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# Origin of abnormal glass transition behavior in metallic glasses

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ABSTRACT

In this paper, the phenomenon of two glass-transition-like appearance in the supercooled liquid region of metallic glasses was investigated. It is confirmed that this abnormal behavior is attributed to the transition process of an amorphous state from higher energy to lower energy. The amorphous state with higher energy comes from the uneven distribution of compositions in glasses, which is mainly caused by the component with significant differences in atomic size and nonnegative values of enthalpy of mixing. The results were verified by high resolution transmission electron microscopy and energy-dispersive spectrometry.



## 1. Introduction

Metallic glasses (MGs) have attracted great attention due to their unique properties, such as ultrahigh strength [1], excellent soft magnetic properties [2,3], and good anticorrosion property [4] suitable in a wide range of applications [5–7]. As an important thermal property, glass transition has been a subject of much discussion since it plays an important role in the definition of MGs [8]. Moreover, the study of glass transition is also essential to explore the nature of glassy forming ability (GFA), thermodynamics, and intrinsic mechanism of glassy formation [9–11,12]. In general, the glass transition behavior during heating is characterized by a single endothermic reaction, i.e., the specific heat increases abruptly to a maximum value, and then remains constantly or slightly decreases down to crystallization onset temperature. Interestingly, two glass-transition-like appearance in supercooled liquid region (SLR) has been observed experimentally in various MGs [13–24]. Recently, many investigations revealed that the abnormal glass transition behavior is directly related to the high GFA and good plasticity of MGs [13,18,21]. Tanner et al. postulated that the abnormal behavior is originated from the phase separation [14]. However, no experimental evidence was found supporting this mechanism [15]. Jiang et al. proposed that this abnormal behavior is strongly correlated to the local atomic structure reordering [19]. Park et al. further suggested that it should be originated from the growth reaction of quenched-in nuclei in the SLR [21,22]. These debates indicate that a physical understanding of the abnormal glass transition behavior in SLR is still unsettled.

In this letter, $(Fe_{0.71}Dy_{0.05}B_{0.24})_{96}Nb_4$ alloy was selected as a model glass to investigate the abnormal behavior of glass transition under uniaxial compression. Based on the concept that the deformation of MGs is actually the same response to the external energy (temperature or force) [25], the origin of abnormal glass transition behavior of MGs was studied systematically.

## 2. Experimental procedures

$(Fe_{0.71}Dy_{0.05}B_{0.24})_{96}Nb_4$ MG was prepared by arc melting the mixtures of Fe (99.99 mass %), Dy (99.99 mass %), Nb (99.99 mass %) metals and B (99.5 mass %) crystals in an argon atmosphere. Glassy ribbons and cylindrical rods with nominal compositions were prepared by a rapid quenching technology on a single copper wheel with a speed of 40 m/s and copper mold casting method, respectively. The structures of samples were identified by X-ray diffraction (XRD) with Cu Kα radiation, high resolution transmission electron microscopy (HRTEM) and energy-dispersive spectrometry

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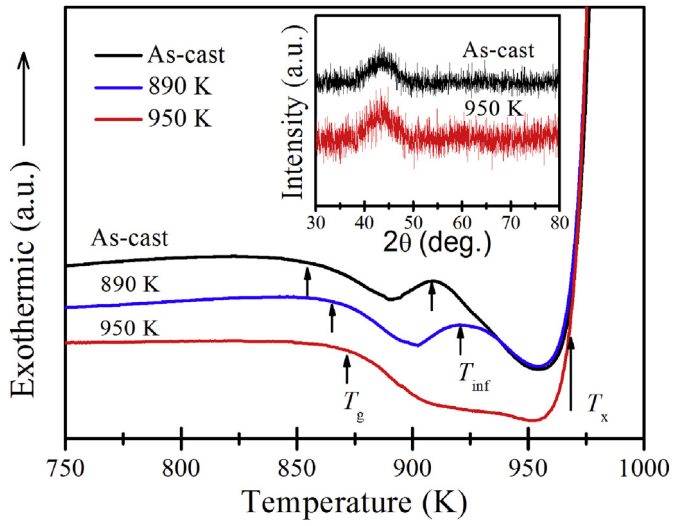


**Fig. 1.** DSC curves for as-quenched and annealed samples; the inset shows the XRD traces of the samples in as-quenched state and annealed at 950 K.

