Physical Aging of Zr$_{65}$Cu$_{17.5}$Ni$_{10}$Al$_{7.5}$ Glassy Alloy

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Abstract. Physical aging of Zr$_{65}$Cu$_{17.5}$Ni$_{10}$Al$_{7.5}$ glassy alloy has been studied after holding its samples with variation of time and temperature of annealing. The results showed that the enthalpy and entropy decreased with time according to a non-exponential kinetics. The Differential Scanning Calorimetry (DSC) heating scan after annealing was analyzed using Tool-Narayanaswamy-Moynihan (TNM) model. The analysis showed that a set of parameters that fitted the heating scan data for one annealing time did not fit the heating scan data for another annealing time. This is explained due to approximations used in the model and the effect of Johari-Goldstein (JG) relaxation to the physical aging.

Keywords: Physical Aging; Glassy Alloys; Glass Transition; Calorimetry; Johari-Goldstein Relaxation

1. Introduction

Structural relaxation on aging of glasses has been studied extensively mainly because it changes the properties of a glass during its use. When a glass is heated toward its glass-softening temperature or when a glass is cooled, all its physical properties change not only with temperature but also with time. Moreover, when a glass is kept at a certain temperature, its properties change with time. Therefore, the properties of a glass depend on its thermal history. By studying the structural relaxation of a glass, one can predict the changes in properties of a glass with time. Change in properties during structural relaxation of glasses has been generally studied [1-4]. Based on the study of structural relaxation in multicomponent metallic glasses, there is a distinction between the topological short range order (TSRO) and the chemical short range order (CSRO) [5]. The change of TSRO and CSRO of metallic glasses is due to annealing or ageing. X-ray and electron diffraction measurements have been used to gain insight of this concept on the atomic diffusion processes occurring either during the isothermal annealing or during heating toward $T_g$. TSRO is a slow process which begins after the completion of the fast CSRO process. From the study of structural relaxation in several Pd- and (Fe, Ni)- based metal-metalloid glasses and Zr-(Cu,Fe,Ni) binary and ternary metallic glasses, at low temperatures structural relaxation occurs by local and medium range rearrangement of the atoms with weak bonding. In contrast, at high temperatures it occurs by the long range cooperative regrouping of metal and metalloid atoms [6].
Johari and coworkers [7] have studied several Ni-based metallic glasses and organic and inorganic glasses. They found that there is no difference between structural relaxation in metallic glasses and other types of glasses when the distribution of self-diffusion times is considered. They showed that structural relaxation of metallic glasses can be simulated by the same stretched-exponential relaxation function of diffusion times and non-linearity of relaxation behavior as used for polymeric and inorganic glasses. This similarity led to the conclusion that structural relaxation of metallic glasses instead involves changes in both TSRO and CSRO. They concluded that the origin of the relaxation is seen in the time- and temperature-dependent regain of the equilibrium state. Those local groups of atoms, whose diffusion is fast enough to allow loss of enthalpy and entropy on their approach to an equilibrium configurational state of low energy on annealing, absorb heat to reach their new equilibrium configuration state of higher energy at a higher temperature on heating at a certain rate. Hence each mode of atomic diffusion in the structure has its own ‘mini glass-transition temperature’, and reversible relaxation is a reflection of a broad distribution of times arising from temporal and spatial variations in the atoms’ environment.

The study described here is intended to further examine the various conclusions reached in earlier studies with both technological and academic viewpoint.

2. Materials and Methods

The bulk metallic glass (BMG) of composition Zr₆₅Cu₁₇.₅Ni₁₀Al₇.₅ were prepared by (i) arc melting of an accurately weighed mixture of pure elements under a titanium-gettered Argon atmosphere and (ii) transferring the melt to a water-cooled copper crucible. To homogenize the melt, the glassy solid was melted two to four times. Plate-like specimens of thickness 1 - 2 mm, width 5 - 8 mm, and length of 50 - 100 mm and rod specimens of diameter 3 - 4 mm and length of 50 - 100 mm were produced by suction casting in a copper mold. Their glassy nature were characterized by diffraction methods and calorimetry.

