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A new method for evaluating structural stability of bulk metallic glasses

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ABSTRACT

This paper proposed a new method for evaluating the structural stability of bulk metallic glasses (BMGs) based on dilatometric measurements. During heating in the dilatometric experiments, the BMGs expanded continuously with increasing temperature. When the temperature reached the glass transition temperature (T_g), viscous shrinkage occurred due to the viscosity of material becoming lower. Since the inhomogeneous nature of the metallic glasses at atomic level, the processes of rigid expansion and the viscous shrinkage co-exist in a certain temperature region. The expansion stopped completely at a temperature (named T_p here) beyond T_g. The values of the temperature region, $\Delta T_{gp} = T_p - T_g$, and the corresponding time interval (Δt_{gp}) and the activation energy (E_p) corresponding to the expansion processes, are the reflection of the structural stability of BMGs. Investigating the co-existing processes kinetically and thermodynamically, we can make an insight into the structural stability of metallic glasses. Based on this idea, the thermal expansion behaviors of Mg-, Pd-, Zr-, Ti- and Fe-based BMG were studied, and their structural stability was evaluated by the parameters of ΔT_{gp}, Δt_{gp} and E_p.

1. Introduction

Understanding the structure of bulk metallic glasses (BMGs) is an attractive and crucial issue in material science, because it closely connects with glass forming ability [1–5] and mechanical properties [6–10]. It is believed that the structure of BMGs is disordered in long range and ordered in short range, suggesting the inhomogeneous nature of BMGs. Several structural models, such as cluster dense packing model [11] and quasi-equivalent cluster model [12], were proposed. Based on the typical cluster structure of BMGs, the BMGs were classified into three types experimentally: the metal-metal type, the Pd-metalloid type and the metal-metalloid type [13]. The structural inhomogeneous nature and the structural stability of BMGs greatly affect their mechanical properties. It was reported that [6] super plasticity was achieved at room temperature in ZrCuNiAl system by uniaxial compression, and microstructure analysis indicated that this BMG was composed of hard regions surrounded by soft regions. Therefore, the study on the structural inhomogeneous nature and the structural stability of BMGs is necessary.

In general, some parameters, such as the value of the supercooled liquid region, ΔT_x (=$T_x - T_g$, T_x and T_g are crystallization temperature and glass transition temperature, respectively) [14], the reduced glass transition temperature, T_{rg} (=T_g/T_m, T_m is melting temperature) [15] and the parameter γ (=$T_x/(T_g + T_l)$, T_l is liquidus temperature) [16], are used to evaluate the thermal stability or structural stability of BMGs. In this paper, based on dilatometric measurements, we propose a new method for evaluating the structural stability of BMGs. It is known that when the temperature reaches T_g, the structure of BMGs becomes unstable and the viscosity decreases intensely. It is reasonably believe that the viscosity change is strongly depended on the “structure stability” of BMGs. Based on the dilatometric measurements, we studied the “structure stability” of BMGs. During the dilatometric experiments, the BMGs expanded continuously with increasing temperature. When the temperature reached T_g, the viscous shrinkage occurred due to the viscosity of material becoming lower. However, since the inhomogeneous nature of the metallic glasses at atomic level, the rigid expansion process and the viscous shrinkage process co-exist in a certain temperature region. The expansion stopped completely at a certain temperature (named T_p here) beyond T_g. The value of the temperature region, $\Delta T_{gp} = T_p - T_g$, the corresponding time interval (Δt_{gp}) and the activation energy (E_p) for the co-existing processes reflect the characteristic of structural stability of BMGs. Based on further study on ΔT_{gp} kinetically and thermodynamically, a new method for evaluating the structural stability of BMGs was proposed.

2. Experimental procedure

$Mg_{58.5}Cu_{30}Dy_{11.5}$, $Pd_{40}Ni_{10}Cu_{30}P_{20}$, $Zr_{55}Al_{10}Ni_5Cu_{30}$, $Ti_{41.5}Cu_{42.5}Zr_{2.5}Ni_{7.5}Hf_5Si_1$ and $Fe_{75}Mo_5P_{10}C_{7.5}B_{8.5}$ (in at%) alloys were studied in the present study. The $Mg_{58.5}Cu_{30}Dy_{11.5}$ alloy ingot was prepared by high-frequency induction melting

