ Z. Altounian¹¹⁾ thinks that the formation of the crystalline Zr₂Ni can be triggered by zirconium oxide nuclei. According to thermodynamic principle, yttrium has a stronger affinity with oxygen atom compared to that of zirconium, because the yttrium has much higher formation enthalpy (1905.0 kJ/mol) than that of Zirconium (1100.8 kJ/mol).¹⁵⁾ Therefore, the reaction between Y and O is favored compared to the reaction between Zr and O, the yttrium addition can substitute zirconium oxide nuclei to yttrium oxide nuclei in the liquid alloy. More yttrium addition leads to the formation of AlNiY crystalline phase although yttrium oxide can greatly hinder the precipitation of Zr₂Ni.¹⁶⁾ Zr₂Cu phase in the Zr₆₅Al_{7.5}Ni₁₀Cu_{17.5} alloy¹⁰⁾ is much more stable than Zr₂Ni phase, which can be triggered by not only zirconium oxide nuclei but also yttrium clusters and other impurities such as Zr₂Ni phase.¹²⁾ This is the reason why the yttrium addition does not take positive effect on the glass formation of the Zr₆₅Al_{7.5}Ni₁₀Cu_{17.5} alloy.

4. Conclusions

With 2 ~ 4 at% yttrium addition, the GFA of the Zr₅₅Al₁₅Ni₁₀Cu₂₀ alloy with low purity raw materials and under a low vacuum condition is greatly improved. The yttrium addition can also modify the thermal properties of the BMGs, but it does not significantly change their elastic properties and hardness. The similar effect is not observed in the Zr₆₅Al_{7.5}Ni₁₀Cu_{17.5} alloy. Our results indicate that the rare earth element addition may be an effective method to obtain the Zr-based BMGs with low purity materials and at a low vacuum.

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