For the DSC measurement, the metallic glass samples were cut from the specimens using diamond cutting saw with oil cooling to keep the specimens at ambient temperature. Before cutting the specimens, the surfaces of the specimens were ground using a sand paper so that the dirt and oxide formed on the surfaces were removed. After the cutting, the samples were cleaned by using ethanol. Aluminum pans were also cleaned by using ethanol. The samples contained in the Al-pans were accurately weighed in 10 to 15 mg amounts. The shape of the samples were made such that the surface of the samples has a good thermal contact with the pans and to obtain further better contacts, the samples were sealed in the pans by crimping them. During the DSC measurement, 99.9% pure argon gas was used as purge gas. The normalized DSC output divided by their mass did not differ by more than 0.5%. Thus the effect of the samples’ mass on the measured values were negligible. Repeat measurements showed that the metallic glass sample or its components did not chemically react or form an alloy with the aluminum pan over the temperature range of the study.

As in a typical study of structural relaxation, the as-cast sample of Zr₆₅Cu₁₇.₅Ni₁₀Al₇.₅ glass was first heated at a rate of 20 K/min in the DSC from 50 °C to 500 °C. This led to its crystallization. The scans obtained are shown in Figure 1. Figure 1 shows two exotherms at high temperature corresponding to the crystallization of the sample. In Figure 1, a broad exotherm was observed due to the structural relaxation on first heating of the as-cast sample over the 50 °C range. From this scan, we obtain the onset crystallization temperature $T_c$, as 424 °C for heating at a rate 20 K/min, and the temperature range of the supercooled ultraviscous liquid of about 380 to 420
°C. From these scans, we obtained the $T_g$ of 325 °C for the heating rate of 20 K/min and $\Delta C_p$ as 19 J/mol K. For the isothermal annealing experiments, the experiments were done for a fixed annealing temperature and different annealing times. The annealing temperatures are 280, 285, 290, 295, and 300 °C. The annealing times for each annealing temperature are 5, 10, 20, 40, 80, 160, and 320 minutes.

![Figure 1. DSC scan for Zr$_{65}$Cu$_{17.5}$Ni$_{10}$Al$_{7.5}$ glass at 20 K/min rate.](image)

In the isothermal annealing experiment, a new as-cast sample was heated from 250 °C (initial temperature, $T_0$) to 400 °C (upper temperature limit, $T_h$) at 20 K/min and cooled from 400 °C to 250 °C at 20 K/min. After this, the sample was heated and cooled again over the same temperature range and the same heating and cooling rate as for the first scan. The second heating scan was obtained for the unannealed sample. After the second cooling, the sample was heated at heating rate of 100 K/min to the annealing temperature, 280 °C, held for 5 minutes at 280 °C, and then cooled at 100 K/min to 250 °C. The sample then heated at a heating rate of 20 K/min to 400 °C and cooled at 20 K/min to 250 °C. The heating scan obtained was the heating scan after annealing at 280 °C for 5 minutes. The DSC scanning was repeated for the annealing times of 10, 20, 40, 80, 160, and 320 minutes. Experiments were done also for annealing temperatures of 285, 290, 295, and 300 K with other new as-cast samples for the same annealing times as given above.