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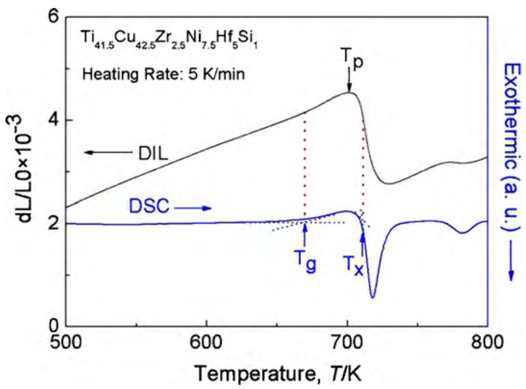

Fig. 1. DSC curve and DIL trace of $Ti_{41.5}Cu_{42.5}Zr_{2.5}Ni_{7.5}Hf_5Si_1$ BMGs at a heating rate of 5 K/min.

under an argon atmosphere. The $Pd_{40}Ni_{10}Cu_{30}P_{20}$ and $Fe_{75}Mo_5P_{10}C_{7.5}B_{8.5}$ master alloys were prepared by arc melting the pure elements, pre-alloyed Pd-P and Fe-P, respectively, under an argon atmosphere. The Zr- and Ti-based alloys were prepared by arc melting the pure metals under a purified argon atmosphere. From the master alloys, rod samples with a diameter of 2 mm were prepared by a copper mold injection casting technique under an argon atmosphere. Glassy structure of the cast rods was confirmed by a Bruker AXS D8 X-ray diffractometer (XRD) with Cu Ka radiation. Thermal characteristics including T_g and T_x were measured with a NETZSCH DSC 404C differential scanning calorimeter (DSC) at heating rates of 5 K/min, 10 K/min, 20 K/min and 40 K/min under a flowing purified argon atmosphere. The dilatometric measurements were conducted with a NETZSCH DIL 402C dilatometer (DIL) with a resolution of ΔL = 1.25 nm at heating rates of 2.5 K/min, 5 K/min, 10 K/min, 15 K/min and 20 K/min under a compressive load of 0.3 N. The test specimens used for liner thermal dilatometric measurements were cylinder rods of 2 mm in diameter and 25 mm in length.

3. Results and discussion

Fig. 1 presents the DSC curve and DIL trace for a typical BMG ($Ti_{41.5}Cu_{42.5}Zr_{2.5}Hf_5Ni_{7.5}Si_1$ alloy) at the heating rate of 5 K/min. It can be seen that this glassy alloy exhibits distinct glass transition behavior. From the corresponding DIL trace, it can be seen that the BMG sample expands continuously with increasing temperature. When the temperature reaches T_g, the sample exhibits subsequent expansion, which stops completely at a certain temperature (named T_p here). It is clear that the T_p is higher than T_g and lower than T_x (as shown in Fig. 1). The values of T_g and T_x obtained by the DSC and DIL experiments, respectively, are almost the same. Therefore, for convenience, the values of T_g that obtained from DSC curves are used henceforth. It is known that when the temperature reaches T_g, the structure of BMGs becomes unstable and the viscosity decreases intensely. It is reasonably believe that the viscosity change is strongly depended on the "structure stability" of BMGs. Since the inhomogeneous nature of BMGs at atomic level, the rigid expansion process and the viscous shrinkage process co-exist in the temperature region from T_g to T_p. It is considered that this temperature region reflects the characteristic of structural breakage or structural stability of BMGs. The DSC curves and DIL traces of $Mg_{58.5}Cu_{30}Dy_{11.5}$, $Pd_{40}Ni_{10}Cu_{30}P_{20}$, $Zr_{55}Al_{10}Ni_5Cu_{30}$ and $Fe_{75}Mo_5P_{10}C_{7.5}B_{8.5}$ glassy alloys were also measured, and their T_g, T_x, ΔT_x (obtained from DSC) and the T_p (obtained from DIL) at the heating rate of 5 K/min are summarized in Table 1.

The value of the temperature region, $\Delta T_{gp} = T_p - T_g$, can evaluate the "structural stability" of BMGs. The larger the value of ΔT_{gp} is, the more stable the structure of the BMG is. The values of ΔT_{gp} of the studied BMGs at the heating rate of 5 K/min are also listed in Table 1, which indicate that the structural stability increases in the order of Mg-, Pd-, Zr-, Ti- and Fe-based BMGs. The time interval (Δt_{gp}) corresponding to ΔT_{gp} also reflects the structural stability from the viewpoint of dynamics. The value of Δt_{gp} can be obtained by dividing ΔT_{gp} by heating rate. Fig. 2 shows the Δt_{gp} of studied

Table 1
Thermal parameters of various BMGs determined by DSC and DIL at a heating rate of 5 K/min.

