Rare Metal Materials and Engineering
Volume 53, Issue 3, March 2024
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Wang Xinghua, Wang Guangtao, Liu Xiaolong, et al. Influence of Hf on Relaxation Behavior of Zr-Al-Ni-Cu Glassy Alloys[J]. Rare Metal Materials and Engineering, 2024, 53(03): 651-659. DOI: 10.12442/j.issn.1002-185X.20230100.

ARTICLE

Influence of Hf on Relaxation Behavior of Zr-Al-Ni-Cu Glassy Alloys

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Abstract: The influence of Hf element on enthalpy and hardness relaxation behavior of $Zr_{70}Al_{7.5}Ni_{8}Cu_{14.5}$ (70Zr), $Zr_{55}Al_{10}Ni_{5}Cu_{30}$ (55Zr) and $(Zr_{0.75}Hf_{0.25})_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ ($65Zr_{0.75}Hf_{0.25}$) bulk glass-type alloys with large diameters of centimeter-level was examined by measuring the temperature dependence of apparent specific heats in as-spun and annealed states. Results show that the structural relaxation of 70Zr and 55Zr alloys occurs through a single-stage mode where the relaxation peak is observed at the annealing temperature (T_a) near glass transition temperature (T_g), while $65Zr_{0.75}Hf_{0.25}$ alloy shows a double-stage reaction with enthalpy relaxation peaks appearing at 523 and 648 K near T_g. The single-stage relaxation mode for 70Zr and 55Zr alloys indicates that these alloys have high resistance to annealing-induced relaxation over the whole temperature range up to T_g, because the distinct relaxation occurs only around the temperature of T_g. $65Zr_{0.75}Hf_{0.25}$ glassy alloy shows a relaxation sub-peak around 523 K presumably due to the weaker bonding nature of Zr-Hf atomic pair with nearly zero in heat of mixing, and the distinct main relaxation occurs near T_g. The Vickers hardness also shows the similar double-stage peak behavior as a function of T_a for $65Zr_{0.75}Hf_{0.25}$ as well as $(Zr_{0.5}Hf_{0.5})_{65}$-$Al_{7.5}Ni_{10}Cu_{17.5}$ ($65Zr_{0.5}Hf_{0.5}$) alloys, so the T_a for the first-stage hardness peak agrees with that for the enthalpy relaxation. These results imply that icosahedral-like medium range ordered structure consisting of Zr, Al, Ni and Cu elements with the three components rule for stabilization of supercooled liquid remains stable during the low T_a relaxation. The double-stage enthalpy and hardness relaxation only appear in $65Zr_{0.75}Hf_{0.25}$ and $65Zr_{0.5}Hf_{0.5}$ glassy alloys which deviate from the three components rule, implying that the unnecessary multiplication for the formation of bulk glassy alloys leads to an increase in structural instability during low-temperature annealing.

Key words: enthalpy relaxation; hardness relaxation; double-stage relaxation; single-stage relaxation; multicomponent glassy alloys

Since the findings of new multicomponent glassy alloys exhibiting high thermal stability of supercooled liquid associated with the formation of bulk glassy alloys around 1990[1–3], many efforts have been made to develop bulk glassy alloys as a new type of metallic material with glassy structure in a bulk form in conjunction with the clarification of fundamental properties and the searches for novel application fields[4–7]. It is known that the syntheses of bulk glassy alloys since 1989 have been made in the order of La-, Mg- and then Zr-based alloy systems[4–7] and their maximum diameters for glass formation exceed largely 10 mm[5–7]. For Zr-based bulk glassy alloys which are important for engineering applications, their alloy systems can be roughly classified to the following three types: Zr-Al-TM (TM=Co, Ni, Cu)[2], Zr-Ti-Be-Ni-Cu[3] and Zr-Cu-Al-Ag[8] types. The first and the second type bulk glassy alloys have been used as practical materials in machinery, optical, pin-spring, casing, sporting goods and medical instrument parts. For instance, the application of pin-type spring glassy alloy used in personal computer, mobile phones and smart phones based on Zr-Al-Ni-Cu system becomes significant year by year[7]. Considering the recently increasing engineering importance of bulk glassy alloys for Zr-Al-Ni-Cu system, it is important to examine the stability to structural relaxation of the Zr-based glassy alloys subjected to annealing at the temperatures below glass transition temperature (T_g)[9–11]. It has been reported that a typical $Zr_{55}Al_{10}Ni_{5}Cu_{30}$

Received date: March 01, 2023

Foundation item: National Natural Science Foundation of China (51901133); The Introduction of Talents and Scientific Research Project (YJ2021-49); Shanghai University Young Teacher Training Funding Program (ZZ202212056)

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bulk glassy alloy has rather high stability to annealing-induced structural relaxation at the temperature well below T_g and exhibits a single-stage change in the annealing-induced enthalpy structural relaxation as a function of annealing temperature[12]. The similar single-stage enthalpy relaxation behavior has also been reported for other typical bulk glassy alloys with optimum alloy composition in each alloy system such as $La_{55}Al_{25}Ni_{10}Cu_{10}$[13], $Pd_{42.5}Cu_{30}Ni_{7.5}P_{20}$[14], $Ni_{40}Pd_{40}P_{16}B_4$[15] and $Ni_{60}Pd_{20}P_{16}B_4$[15].

For engineering Zr-Al-Ni-Cu bulk glassy alloys, it has been reported that the enrichment of Zr ranging from 55% to 70%, namely, from $Zr_{55}Al_{10}Ni_5Cu_{30}$ (55Zr) to $Zr_{70}Ni_{16}Cu_6Al_8$, causes distinct increase in Poisson's ratio, plastic strain, fracture toughness, corrosion resistance and stress-corrosion cracking resistance, though the yield strength, Young's modulus and hardness decrease slightly[16]. The 70Zr bulk glassy alloy has still high glass-forming ability with a large diameter of 10 mm and hence can be regarded as a more interesting engineering structural material. In addition, the enrichment of Zr content from 55% to 70% is presumed to increase the annealing-induced structural relaxation owing to the increase in the number of Zr-Zr atomic pairs with weak bonding nature as compared with 55Zr alloy. Recently, there has been a rapidly increasing interest in high entropy type and pseudo high entropy type bulk glassy alloys. However, little is known about the structural relaxation behavior of their multicomponent glassy alloys upon annealing. The clarification is essential for future extension as engineering materials. Here, multicomponent (Zr, Hf)$_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ glassy alloys were selected to examine the change in the enthalpy and hardness relaxation stabilities of glassy phase by the addition of Hf which has nearly zero heat of mixing to Zr. There are few reports on the annealing-induced enthalpy relaxation behavior of Zr-rich 70Zr and (Zr, Hf)$_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ bulk glass-type alloys which are expected to exhibit improved characteristics.

