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Dmitri V. Louzguine-Luzgin

Ichiro Seki

Tokujiro Yamamoto

Hitoshi Kawaji

C. Suryanarayana

University of Central Florida

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Authors

Dmitri V. Louzguine-Luzgin, Ichiro Seki, Tokujiro Yamamoto, Hitoshi Kawaji, C. Suryanarayana, and Akihisa Inoue

Double-stage glass transition in a metallic glassDmitri V. Louzguine-Luzgin,^{1,2,*} Ichiro Seki,² Tokujiro Yamamoto,² Hitoshi Kawaji,³ C. Suryanarayana,^{2,4} and Akihisa Inoue^{1,2}¹*WPI Advanced Institute for Materials Research, Tohoku University, Katahira 2-1-1, Aoba-Ku, Sendai 980-8577, Japan*²*Institute for Materials Research, Tohoku University, Katahira 2-1-1, Aoba-Ku, Sendai 980-8577, Japan*³*Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8503, Japan*⁴*Department of Mechanical, Materials and Aerospace Engineering, University of Central Florida, Orlando, Florida 32816-2450, USA*

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Glass-transition region is still a somewhat “dark area” in the field of materials science. In order to shed more light on this phenomenon, the glass-transition behavior was studied in a $Zr_{55}Cu_{30}Al_{10}Ni_5$ glassy alloy by monitoring its specific-heat capacity measured using a differential scanning calorimeter during heating in a step-scan mode. This reduces the influence of kinetic effects which shield the transition. It is suggested that two types of relaxation (likely related to the diffusivities of different alloying elements Cu and Ni on the one hand as well as Zr and Al on the other hand) take place and compete in the glass-transition region.

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I. INTRODUCTION

Active research on metallic glassy alloys (or metallic glasses) started since the first synthesis of an amorphous phase by rapid solidification of an Au-Si alloy in 1960.¹ Depending on the glass-forming ability (GFA) of the system, glassy/amorphous alloys can be produced using different methods. Materials having a very low GFA, e.g., pure metals, can be prepared in the amorphous state by condensation from the vapor phase² which is highly power intensive and not efficient. Much more effective is rapid (compared to conventional metallurgical methods) solidification from a liquid phase³ by techniques such as melt spinning, Cu-mold casting, liquid forging, and so on. A large number of bulk glassy alloys (also called bulk metallic glasses) defined as three-dimensional massive glassy (amorphous) articles with a size of not less than 1 mm in any dimension (10 mm by another definition) have also been produced during the last 20 years in the thickness range of up to 72 mm by using various casting processes.⁴⁻⁷

Even though metallic glasses have a liquidlike structure, they behave as solids in general but also have similarities with solids and with liquids. The packing density of noncrystalline structures is an important geometrical factor influencing GFA. The importance of efficient atomic packing for the formation of metallic glasses was shown recently.^{8,9} It has been emphasized that specific radius ratios of the constituent elements are preferred for the formation of metallic glasses at certain composition ranges.

Glass formation is a complex phenomenon. Upon fast enough cooling of a liquid alloy, crystallization is suppressed and it solidifies producing a glass.¹⁰ The properties of the liquid and glass vary continuously and the specific volume of a crystal at a given temperature is lower than that of the glassy phase.

The glass-transition phenomenon in metallic glasses has been studied extensively for many years.¹¹⁻¹⁴ Nevertheless, the glass-transition process is still somewhat a “dark area” in the field of materials science. The nature of the glassy state and of the glass transition is not clear and is still being in-

vestigated. An important question which is still not fully answered is: do glassy and liquid phases belong to essentially the same phase, just observed at different temperatures, or are they two completely different phases? In other words, does the liquid→glass phase transformation (called glass transition) and the reverse (glass→liquid transformation) indeed take place or it is just the reaction of the machine on different relaxation times.^{15,16} A thermodynamic treatment of glass transition has been suggested by Kauzmann.¹⁷ Several theories are used to describe the glass transition,^{18,19} though none is so far comprehensive. It is known that the temperatures of the beginning/start and finish of the glass transition depend on the heating rate. At lower heating rates, T_g is lower and the width of the glass-transition region decreases.

