Science in China Series G: Physics, Mechanics & Astronomy

© 2008 SCIENCE IN CHINA PRESS
Springer-Verlag

www.scichina.com
phys.scichina.com
www.springerlink.com

Physical aging in $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ typical bulk metallic glass manifested as enthalpy relaxation

WEN Ping†, ZHAO ZuoFeng & WANG WeiHua

Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

Enthalpy recovery is not only an important characteristic of physical aging of glass, but also a good tool to investigate the physical aging. Using differential scanning calorimeter (DSC), the enthalpy recovery of $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ bulk metallic glass (BMG) was studied. The typical characteristics of enthalpy recovery of glass including the sub-T_g peak and 'overshot' were found in BMG. The evolution of the sub-T_g peak and 'overshot' were described by the free volume theory and Hodge's model, respectively. It was found that the former failed to describe the enthalpy recovery in the BMG, while the latter could give a qualitative explanation. In combination with the dynamics in the BMG, the origin of the enthalpy recovery in the BMG was discussed. The results show that BMGs are an ideal material to investigate the physical aging. The further understanding of physical aging of BMGs is useful to clarify the nature of glass and improve the application and device of new types of BMGs.

bulk metallic glass, enthalpy recovery, physical aging

1 Introduction

Strictly speaking, glass is formed by cooling liquid. Without crystallization the structural relaxation time τ and corresponding viscosity η of liquid increase with the decrease in temperature. As η approaches 10^{13} poise, τ is close to the scale of the experimental time. With further cooling, the increasing τ makes the observation of the structural relaxation unavailable within the experimental time scale, and correspondingly the rigid glass is formed[1,2]. Usually the temperature at the viscosity of 10^{13} poise is considered as the glass transition temperature T_g, even though T_g depends on the experimental time scale. No difference between the liquid and its glass can be found in microstructure[3]. From the point of view of dynamics, glass is a frozen liquid. Glass has excess free

---

Received April 2, 2007; accepted January 4, 2008
doi: 10.1007/s11433-008-0048-z
† Corresponding author (email: pwen@aphy.iphy.ac.cn)
Supported by the National Natural Science Foundation of China (Grant No. 50671118)

energy, compared with its equilibrium at the same temperature. Its density and energy always relax toward its equilibrium values. The rate of relaxation is a function of the formation and history of the glass[4]. The process is companied with the change of the physical properties of glass that is sensitive to the structure, and termed firstly as physical aging by Struik[5]. Physical aging is a long-running issue, which is not only interesting to the basic theory, but also important in the practical application of amorphous materials[6].

In principle, the physical aging can be detected by all of structure-sensitive physical properties. Due to the application of differential scanning calorimeter (DSC) of high accuracy, sensitivity and stability, enthalpy becomes a convenient property to monitor physical aging[7]. Enthalpy recovery is one of characteristics of physical aging. Its endothermic process is characterized as a maximum in differential scanning calorimeter (DSC) curves. It is called the overshot when the maximum appears at the upper edge of the glass transition, while the sub-T_g peak when it appears at or below the lower edge of the glass transition. A vast amount of experiments affirm that the enthalpy relaxation is an important characteristic of glass. But no consensus has been reached on its nature yet. In the current phenomenological models, based on the idea of the fictive glass transition temperature T_f, the enthalpy recovery has been considered to be related to the primary structural relaxation in supercooled liquid, and arises from the stretched-exponential and nonlinear relaxation[8,9]. In the free volume theory[10], the enthalpy relaxation is thought as a simple process that is similar to the annihilation and germination of point 'defect' in crystalline phases[11]. It has also been explained with the heterogeneity of the microstructure of the metallic glasses by H. S. Chen and his coworkers[12]. In fact, the accumulated results affirm that the enthalpy recovery is related to the glass transition, and is a fundamental problem in amorphous physics[6,9,13].

