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Structural relaxation of Ti₄₀Zr₂₅Ni₈Cu₉Be₁₈ bulk metallic glass

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Abstract

The enthalpy relaxation behavior of Ti₄₀Zr₂₅Ni₈Cu₉Be₁₈ bulk metallic glass follows the general characteristics of that for amorphous materials although its unique quenched-in nuclei/amorphous matrix structure: the annealing time dependence of recovery enthalpy follows a stretched exponential function with the mean relaxation time obeying an Arrhenius law, which may be due to the longer incubation time for crystallization τ_{inc} than the relaxation time τ leading to the enthalpy relaxation almost not being disturbed by the crystallization of quenched-in nuclei. The equilibrium recovery enthalpy ΔH_T^{eq} , mean relaxation time τ and stretching exponent β are all dependent on the annealing

temperature, and the higher the annealing temperature, the lower the values of ΔH_T^{eq} , τ and higher of β .

Two parameters, β_g and τ_g , representing the stretching exponent and the mean structural relaxation time at the calorimetric glass transition temperature, respectively, are correlated with glass forming ability and thermal stability, respectively. The high value of β_g for Ti₄₀Zr₂₅Ni₈Cu₉Be₁₈ BMG that is much higher than 0.84 and approaches unity reveals its good glass forming ability; however, its low value of τ_g indicates a worse thermal stability compared with typical BMGs.

Keywords: Bulk metallic glass; Titanium alloy; Structural relaxation; Quenched-in nuclei; Glass forming ability; Thermal stability

1. Introduction

Since a glass can be described as an undercooled melt, such glassy structure is thermodynamically metastable compared with the ideal glassy state and tends to undergo structural rearrangement to reach the ideal glassy state (structural relaxation) [1,2] or transform to an equilibrium crystalline structure through a series of continuous transformations once the external energies are supplied either thermally by heat treatments or mechanically by application of external stresses, leading to continuous changes in physical, chemical and mechanical properties.

Ti-based bulk metallic glasses (BMGs), as promising lightweight structural materials, have attracted more and more attention during recent years [3-12]. Ti₄₀Zr₂₅Ni₈Cu₉Be₁₈ BMG, as one of the best Ti-based BMGs known today, was found to exhibit a good combination of glass forming ability (GFA, the maximum diameter could be 8 mm) and mechanical properties (high compressive strength and large compressive plastic strain) [9,13,14], which could be a potential structural material. Our recent study has investigated its crystallization behavior, and found its unique quenched-in nuclei/amorphous matrix structure [14,15], suggesting that this alloy is a marginal BMG. Actually such marginal glassy alloys exist extensively and are complex with respect to typical fully glassy alloys, accordingly may lead to the different thermally induced transformation behaviors for their different structural nature and the microstructure sensitivity to thermal activation. However, so far there is no detailed investigation on structural relaxation of such complex marginal BMGs. Ti₄₀Zr₂₅Ni₈Cu₉Be₁₈ BMG could be a good

medium for investigating the structural relaxation behavior of such complex metallic glasses. Therefore, the present work aims to investigate the structural relaxation behavior of $\text{Ti}_{40}\text{Zr}_{25}\text{Ni}_8\text{Cu}_9\text{Be}_{18}$ BMG.

2. Experiment

The ingots of master alloy with nominal composition of $\text{Ti}_{40}\text{Zr}_{25}\text{Ni}_8\text{Cu}_9\text{Be}_{18}$ (at.%) were prepared by melting elements of 99.8 to 99.999 wt.% purity with high frequency electromagnetic induction in a water-cooled copper crucible under a high purity argon atmosphere. The ingot alloys were remelted at high temperature several times to ensure the compositional homogeneity. Cylindrical samples with 2 mm in diameter and 40 mm in length were prepared by injection casting into a water-cooled copper mould via an electromagnetic levitation-melt state under a high purity argon atmosphere before casting to obtain a completely melted state. Alloy's oxygen content was measured <400 ppm.

The glass transition temperature (T_g) and the onset crystallization temperature (T_{x1}) were determined to be 313 and 372 °C, respectively, by differential scanning calorimetry (DSC, Netzsch DSC 404s) measurement at a heating rate of 20 K/min in a flowing argon atmosphere. The microstructure was observed by high-resolution transmission electron microscopy (HRTEM, JEM-3010).

