Investigation on Kinetic Glass Transition and Relaxation of Vit1 Bulk Metallic Glass by Calorimetric Method

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Abstract: The kinetic glass transition of the Vit1 ($Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$) bulk metallic glass (BMG) was calorimetrically studied by using the differential scanning calorimetry (DSC). A wide range of heating rate, q=0.5~100 K min^{-1}, was adopted in the calorimetric experiments. The apparent values of the glass transition temperatures were determined from the DSC curves. Then the kinetic glass transition was analyzed by adopting the function in the form of the Vogel-Tammann-Fucher (VTF) type. In addition, by considering the glass transition of the BMG from non-equilibrium to kinetic equilibrium during the process of heating experiments, a new model which can be used to calculate the relaxation time near the glass transition temperature region was established. The relaxation time of the Vit1 BMG near the glass transition temperature region calculated by the new model was used to compare with the glass transition time (t_{trans}), as well as the relaxation time calculated by the viscosity and diffusion methods. The result shows that the relaxation time calculated based on the model can reflect the relaxation event reasonably near the glass transition temperature region. This work may provide some new perspectives or ideas for the study of the glass transition and relaxation of metallic glass.

Keywords: Kinetic Glass Transition, Calorimetry, Relaxation Time, Metallic Glass, Vit1 Alloy

1. Introduction

Glass transition during the solidification of liquid metal is attributed to the loss of the structural equilibrium in liquid. For the metastable metallic glass (MG), the non-equilibrium state will be gradually returned to its quasi-equilibrium state by relaxation in time scale when it is under some favorable conditions. For example, the large-scale motion or hopping of the atoms will be activated when the temperature of MG is high enough during heating, and thus the kinetic condition of the relaxation is provided. Therefore, the kinetic characteristics and time scale of the relaxation in MG, especially the kinetic glass transition, have been interested a great number of researchers. A universal viewpoint is that the glass transition is kinetically "frozen" from the supercooled liquid, which depends on the cooling rate [1]. On the other hand, the glass transition during reheating (or named α-relaxation), however, depends on the heating rate [2].

In traditional studies, various kinds of methods, such as the measurements of the shear viscosity [3], atomic diffusion [4] and internal friction [5], can be used to analyze the relaxation of MG near the glass transition temperature. In the past few decades, the dependence of the glass transition temperature on the heating rate of the reheating process or the cooling rate of the supercooled liquid has been investigated extensively for the glass forming alloy systems, and an obvious kinetic effect was observed. For the heating process, it is found that the α-relaxation time (τ) and the experimental time of the glass transition (t_{trans}) are roughly in the same order near the glass transition temperature (T_g). Based on this nature, the equations in the form of Vogel–Tammann–Fulcher (VTF) and Arrihenius types are often used to investigated the glass transition.

In this work, the kinetic glass transition of a typical MG was investigated by using the differential scanning calorimetry (DSC). Then it was fitted by a function in the form of VTF type. The τ dependence of the temperature was calculated by considering the calorimetric glass transition. In addition, the curves of τ obtained by other methods, e.g., by

viscosity or diffusion measurement, were referred as well and used to compare with the present results.

2. Experimental

In order to obtain the precise characteristic temperatures of the glass transition, especially the temperature at which the MGs can be completely transformed into their quasi-equilibrium liquid state, it is required that the supercooled liquids of the glass forming alloys can exist stably in laboratory time scale. Therefore, the MGs with high glass-forming ability (GFA) are the appropriate materials for the present experiments. The experimental material used in the work is $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ (Vit1) [6] bulk metallic glass (BMG), and the preparation process can be found in reference [7]. The as-cast BMG were cut into small pieces for the DSC experiments. Then, the specimens were investigated with a STA 449F3 DSC, which has the specifications as follows: the measurable temperature range is 150~2400 K, the heating rate range is 0.001~150 K min^{-1}, and the mistake of the heat flow is less than 0.1 µW. New specimen was always used in each DSC experiment. The ultrahigh purity argon was used to purge the DSC and protect the specimen from oxidation. The calorimeter of the DSC was recalibrated for each heating rate with the indium and zinc standards. A second run for each specimen was directly carried out after the first cycle without changing the conditions of the measurement to construct a baseline. The heat flow of the specimens near the glass transition temperature region was monitored at different heating rates (q) ranging from 0.5 to 100 K min^{-1}.