BMGs	T_g (K)	T_x (K)	ΔT_x (K)	T_p (K)	ΔT_{gp} (K)
$Mg_{58.5}Cu_{30}Dy_{11.5}$	416	475	59	429	13
$Pd_{40}Ni_{10}Cu_{30}P_{20}$	562	644	82	576	14
$Zr_{55}Al_{10}Ni_5Cu_{30}$	671	744	73	691	20
$Ti_{41.5}Cu_{42.5}Zr_{2.5}Hf_5Ni_{7.5}Si_1$	677	716	39	701	24
$Fe_{75}Mo_5P_{10}C_{7.5}B_{8.5}$	695	726	31	721	26

BMGs at the heating rate of 20 K/min. It can be seen from Fig. 2 that the values of Δt_{gp} also reflect increasing structural stability in the order of Mg-, Pd-, Zr-, Ti- and Fe-based BMGs.

The thermal expansion behavior is a kind of thermal activation process. It can be described by Arrhenius equation:

$$A = A_0 \exp\left(-\frac{E}{RT}\right) \quad (1)$$

where A is a rate constant, A_0 is the frequency factor, E is the apparent activation energy, R is gas constant and T is the temperature. Based on Eq. (1), Chen derived the following equation [17]:

$$\ln\left(\frac{T^2}{B}\right) = -\frac{E}{RT} + C \quad (2)$$

where T represent the specific temperature, such as T_p, B is the heating rate and C is a constant. In this study, the activation energy E_p reflecting the structural breakage from the thermodynamic point can be obtained by Eq. (2).

Fig. 3 shows the position of the peak of T_p in DIL traces for the $Ti_{41.5}Cu_{42.5}Zr_{2.5}Ni_{7.5}Hf_5Si_1$ alloy at the different heating rates. It is seen that the T_p of the Ti-based BMG shifts to higher temperature with increasing heating rate. The change in T_p with the heating rate for the Mg-, Pd-, Zr- and Fe-based glassy alloys exhibited the same trend with that of the Ti-based glassy alloy. By plotting $\ln(B/T_p{}^2)$ versus $1/T_p$, a straight line with the slope of E_p is obtained, as shown in Fig. 4. The E_p of $Mg_{58.5}Cu_{30}Dy_{11.5}$, $Pd_{40}Ni_{10}Cu_{30}P_{20}$, $Zr_{55}Al_{10}Ni_5Cu_{30}$, $Ti_{41.5}Cu_{42.5}Zr_{2.5}Ni_{7.5}Hf_5Si_1$ and $Fe_{75}Mo_5P_{10}C_{7.5}B_{8.5}$ BMGs are 96.5 ± 7.4 kJ/mol, 228.0 ± 10.9 kJ/mol, 297.2 ± 14.0 kJ/mol, 317.5 ± 19.3 kJ/mol and 435.6 ± 28.3 kJ/mol, respectively, as listed in Table 2. The larger the value of E_p is, the more stable the structure of the BMG is. It is obvious that the structural stability of these BMGs increases in the order of Mg-, Pd-, Zr-, Ti- and Fe-based BMGs. By comparing the values of ΔT_{gp}, Δt_{gp} and E_p of these alloys, the order of E_p coincides approximately with those of ΔT_{gp} and Δt_{gp}.

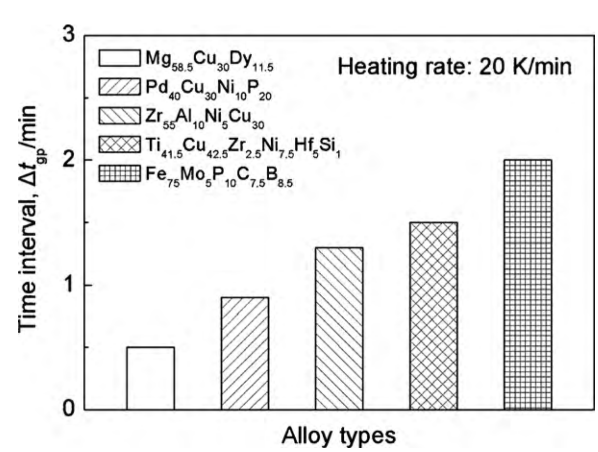

Fig. 2. The Δt_{gp} of various BMGs at a heating rate of 20 K/min.