Structural relaxation was investigated through measuring the relaxation of the frozen-in enthalpy towards the equilibrium state as a function of time at a certain constant temperature by using DSC. The enthalpy reduction during an isothermal relaxation below the calorimetric glass transition is recovered as an “overshooting” at the glass transition during a subsequence DSC run. The detailed temperature program can be summarized as followed: to erase the thermal history of metallic glasses, each sample was heated from room temperature to a certain temperature (about 20 °C above T_g) at a heating rate of 20 K/min, and then immediately cooled down to room temperature at a cooling rate of 50 K/min, then heated the sample to the isothermal annealing temperature T (273, 283, 293 and 303 °C) at a heating rate of 30 K/min and annealed for different period of time t (5 min-6 h). After each isothermal annealing, the sample was heated up to high temperature to complete the crystallization (600 °C) at a heating rate of 20 K/min and then immediately cooled down to room temperature at a heating rate of 50 K/min for the following calculation of recovery enthalpy. Finally, this heating and cooling cycle was repeated using the same procedure as before for baseline correction. The relaxation recovery enthalpy ($\Delta H_T(t)$) was determined by measuring the overshoot endothermic enthalpy around T_g of an annealed sample with respect to the as-cast sample.

3. Results

Fig. 1 shows the recovery enthalpy $\Delta H_T(t)$ as a function of annealing time t at various annealing temperatures T of 273, 283, 293 and 303 °C for $\text{Ti}_{40}\text{Zr}_{25}\text{Ni}_8\text{Cu}_9\text{Be}_{18}$ BMG. It can be seen that the value of $\Delta H_T(t)$ increases rapidly with increase in t at the initial stage of relaxation, then changes to increase gradually, finally tends to saturate. Further investigation find that the $\Delta H_T(t)$ - t relation does not follow a simple exponential relaxation function, which could be due to the microstructural heterogeneities of the sample, and suggests that the enthalpy relaxation of the $\text{Ti}_{40}\text{Zr}_{25}\text{Ni}_8\text{Cu}_9\text{Be}_{18}$ liquid does not involve a single Debye relaxation event, as is in accordance with the previous report related to amorphous materials.

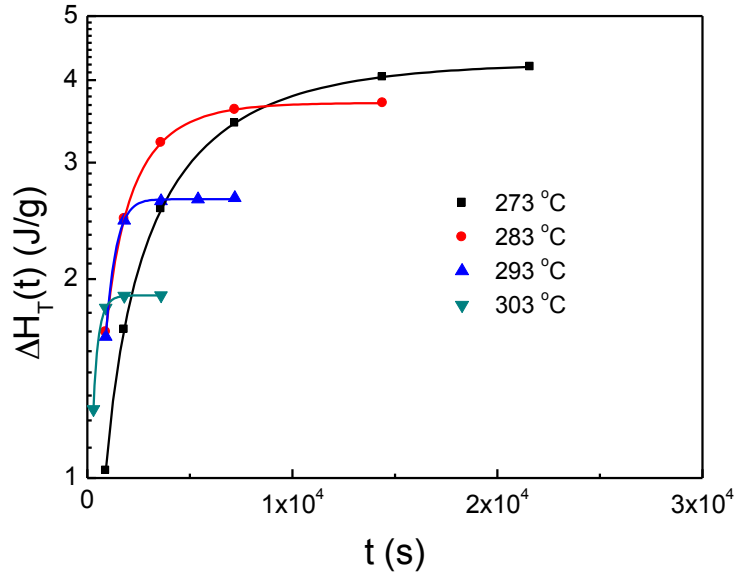


Fig. 1 Relaxation recovery enthalpy $\Delta H_T(t)$ as a function of annealing time t at various temperatures for $\text{Ti}_{40}\text{Zr}_{25}\text{Ni}_8\text{Cu}_9\text{Be}_{18}$ BMG. The stretched exponential function was used to fit the experimental data.