In the present study, we have investigated the glass-transition phenomenon in a $Zr_{55}Cu_{30}Al_{10}Ni_5$ glassy alloy. In order to minimize the kinetic effects associated with structural relaxation upon continuous heating, we have measured the specific-heat capacity as a material property, on annealing the glassy alloy for different times in a step-scan mode. Step-scan measurements allow one to equilibrate the glassy phase before each measurement.²⁰ The studied alloy has a high enough GFA and stability of the supercooled liquid for such an investigation.

Another target was to test the relaxation behavior of the glassy phase toward the liquid phase in the glass-transition region and infer whether the glass transition is just a reaction of the instrument (DSC) on the characteristic time scales or whether the glassy phase indeed transforms gradually to the liquid state above the glass-transition temperature. With this purpose in mind, measurements have been made for different time scales in a step-scan mode.

II. EXPERIMENTAL PROCEDURE

The ingot of a $Zr_{55}Cu_{30}Al_{10}Ni_5$ alloy (the composition is given in nominal at. %) was prepared by arc-melting mixtures of high-purity elemental metals >99.9 wt% purity in an argon atmosphere. Since crystallization of this alloy was found to be quite sensitive to the presence of impurities,²¹

pure metals were used to synthesize the samples in the present investigation. From this ingot, glassy ribbon samples of about 20 μm in thickness and 1 mm in width were prepared by rapid solidification of the melt on a single copper roller at a tangential wheel velocity of 40 m/s.

The glass-transition phenomenon was studied on heating in a Perkin-Elmer Diamond DSC in a step-scan mode. The ribbon samples of glassy $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ alloys were heated at a heating rate of 0.083 K/s (5 K/min) while the annealing (waiting) time between steps was maintained at 60, 600, and 1200 s (1 min, 10 min, and 20 min, respectively). The specific-heat capacity at constant pressure (C_p) was measured by using heat release (ΔH) at each heating step. The specific-heat capacity near a certain temperature (696 K) within the glass-transition region was measured on heating and cooling by 5 K separated by isothermal keep time of 60 s. In a separate run of the experiments, different heating rates of 0.05 and 0.167 K/s (3 and 10 K/min) were also used.

III. RESULTS

Figure 1(a) shows the variation in specific-heat capacity C_p of the alloy as a function of temperature on continuous heating in the DSC at a heating rate of 0.67 K/s (40 K/min). The plot obtained is typical showing that the specific heat increases with increasing temperature suggesting that relaxation occurs initially and then crystallization sets in above 760 K. The specific heat is found to increase more abruptly in the glass-transition temperature range of 660–720 K. The specific heat remains virtually constant in the (supercooled) liquid state, and decreases to a low value (similar to that of the glassy state) on crystallization. It is also interesting to note that one can see a clear overshoot in the continuous C_p curve.

Figure 1(a) also shows the variation in specific heat with increasing temperature and for an annealing time of 1 min (60 s) per step. It is shown that C_p has an initial value below 25 J/mol \cdot K in the as-quenched glassy state and starts to increase more-or-less monotonically with temperature. The slope changes drastically starting from about 670 K and C_p reaches a maximum of about 38 J/mol \cdot K at about 700 K in the liquid state (C_p^L). Similar plots were obtained when the annealing (hold) time was maintained at 10 min (600 s) and 20 min (1200 s) Fig. 1(b). The C_p values measured at the annealing times of 1 min (60 s), 10 min (600 s), and 20 min (1200 s) are referred to as C_p^1 , C_p^{10} , and C_p^{20} , respectively. The most stable value of $C_p = 38.22 \pm 0.06$ J/mol \cdot K was obtained at 1 min (60 s) annealing time and is taken as a reference value.

Depending on the annealing time, the (supercooled) liquid crystallizes forming crystalline phases and the specific-heat capacity in this case decreases back close to that of the glassy phase. One may also point out that no prolonged exothermic peak is noted below the glass-transition region upon the step-scan measurement compared to continuous heating [Fig. 1(a)]. Thus one can assume that the sample mostly relaxes during the annealing time of the measurement. One can also see that compared to continuous heating curve [Fig. 1(a)], no clear overshoot is seen in C_p^1 produced in a step-scan mode.