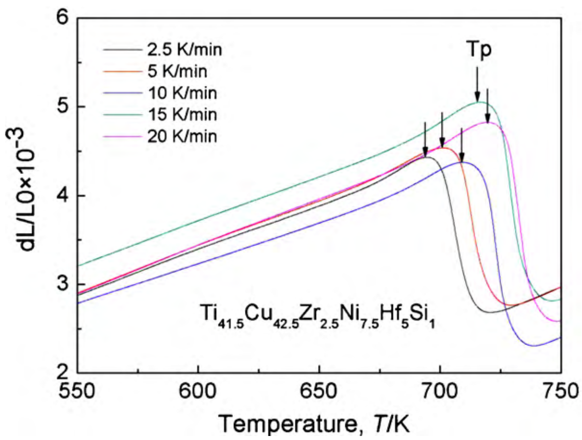

Fig. 3. The DIL curves of $Ti_{41.5}Cu_{42.5}Zr_{2.5}Ni_{7.5}Hf_5Si_1$ BMG at different heating rates.

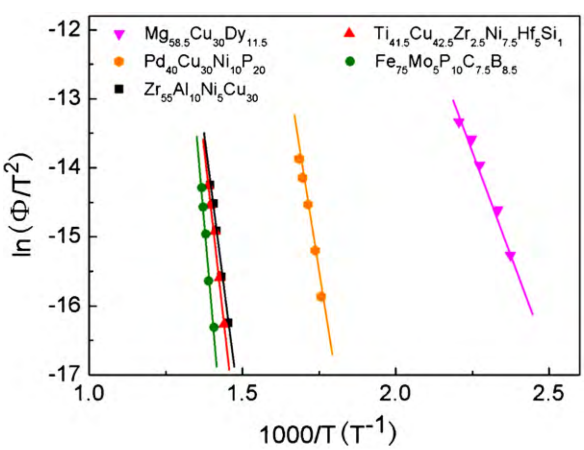

Fig. 4. The plot of $\ln(\varphi/T_p)$ vs. $1/T_p$ for E_p of various BMGs.

Table 2
The E_g, E_x and E_p of various BMGs.

BMGs	E_p (kJ/mol)	E_g (kJ/mol)	E_x (kJ/mol)
$Mg_{58.5}Cu_{30}Dy_{11.5}$	96.5 ± 7.4	115.5 ± 8.2	129.0 ± 9.2
$Pd_{40}Ni_{10}Cu_{30}P_{20}$	228.0 ± 10.9	254.8 ± 9.3	233.1 ± 12.1
$Zr_{55}Al_{10}Ni_5Cu_{30}$	297.2 ± 14	333.3 ± 12.0	388.0 ± 10.4
$Ti_{41.5}Cu_{42.5}Zr_{2.5}Hf_5Ni_{7.5}Si_1$	317.5 ± 19.3	292.8 ± 15.9	355.1 ± 9.8
$Fe_{75}Mo_5P_{10}C_{7.5}B_{8.5}$	435.6 ± 28.3	342.5 ± 13.7	533.0 ± 19.3

We also calculate the activation energy of glass transition (E_g) and crystallization (E_x) by Kissinger method (Eq. (2)) based on the DSC curves. The values of E_g and E_x are also summarized in Table 2. It can be seen that the values of E_p are slightly lower than those of E_g and E_x. It should be indicated that the E_g, E_x and E_p are the parameters describing the structural stability of metallic glasses, but they imply the different physical meaning, which are deeply being studied in our research group. The study on structural stability would be beneficial to further understanding the viscous flow and deformation mechanism.

4. Summary

In this paper, we proposed a new method to evaluate the structural stability of BMGs based on dilatometric measurements. By using this method, the structural stability of $Mg_{58.5}Cu_{30}Dy_{11.5}$, $Pd_{40}Ni_{10}Cu_{30}P_{20}$, $Zr_{55}Al_{10}Ni_5Cu_{30}$, $Ti_{41.5}Cu_{42.5}Zr_{2.5}Ni_{7.5}Hf_5Si_1$ and $Fe_{75}Mo_5P_{10}C_{7.5}B_{8.5}$ BMGs were evaluated. It is revealed that the structural stability increases in the order of Mg-, Pd-, Zr-, Ti- and Fe-based BMGs.

Acknowledgements

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