It is well known that the time dependence of $\Delta H_T(t)$ at a given temperature of amorphous materials generally can be fitted by a stretched exponential relaxation function [16-18]

$$\Delta H_T(t) = \Delta H_T^{eq} \left\{ 1 - \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right] \right\} \quad (1)$$

where τ is the mean structural relaxation time, ΔH_T^{eq} is the equilibrium value of $\Delta H_T(t)$ for $t \rightarrow \infty$ at the annealing temperature T , β is the stretching exponent whose value is between zero and unity $0 < \beta \leq 1$, reflecting the width of relaxation time distribution spectrum originating from the inhomogeneity of the supercooled liquid. The value of $\beta=1$ corresponds to a single relaxation time with exponential behavior. The smaller the value of β , the more the distribution of atomic motions deviates from a single exponential behavior. So, if the relaxation time distribution becomes broader, the value of β will be reduced, and the enthalpy recovery curve will be spread out over a wider temperature range. Obviously, the experimental $\Delta H_T(t)$ - t relation for $\text{Ti}_{40}\text{Zr}_{25}\text{Ni}_8\text{Cu}_9\text{Be}_{18}$ BMG can be well fitted with stretched exponential relaxation function. The obtained ΔH_T^{eq} , τ and β , at various annealing temperatures are listed in **Table 1**. It is found that the values of ΔH_T^{eq} , τ and β are dependent on the annealing temperature, and the higher the annealing temperature, the lower the values of ΔH_T^{eq} , τ and higher of β , indicating that the enthalpy recovery is determined by the annealing temperatures. The annealing temperature dependence of ΔH_T^{eq} , τ and β is mainly ascribed to the degree of the amorphous phase deviating from its equilibrium state at each annealing temperature. It should be pointed out that for $\text{Ti}_{40}\text{Zr}_{25}\text{Ni}_8\text{Cu}_9\text{Be}_{18}$ BMG, stretching exponent β is not constant but slightly increasing with annealing temperature. Such annealing temperature dependence of stretching exponent β has been found in some

BMGs, for example, $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ [19], $Pd_{43}Cu_{27}Ni_{10}P_{20}$ [18] and $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ [20] BMGs, indicating that the structural relaxation behavior of BMGs are complex.

Table 1 The values of ΔH_T^{eq} , τ and β obtained from the fitting of $\Delta H_T(t)$ vs. t curves based on the stretched exponential relaxation function for $Ti_{40}Zr_{25}Ni_8Cu_9Be_{18}$ BMG.

T (°C)	ΔH_T^{eq} (J/g)	τ (s)	β
273	4.2	3997	0.86201
283	3.7	1616	0.87987
293	2.6	624	0.91135
303	1.9	266	0.93578

In the literature, Vogel-Fulcher-Tammann (VFT) equation is used to describe the non-Arrhenius behavior of the mean relaxation time τ [21]

$$\tau = \tau_0 \exp\left(\frac{D^*T_0}{T - T_0}\right) \quad (2)$$

where τ_0 is the pre-exponential factor related to relaxation time constant, D^* is the fragility parameter and T_0 is the VFT temperature at which barriers with respect to flow would go to infinity and is believed to correspond to the theoretical Kauzmann temperature T_k . In most enthalpy relaxation studies, T_0 in VFT equation is assumed to be 0 and accordingly the mean relaxation time τ for the enthalpy relaxation is assumed to follow an Arrhenius behavior [21]

$$\tau = \tau'_0 \exp\left(\frac{E_a}{RT_a}\right) \quad (3)$$

where τ'_0 is the pre-exponential factor, R is the ideal gas constant, E_a is the apparent activation energy [18,20]. It is found that the experimental annealing temperature dependence of the mean relaxation time τ for $Ti_{40}Zr_{25}Ni_8Cu_9Be_{18}$ BMG can be well fitted with an Arrhenius plot as shown in Fig. 2, and yields a τ'_0 of 1.96×10^{-19} s and an E_a of 233 kJ/mol (2.42 eV). It should be pointed out that such Arrhenius behavior cannot hold over a wide temperature since that actually T_0 is not equal to 0 and approximately several tens of Kelvins below T_g for glasses. However, the T_0 item in VFT equation can be ignored when considering the temperature dependence of τ in the experimental annealing temperature range.