3. Results and Discussion

The preliminary objective of the DSC measurement is to determine the influence of the heating rate on the kinetic behavior of the glass transition. The heat flow curves of the specimens measured at different heating rates are illustrated in figure 1. Note the curve measured at the q of 1 K min^{-1} as the typical example. The onset temperature of the glass transition (T_g^{on}) at which the glass begins to respond to the ascending of the endothermic peak can be obtained by intercepting the extrapolated heat flow of the glass and the maximum slope of the increased heat flow curve during the glass transition [8-10]. In addition, the end temperature of the glass transition (T_g^{end}), above which the alloy can fully equilibrate into the metastable supercooled liquid state during heating, can be obtained by intercepting the extrapolated heat flow of the supercooled liquid and the maximum slope of the increased heat flow curve during the glass transition [7-8]. According to figure 1, it is concluded that the kinetic glass transition behavior of the BMG is strongly depended on the heating rate. Namely, the higher the heating rate, the higher the characteristic temperatures of the glass transition.

According to the viewpoint proposed by Busch, the relaxation of a glass near the glass transition temperature depends on the experimental time scale of the heating process [11]. Namely, the relaxation time or the glass transition time

dependence of the heating rate q can be formulated as [11-12]:

$$\tau_{(T)|T=T_g} = t_{trans} = (T_g^{end} - T_g^{on})/q \qquad (1)$$

In addition, the τ can also be derived by using the viscosity of the material near the glass transition region, and it is well fitted with the VTF relation [13]:

$$\tau = A\exp[B/(T-T_0)] \qquad (2)$$

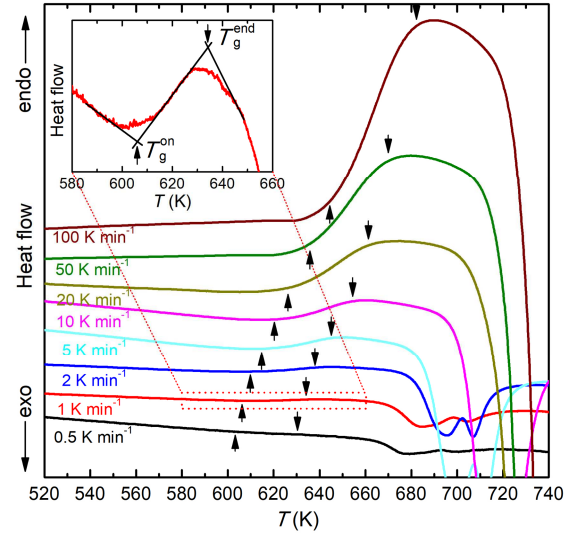Where A, B and T_0 are constants.

Figure 1. *Heat flow of the Vit1 alloy near T_g measured at different q.*

Hereby, it was presumed by Brüning and Samwer [14] that the VTF relation should be valid as well for fitting the characteristic glass transition temperature. The functional form of the VTF type which can be used to fit the experiment result of T_g^{on}-vs-q is expressed as:

$$q = B\exp[A/(T_{g0}^{on} - T_g^{on})] \Leftrightarrow T_g^{on} = T_{g0}^{on} + A/\ln(B/q) \quad (3)$$

Since T_g^{on} and T_g^{end} are equivalent characteristic temperatures in calculating the time scale or α-relaxation time of the glass transition as shown in equation (1), it can be presumed that the functional form of the VTF type can be used to fit the experiment result of T_g^{end}-vs-q as well. Thus, the functions which are suitable to fit the characteristic glass transition temperatures of the DSC experiments are:

$$\begin{cases} T_g^{on} = T_{g0}^{on} + A/\ln(B/q) \\ T_g^{end} = T_{g0}^{end} + C/\ln(D/q) \end{cases} \qquad (4)$$

Where C and D are constants as well, T_{g0}^{on} and T_{g0}^{end} are the ultimate characteristic temperatures of the glass transition for $q \to 0$.