This research aims to examine enthalpy relaxation behavior of 70Zr and $(Zr_{0.75}Hf_{0.25})_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ ($65Zr_{0.75}Hf_{0.25}$) bulk glass-type alloys subjected to annealing in a wide temperature range below T_g in comparison with 55Zr alloy, and to clarify the change in the annealing-induced enthalpy relaxation with the shift to Zr-rich composition and the significant replacement of Zr by Hf for Zr-Al-Ni-Cu base bulk glassy alloys. In addition to the enthalpy relaxation, we have also examined, for comparison, the change in Vickers hardness with T_a for 70Zr, 55Zr, $65Zr_{0.75}Hf_{0.25}$ and $(Zr_{0.5}Hf_{0.5})_{65}Al_{7.5}Ni_{10}Cu_{17.5}$($65Zr_{0.5}Hf_{0.5}$) alloys. Based on the structure and hardness relaxation data, we further investigated the feature of annealing-induced structural and hardness relaxations for the high-order multicomponent bulk glass-type alloys.

1 Experiment

Bulk glass-type alloys with nominal atomic composition of $Zr_{70}Al_{7.5}Ni_8Cu_{14.5}$ (70Zr), $Zr_{55}Al_{10}Ni_5Cu_{30}$ (55Zr), $(Zr_{0.75}Hf_{0.25})_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ ($65Zr_{0.75}Hf_{0.25}$) and $(Zr_{0.5}Hf_{0.5})_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ ($65Zr_{0.5}Hf_{0.5}$) were chosen because they have a large supercooled liquid region and high glass-forming ability with large diameters of centimeter-class in spite of significant difference in the major host metal contents[17–19]. Besides, hypoeutectic bulk glassy alloy with Zr content as high as 70% exhibits excellent mechanical and chemical properties[19]. The specimens used for the present structure and hardness relaxation studies were in a ribbon form with about 25 μm in thickness and 1.2 mm in width, and prepared by the single roller melt spinning method. The amorphous structure was identified by X-ray diffraction (XRD) and ordinary DSC measurement. The measurement of temperature dependence of apparent specific heat was conducted by DSC equipment (PerkinElmer DSC8000 type) at a scanning rate of 0.67 K/s in a flowing argon atmosphere. The annealing treatments at 473–553 K for 1 – 12 h were carried out in a flowing argon atmosphere. Vickers hardness as a function of annealing temperature was also measured at room temperature by a Vickers hardness tester under a load of 0.49 N.

2 Results

Fig. 1 shows apparent specific heat curves of the as-spun 70Zr, 55Zr, $65Zr_{0.75}Hf_{0.25}$ and $65Zr_{0.5}Hf_{0.5}$ glassy alloys. These four alloys exhibit distinct glass transition, followed by a large supercooled liquid region and crystallization. The glass transition temperature (T_g), onset temperature of crystallization (T_x) and supercooled liquid region (ΔT_x) are 604, 710 and 106 K for 70Zr alloy, respectively; 665, 780 and 104 K for 55Zr alloy, respectively; 676 , 757 and 92 K for $65Zr_{0.75}Hf_{0.25}$ alloy, respectively; 690, 770 and 80 K for $65Zr_{0.5}Hf_{0.5}$ alloy, respectively. The increase in Zr content as well as the replacement amount of Zr by Hf increase T_g and T_x, while the ΔT_x decreases with increasing the replacement amount of Zr by Hf through the rapid increase in T_g.

Fig. 2 shows the temperature dependence of apparent specific heats C_p for 70Zr alloy in as-quenched state and annealed at the temperatures between 423 and 623 K for 1, 3, 6 and 12 h. The $C_{p,q}$, $C_{p,s}$ and $C_{p,a}$ represent the apparent specific heats of the as-quenched sample, the reference sample heated at a heating rate of 0.67 K/s up to 653 K followed by holding at 653 K for 60 s, and then cooled to room temperature at 0.67 K/s, and the samples annealed at different temperatures of 423–623 K for 1, 3, 6 and 12 h, respectively.

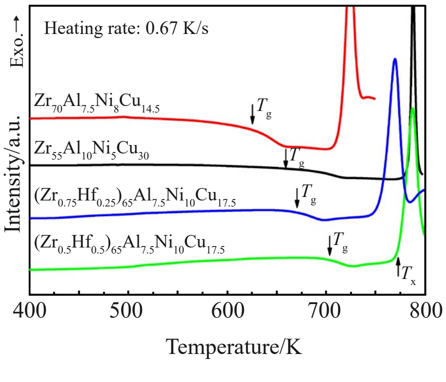

Fig.1 Apparent specific heat curves of as-spun glassy alloys

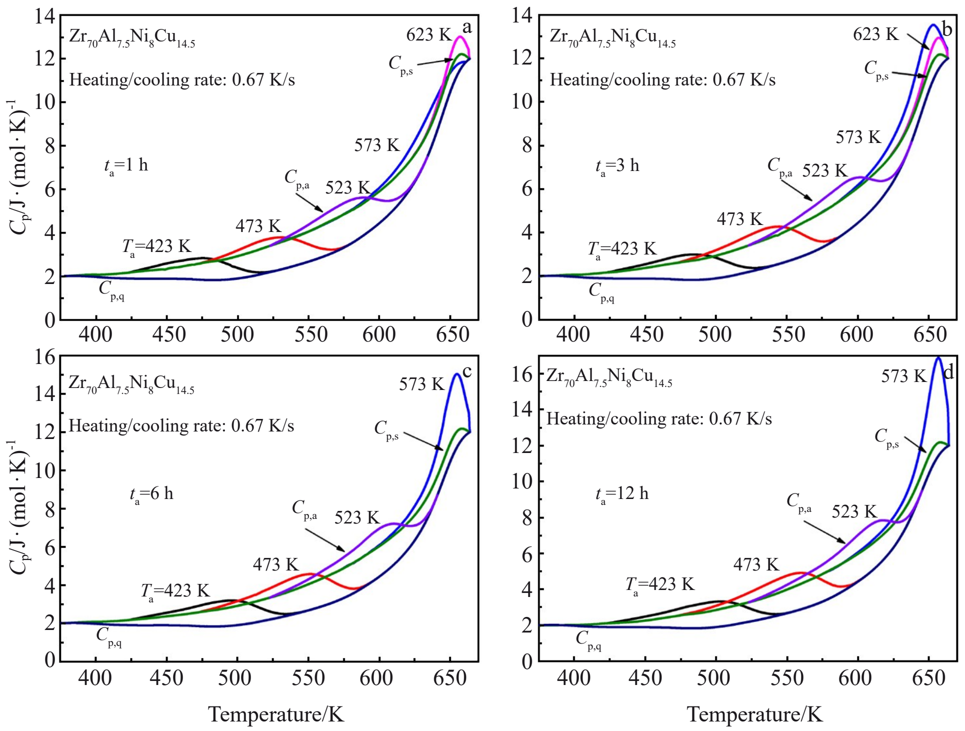

Fig.2 Temperature dependence of apparent specific heats of $Zr_{70}Al_{7.5}Ni_8Cu_{14.5}$ glassy alloy in the as-quenched state ($C_{p,q}$), heated to 653 K for 60 s ($C_{p,s}$), and annealed at 423–623 K ($C_{p,a}$) for different annealing time (t_a): (a) 1 h, (b) 3 h, (c) 6 h, and (d) 12 h