The microstructure of metallic glasses (MGs) has been considered as the random packing of hard/soft spheres[14]. Thus they are ideal materials used to clarify some fundamental problems in the glasses[1]. But due to the poor glass-forming ability of conventional MGs, a high cooling rate (around 10^5 K/s) is necessary for their formation. So the size of conventional MGs is too small to measure their properties. Moreover, the interference of crystallization of conventional MGs cannot be avoided since they are unstable against crystallization. Recently, a new type of metallic glass (bulk metallic glasses (BMGs)) has been developed. Most of BMGs contain no metalloids[15]. Their microstructure is simple. It is important that these BMGs as well as their supercooled liquids have higher stability against crystallization. BMGs offer a good opportunity to investigate such fundamental problems as the mechanism of diffusion[16], the structural relaxation[17] and "crossover" phenomenon[18]. But few enthalpy recoveries in BMGs have been carried out. The investigation in details of enthalpy recoveries in BMGs is necessary.

2 Experimental method

$Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ BMG was prepared by suck casting in an arc furnace. Its cooling rate was more than 100 K/s. The as-cast cylinder is 3 mm in diameter and 70 mm in length. The samples taken from different parts of the rod were tested by measuring the calorimetric behavior of samples. No indication of heterogeneity was found. The samples used for aging and DSC measurements are about 0.5 mm in thickness. The aging and DSC measurements were carried out in the Perkin Elmer DSC-7 under a protection of purified argon gas.

3 Results and analysis

3.1 Effects of the formation of BMG on the enthalpy recovery

Figure 1 exhibits the temperature dependence of the heat capacity (C_p) of the samples formed with different cooling rates. The C_p curves are deduced from the DSC curves measured at the heating rate of 40 K/min. Except the as-cast sample, the samples formed at different cooling rates were produced by DSC. That is, the as-cast samples were sealed in an aluminum pan, and heated to the supercooled liquid region, then cooled down to room temperature with a given cooling rate by DSC. The temperature dependence of C_p of the glass is same to the heat capacity C_p^{Cryst} of the crystalline phases at low temperature (around room temperature). Its value is about 25 J/mol (about 3R, gas constant), equal to that calculated from ultrasonic measurements[19], indicating that the thermal physical properties of BMG are dominated by the vibrational motions of atoms at low temperature around room temperature. In Figure 1, an exothermal process can be found from 425 K up to T_g during heating in the as-cast sample DSC curve. This corresponds to its fast forming rate, which can be found in other glass-forming systems[20]. The exothermic process disappears in other samples. On the contrary, a weak endothermic process is observed at the beginning of 500 K, here called excess heat capacity of low temperature (HPLT). In Figure 1 the overshot in the C_p curve increases with the decreasing cooling rate. C_p of metallic supercooled liquid is temperature-independent, affirming that the metallic supercooled liquid is metastable equilibrium.

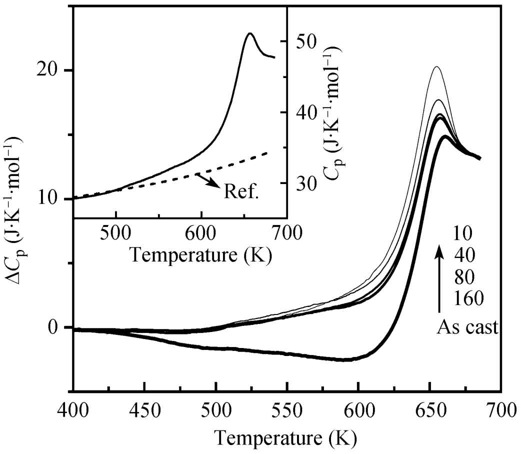

Figure 1 The temperature dependence of the heat capacity for $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ BMG formed with different cooling rates. The inset exhibits the relative heat capacity of the BMG formed by the cooling rate of 40 K/min and its corresponding crystalline phases.

Figure 1 shows that the glassy state of BMG is related to its formation. According to the free volume theory, the glass is the frozen glass-forming liquid. On the basis of the free volume theory, one parameter, the free volume, can be used to describe the supercooled liquid (SL). The free volume in SL is a function of temperature and pressure, while the free volume of glass is invariable. The varying free volume in a glass means the change of glassy state and physical aging occurs. In order to quantify the glassy states, the defect concentration c_D was introduced by Spaepen et al.[11,21]. According to the free-volume theory, the defect concentration is a function of the reduced free volume x: $c_D = \exp(-1/x)$. The change in defect concentration due to physical aging during the annealing process is governed by the differential equation:

$$\frac{\mathrm{d}c_\mathrm{D}}{\mathrm{d}t} = -k_\mathrm{r} c_\mathrm{D} (c_\mathrm{D} - c_\mathrm{D}^\mathrm{eq}), \tag{1}$$

where c_D and c_D^eq ($c_\mathrm{D}^\mathrm{eq} = \exp(-1/x_\mathrm{eq})$, x_eq is the reduced free volume in metastable equilibrium) are the defect concentrations in glassy state and metastable equilibrium. The reduced free volume in thermodynamic equilibrium x_eq has the form: $x_\mathrm{eq} = \frac{T - T_0}{B}$, where T_0 is the Vogel-Fulcher temperature[22] and B is a constant. t denotes time and k_r is a temperature-dependent rate factor for structural relaxation. k_r has the form: $k_\mathrm{r} = k_0 \exp\left(-\frac{E_\mathrm{f}}{k_\mathrm{B}T}\right)$, where E_f is the relaxation activation energy and k_0 is a constant. The calculated DSC signal is obtained by assuming the observed apparent heat capacity, given here as $\Delta C_\mathrm{p} = A\mathrm{d}x/\mathrm{d}T$. Figure 2 shows the results with the parameters of E_f, k_0, A, and the excess free volume x_0 in glass. The changes of the DSC curves are only related to initial x_0. The values of E_f, k_0 and A used are 1.75 eV, 2.4×10^{27} $\mathrm{s}^{-1}$and 0.7 eV, respectively. Based on the calculation, it is found that the high content of x_0 frozen in the as-cast sample approaching low x_eq brings up an exothermic process during heating. With increasing temperature, x becomes smaller than the equilibrium value since the kinetic is too slow to follow x_eq. The free volume begins to increase in order to attain equilibrium. The production of the free volume is an endothermic process, which corresponds to the glass transition process. The value of x in BMG is dependent on the cooling rate of the formation, and becomes large with the increase in the cooling rate of the formation. Correspondingly, the overshot is not obvious. It is noted here that the model based on the free theory cannot simulate the DSC curves since the temperature range for the glass transition in Figure 1 is about 25 K, but 15 K in calculation results (see Figure 2). The HPLT cannot be explained by the model.

Using the idea of fictive glass transition temperature T_f, Hodge and his coworkers have described successfully DSC curves in polymer glass system[7,23], based on the understanding of the nonlinear and nonexponential behavior of the glass transition[24]. T_f[9] has the form as $\frac{\mathrm{d}T_\mathrm{f}}{\mathrm{d}T} =$

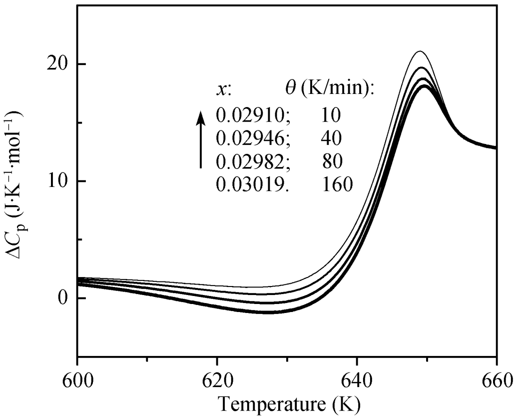

Figure 2 The calculation results for the temperature dependence of ΔC_p of BMG (the same as in Figure 1) based on the free volume theory.