3. Results and Discussion

An isothermally annealed or structurally relaxed glass generally shows an endothermic feature or an ‘overshoot’ in the DSC scan. The reversibility of this effect on thermal cycling between $T_0$ and $T_h$ indicates that the underlying atomic diffusion processes are reversible in nature. The DSC scans, of the annealed and unannealed samples of Zr$_{65}$Cu$_{17.5}$Ni$_{10}$Al$_{7.5}$ bulk metallic glass obtained during heating at 20 K/min after annealing at 285 °C for annealing times of 5, 10, 20, 40, 80, 160, and 320 minutes are shown in Figure 2. The plot for annealed sample shows an excess endothermic heat flow or an overshoot. The $dH/dt$ measured in the scan was multiplied by molecular weight and divided by the mass of the sample and by the heating rate, $q_h$, and thus
converted to \( (dH/dT) \) in units of J/mol K. The difference between the annealed DSC scan and unannealed DSC scan, i.e., \([ (dH/dT)_{an} - (dH/dT)_{un} ] \) is plotted against \( T \) in Figure 3 for annealing temperatures of 285 °C. The plots of \( (dH/dT) \) and \([ (dH/dT)_{an} - (dH/dT)_{un} ] \) for other annealing temperatures are not shown in this report.

Figure 2. DSC scan for Zr\(_{65}Cu_{17.5}Ni_{10}Al_{7.5} \) glass at 20 K/min rate after annealing at 285 °C for annealing times of 5, 10, 20, 40, 80, 160, and 320 min.

Figure 3. The plots of \( (dH/dT)_{an} - (dH/dT)_{un} \) for Zr\(_{65}Cu_{17.5}Ni_{10}Al_{7.5} \) glass at 20 K/min rate after annealing at 285 °C for annealing times of 5, 10, 20, 40, 80, 160, and 320 min.
In these isothermal annealing experiments, a great amount of time and effort was made to repeat the measurement for different samples so that no crystallization occurred. If the sample showed crystallization, $\frac{dH}{dt}$ in its ultraviscous liquid state was lesser than before, and all data were rejected. In most of the experiments after annealing 10 or 20 minutes at fixed annealing temperature the samples partially crystallized.

A rapid and large magnitude of structural relaxation in metallic glasses, as found for Zr$_{65}$Cu$_{17.5}$Ni$_{10}$Al$_{7.5}$, is observed when an as-cast sample or a metallic glass kept for a long period at ambient temperature is heated more slowly than it was cooled from the liquid state. Thermodynamically, its state during heating approaches a structure of lower energy and entropy. Usually, in the production of a metallic glass, a high cooling rate is required to convert its liquid state to glassy state. The high cooling rate during the glass formation in a mold creates also stored-strains in the specimen across its thickness, because of the different rate of cooling in its bulk. When a sample of this specimen is heated, enthalpy, entropy as well as some of the elastic energy stored in the sample are released. These effects appear as an exothermic feature in the DSC scan, as is seen in the first heating scan in Figure 1. After the first heating of the as-cast sample from its glass to its supercooled liquid, any further relaxation that occurs on thermal cycling is referred to as reversible relaxation. In this reversible relaxation, the physical properties are recovered after subjecting the glass to a variety of thermal histories.

During the course of structural relaxation, the enthalpy and entropy of a glass decrease. The decrease in enthalpy and entropy is a combined effect of two occurrences, first, loss of the configurational enthalpy and entropy as a result of localized atomic diffusion in the disordered structure, and second, changes in the phonon frequencies and the corresponding density of states [7]. Contributions from these two effects can be seen in the exothermic and endothermic features of the DSC scan shown in Figure 2. In the figure, the features show generally how the recovery of the configurational enthalpy and entropy by local atomic diffusion and by changes in phonon behavior produce an endothermic feature when a sample, after having been annealed is heated to its ultraviscous liquid state.