The $C_{p,q}$ shows an irreversible exothermic reaction with an onset temperature of about 395 K. The $C_{p,a}$ starts to deviate from the $C_{p,s}$ curve at each annealing temperature (T_a), which shows an excess endothermic reaction, followed by a maximum peak, and then merges with the $C_{p,q}$ curve. The endothermic reaction occurs reversibly and its peak, temperature and endothermic enthalpy quantity are dependent on annealing condition. The irreversible reaction is due to the change from as-quenched disordered atomic configurations to relaxed disordered configurations upon heating, while the reversible endothermic peak is due to the change of annealing-induced relaxed atomic configurations to disordered configurations which are in an internal equilibrium state at higher heating temperatures.

Fig.3 shows the temperature dependence of $C_{p,q}$, $C_{p,s}$ and $C_{p,a}$ of 55Zr alloy in as-quenched and annealed states at the temperatures between 423 and 673 K for 1, 3, 6 and 12 h. The $C_{p,s}$ was obtained for the sample heated at a heating rate of 0.67 K/s to 725 K followed by holding for 60 s, and then cooled at 0.67 K/s to room temperature. The $C_{p,a}$ presents the apparent specific heat of the samples annealed for 1, 3, 6 and 12 h at temperatures of 423 – 673 K. The features of the temperature dependence of $C_{p,q}$, $C_{p,s}$ and $C_{p,a}$ are nearly the same as those (Fig.2) obtained for 70Zr alloy.

Fig.4 shows the temperature dependence of $C_{p,q}$, $C_{p,s}$ and $C_{p,a}$ of $65Zr_{0.75}Hf_{0.25}$ alloy in as-quenched and annealed states at the temperatures between 473 and 648 K for 1, 3, 6 and 12 h. The $C_{p,s}$ was obtained for the sample heated at a heating rate of 0.67 K/s to 718 K followed by holding for 60 s, and then cooled at 0.67 K/s to room temperature. The $C_{p,a}$ also presents the apparent specific heat of the samples annealed at different temperatures of 473 – 648 K for 1 – 12 h. The features of the temperature dependence of $C_{p,q}$ and $C_{p,s}$ are nearly the same as those for 70Zr (Fig. 2) and 55Zr (Fig. 3) alloys, while the $C_{p,a}$ shows a distinct difference in the endothermic peak behavior with annealing temperature (T_a). The endothermic amount of $C_{p,a}$ curve shows a maximum at T_a=523 K, then decreases with increasing T_a and then increases again rapidly at T_a near T_g. It is thus noticed that the change in $C_{p,a}$ with T_a for $65Zr_{0.75}Hf_{0.25}$ alloy is obviously different from that for 70Zr and 55Zr alloys.

Fig. 5 shows the temperature dependence of $\Delta C_{p,a}$ ($\Delta C_{p,a}$= $C_{p,a}$–$C_{p,s}$) of 70Zr, 55Zr and $65Zr_{0.75}Hf_{0.25}$ alloys on the basis of the data shown in Fig. 2–Fig. 4. The $\Delta C_{p,a}$ of the former two alloys increases gradually with increasing T_a and then increases rapidly at T_a=573 K. The change in $\Delta C_{p,a}$ as a function of T_a is monotonous and no distinct sub-peak is recognized. In addition, $65Zr_{0.75}Hf_{0.25}$ alloy shows a distinctly different $\Delta C_{p,a}$ behavior compared with 70Zr and 55Zr alloys. The $\Delta C_{p,a}$ value shows the maximum at T_a=523 K, followed by the decrease to the minimum at T_a=573 K and a rapid increase at T_a near T_g. The change in $\Delta C_{p,a}$ as a function of T_a does not occur in a monotonous mode, indicating the separable two maximum peaks for annealing-induced enthalpy relaxation.

To show more clearly the T_a dependence of annealing-induced enthalpy relaxation, the maximum value of $\Delta C_{p,a}$ and the calculated $\Delta H_a = \int (C_{p,a} - C_{p,s})dT$ value of 70Zr, 55Zr and $65Zr_{0.75}Hf_{0.25}$ alloys obtained from Fig. 5 are plotted as a

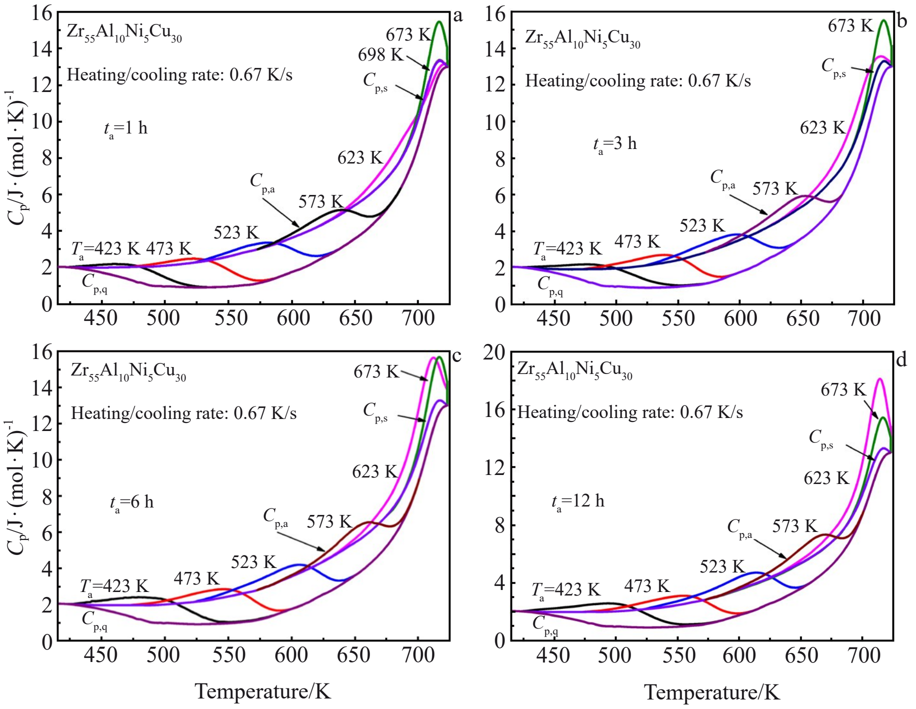

Fig.3 Temperature dependence of apparent specific heats of $Zr_{55}Al_{10}Ni_5Cu_{30}$ glassy alloy in the as-quenched state ($C_{p,q}$), heated to 725 K for 60 s ($C_{p,s}$), and annealed at 423–673 K ($C_{p,a}$) for different annealing time (t_a): (a) 1 h, (b) 3 h, (c) 6 h, and (d) 12 h