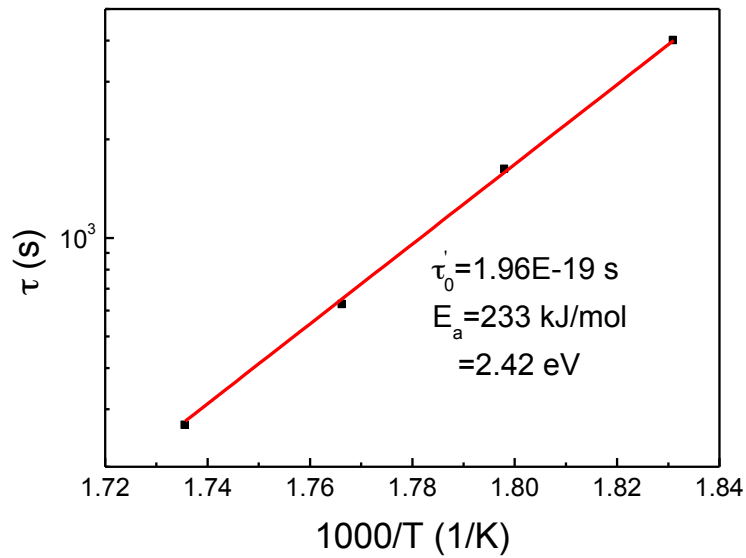


Fig. 2 Mean enthalpy relaxation time as a function of inverse temperature for $\text{Ti}_{40}\text{Zr}_{25}\text{Ni}_8\text{Cu}_9\text{Be}_{18}$ BMG fitted with the Arrhenius equation.

4. Discussion

Although the unique quenched-in nuclei/amorphous matrix structure, surprisingly, its enthalpy relaxation behavior follows the general characteristics of amorphous materials without being disturbed (at least not obviously) by the crystallization of quenched-in nuclei: the annealing time dependence of recovery enthalpy $\Delta H_T(t)$ follows a stretched exponential function with the mean relaxation time obeying an Arrhenius law. In order to confirm such phenomenon, we performed low temperature isothermal annealing on the as-cast $\text{Ti}_{40}\text{Zr}_{25}\text{Ni}_8\text{Cu}_9\text{Be}_{18}$ BMG at 293 °C for various times from 15 min to 6 h to observe its microstructure evolution. It is found that no crystals are formed until the sample is annealed for 6 h, as shown in **Fig. 3**, suggesting that the crystallization of quenched-in nuclei will not significantly disturb its structural relaxation behavior.

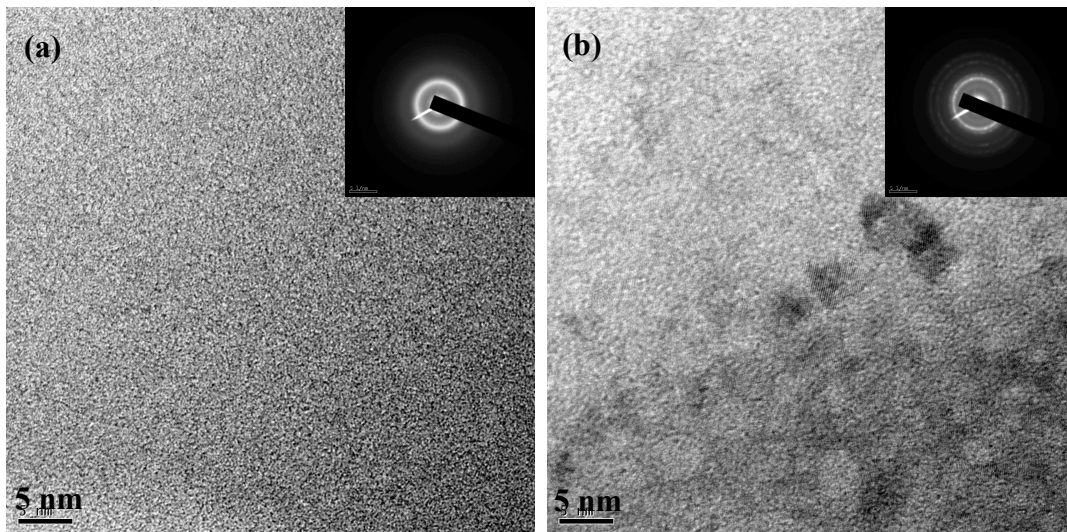


Fig. 3 Bright field image and corresponding SADP obtained from annealed $\text{Ti}_{40}\text{Zr}_{25}\text{Ni}_8\text{Cu}_9\text{Be}_{18}$ samples

at 293 °C for (a) 2 h and (b) 6 h.