Structural relaxation can be appropriately described in the terms of changes in the thermodynamic state functions without using a model. For that purpose, the decrease in enthalpy on annealing, $d\Delta H_a$, may be written as the sum of several contributions [7],

$$d\Delta H_a = \left( \frac{\partial \Delta H}{\partial t_a} \right)_{T_a, q_h, q_c} dt_a + \left( \frac{\partial \Delta H}{\partial q_h} \right)_{T_a, t_a, q_c} dq_h + \left( \frac{\partial \Delta H}{\partial q_c} \right)_{T_a, t_a, q_h} dq_c \quad (1)$$

where $d\Delta H_a$ is the difference between the enthalpy of the material before and after the annealing experiment. The prefix $\Delta$ is used to maintain that quantities determined by experiments are $[H - H(0 \text{ K})]$ and $[S - S(0 \text{ K})]$, where $H(0 \text{ K})$ and $S(0 \text{ K})$ are the enthalpy and entropy of a material at 0 K. It should be noted also that $H(0 \text{ K})$ decreases on annealing as the structure densifies, as does $S(0 \text{ K})$ because the randomness of the zero-point energy changes.

The first term on the right hand side of equation (1) represents the enthalpy loss with respect to temperature for constant annealing time, $t_a$, heating rate, $q_h$, and cooling rate, $q_c$, and the second term represents this loss with respect to $t_a$, for constant $T_a$, $q_h$, and $q_c$. The third term represents the enthalpy loss over a certain temperature range with respect to the heating rate, for constant $t_a$, $T_a$, and $q_c$ and the fourth term represents the enthalpy loss over a certain temperature range...
with respect to the cooling rate, for constant \( t_a, T_a, \) and \( q_h. \) Because \( q_h \) and \( q_c \) for the experiments are kept constant, the magnitudes of the third and fourth terms are zero. The corresponding decrease in entropy is given by \([7]\),

\[
d\Delta S_a = \left( \frac{\partial \Delta S}{\partial T} \right)_t dT + \left( \frac{\partial \Delta S}{\partial t} \right)_T dt_a + \left( \frac{\partial \Delta S}{\partial q_h} \right)_{T, t, q_c} dq_h + \left( \frac{\partial \Delta S}{\partial q_c} \right)_{T, t, q_h} dq_c \tag{2}
\]

where the terms have the same meaning as in equation (1). These two equations describe how \( H \) and \( S \) of a glass will change during annealing or during aging if the temperature fluctuates at a certain rate.

Effects of the Annealing Temperature

To investigate the effects of the annealing temperature for a constant annealing time, we first determine the first term on the right hand side of equations (1), and (2), i.e., the enthalpy and entropy loss when a vitrified sample is annealed at a selected \( T_a \) for a fixed period. The magnitude of \( d\Delta H_a \) of equation (1) was determined from the area of the difference between the annealed DSC scan and unannealed DSC scan, i.e., \([dH/dT]_{an} - (dH/dT)_{un}\) plotted on a linear temperature scale using equation (3) shown in Figure 4 and \( d\Delta S_a \) was determined from the area of the difference curve plotted on a logarithmic temperature scale using equation (4).

\[
d\Delta H_a = \int_{T_1}^{T_2} \left[ \left( \frac{dH}{dT} \right)_{an} - \left( \frac{dH}{dT} \right)_{un} \right] dT \tag{3}
\]

\[
d\Delta S_a = \int_{T_1}^{T_2} \left[ \left( \frac{dH}{dT} \right)_{an} - \left( \frac{dH}{dT} \right)_{un} \right] d\ln(T) \tag{4}
\]

Figure 4. The enthalpy loss for \( \text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5} \) glass after annealing for annealing times of 5, 10, 20, 40, 80, 160, and 320 min at 280, 285, 290, 295, and 300 °C.
The area under the peaks in the difference curves in Figure 3 was integrated against $T$ with a baseline at $dH/dT = 0$ and this gave the value of the enthalpy recovered on heating the annealed sample, which should be the same as the enthalpy lost on structural relaxation during isothermal annealing at a chosen $T_a$ and $t_a$, plus any other enthalpy lost on heating when the sample does not crystallize or chemically react during cooling, annealing, or heating. To determine the entropy decrease on structural relaxation, the difference $[(dH/dT)_{ann} - (dH/dT)_{eq}]$ can be constructed against $\ln(T)$ instead of against $T$. The peak area in the difference curve of such a plot yielded the entropy recovered on heating, which should be the same as the entropy decrease on structural relaxation at a chosen $T_a$ and $t_a$. The enthalpy loss on annealing of Zr$_{65}$Cu$_{17.5}$Ni$_{10}$Al$_{7.5}$ at a fixed annealing temperature and different annealing times is plotted against time in Figure 4. Since $H$ and $S$ of an equilibrium liquid at a temperature substantially above its $T_g$ is independent of the path by which it is reached from the glassy state, we can determine the enthalpy and entropy at all temperatures between $T_a$ and $T_{eq}$ from the relation,