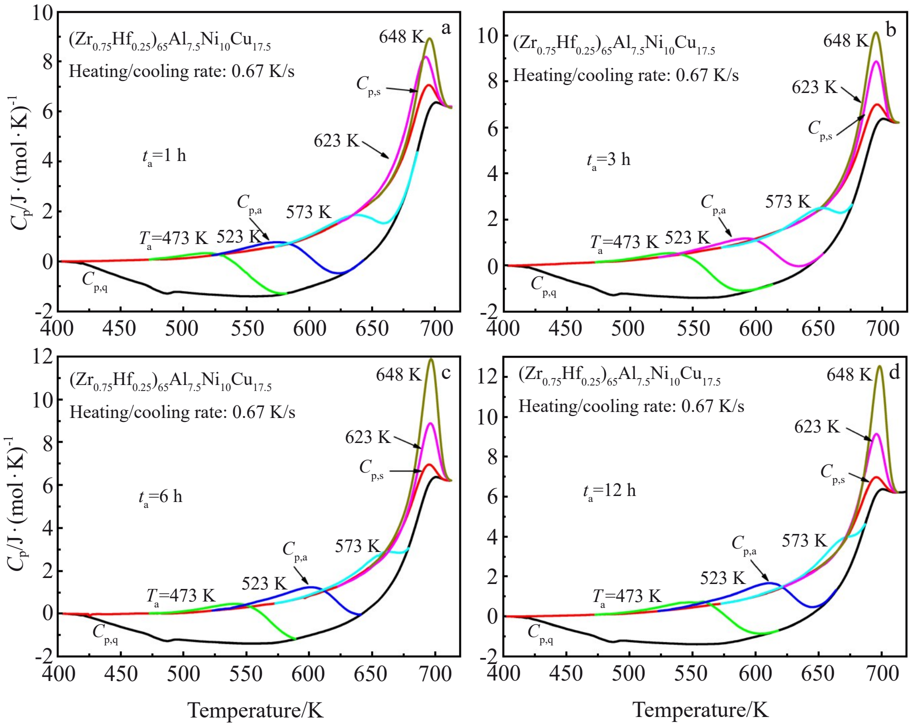

Fig.4 Temperature dependence of apparent specific heats of $(Zr_{0.75}Hf_{0.25})_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ glassy alloy in the as-quenched state ($C_{p,q}$), heated to 718 K for 60 s ($C_{p,s}$), and annealed at 473–648 K ($C_{p,a}$) for different annealing time (t_a): (a) 1 h, (b) 3 h, (c) 6 h, and (d) 12 h

function of T_a in Fig. 6. The former two alloys exhibit a monotonous increase in the values of $\Delta C_{p,a,max}$ and ΔH_a and show the largest values at T_a=573 K near T_g, indicating the rapid increase due to the easy structural relaxation owing to the ordinary glass transition. $65Zr_{0.75}Hf_{0.25}$ alloy shows an appreciable sub-peak phenomenon in the $\Delta C_{p,a,max}(T_a)$ and ΔH_a (T_a) behavior accompanied with the minimum phenomenon around T_a=573 K, and with further increasing T_a to T_g, their

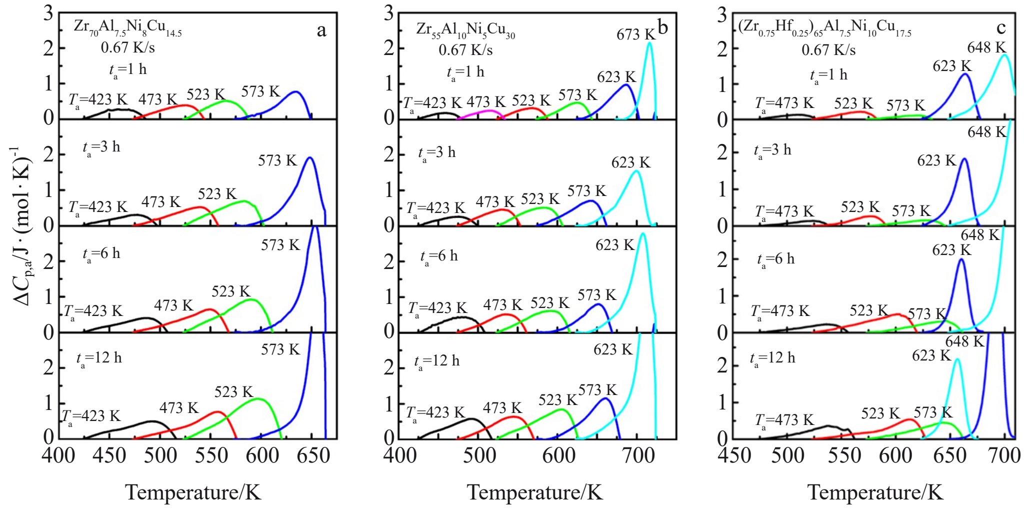

Fig.5 Temperature dependence of endothermic peak $\Delta C_{p,a}$ for $Zr_{70}Al_{7.5}Ni_8Cu_{14.5}$ (a) and $Zr_{55}Al_{10}Ni_5Cu_{30}$ (b) glassy alloys annealed at 423–623 K for 1–12 h, and for $(Zr_{0.75}Hf_{0.25})_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ glassy alloy annealed at 473–648 K for 1–12 h (c)

values increase rapidly due to the glass transition relaxation. Fig.7 shows the normalized curves of endothermic peak $\Delta C_{p,a}$ and relaxation endothermic enthalpy ΔH_a as a function of T_a/T_g. The 70Zr and 55Zr alloys also exhibit a monotonous increase in the values of $\Delta C_{p,a,max}$ and ΔH_a, but the $65Zr_{0.75}Hf_{0.25}$ alloy shows an appreciable II-stage phenomenon. It is thus judged that the annealing-induced enthalpy relaxation occurs through a single stage with a peak at T_a=573 K near T_g for 70Zr and 55Zr alloys, while it occurs through distinguishable two stages for $65Zr_{0.75}Hf_{0.25}$ alloy.