Whether the quenched-in nuclei in the as-cast $\text{Ti}_{40}\text{Zr}_{25}\text{Ni}_8\text{Cu}_9\text{Be}_{18}$ BMG influence on the structural relaxation or not? It depends on the stability of the quenched-in nuclei, i.e. if the incubation time for crystallization of the quenched-in nuclei τ_{inc} is longer than the relaxation time of the amorphous matrix τ , in other words, these two events (structural relaxation and crystallization of quenched-in nuclei) do not overlap, in this case the structural relaxation will not be disturbed by the crystallization of quenched-in nuclei, accordingly its enthalpy relaxation behavior should be similar to that of typical amorphous materials; or else, the enthalpy relaxation behavior should be different due to the disturbance of the crystallization of quenched-in nuclei. For $\text{Ti}_{40}\text{Zr}_{25}\text{Ni}_8\text{Cu}_9\text{Be}_{18}$ BMG, the above microstructure evolution observation at isothermal annealing temperature of 293 °C has confirmed the very limited crystallization of the quenched-in nuclei at the later stage of structural relaxation, indicating that the overshoot of the endothermic reaction in the vicinity of glass transition of the annealed samples with respect to the as-cast samples is mainly ascribed from the structural relaxation and the crystallization of quenched-in nuclei is so limited that can be ignored, especially at low annealing temperature and short annealing time. Accordingly, the enthalpy relaxation behavior of $\text{Ti}_{40}\text{Zr}_{25}\text{Ni}_8\text{Cu}_9\text{Be}_{18}$ BMG follows the general law.

The characteristic parameters, stretching exponent β and mean structural relaxation τ derived from the stretched exponential relaxation function, are essential for the analysis of enthalpy relaxation, which are believed to be correlated with the GFA and thermal stability of metallic glasses, respectively. However, their characteristic of temperature dependence brings about difficulties for constructing the correlation between stretching exponent β and GFA, and correlation between mean structural relaxation τ and thermal stability. In this study, two parameters, β_g and τ_g , representing the stretching exponent and the mean structural relaxation time at the calorimetric glass transition temperature, respectively, were proposed to be the indicators of enthalpy relaxation properties.

The relation between β_g and GFA of metallic glasses was constructed through fragility index m as a chain, since the stretching exponent β has a correlation with the fragility index m which is an indicator of the fragility of supercooled liquid and the strong liquid (with small fragility index) is generally correlated with the good GFA. It is known that most of the bulk metallic glasses show strong liquid behavior and generally have a fragility index of less than 50 [19,22,23]. And a reduced $m=42/\beta$ relation can be derived from a relation between the fragility index m and stretching exponent β based on the defect diffusion model proposed by Bendler et al. [24], this expression has been confirmed to be suitable for describing the m - β relation for polymeric, alcoholic and metallic glasses. Accordingly, the value of stretching exponent β for the metallic glasses who exhibit a good GFA empirically should be larger than 0.84. Fig. 4 shows the stretching exponent β as a function of annealing temperature T for $\text{Ti}_{40}\text{Zr}_{25}\text{Ni}_8\text{Cu}_9\text{Be}_{18}$ BMG as well as typical Zr-based BMGs (Vit 4 and Vit 106a alloys), the β_g values can be obtained through linear extrapolation. It is found that the value of β_g for $\text{Ti}_{40}\text{Zr}_{25}\text{Ni}_8\text{Cu}_9\text{Be}_{18}$ BMG is comparable with other typical BMGs, much higher than 0.84 and approaches unity, implying its strong liquid behavior and accordingly good GFA.

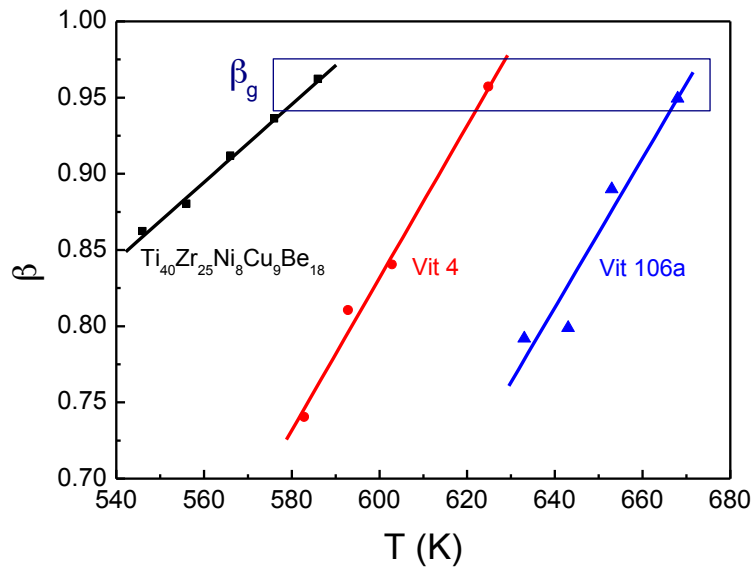


Fig. 4 Stretching exponent β as a function of annealing temperature T for $\text{Ti}_{40}\text{Zr}_{25}\text{Ni}_8\text{Cu}_9\text{Be}_{18}$ as well as Vit 4 and Vit 106a BMGs.