$\left.\frac{C_{\mathrm{p}} - C_{\mathrm{pg}}}{C_{\mathrm{pe}} - C_{\mathrm{pg}}}\right|_T$, where C_{p} is the heat capacity measured, C_{pg} is the heat capacity of glass, and C_{pe} is the heat capacity of supercooled liquid. Thence, the DSC curves can be transformed into $\frac{\mathrm{d}T_{\mathrm{f}}}{\mathrm{d}T}$ curves with the known C_{pg} and C_{pe}. The temperature dependence of C_{pe} in the glassy region is usually deduced from the linear extrapolation of the heat capacity of the supercooled liquid[25]. C_{pg} at temperature higher than T_{g} results from the extrapolation of the heat capacity of the glass[25]. But the extrapolation for C_{pg} cannot be used here because the heat capacity of glass near T_{g} is dependent of the cooling rates (see Figure 1). Since C_{pg} is equal to $C_{\mathrm{p}}^{\mathrm{Cryst}}$ at low temperature in Figure 1, the temperature dependence of C_{pg} is displaced by that of $C_{\mathrm{p}}^{\mathrm{Cryst}}$. This replacement has been discussed in details and thought to be reasonable[26]. So the temperature dependence of C_{pg} (the unit of $\mathrm{J \cdot g^{-1} \cdot K^{-1}}$) has the form of $a+bT+cT^2$. The constants a, b and c are 0.42, -3.6×10^{-4}, and 1.1229×10^{-6}, respectively. Thence, corresponding to Figure 1, the temperature dependence of $\frac{\mathrm{d}T_{\mathrm{f}}}{\mathrm{d}T}$ can be plotted as Figure 3. The inset in Figure 3 exhibits an obvious linear relationship between $1000/T_{\mathrm{f}}$ and $\ln Q$. Q is the cooling rate. A linear relationship is followed as $\ln Q = 91.96 - 54070/T_{\mathrm{f}}$. The similar linear relationship has been derived by Moynihan, and found to exist in the polymer glass-forming system[27]. With the equation the cooling rate of the formation of the as-cast sample is 1.2215×10^4 K/min.

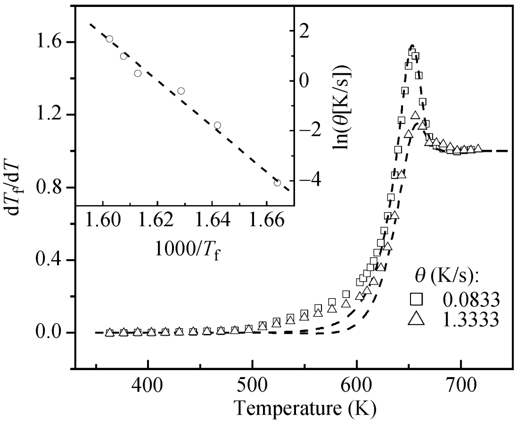

Figure 3 The plots of $\frac{\mathrm{d}T_{\mathrm{f}}}{\mathrm{d}T}$ of the sample formed with the cooling rates of 0.0833 (□) and 1.3333 (△) K/s. The dash lines are the best fit with Hodge's method. Inset exhibits the relationship between the cooling rate and T_{f}: $\ln\theta = 91.96 - 54070/T_{\mathrm{f}}$.

In Hodge's model the non-expomentiality in the cooing and heating processes can be treated as the Boltsmann's superposition of a series of isothermal temperature steps. At a given temperature T the response function is of the Kohlrausch-Willians-Watts form[28]:

$$\phi(t) = \exp[-(t/\tau_0)^{\beta}],$$

where $1 \geqslant \beta \geqslant 0$. τ_0 is a relaxation time that depends on T and T_{f}:

$$\tau_0 = A\exp\left[\frac{x\Delta h}{RT} + \frac{(1-x)\Delta h}{RT_{\mathrm{f}}}\right],$$

where A, x ($1 \geqslant x \geqslant 0$), and Δh are parameters and R is the ideal gas constant[7]. The four parameters of β, A, x, and Δh are assumed to be independent of T and T_{f}. Δh can be determined from the cooling rate dependence of the frozen fictive temperature T_{f} in glass. Thus, T_{f} originating from the response of $T_{\mathrm{f}}(T)$ to temperature (T) perturbation can be given by

$$T_{\mathrm{f}}(T) = T_0 + \int_{T_0}^{T} \mathrm{d}T' \left\{1 - \exp\left[-\left(\int_{T'}^{T} \mathrm{d}T''/Q\tau_0\right)^{\beta}\right]\right\},$$

where T_0 is a starting temperature well above T_{g}. From the result of the inset in Figure 3, the value of $\Delta h/R$ is 54070 K. h is input, and the values of A, x, and β will be output from the best-fit. The value of A, x, and β is 2.44×10^{-36} s, 0.55 and 0.5, respectively. Beyond the temperature region from 480 K to T_{g}, Hodge's model can describe quantitatively the experimental data (see Figure 3).