$$\Delta H(T) = \Delta H(T_a) - \int_{T_a}^{T} \frac{dH}{dT}dT$$

$$\Delta S(T) = \Delta S(T_a) - \int_{T_a}^{T} \frac{dH}{dT}d\ln T$$

where $(dH/dT)$ is determined from DSC. Thus the $\Delta H(T)$ and $\Delta S(T)$ plots against $T$ for all $T_a$ and $t_a$ condition would merge in the equilibrium liquid state. The values of $\Delta H(T_a)$ and $\Delta S(T_a)$ are taken from Figure 2 and the starting of the integration is from $T_{eq}$ of 250 °C.

**Theoretical Consideration**

The observations of a similarity of structural relaxation in glassy polymers and in metallic glasses [7] indicate that either the conceptual and mathematical treatments in terms of a two-level system used for metallic glasses may be useful for the glassy state in general, or that, the concept and mathematical models which are used currently for interpreting the structural relaxation in other glasses be extended to metallic glasses. It is expected that the atomic level processes in all glasses be similar, and that, during the annealing of a glass, localized diffusion leading to a spontaneous decrease in $H$ and $S$ of a glass is a reflection of the spontaneous change in either the overall glass structure to a lower configurational energy state, or of only those group of atoms in it that have been trapped in a deep energy minimum. In one general model, which is independent of the molecular or atomic details, developed by Perez and coworkers [8], the high energy sites in configurational space are termed defects. These defects are the local groups of atoms where potential energy correspond to a point on either the attractive side of the potential energy minimum or the repulsive side of it. There are also alternative representations referred to as “rugged energy landscape” models containing numerous minima of varying depth. The potential energy landscapes are now regarded also as time-dependent.

Variations in the atomic environment in a glass structure, in either representation, leads to a distribution of diffusion coefficients, which may be expressed as a distribution of mainly the activation energy, $E$, in the Arrhenius equation, $D = D_0 \exp(-E/kT)$, where $D_0$ is the pre-exponential term and $k$ the Boltzmann constant. On cooling at a certain rate, those atoms which diffuse too slowly to achieve their lowest configurational enthalpy and entropy in the glass structure, become kinetically frozen. As cooling causes a progressively rapid decrease of the self-diffusion coefficient, the majority of the atoms in a glass structure becomes kinetically frozen-in just below $T_g$. The fraction of the atom population that ceases to contribute to a
thermodynamic function during the cooling of a glass leads to further development of a kinetic instability with respect to those parts of the structure that fail to attain a thermodynamic equilibrium with decrease in $kT$. This appears as a gradual decrease in $C_p$, $H$ and $S$ of a glass over a temperature range extending to 0 K. On isothermal annealing, only those local configurations in which atomic diffusion is sufficiently rapid, approach an equilibrium structure within a given annealing time. On heating an annealed glass, self diffusion in the local regions becomes faster according to the same Arrhenius equation as on cooling. And $C_p$, $H$ and $S$ become equal to the sum of contributions from all states that achieve configurational equilibrium on heating plus the vibrational contributions. For each structural state that had attained a configurational equilibrium and reached its $T_f$, defined as the temperature at which a glass is kinetically stable with respect to its equilibrium liquid, on heating at a certain rate, the slopes of the $H$ and $S$ curves rapidly increase once the temperature exceeds $T_f$, goes through a point of inflexion and the curves meet the curves for the configurationally equilibrated state from below the equilibrium state curve.