Such a single-stage enthalpy relaxation behavior is similar to that for other multicomponent bulk glassy alloys with an optimum alloy component, i.e., $La_{55}Al_{25}Ni_{20}$[20], $Pd_{40}Cu_{30}Ni_{10}P_{20}$[21], $Pd_{42.5}Cu_{30}Ni_{7.5}P_{20}$[22], $Ni_{40}Pd_{40}P_{16}B_4$ and $Ni_{60}Pd_{20}P_{16}B$[15]. This is different from the double-stage enthalpy relaxation behavior with distinctly separated sub-peak and main peak for metal-metal-metalloid type amorphous alloys containing two metallic elements or more such as Fe-Ni-P[23], Fe-Ni-B[23] and Fe-Ni-Co-Si-B[24]. On the contrary, the present single-stage relaxation behavior is similar to that for metal-metalloid type amorphous alloys such as Fe-P, Fe-B and Ni-P systems[25], though there is an essential difference in alloy components

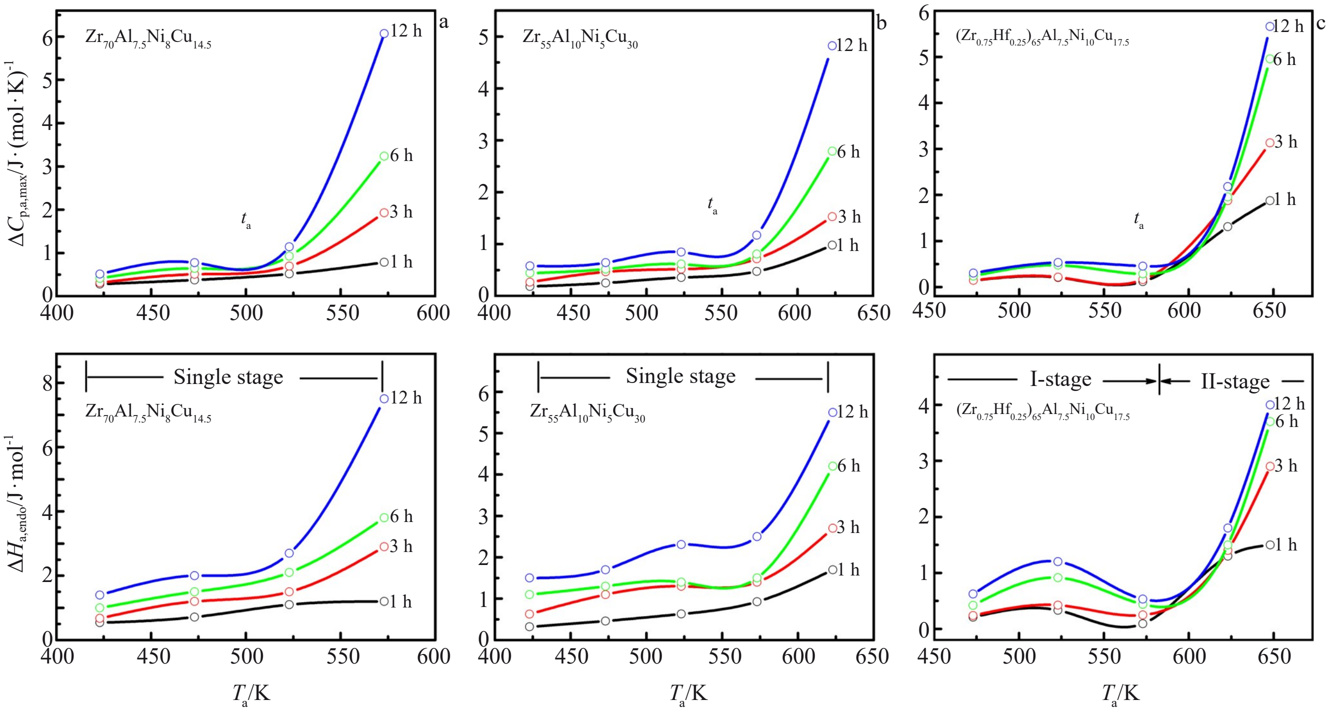

Fig.6 Changes in the maximum values of endothermic peak $\Delta C_{p,a,max}$ and relaxation endothermic enthalpy ΔH_a with annealing temperature (T_a): (a) $Zr_{70}Al_{7.5}Ni_8Cu_{14.5}$, (b) $Zr_{55}Al_{10}Ni_5Cu_{30}$, and (c) $(Zr_{0.75}Hf_{0.25})_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloys

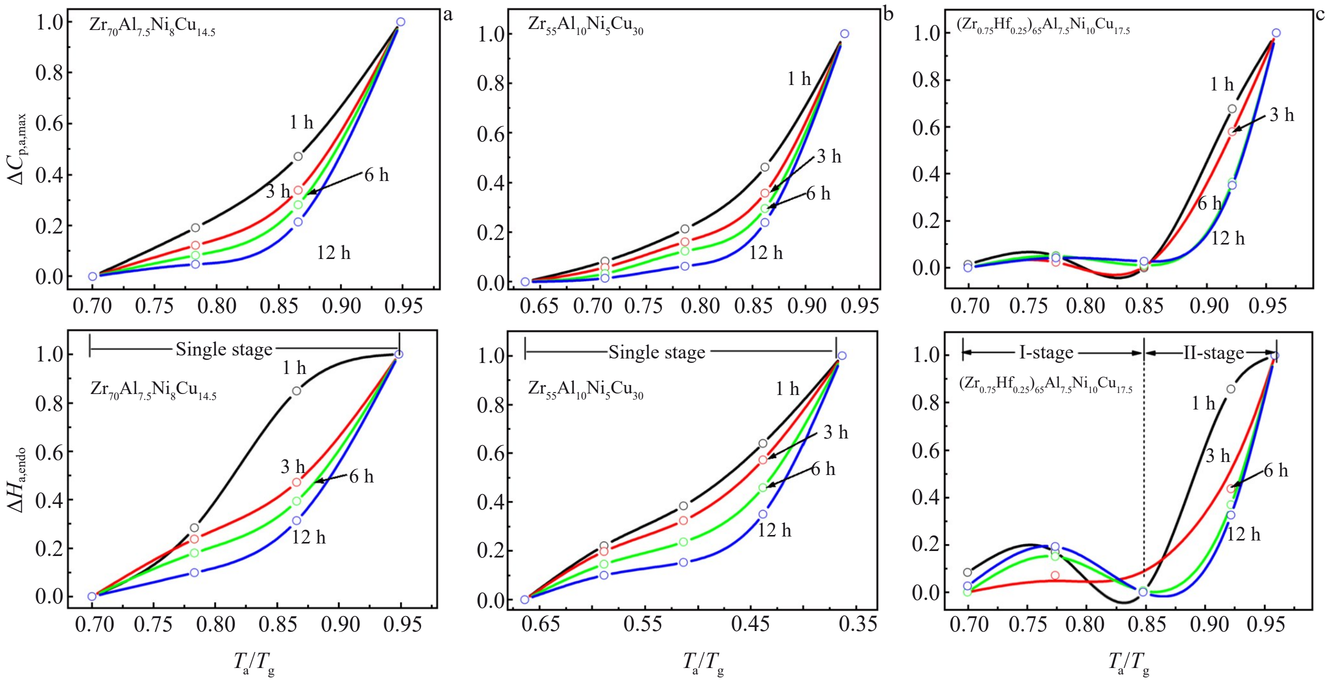

Fig.7 Normalized curves of endothermic peak $\Delta C_{p,a,max}$ and relaxation endothermic enthalpy ΔH_a as a function of annealing temperature (T_a)/glass transition temperature (T_g): (a) $Zr_{70}Al_{7.5}Ni_8Cu_{14.5}$, (b) $Zr_{55}Al_{10}Ni_5Cu_{30}$, and (c) $(Zr_{0.75}Hf_{0.25})_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloys

between the multicomponent bulk glassy alloys consisting of three kinds of metallic elements or more and the amorphous type binary alloys.

Fig. 8 shows the change in Vickers hardness (HV) with T_a for 70Zr, 55Zr, $65Zr_{0.75}Hf_{0.25}$ and $65Zr_{0.5}Hf_{0.5}$ alloys. The HV increases gradually with increasing T_a and significantly at the T_a near T_g for 70Zr and 55Zr alloys, while the T_a dependence of HV for $65Zr_{0.75}Hf_{0.25}$ and $65Zr_{0.5}Hf_{0.5}$ alloys is different, i.e., the HV increases with T_a, followed by the maximum at T_a=523 K, a slight decrease at T_a=573 K and then an increase at T_a near T_g. The T_a dependence of HV for the four glassy alloys is quite similar to the enthalpy relaxation peak behavior. The confirmation of the double-stage relaxation behavior through the measurement of HV is believed to be the first evidence, indicating that the enthalpy-relaxation is closely related to other properties.

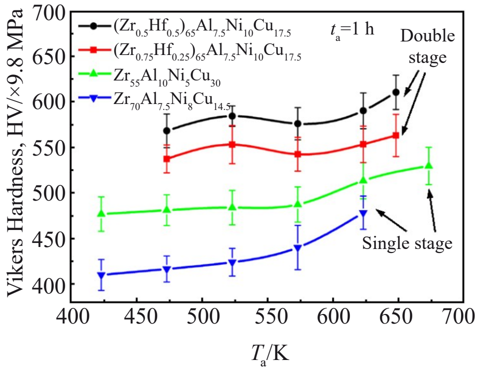

Fig.8 Change in Vickers hardness (HV) with T_a for glassy alloys

3 Discussion

It is known that Zr-Al-Cu ternary alloys can have a typical glassy structure with distinct glass transition and wide supercooled liquid region[2], and the most stable glass with nearly eutectic alloy composition and large supercooled liquid region is obtained for $Zr_{50}Al_{10}Cu_{40}$[16]. Besides, the high stability of supercooled liquid to crystallization is due to the formation of medium-range ordered atomic configurations consisting of three elements of Zr, Al and Cu which include Al-centered first shell clusters[26]. The highest stability of the composition of $Zr_{50}Al_{10}Cu_{40}$ implies that this atomic ratio is the most suitable for the construction of the medium-range ordered atomic configurations. Besides, it has been reported that the partial replacement of Cu by about 5wt% Ni causes further increase in ΔT_x and glass-forming ability[27]. These previous results also suggest that the Zr-rich composition of $Zr_{70}Al_{7.5}Ni_8Cu_{14.5}$ deviates significantly from the optimum atomic ratio to Zr-rich side. The extra Zr element is presumed to allow the generation of Zr-Zr atomic pair with weaker bonding nature and shorter relaxation time in the base structure of the optimum medium-range ordered atomic configurations with longer relaxation time. The cooperative atomic rearrangement of the medium-range ordered atomic configuration corresponds to the ordinary glass transition, while the easy rearrangement of Zr-Zr atomic pair with much shorter relaxation time is presumed to cause the extra endothermic sub-peak reaction at the lower annealing temperature side. However, these presumption and expectation are not consistent with the experimental data where no sub-peak behavior is observed.

Here, it is important to point out that the single-stage enthalpy relaxation behavior for the 70Zr and 55Zr glassy alloys with large diameters of centimeter-class is similar to that for $Pd_{42.5}Cu_{30}Ni_{7.5}P_{20}$ and $Ni_{60}Pd_{20}P_{17}B_3$ bulk glassy alloys with large maximum diameters of 80[28] and 15 mm[29], respectively, belonging to metal-metalloid type. The disappearance of the first-stage sub-peak reaction suggests that the present Zr-based bulk glassy alloys can keep the skeleton structure of medium-range ordered atomic configurations even in the significantly deviated alloy composition of 70Zr. The medium-range ordered atomic configuration is dominated by the coexistence of larger atomic size of Zr, medium atomic size of Al, and smaller atomic size TM (Ni and Cu) elements with large negative heats of mixing among Zr, Al and TM elements, and almost independent of Zr content in the range of 55at% – 70at%. The maintenance of the medium-range ordered atomic configuration in the wide Zr content range is presumed to promote the high glass-forming ability, leading to the formation of bulk glassy alloys with 10 mm in diameter even for 70Zr alloy, in addition to the appearance of the large supercooled liquid region[16].