The relation between τ_g and thermal stability of metallic glasses was constructed based on the simple idea that the long structural relaxation time corresponds to a good thermal stability. There exists a linear relationship between the logarithmic relaxation time $\ln\tau$ and the difference between the glass transition temperature and annealing temperature ΔT , $\ln\tau = \ln\tau_g + A\Delta T$. **Fig. 5** shows the τ vs. ΔT curves of $\text{Ti}_{40}\text{Zr}_{25}\text{Ni}_8\text{Cu}_9\text{Be}_{18}$ as well as other typical BMGs. It is generally believed that the structural relaxation time at glass transition temperature is around 100 s. The τ_g value of $\text{Ti}_{40}\text{Zr}_{25}\text{Ni}_8\text{Cu}_9\text{Be}_{18}$ BMG is around 105 s, much lower than that of $\text{La}_{55}\text{Al}_{25}\text{Ni}_{10}\text{Cu}_{10}$ BMG (~ 1720 s) [25], $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$ BMG (~ 145 s) [18] and $\text{Zr}_{58.5}\text{Cu}_{15.6}\text{Ni}_{12.8}\text{Al}_{10.3}\text{Nb}_{2.8}$ BMG (~ 145 s) [20], suggesting that $\text{Ti}_{40}\text{Zr}_{25}\text{Ni}_8\text{Cu}_9\text{Be}_{18}$ BMG is more relaxed and only need short relaxation time to reach the internal equilibrium state, which may be due to the smaller activation energy for structural relaxation and free volume, as indicates its worse thermal stability than other typical BMGs.

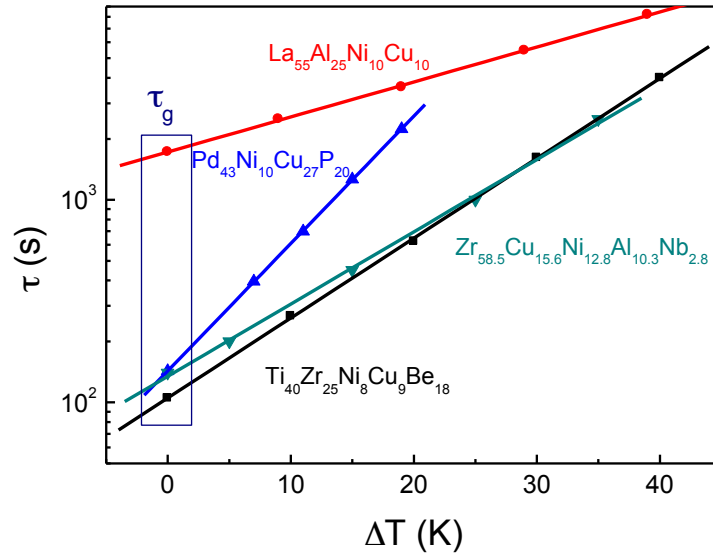


Fig. 5 Mean structural relaxation time τ as a function of ΔT for $\text{Ti}_{40}\text{Zr}_{25}\text{Ni}_8\text{Cu}_9\text{Be}_{18}$ as well as typical BMGs. The solid lines are the linear fitting curves based on $\ln \tau = \ln \tau_g + A\Delta T$.

5. Conclusions

Enthalpy relaxation from the amorphous state into the supercooled liquid state was investigated on the $\text{Ti}_{40}\text{Zr}_{25}\text{Ni}_8\text{Cu}_9\text{Be}_{18}$ bulk metallic glass below the calorimetric glass transition. The enthalpy relaxation behavior of this alloy follows the general characteristics of enthalpy relaxation for glasses although its unique quenched-in nuclei/amorphous matrix structure: a stretched exponential function with the relaxation time obeying an Arrhenius law, which is due to the incubation time for crystallization τ_{inc} is longer than the relaxation time τ and the enthalpy relaxation is almost not disturbed by the crystallization of quenched-in nuclei. Two parameters, β_g and τ_g , representing the stretching exponent and the mean structural relaxation time at the calorimetric glass transition temperature, respectively, were proposed to correlate with GFA and thermal stability, respectively. The high value of β_g that is much higher than 0.84 and approaches unity for $\text{Ti}_{40}\text{Zr}_{25}\text{Ni}_8\text{Cu}_9\text{Be}_{18}$ BMG confirms its good GFA as typical Zr-based BMGs; however, its low value of τ_g (105 s) indicates a worse thermal stability compared with typical BMGs.