3.2 Effect of annealing temperature

Higher T_{f} of the as-cast sample indicates that the as-cast sample has higher excess energy. The higher excess energy will drive the sample to approach a low energy state even at the temperature well below T_{g}. Obviously, the approaching rate is dependent on temperature and time. Figure 4(a) exhibits the effect of the annealing temperature on the enthalpy recovery. The annealing temperature is from 437 K (150 K lower than T_{g} (630 K)) to 683 K. In order to exhibit the aging temperature effect on the enthalpy relaxation, the as-cast sample was heated up to a given annealing temperature at the heating rate of 40 K/min and cooled down immediately at the cooling rate of 80 K/min when the annealing temperature is reached. It is found that the onset temperature of the exothermic shifts to a higher temperature as the aging temperature increases. The exothermic process disappears when the aging temperature is higher than 613 K. While the exothermic process is disappearing, enthalpy recovery appears and becomes dominated gradually. The evolution of the characteristic maximum with the annealing temperature is similar to sub-T_{g} peak. The height and temperature of the maximum increase with the increasing annealing temperature. It is interesting that the sub-T_{g} lies on the temperature of HPLT. Its formation can be considered as the superposi-

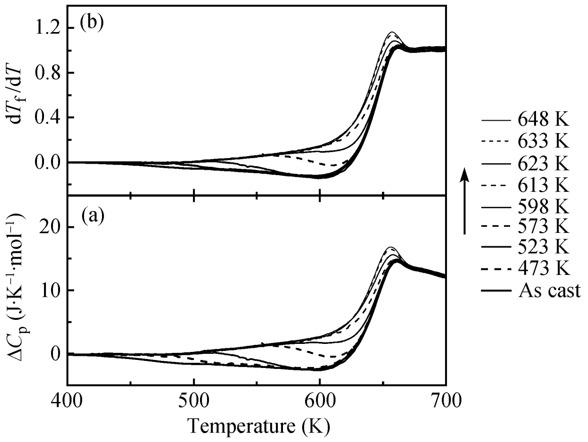

Figure 4 (a) The temperature dependence of ΔC_{p} for the samples annealed at different temperatures for 0 s; (b) the temperature dependence of $\frac{\mathrm{d}T_{\mathrm{f}}}{\mathrm{d}T}$ of the corresponding samples shown in (a).

tion of the HPLT and the exothermic process. As the annealing temperature is higher than 613 K, the glass transition is affected. The sub-T_g is merged into the endothermic process of the glass transition (see 613 and 623 K), and finally is transformed into overshot (see 633). When the annealing temperature is up to the supercooled liquid region, the C_p curve is independent of the annealing temperature. The sub-T_g peak cannot be consistent with the free volume theory, in which relaxation makes the free volume decrease to metastable equilibrium. Thus below T_g no endothermic process exists. Corresponding to Figure 4(a), Figure 4(b) is the temperature dependence of $\frac{dT_f}{dT}$. It is found that they are equal to exhibit the enthalpy recovery.

Figure 5 shows the simulation results based on the Hodge's phenomenological model. The parameters in the simulation are the same as those used in Figure 3. An obvious sub-T_g peak is formed by the 623 annealing. The evolvement of the sub-T_g peak upon the annealing temperature is the same as that shown in Figure 4(b). The evolvement of the endothermic process exhibits that the endothermic process is only superposited on the endothermic process of the glass transition, but changes it. That implies that the endothermic process has a different nature from that of the calorimetric glass transition. Since the overshot has the same nature of the endothermic process of the maximum, the overshot should be distinguished from the calorimetric glass transition. Based on Hodge's phenomenological model the retardation times of the relaxation of BMG are widely distributed. The long averaged retardation times associated with low annealing and heating temperature contribute to short reduced times $\sum t_i / \tau_i$. The short reduced times correspond to the sub-T_g peak. Longer anneals and/or higher annealing temperatures associated with the long averaged retardation time can also produce longer reduced times. When the reduced time for annealing approaches that of the glass transition, the sub-T_g annealing peak merges with the glass transition. As the reduced time lengthens further, the overshot appears. On the contrary, the glass transition results from longer characteristic reduced time formed by shorter averaged retardation time associated with high temperature.