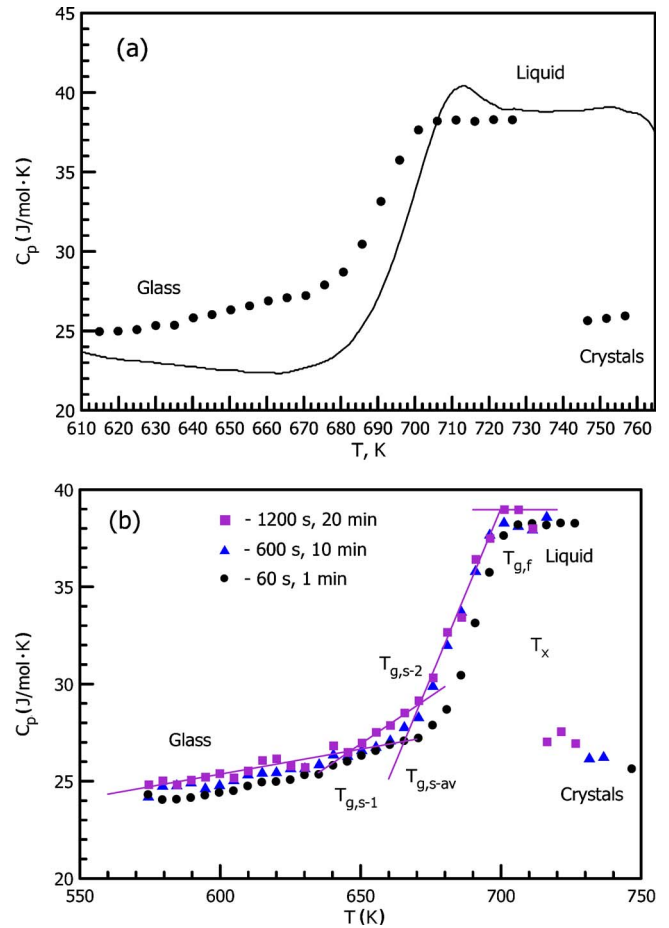


FIG. 1. (Color online) (a) Solid line C_p on continuous heating at 0.67 K/s (40 K/min). Circles— C_p^1 as a function of temperature measured in a step-scan way (heating rate 0.083 K/s or 5 K/min). (b) C_p as a function of temperature and annealing time measured in a step-scan way (heating rate 0.083 K/s or 5 K/min).

Unlike in the continuous mode of heating, the C_p curves in the step-scan mode change the slope several times and this is clearly illustrated for C_p^{20} in Fig. 1(b). One can distinguish several break points in the curves, which could be designated as the start of the glass-transition temperature (ergodicity making²²) ($T_{g,s}$) consisting of ($T_{g,s-1}$), ($T_{g,s-av}$), and ($T_{g,s-2}$) as well as finish ($T_{g,f}$) glass-transition temperature. These temperatures could be obtained by drawing tangents to the plot below, inside and above the glass-transition region as shown by straight solid lines in case of C_p^{20} in Fig. 1(b). Clear existence of at least two slopes within the glass-transition region (especially at high enough annealing time of 20 min) between $T_{g,s-1}$ and $T_{g,f}$ indicates two glass-transition processes: low- and high-temperature glass-transition processes which cannot be a result (or an artifact) of the machine used to determine the specific-heat values. The changes in slopes may actually indicate a competition between the α - and β -relaxation processes.

A very weak peak may also be noticed at about 615–620 K in Fig. 1(b). This may indicate the beginning of the release of the excess volume upon structural relaxation leading to densification of the glass. According to the work of Yavari *et*

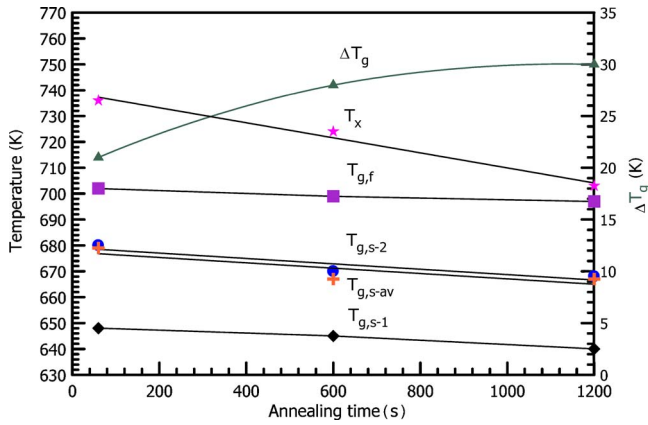


FIG. 2. (Color online) The glass-transition and crystallization temperatures as well as the width of the glass-transition region (ΔT_g) as a function of annealing time.