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References

- [1] H.S. Chen, Glassy metals, Rep. Prog. Phys. 1980, 43: 353-432.
- [2] A. Van den Beukel, J. Non-Cryst. Solids 1986, 83: 134-140.
- [3] G. Duan, A. Wiest, M.L. Lind, A. Kahl and W.L. Johnson, Scripta Mater. 2008, 58: 465-468.

- [4] C.L. Ma, S. Ishihara, H. Soejima, N. Nishiyama and A. Inoue, *Trans. JIM*. 2004, 45: 1802-1806.
- [5] C.L. Ma, H. Soejima, S. Ishihara, K. Amiya, N. Nishiyama and A. Inoue, *Mater. Trans. JIM*. 2004, 45: 3223-3227.
- [6] K.B. Kim, X.F. Zhang, S. Yi, M.H. Lee, J. Das and J. Eckert, *Philos. Mag. Lett.* 2008, 88: 75-81.
- [7] F.Q. Guo, H.J. Wang, S.J. Poon and G.J. Shiflet, *Appl. Phys. Lett.* 2005, 86: 091907.
- [8] Y.C. Kim, J.H. Na, J.M. Park, D.H. Kim, Y.H. Lee and W.T. Kim, *Appl. Phys. Lett.* 2003, 83: 3093-3095.
- [9] Y.C. Kim, W.T. Kim and D.H. Kim, *Mater. Sci. Eng. A* 2004, 375-377:127-135.
- [10] J.M. Park, H.J. Chang, K.H. Han, W.T. Kim and D.H. Kim, *Scripta Mater.* 2005, 53: 1-6.
- [11] T. Ohkubo, D. Nagahama, T. Mukai and K. Hono, *J. Mater. Res.* 2007, 22: 1406-1413.
- [12] J. Fornell, A. Concustell, S. Suriñach, W.H. Li, N. Cuadrado, *Int. J. Plasticity*. 2009, 25: 1540-1559.
- [13] W.F. Ma, H.C. Kou, J.S. Li, H. Chang and L. Zhou, *J. Alloy. Comp.* 2009, 472: 214-218.
- [14] J.N. Mei, J.L. Soubyeroux, J.J. Blandin, J.S. Li, H.C. Kou, H.Z. Fu and L. Zhou, submitted to
- [15] J.L. Soubyeroux, J.N. Mei, *J. Alloy. Compd.* Accepted.
- [16] T.A. Vilgis, *Phys. Rev. B* 1993, 47: 2882-2885.
- [17] R. Busch and W.L. Johnson, *Appl. Phys. Lett.* 1998, 72: 2695-2697.
- [18] G.J. Fan, J.F. Löffler, R.K. Wunderlich and H.J. Fecht, *Acta Mater.* 2004, 52: 667-674.
- [19] R. Busch, A. Masuhr and W.L. Johnson, *Mater. Sci. Eng. A* 2001, 304-306: 97-102.
- [20] I. Gallino, M.B. Shah and R. Busch, *J. Alloy. Compd.* 2007, 434-435: 141-144.
- [21] Y. Liu, B. Bhandari and W.B. Zhou, *J. Agric. Food Chem.* 2006, 54: 5701-5717.
- [22] R. Busch, W. Liu and W.L. Johnson, *J. Appl. Phys.* 1998, 83: 4134-4141.
- [23] K.M. Flores, D. Suh, R.H. Dauskardt, P. Asoka-Kumar, P.A. Sterne and R.H. Howell, *J. Mater. Res.* 2002, 17: 1153-1161.
- [24] J.T. Bendler, J.J. Fontanella and M.F. Shlesinger, *J. Chem. Phys.* 2003, 118: 6713-6716.
- [25] T. Zhang, Structural relaxation behavior of LaAlNiCu bulk metallic glass, thesis University of Science and Technology of Beijing, 2007.