In this work, the dependence of the characteristic glass transition temperatures (T_g^{on} and T_g^{end}) of the Vit1 BMG on the q are given in figure 2 by solid squares and dots respectively. It shows clearly that the values of the T_g^{on} and

T_g^{end} increase with the increase of q, and their changes are nonlinear. In addition, equation (4) was used to fit the experimental glass transition temperature points. The fitted curves are plotted in figure 2 in solid line form, and the results seem to be quite reasonable. The fitted parameters T_{g0}^{on}, T_{g0}^{end}, A, B, C and D are 562.2 K, 572.1 K, 444.6 K, 340.4 K s^{-1}, 628.6 K and 501.5 K s^{-1}, respectively, which can be found in our previous work [15]. According to the fitted results, the lower limit T_{g0}^{on} seems close to the Kauzmann temperature (T_K) of 560 K calculated by Busch et al. [7], which is considered to be the formation temperature of the ideal glass. This result proves that the glass transition cannot take place at the temperature below T_K. In other words, the T_{g0}^{on} or T_K is the characteristic temperature that signals the arrest of the glass transition and α-relaxation [16-19].
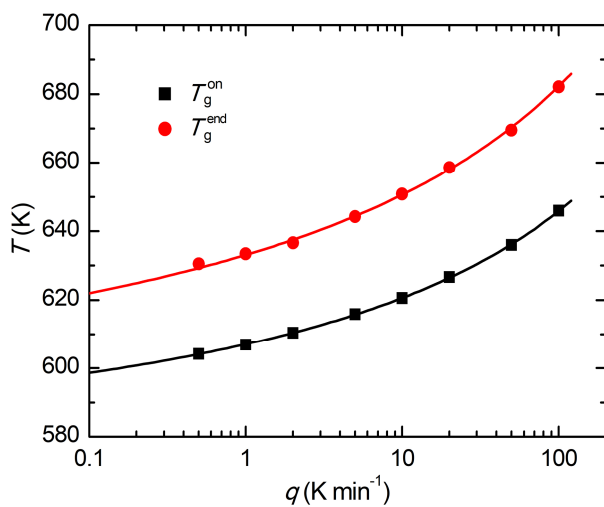

Figure 2. *The dependence of the glass transition temperatures (T_g^{on} and T_g^{end}) on the q. The solid lines are the curves fitted by using the functions in the form of VTF type.*

The primary relaxation event of liquid which is named as α-relaxation has been studied in different ways by the previous researchers. For example, by visualizing the liquid as a solid-like material on the instantaneous time scale, the relaxation time was given as [20]:

$$\tau = \eta / G_\infty \qquad (5)$$

Where η is the viscosity, and G_∞ is the instantaneous shear modulus of the liquid. The equation (5) which is named as the Maxwell relaxation time provides the key to understand the glass transition. Since the viscosity of the glass-forming alloy system at the glass transition temperature is about 10^{12} Pa s, and the G_∞ is about 1~10 GPa, the $\tau = 10^2 \sim 10^3$ s can be determined.

The kinetic theory for the relaxation of the glass-forming alloy systems was considered to be related to the process of the structural equilibrium transformation. By connecting the η with the particle diffusion of the liquid system, the kinetic theory of the relaxation can be understood with the Stokes-Einstein relation:

$$D = \kappa_B T / (3\pi d\eta) \qquad (6)$$

Where D is the diffusion coefficient, d is the particle radius, and κ_B is the Boltzmann constant.

From the above theory, it can be understood that the α-relaxation of the glass forming alloy is the process of the system transiting from the non-equilibrium state to the equilibrium state. In other words, the τ can be considered as the time that is needed for the system to undergo the whole equilibriun transformation process. Based on this interpretation, the equation (1) which is used to calculate the glass transtion time seems quite reasonable in analyzing the α-relaxation time of the glass forming alloy systems. However, the calculation of the whole equilibrium transformation process with this equation is still not deep enough since the lower limit of the glass transition temperature is not taken into account precisely.

In this work, the dependence of the T_g^{on} and T_g^{end} of the Vit1 BMG on the q has been obtained from the DSC experiments. The T_g^{end} can be considered as the end temperature of the equilibrium transformation [21]. On the other hand, the T_g^{end} represents the end of the kinetic glass transition or relaxation during the heating process. In addition, the T_g^{on} measured at a certain q is the result of the kinetic effect of the calorimetric experiment, and it closes to T_{g0}^{on} when the $q \rightarrow 0$, which means that the T_{g0}^{on} should be the equilibrium onset temperature of the glass transition. In other words, the thermal effect for the glass transition of the BMG at the temperature region ranging from T_{g0}^{on} to T_g^{on} cannot be reflected in the DSC curve since the time scale that the sample goes through this temperature region is so short when it is heated at higher q. Therefore, the glass transition temperature range of the whole process for the sample transforming from the non-equilibrium state to the kinetic equilibrium state in heating experiment can be considered as from T_{g0}^{on} to T_g^{end}.