In addition, as shown in Fig. 5 – Fig. 8, the two-stage relaxations of enthalpy and hardness (HV) are recognized for $65Zr_{0.75}Hf_{0.25}$ and $65Zr_{0.5}Hf_{0.5}$ glassy alloys. Considering that the single-stage enthalpy and hardness relaxations are observed for 70Zr and 55Zr alloys, the appearance of the two-stage enthalpy and hardness relaxations for $65Zr_{0.75}Hf_{0.25}$ and $65Zr_{0.5}Hf_{0.5}$ alloys is concluded to originate from the generation of additional Zr-Hf atomic pair with weaker bonding and shorter relaxation time compared with other atomic pairs of Zr-Al, Zr-Ni, Zr-Cu, Hf-Al, Hf-Ni and Hf-Cu with larger negative heats of mixing[30]. The weaker bonding nature of Zr-Hf pair can be easily estimated from the nearly zero heat of mixing[30]. It is thus said that the significant replacement of major metallic element by other elements with nearly zero heat of mixing makes the structural relation easy in the low temperature region of about T_g – 150 K. This information also proves that the component multiplication to synthesize high entropy glassy alloys by adding the elements with nearly zero heat of mixing leads to the formation of glassy alloys with easier structural relation even at low temperatures in conjunction with the change in fundamental properties.

With the aim of investigating the effect of the Hf replacement on the double-stage relaxation of enthalpy and hardness for $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ glassy alloy, we calculated five parameters, i. e., chemical mixing enthalpy (ΔH_{mix}), atomic size difference (δ), entropy of mixing (ΔS_{mix}), valence electron concentration (VEC) and electron negativity difference ($\Delta\chi$) for the present 70Zr, 55Zr, $65Zr_{0.75}Hf_{0.25}$ and $65Zr_{0.5}Hf_{0.5}$ glassy alloys. The ΔH_{mix} can be calculated according to the extended regular solution mode shown in Ref.[31–32]. The atomic size, electronegativity and VEC for Zr, Hf, Al, Ni and Cu elements used for the calculation are listed in Table 1. The calculated results of five parameters for 55Zr, 70Zr, $65Zr_{0.75}Hf_{0.25}$ and $65Zr_{0.5}Hf_{0.5}$ alloys are shown in Table 2. As can be seen in Table 2, no distinct difference is recognized for ΔH_{mix}, δ, VEC and $\Delta\chi$, while the ΔS_{mix} shows clearly distinguishable values. The ΔS_{mix} values of $65Zr_{0.75}Hf_{0.25}$ and $65Zr_{0.5}Hf_{0.5}$ alloys are 11.43 and 12.14 $J\cdot(mol\cdot K)^{-1}$, respectively, which are considerably larger than those (7.699–8.896 $J\cdot(mol\cdot K)^{-1}$) for 70Zr and 55Zr alloys. Based on this data, it is confirmed that the multiplication of glassy alloy by the element with nearly zero heat of mixing to increase the mixing entropy value is effective for the enhancement of the first-stage relaxation tendency monitored by enthalpy or hardness at T_a in the vicinity of T_g–150 K.

It has previously been reported that the double-stage enthalpy relaxation behavior occurs through the generation of Fe-Ni, Fe-Co and Co-Ni atomic bonds with shorter relaxation time as compared with metal-metalloid atomic pairs for $Fe_{41.5}Ni_{41.5}P_{17}$[23], $Fe_{41.5}Ni_{41.5}B_{17}$[23] and $(Fe, Co, Ni)_{75}Si_{10}B_{15}$[24] amorphous alloys where atomic configurations consisting of short-range ordered trigonal prisms are formed in a skeleton structure[33]. The present recognition of the double-stage enthalpy and hardness relaxations is believed to be the first evidence for metal-metal type multicomponent bulk glass-type alloys.

Fig. 9 shows a schematic illustration of the changes in the $\Delta C_{p,\,endo}$, ΔH_{endo} and HV with T_a for 70Zr, 55Zr, $65Zr_{0.75}Hf_{0.25}$ and $65Zr_{0.5}Hf_{0.5}$ glassy alloys, together with the previous data of other typical bulk glassy alloys such as Zr-Al-Cu[2], Zr-Al-Ni[2] and Pd-Cu-Ni-P[21] systems. Besides, the data of typical amorphous alloys such as Fe-B[25], Fe-P[25], Ni-P[25], Fe-Ni-P[23],

Table 1 Atomic size, electronegativity and VEC for Zr, Al, Ni, Cu and Hf elements[28]

Parameter	Zr	Al	Ni	Cu	Hf
Atomic size/$\times10^{-1}$ nm	1.603	1.432	1.246	1.278	0.158
Electronegativity	1.33	1.61	1.91	1.90	1.30
VEC	4	3	10	11	4

Table 2 Calculated parameters of ΔH_{mix}, δ, ΔS_{mix}, VEC and $\Delta\chi$ for $Zr_{70}Al_{7.5}Ni_8Cu_{14.5}$, $Zr_{55}Al_{10}Ni_5Cu_{30}$, $(Zr_{0.75}Hf_{0.25})_{65}Al_{7.5}Ni_{10}Cu_{17.5}$, $(Zr_{0.5}Hf_{0.5})_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloys

Alloy	ΔH_{mix}/kJ·mol^{-1}	δ	ΔS_{mix}/J·(mol·K)$^{-1}$	VEC	$\Delta\chi$
$Zr_{55}Al_{10}Ni_5Cu_{30}$	–30.57	10.41	8.896	6.3	0.2649
$Zr_{70}Al_8Ni_{16}Cu_6$	–36.66	9.56	7.597	5.3	0.2393
$Zr_{70}Al_{7.5}Ni_8Cu_{14.5}$	–29.94	9.31	7.699	5.42	0.2396
$(Zr_{0.75}Hf_{0.25})_{65}Al_{7.5}Ni_{10}Cu_{17.5}$	–30.84	9.83	11.43	5.75	0.2574
$(Zr_{0.5}Hf_{0.5})_{65}Al_{7.5}Ni_{10}Cu_{17.5}$	–29.46	9.67	12.14	5.75	0.2610

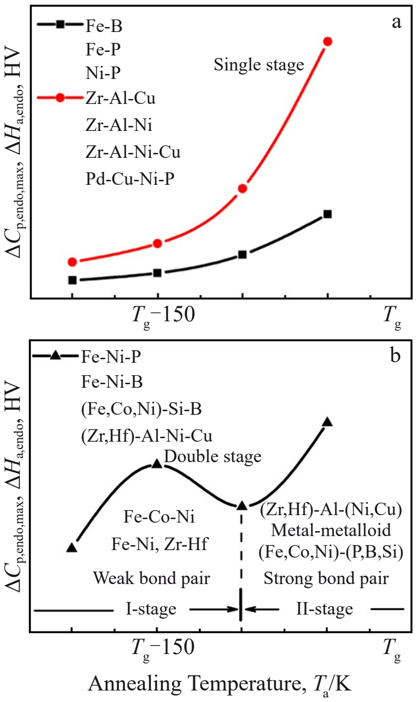

Fig.9 Change in enthalpy relaxation amounts ($\Delta C_{p,a}$ and ΔH_a) and HV with T_a for glassy alloys (the previous data of other typical bulk glass-type alloys and amorphous-type alloys are also shown for comparison)