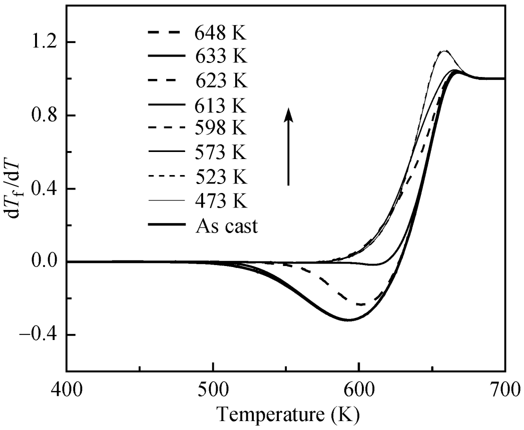

Figure 5 The simulation results for Figure 4 based on the Hodge's model.

4 Discussion

The similarity of the characteristics and evolvement of the enthalpy recovery in BMG with those in polymer, oxide and conventional MGs further affirms that enthalpy recovery is a common characteristic in the glassy state. Enthalpy recovery rises from a wide distribution of relaxation time in the glassy system. Compared with the free volume theory, the model based on a wide distribution of relaxation time has an obvious advantage. It is consistent with the understanding of the primary relaxation of supercooled liquids (SLs) of the glass-forming system. The primary microstructure relaxation of SL has a wide distribution of relaxation time, but is not a process of overcoming a common barrier for correlated particles.

The wide distribution of the relaxation time indicates that the corresponding dynamical microstructure of SL is heterogeneous. No consensus has been reached so far on whether the heterogeneity in dynamics is related to the heterogeneity in space or not. The investigation of the dynamics in polymer and oxide amorphous systems with a complex microstructure is not useful to clarify the disputation. Currently the mechanical relaxation of the $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ supercooled liquid has been investigated[20]. It has been found that the spectrum of the primary relaxation of the SL is widened. The result supports that the microstructure of the SL is heterogeneous in space since the heterogeneity of the mechanical relaxation in the metallic SL is related to the heterogeneity of the translational diffusions. The parameter in the WLT equation used to describe the spectrum is about 0.5, consistent with that used in Hodge's model.

It is important that an excess wing has been observed at the high frequency tail of the spectrum mechanical relaxation. This means that the slow β relaxation exists in the metallic SL. One obvious peak of the slow β-relaxation is due to the intrinsic dynamical characteristic of the metallic SL. According to the definition of Angell's liquid, the metallic SL is a rather strong liquid. So the structural relaxation is coupled[29]. Thus, from the point of view of dynamics the formation of BMG is the freezing of the primary relaxation. Below T_g, the β-relaxation should exist in a certain temperature range. The motions representing the slow β-relaxation can contribute to the heat capacity. The excess heat capacity in BMG (see Figures 1 and 3) at temperature close to T_g is a strong evidence. The existence of the β-relaxation in the BMG has been affirmed by the measurement of the mechanical relaxation. The relationship between the primary relaxation and the β-relaxation and their effect on the physical aging are beyond the paper, and will be an important object to study in future.

5 Conclusions

The enthalpy recovery in $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ BMG was investigated by DSC. Compared with Hodge's model, the free volume theory is not a good way to describe the enthalpy recovery in BMG. An endeavor should be needed to give a quantitative description of the enthalpy recovery. In combination with the investigation of dynamics of the metallic SL, it is found that the enthalpy recovery is mainly contributed from the freezing of the primary relaxation, but the effect of the slow β relaxation cannot be neglected in order to understand the origin of the enthalpy recovery.