al., a significant decrease in volume of Zr-based alloys was noted in this temperature range.²³

Figure 2 plots the variation in the different glass-transition temperatures ($T_{g,s-1}$, $T_{g,s-av}$, $T_{g,s-2}$, $T_{g,f}$, T_x), and ΔT_g as a function of annealing (hold) time. It is interesting to note that while all the temperatures related to glass-transition decrease, the ΔT_g values show a moderate increase with increasing annealing time. This is rather surprising since the temperature range is expected to be narrower at longer hold times.¹⁴ Further, from the trend of variation in crystallization temperature (T_x) and $T_{g,f}$, it appears that, at annealing times longer than 20 min (1200 s), T_x will be lower than even $T_{g,f}$ and the sample will behave like an amorphous solid. This indicates the complex mechanism of glass transition in this alloy.

The relaxation velocity, $\Delta C_p R$ related to the specific-heat capacity, of the liquid C_p^L can be calculated using the relationship: $\Delta C_p R = C_p^x - C_p^1 / C_p^L - C_p^1$ ($x=10$ or 20) and the values of $\Delta C_p R$ for C_p^{20} and C_p^{10} are presented in Fig. 3, along with the absolute $\Delta C_p A$ values. Absolute values of the relaxation velocity have a maximum close to $T_{g,s}$ while the values relative to C_p^1 attain a maximum at close to $T_{g,f}$. As the ab-

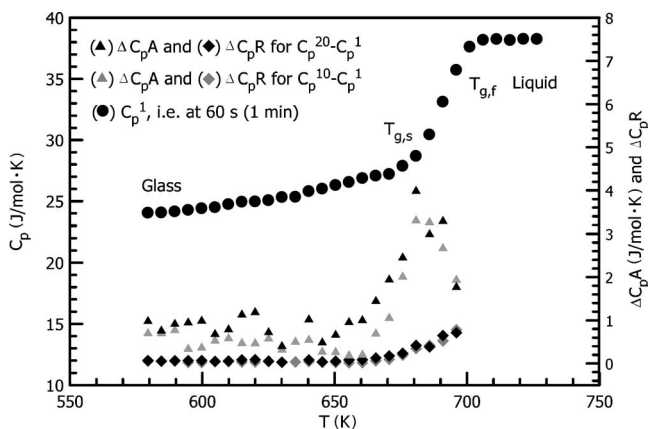


FIG. 3. Transition of glassy phase toward liquid phase as a function of annealing time. $\Delta C_p A$ and $\Delta C_p R$ are absolute and relative C_p difference values, respectively.

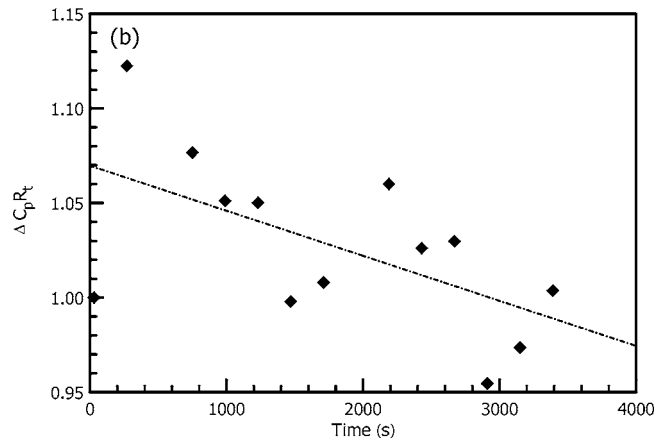
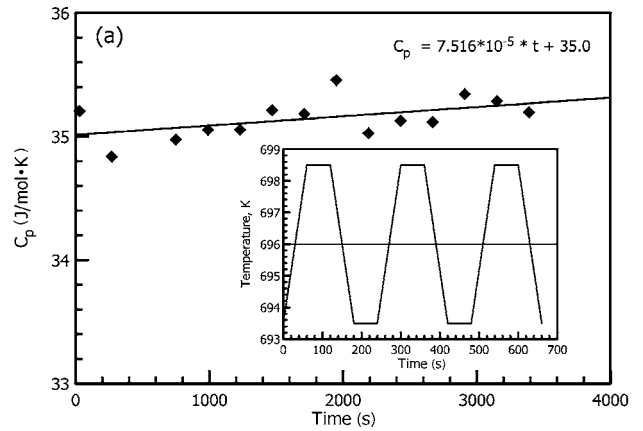


FIG. 4. (a) C_p^1 at 696 K as a function of time measured on heating cycle. Heating scheme is illustrated in the inset and (b) the corresponding derived $\Delta C_p R_t$ data.

solute difference between C_p^{20} and C_p^{10} is much smaller than the difference between C_p^{10} and C_p^1 , one can confirm that although transition of glassy phase toward liquid is a damped process it really takes place above $T_{g,s}$.