Here, we propose the following hypothesis: the whole relaxation process of the BMG is gradually carried out at the temperature region ranging from T_{g0}^{on} to T_g^{end} when the sample is heated at the heating rate of q; the isothermal relaxation time of the BMG at the temperature T near the glass transition temperature region is $\tau_{(T)}$. Thus, the time scale that the sample is heated up by 1 K during the heating process is $1/q$, and the whole relaxation process can be expressed as:

$$\int_{T_{g0}^{on}}^{T_g^{end}} \frac{1}{q\tau_{(T)}} \cdot dT = 1 \qquad (7)$$

In addition, the total time scale that is required for the whole equilibrium transformation when the sample is heated at the heating rate of q can be calculated as:

$$t_{(T_{g0}^{on}, T_g^{end})} = (T_g^{end} - T_{g0}^{on}) / q \qquad (8)$$

Then, by combing equations (7) and (8), the expression for the isothermal relaxation time $\tau_{(T)}$ at the end temperature of the glass transition is:

$$\tau_{(T)|T=T_g^{\mathrm{end}}} = \left| \frac{\mathrm{d}\, t_{(T_{g0}^{\mathrm{on}}, T_g^{\mathrm{end}})}}{\mathrm{d}\ln\Delta T} \right| \qquad (9)$$

Where $\Delta T = T_g^{\mathrm{end}} - T_{g0}^{\mathrm{on}}$. For the investigated Vit1 BMG, the value of T_{g0}^{on} and the dependence of the T_g^{end} on the q have been fitted with equation (4). Based on this, the data map of the $t_{(T_{g0}^{\mathrm{on}}, T_g^{\mathrm{end}})}$ which depends on the q and T_g^{end} can be depicted, and thus the $t_{(T_g^{\mathrm{end}})}$ can be calculated as well.

In figure 3, the dependence of the isothermal relaxation time $\tau_{(T)}$ on the T_g^{end} for the investigated Vit1 BMG is plotted based on the calculated method expressed as equation (9). The values of $\tau_{(T)}$ calculated according to equation (1) and based on the viscosity and particle diffusion of the liquid are plotted as well, which are used to compare with the current result. Among them, the data of the viscosity and diffusion was cited from the results obtained by Masuhr [22] and Meyer [23], respectively. It is shown from figure 3 that the curves of $\tau_{(T)}$ calculated according to equations (1) and (9) are close to the ones calculated by the viscosity and diffusion methods at the temperature interval ranging from 610 K to 660 K (the temperature is expressed as $1000/T$ in the figure), which means that the relaxation time calculated by the calorimetric methods can basically reflect the α-relaxation event near the glass transition temperature. In addition, it seems clear that the temperature range within which the $\tau_{(T)}$ calculated according to equation (9) is approximate to the curves calculated by the viscosity and diffusion methods is larger than the one that calculated according to equation (1), which means that the $\tau_{(T)}$ calculated according to equation (9) reflects the relaxation event more reasonably than the one calculated according to equation (1).
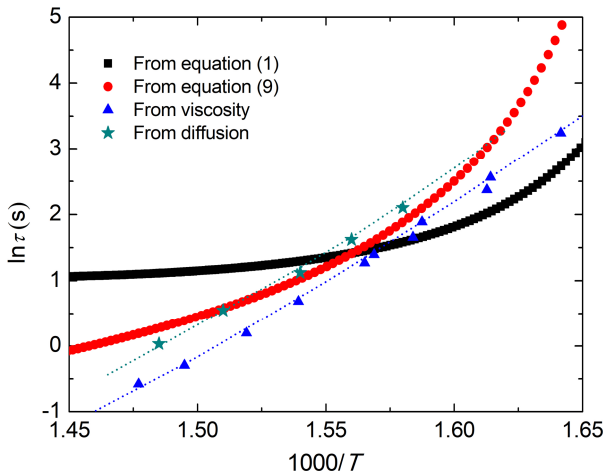

Figure 3. *The relaxation time of the Vit1 BMG near the glass transition temperature region calculated by different methods.*

4. Conclusions

In summary, the kinetic glass transition of the Vit1 BMG was monitored at a wide range of q by using DSC. The dependence of the apparent values of T_g^{on} and T_g^{end} on the q was fitted by the functions in the form of the VTF type. By considering the whole glass transition process from non-equilibrium to kinetic equilibrium, a model of the relaxation time near the glass transition temperature region was established. The calculation results of the Vit1 BMG indicate that the $\tau_{(T)}$ calculated based on the model can reflect the relaxation event reasonably near the glass transition temperature region.

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