1 Beck H, Güntherodt H J. Glassy Metals II. Berlin: Springer-Verlag, 1983. Chapter 6
2 Leutheusser E. Dynamical model of the liquid-glass transition. Phys Rev A, 1984, 29: 2765－2773[DOI]
3 Torquato S. Glass transition: Hard knock for thermodynamics. Nature, 2000, 405: 521－523[DOI]
4 Kovacs A J, Aklonis J J, Hutchinson J M, et al. Isobaric volume and enthalpy recovery of glass (II): A transparent multiparameter theory. J Polym Sci, 1979, 17: 1097－1162
5 Struik L C E. Physical Aging in Amorphous Polymers and Other Materials. Amsterdam: Elsevier, 1978

6 Hodge I M. Physical aging in polymer glasses. Science, 1995, 267: 1945[DOI]

7 Hodge I M. Relaxation in Complex Systems. Washington, D.C.: Office of Naval Research, 1983. 65

8 Tool A Q, Eichlin C G. Variation caused in the heating curves of glass by heat. J Am Ceram Soc, 1931, 14: 276 [DOI]

9 Hodge I M. Enthalpy relaxation and recovery in amorphous materials. J Non-Cryst Solids, 1994, 169: 211[DOI]

10 Cohen M H, Grest G S. Liquid-glass transition, a free volume approach. Phys Rev B, 1979, 20: 1077[DOI]

11 Taso S S, Spaepen F. Structural relaxation of a metallic glass near equilibrium. Acta Metal, 1985, 33: 881[DOI]

12 Chen H S, Inoue A, Masumoto T. Two-stage enthalpy relaxation behavior of $(Fe_{0.5}Ni_{0.5})_{83}P_{17}$ and $(Fe_{0.5}Ni_{0.5})_{83}B_{17}$ amorphous alloys upon annealing. J Mater Sci, 1985, 20: 2417[DOI]

13 Donth E. The Glass Transition: Relaxation and Thermodynamics in Polymers: Glass Transition. Berlin Heidelberg: Springer-Verlag, 2001

14 Greer A L. Metallic glasses. Science, 1995, 267: 1947[DOI]

15 Johnson W L. Bulk glass-forming metallic alloy: Science and technology. MRS Bull, 1999, 24(10): 42

16 Tang X P, Geyer U, Busch R, et al. Diffusion mechanisms in metallic supercooled liquids and glasses. Nature, 1999, 402: 160 [DOI]

17 Wen P, Zhao D Q, Pan M X, et al. Relaxation of metallic $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ bulk glass-forming supercooled liquid. Appl Phys Lett, 2004, 84: 279

18 Meyer A, Busch R, Schober H. Time-temperature superposition of structural relaxation in a viscous metallic liquid. Phys Rev Lett, 1999, 83: 5027[DOI]

19 Wen P, Johari G P, Wang R J, et al. Change in the vibrational properties in the metallic glass with time. Phys Rev B, 2006, 73: 224203[DOI]

20 Yue Y, Angell C A. Clarifying the glass transition behavior of water by comparison with inorganic glasses. Nature, 2004, 427: 717[DOI]

21 van den Beukel A, Sietsma J. The glass transition as a free volume related kinetic phenomenon. Acta Metall Mater, 1990, 38: 383[DOI]

22 Bakke E, Busch R, Johnson W L. The viscosity of the $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ bulk metallic glass forming alloy in the supercooled liquid. Appl Phys Lett, 1995, 67: 326

23 Kovacs A J, Aklonis J J, Hutchinson J M, et al. Isobaric volume and enthalpy recovery of glasses. 2. A transparent multi-parameter theory. J Polym Sci Part B: Polym Phys, 1996, 34: 2467[DOI]

24 Narayanaswamy O S. A model of structural relaxation in glass. J Am Ceram Soc, 1971, 53: 380

25 Hodge I M. Effects of annealing and prior history on enthalpy relaxation in glass polymer. 4. Comparsion of five polymers. Macromolecules, 1983, 16: 898[DOI]

26 Angell C A, Borick S. Glass transitions and first order liquid-metal-to-semiconductor transitions in 4-5-6 covalent systems. J Non-Cryst Solids, 2002, 307-310: 393[DOI]

27 Kubaschewski O, Alcock C B, Spencer P J. Materials Temochemistry. 6th ed. New York: Permagon, 1993

28 Debenedetti P G, Stillinger F H. Supercooled liquids and the glass transition. Nature, 2001, 410: 259[DOI]

29 Tanaka H. Origin of the excess wing and slow β relaxation of glass formers: A unified picture of local orientational fluctuations. Phys Rev E, 2004, 69: 021502[DOI]