Figure 4 shows the relaxation behavior of the glassy alloy ribbon during a heating-cooling cycle around the temperature of 696 K, which is in the glass-transition region. In this experiment, the sample was heated (or cooled) by 5 K in such a way that 696 K is an average value at a rate of 0.083 K/s, held there for 1 min (60 s) of annealing time and then cooled (or heated). C_p^1 was measured and the results are shown in Fig. 4. Both C_p and $\Delta C_p R_t$, calculated using the relationship $\Delta C_p R_t = C_p^1(t) - C_p^L / C_p^1(t=1) - C_p^L$ are plotted as a function of time. In this relationship, $C_p^1(t)$ is heat capacity at time t , C_p^L is that of a liquid (taken 38.22 J/mol·K), and $C_p^1(t=1)$ is heat capacity after 60 s. Here the target was to examine the behavior of the glassy phase, when it is allowed to relax within the glass-transition region. With this repeated heating-cooling cycling, the C_p value of the glassy phase gradually increased toward the value of the liquid. In other words, glass tends to become a liquid with time.

Figure 5 shows C_p^1 and relaxation time calculated using the viscosity data²⁴ as a function of temperature obtained at a heating rate of 20 K/min (0.33 K/s). It is generally expected that the glass transition takes place when the Maxwell relax-

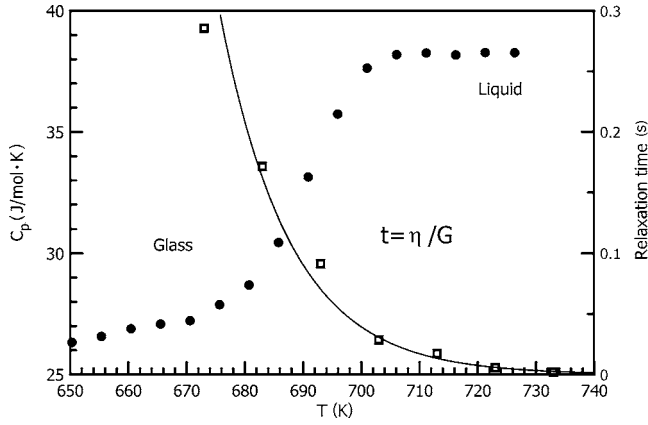


FIG. 5. C_p^1 (●) and relaxation time (□) calculated using viscosity data (Ref. 24) as a function of temperature.

ation time is on the order of 100 s. Further, the viscosity value is expected to be about 10^{12} Pa*s at the start of glass transition on heating. However, in the present investigation, it is noted that the viscosity and calculated relaxation time at $T_{g,s}$ are rather low—about 10^{10} Pa*s and 0.3 s, respectively, at 673 K (Ref. 24) and, these values change only about an order of magnitude within the glass-transition region. Of course, it is accepted that these values measured at 0.33 K/s (20 K/min) are far from equilibrium.

Figure 6 presents the variation in C_p and ΔC_p as a function of temperature at different heating rates. Annealing time between the heating steps was 60 s. Here, the values of ΔC_p (ΔC_p^{3-5} , ΔC_p^{5-10} , ΔC_p^{3-10}) are the absolute differences between the corresponding heat capacities C_p^3 , C_p^5 , and C_p^{10} measured at different heating rates of 3 K/min, 5 K/min, and 10 K/min, respectively. These values are increasing slightly with the cooling rate.

Figure 7 shows the variation in C_p^1 on heating and cooling as a function of temperature within the glass-transition range, at two different rates, viz., 5 and 10 K/min. There is only a very weak, almost undetectable hysteresis in C_p on heating and cooling. A weak overshoot is also observed on heating at 5 K/min. The overshoot and the hysteresis relate the enthalpy relaxation in this glass.