Fe-Ni-B[23] and (Fe, Co, Ni)-Si-B[24] systems are also shown for comparison. The features of the figure can be summarized as follows: (1) clear difference in the annealing-induced enthalpy or hardness relaxation behavior between the quaternary 70Zr and 55Zr glassy alloys and the quaternary $65Zr_{0.75}Hf_{0.25}$ and $65Zr_{0.5}Hf_{0.5}$ glassy alloys, i.e., the single-stage relaxation for the quaternary alloys and the double-stage relaxation for the quaternary alloys; (2) no difference in the relaxation behavior for the quaternary metal-metal type bulk glassy alloys and the quaternary metal-metalloid type (Pd-Ni-Cu-P) bulk glassy alloys; (3) no difference in the relaxation behavior among the ternary and quaternary glassy alloys; (4) no close relation between the relaxation behavior and glass-forming ability; (5) no appreciable difference in relaxation behavior between enthalpy and hardness. Thus, the single-stage relaxation can be observed for the multicomponent glassy type alloys with the three components rule, and the replacement of the main constituent metal by other elements with nearly zero heat of mixing causes the change to the double-stage relaxation mode.

In addition, when the enthalpy relaxation data (Fig.2, Fig.5 and Fig.6) of 70Zr alloy are compared with those (Fig.3, Fig.6 and Fig. 8) for 55Zr alloy, one can recognize the following differences: (1) the temperature at which the irreversible exothermic relaxation begins to occur is about 395 K for 70Zr alloy, which is much lower than that (about 425 K) for 55Zr alloy; (2) the annealing-induced endothermic quantity for 70Zr alloy is considerably larger than for 55Zr alloy in spite of the much lower annealing temperature condition; (3) the temperature leading to an internal equilibrium supercooled liquid for 70Zr alloy is considerably lower than for 55Zr alloy. These differences also indicate that 70Zr alloy has a more unstable glassy structure which enables the progress of structural relaxation in the lower annealing temperature side, because of a looser medium-range ordered atomic configurations resulting from the deviation from the optimum Al and TM concentrations, though no distinct sub-peak relaxation behavior occurs.

Thus, the deviation of alloy component from the nearly optimum multicomponent alloy composition in the Zr-based bulk glassy alloys does not cause distinguishable double-stage reaction in the annealing-induced enthalpy or hardness structural relaxation behavior, which may be useful to understand the glass-forming ability of Zr-based bulk glassy alloys and to provide a guiding principle to search for an optimum alloy composition of highly ductile bulk glassy alloy. This expectation is supported by the favorable experimental evidence that the 70Zr bulk glassy alloy exhibits very high compressive plastic strain without final fracture[16], high fracture toughness[34] and high resistance to stress corrosion cracking[35].

4 Conclusions

1) Both $Zr_{70}Al_{7.5}Ni_8Cu_{14.5}$ (70Zr) and $Zr_{55}Al_{10}Ni_5Cu_{30}$ (55Zr) alloys show a single-stage enthalpy or hardness relaxation behavior with the peak at the temperature near T_g. No obviously distinguishable sub-peak relaxation behavior is recognized in the wide low T_a range even for the Zr-rich 70Zr alloy where a large number of Zr-Zr atomic pairs are included.

2) $(Zr_{0.75}Hf_{0.25})_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ ($65Zr_{0.75}Hf_{0.25}$) and $(Zr_{0.5}Hf_{0.5})_{65}$-$Al_{7.5}Ni_{10}Cu_{17.5}$ ($65Zr_{0.5}Hf_{0.5}$) alloys exhibit distinguishable two-stage enthalpy or hardness relaxation behavior where each peak appears at T_a=T_g – 150 K and $T_a \cong T_g$. The first-stage enthalpy or hardness peak is due to the atomic rearrangement of Zr-Hf atomic pair with shorter relaxation time via weaker bonding nature compared with other atomic pairs with longer relaxation time via stronger bonding nature resulting from large negative heats of mixing. The single-stage enthalpy or hardness relaxation as well as their relaxations at the higher temperature side in the second-stage enthalpy relaxation are due to the ordinary glass transition caused by the long-range cooperative atomic rearrangements of the constituent elements.

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Hf对Zr-Al-Ni-Cu金属玻璃弛豫行为的影响

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摘　要：通过测定快淬态和退火态比热与温度的关系，研究了Hf元素对$Zr_{70}Al_{7.5}Ni_8Cu_{14.5}$（70Zr）、$Zr_{55}Al_{10}Ni_5Cu_{30}$（55Zr）和$(Zr_{0.75}Hf_{0.25})_{65}Al_{7.5}Ni_{10}Cu_{17.5}$（$65Zr_{0.75}Hf_{0.25}$）厘米级金属玻璃焓和硬度弛豫的影响。结果显示：70Zr和55Zr合金的结构弛豫表现为单峰现象，在退火温度（T_a）接近玻璃转变温度（T_g）时出现弛豫峰；而$65Zr_{0.75}Hf_{0.25}$合金的结构弛豫表现为双峰现象，分别在523和648 K（接近T_g）时出现焓弛豫峰。70Zr和55Zr合金在T_g温度附近出现明显的单峰弛豫行为，表明合金在T_g之前的整个温度范围内具有较高的抵抗退火诱导结构弛豫的能力；另一方面，$65Zr_{0.75}Hf_{0.25}$合金在523 K附近出现一个弛豫子峰，可能是由于Zr-Hf原子对的键合性较弱，混合焓接近于零，随后在T_g附近出现明显的主弛豫。$65Zr_{0.75}Hf_{0.25}$和$(Zr_{0.5}Hf_{0.5})_{65}Al_{7.5}Ni_{10}Cu_{17.5}$（$65Zr_{0.5}Hf_{0.5}$）合金的硬度也表现出类似的双峰现象，导致第一峰的$T_a$与焓弛豫峰的$T_a$一致。结果表明，满足非晶形成三原则的Zr、Al、Ni和Cu组成的类二十面体中程有序结构在低T_a温度下保持稳定；只有背离非晶形成三原则的$65Zr_{0.75}Hf_{0.25}$和$65Zr_{0.5}Hf_{0.5}$金属玻璃焓弛豫和硬度弛豫出现了双峰，表明形成大块金属玻璃非必要组元的增加将导致合金结构在低温退火过程中的不稳定性。

关键词：焓弛豫；硬度弛豫；双级弛豫；单级弛豫；多组分金属玻璃

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