In the usual DSC scan, when an annealed glass is heated towards its equilibrium liquid state, this recovery appears as an overshoot at $T > T_g$, before the equilibrium liquid state is reached. The area of the overshoot is a measure of the $H$ and $S$ lost during the annealing. Even when the majority of the atoms in a glass structure at $T < T_g$ are kinetically frozen-in, the rapid approach towards an equilibrium of a small, but increasing number of locally diffusing atoms produces a small overshoot at a temperature determined by its diffusion rate and the rate of heating. In this view, the endothermic peak observed on heating an annealed glass is a reflection of the sum of a multitude of $C_p$ overshoots, each corresponding to a “mini glass-liquid transition” of the localized groups of atoms or molecular segments.

In previous studies on physical aging of several metallic glasses where the effect of the distribution of relaxation times was investigated in the glassy state [7,9-14], the glasses were cooled from $T < T_g$, annealed and then heated back to the same $T < T_g$. Johari and coworkers [7,9] observed small endothermic peak in the DSC scan. However, such endothermic was not observed in the DSC scan [10-14] which is similar to the result in the present work. The different findings for this thermally cycling in a $T$ range below $T_g$ can be explained by the competition between two processes: $\alpha$-relaxation and JG relaxation. The endothermic peak observed in Refs. 7 and 9 was attributed to the unfreezing of the faster relaxation modes in the distribution of the $\alpha$-relaxation process [15,16]. If the rate of the JG relaxation occurs is comparable to these faster modes, its process strength would decrease on annealing and on heating, it would be recovered [15,16]. The recovery would be observed as an overshoot at $T > T_g$ and attributed to the $\alpha$-relaxation. On contrary, when the rate of the JG relaxation is close to that of the $\alpha$-relaxation, recovery of the JG relaxation configurations would be accompanied by the recovery of the $\alpha$-relaxation contributions. Therefore the JG relaxation in a DSC scan can be observed only if its relaxation rate is much faster than that of the $\alpha$-relaxation and its magnitude relatively large.

Modeling

To examine whether or not the reversible relaxation in metallic glasses may be attributed to a distribution of relaxation time in the same manner as for other glasses, we qualitatively simulate its feature by using the TNM equations for the structural relaxation of organic and inorganic polymers as done by Hodge [17]. As mentioned earlier, the main observations of this study are: (i) the broad temperature range of structural relaxation, and (ii) the appearance of an endothermic feature on annealing. The kinetics of atomic and segmental motion involves a broad distribution of relaxation times which can be represented in two ways: (i) a set of a
separate relaxation mechanisms for the various relaxation time components of \( g(\tau) \) which represents the distribution of relaxation times, and (ii) an empirical nonexponential relaxation function.

The relaxation function for the irreversible change in the structure is written in terms of a distribution of relaxation times. This distribution of relaxation time is written in the form of a relaxation function,

\[
\phi(t) = \exp \left[ -\left(\frac{t}{\tau}\right)^\beta \right]
\]

where \( \phi(t) = \frac{H(t) - H(\infty)}{H(0) - H(\infty)} \), \( H(t) \) is the value of enthalpy at time \( t \), \( H(\infty) \) is the value of the enthalpy at equilibrium (infinite time), \( H(0) \) is the value of the enthalpy at initial time (the value at \( t = 0 \)), \( \tau \) is characteristic relaxation time, \( \beta \) is a parameter that expresses the breadth of the distribution of relaxation time \( (0 < \beta \leq 1) \). A single relaxation time is denoted by \( \beta = 1 \). Equation (2.13) is equivalent to a set of separate relaxation mechanisms for the various relaxation time components of \( g(\tau) \) which represents the distribution of times:

\[
\phi(t) = \int_0^\infty g(\tau) \exp \left[ -\frac{t}{\tau} \right] d\tau
\]

for \( \int_0^\infty g(\tau) d\tau = 1 \), and,

\[
\tau(T,T_f) = A \exp \left[ \frac{x\Delta h^*}{RT} + \left(\frac{(1-x)\Delta h^*}{RT_f}\right) \right]
\]

where \( \phi(t) \) is the relaxation function, \( \Delta h^* \) is the activation energy, \( T_f \) is fictive temperature, \( A \) is a parameter equal to \( \tau \) when both \( T \) and \( T_f \) are formally infinity, and \( x < 1 \) is an empirical parameter referred to as the nonlinearity parameter. For \( x = 1 \), equation (9) becomes the Arrhenius equation.

The DSC scans of our experimental data were qualitatively simulated by using the parameters: \( \ln A = -76 \), \( x = 0.29 \), \( \beta = 0.69 \) and \( \Delta h^* = 408,000 \) J/mol. The simulated curves are shown in Figure 5 for the annealed sample at 285 °C for annealing times 5, 10, 20, 40, 80, 160, and 320 minutes. In the simulation, a glass was cooled at 100 K/min from 407 °C to 250 °C and heated to 285 °C at 100 K/min then held at 285 °C for a certain annealing time. The heating curve of annealed glass thus could be obtained. These parameters should describe the curves for all the samples, whether annealed or unannealed.

It is evident in Figure 5 that a good fit is obtained for the sample after annealing for 5 minutes, and somewhat satisfactory fit is obtained for the sample annealed for 10 minutes. But the fit is quite unsatisfactory for the samples that were annealed other annealing times. The discrepancy between the simulated results and the experimental data for the metallic glasses seems to support the premise that only for a few cases structural relaxation of a metallic glass may be described in terms of a distribution of relaxation times. The above-given comparison of simulation of the DSC scans for metallic glasses, even though they fail to predict the structural
relaxation or annealing over a long time period, shows that the structural relaxation observed in metallic glasses, whether irreversible or reversible, has a broad distribution of atomic diffusion time. Formalisms used for glasses in general can be used to describe the structural relaxation in metallic glasses.

The simulations also have been performed previously for several Zr-based metallic glasses [10-14]. The simulation results were similar to our finding where results indicated that the glasses had a broad glass transition region. According to Hammond et. al. [11], Wunderlich’s model may be used to explain that structural relaxation in these glasses involved the cooperative motion of a single bead. Similar to previous studies of other Zr-based metallic glasses [10-14], relaxation behavior was well described by the TNM model. Qiao et. al. [14] further elaborated that the values of $\beta$ and relaxation times were sensitive to the composition of the metallic glasses. The enthalpy relaxation that we observed in the present work were sensitive to both annealing time and temperature, which is in a good agreement with the results relative to other metallic glasses [11,14].

4. Conclusions

The structural relaxation studies of metallic glasses presented in this section leads to the following conclusions:

1. There are two types of relaxation observed in a metallic glass. The first relaxation is irreversible relaxation and the second is reversible relaxation. The irreversible relaxation is observed as an exothermic feature during the first heating of the as-cast sample. The exotherm is due to the very large enthalpy frozen-in during the high cooling rate in the preparation of the metallic glass and its release during the slower heating rate of the first heating in the DSC.

2. Isothermally annealing of a sample at a certain temperature and a certain time produces also endothermic effect during the sample’s heating, which are the reversible relaxations. The
peaks area is larger than that for the unannealed sample. For a fixed annealing temperature but different annealing times, the peaks area continuously increases as annealing time increases. These features correspond to the enthalpy and entropy loss during annealing.

3. Simulation of the heat capacity curves obtained from the DSC scans in terms of a nonexponential and nonlinear relaxation concept for metallic glasses fit satisfactorily for some isothermal annealing experiment results but do not do so for other experimental results.

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6. References

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