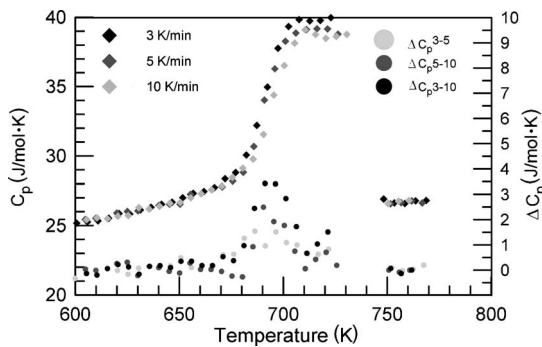


FIG. 6. C_p^3 , C_p^5 , and C_p^{10} as a function of temperature. ΔC_p^{3-5} , ΔC_p^{5-10} , and ΔC_p^{3-10} are the absolute differences between the corresponding heat capacities. Note that here the meaning of the superscript above C_p is slightly different than that in previous figures.

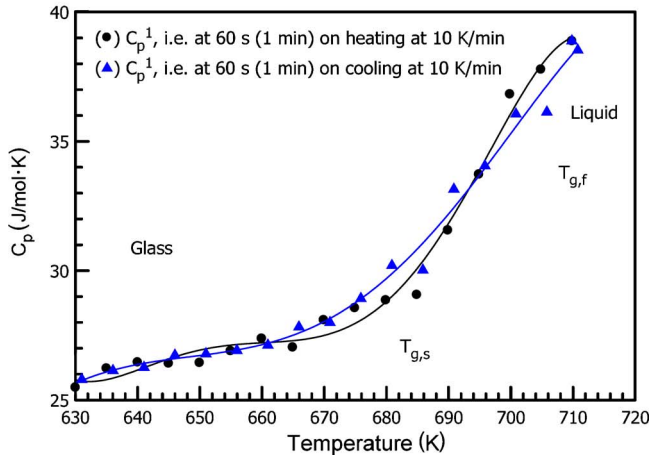
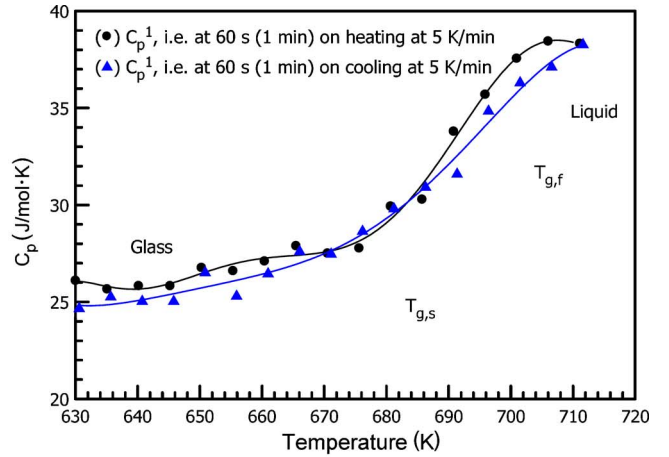


FIG. 7. (Color online) C_p^1 on heating and cooling as a function of temperature at two different heating rates. (a) 5 K/min and (b) 10 K/min.

IV. DISCUSSION

The phenomenon of glass transition is very important in understanding the transformation behavior of a liquid into the glassy state. However, as mentioned earlier, there are several gaps in obtaining a clear picture of the glass transition, especially in metallic liquids. One may refer to Angell (Ref. 14), Ngai and Capaccioli,²⁵ and Hodge²⁶ for the issues that continue to puzzle the scientists. The present investigation has been undertaken to shed more light on this issue.

As shown in Fig. 1(b), two slopes were clearly observed within the glass-transition region between $T_{g,s-1}$ and $T_{g,f}$. These slopes indicate that two glass-transition processes are occurring one at a low temperature and the other at a high temperature. These changes in slopes representing the glass-transition processes are not the artifacts produced by the machine but they are genuine. The change in slopes may be explained on the basis of the different diffusivities of the constituent elements in the glass.

It is known that at low temperatures, diffusion of atoms by cooperative shearing is several orders of magnitude slower and therefore they move predominantly by atomic hopping.^{14,27} At higher temperatures, however, diffusion of Ni atoms becomes comparable to the hopping time. This is because Ni has a significantly higher diffusion coefficient

($D \sim 10^{-18}$ m²/s at 650 K) than Al ($D \sim 5 \times 10^{-20}$ m²/s at 650 K)²⁸ and therefore the time scale for shear of Ni atoms becomes comparable to the hopping time and the liquidlike motion is predominant for these atoms. According to the formula ($l=2\sqrt{Dt}$), where l is the diffusion length, D is the diffusion coefficient, and t is the time, the diffusion length (l) at 650 K is calculated to be 60 nm in 100 s for Ni which is about 200 interatomic distances while for Al, the diffusion length corresponds to only 4 nm or nearly 10 interatomic distance. The behavior in Fig. 1 may illustrate that each alloying element undergoes a different transition range below which it moves in a solidlike manner. In fact, Egami²⁹ suggests that glass transition in a multicomponent system does not occur uniformly but gradually over a range of temperature reflecting the inhomogeneity at the atomic level. Thus, based on the complexity of the alloy consisting of the different constituent elements which present in the glass, one may observe more than two slopes in the glass transition. If the number of steps is too large, due to the presence of small changes in the inhomogeneity in the entire glass, then a large number of changes in the slope will occur at very short intervals, and consequently the glass transition will appear relatively smooth. On the other hand, if the inhomogeneity level is relatively high, i.e., on a scale larger than the atomic level (but the glass is still “homogeneous” on a macroscopic level), then it is possible that clear changes in slope may be observed in the glass transition. It is very likely that is what is happening in the present alloy.

Based on the above calculations, 650 K may be considered as a freezing temperature for Ni atoms (and possibly for Cu also since both Cu and Ni are quite similar in many respects) whereas Al atoms become mobile only above about 670 K when its D_{Al} reaches about 10^{-18} m²/s.²⁸ This may explain the widening of the glass-transition range in Fig. 2 because $T_{g,s-1}$ decreases with increase in the annealing time while $T_{g,f}$ is related to an ergodic liquid and is less dependent on the annealing time.

Relaxation speed³⁰ in isothermal conditions at 696 K, which is about 0.3 J/mol*K at about 3000 s (Fig. 4), roughly corresponds to the difference obtained upon step-scan heating.

Relaxation of the glassy phase toward liquidlike behavior takes place in the glass-transition region. According to the obtained results apart from the instrumental manifestation of T_g , the glassy phase indeed changes its properties/relaxes even above $T_{g,s}$ and the relative relaxation speed increases as

the temperature approaches $T_{g,f}$. One can suggest that the glassy phase tends to be more like a liquid with time. On the other hand, the absolute relaxation-time values are higher in the middle of the glass-transition region.

The interesting question, however, is how far can the glassy phase relax in the glass-transition region and if we can expect it to ever reach the liquid state below $T_{g,f}$? $T_{g,s}$ decreases faster than $T_{g,f}$ with annealing time, and therefore this transformation may not be ever realized, at least in these cases. But, if the rate of decrease in $T_{g,s}$ is slower than that of $T_{g,f}$, then only it may be possible for the glass to reach the true liquid state.

Hysteresis which is very well seen in the samples heated and cooled at continuous scan mode is much less pronounced if the sample is studied under step-scan mode (Fig. 7) when the heating and cooling traces almost coincide.

V. CONCLUSIONS

In the present paper, the glass-transition phenomenon in a Zr-based metallic glass has been studied using a step-scan calorimetry technique. The clear existence of two slopes within the glass-transition region between $T_{g,s-1}$ and $T_{g,f}$ indicates the occurrence of two glass-transition processes. These two processes occurring one at low temperatures and the other at high temperatures, indicate two relaxations competing with each other. This phenomenon is likely related to the different diffusion coefficients (mobility) of the alloying elements.

Relaxation of the glassy phase toward liquidlike behavior takes place in the glass-transition region. According to the obtained results apart from the instrumental manifestation of T_g , the glassy phase indeed changes its properties/relaxes even above $T_{g,s}$ and the relative relaxation speed increases as the temperature approaches $T_{g,f}$. One can suggest that the glassy phase tends to be more like a liquid with time. On the other hand, the absolute relaxation-time values are higher in the middle of the glass-transition region.

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*FAX: +081 (22) 217-5956; dml@wpi-aimr.tohoku.ac.jp

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