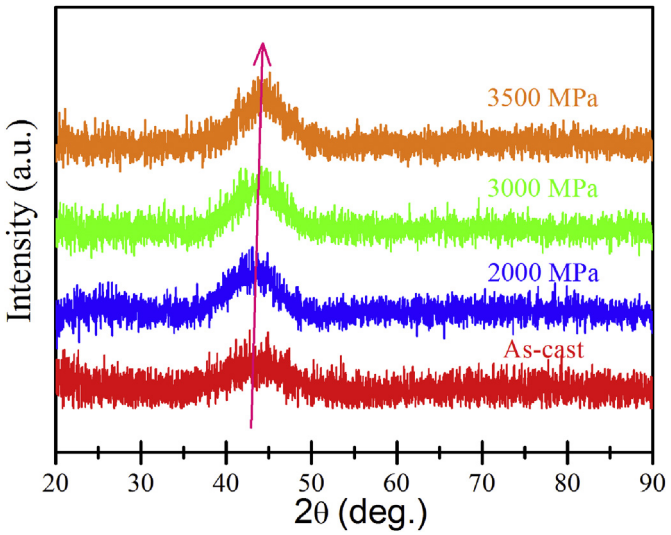


**Fig. 2.** XRD patterns of $(Fe_{0.71}Dy_{0.05}B_{0.24})_{96}Nb_4$ BMG in as-cast state and ones after compression.

(EDS). The thermal stability of the glassy samples was examined using a NETZSCH 404 C differential scanning calorimeter (DSC) at a heating rate of 0.67 K/s under a flow of high purity argon. The glassy rods ($\Phi = 2$ mm) were cut to about 4 mm in length and their ends were carefully polished so as to be flat and parallel. The cylindrical rods were loaded for 5 min under each stress level of 2000, 3000, and 3500 MPa at room temperature by compression testing with an Instron testing machine with strain rate $5 \times 10^{-4}$ $s^{-1}$. The rods after uniaxial compression were re-examined by XRD and DSC. The density of samples in as-cast state and annealed state at 950 K for 0.5 h in vacuum was measured using Archimedes's method with the uncertainty less than 0.5%.

## 3. Results and discussion

Fig. 1 shows the XRD and DSC traces of specimens after annealing at different temperatures in SLR below the crystallization temperature ($T_x$). The XRD patterns of the as-quenched and annealed (at 950 K) samples display broad diffraction maxima, which is the characteristic of an amorphous structure. The sample annealed at 890 K shows a second inflection like the as-quenched samples. However, the second inflection of the annealed samples (at 950 K) almost disappears. Meanwhile, the glass transition temperature ($T_g$) increases from 860 K for the as-quenched sample to 875 K for that annealed at 950 K. The constant value of $T_x$ after heating at different temperatures implies that there is no obvious progress in crystallization, which is in agreement with the XRD results. On the other hand, the slight rise in $T_g$ suggests that the state of the amorphous phase changes during the heating through the second inflection temperature ($T_{inf}$).

Fig. 2 shows the XRD patterns of $(Fe_{0.71}Dy_{0.05}B_{0.24})_{96}Nb_4$ BMG in as-cast and compression states. No sharp Bragg peaks are detected for the compression samples, indicating that the glassy nature of these samples is quite stable at room temperature. However, with an increase of the compression pressure, the broad diffusive amorphous halo peak obviously shifts to a higher wave vector. According to the Bragg equation: $2r_1\sin\theta = \lambda$, the position of an X-ray halo maximum is directly related to the average radius of the first coordination shell $r_1$, the X-ray wave length $\lambda$, and the scatter angle corresponding to the halo maximum $2\theta$. The shifts may indicate the changes of configuration coordination and topological rearrangements of atoms by compressing [26].

Fig. 3 gives the DSC curves of $(Fe_{0.71}Dy_{0.05}B_{0.24})_{96}Nb_4$ MG in as-quenched ribbon, as well as as-cast and compressed rods. We can see that the exothermic event in the SLR is more noticeable for the ribbon than that for the rods. For the compressed rods, the amplitude of the first endothermic event decreases with the increasing pressure. The endothermic event $\Delta H$ were estimated to be −156.1 J/mol for ribbons, −89.4 J/mol for the uncompressed rod, −74.9 J/mol for the rod with 2000 MPa load, −71.6 J/mol for the rod with 3000 MPa load, and −64.0 J/mol for the rod with 3500 MPa load.

In glassy systems, the addition of elements with different atomic size and nonnegative values of enthalpy of mixing with others is likely to lead to a energy rise of the amorphous phase [27]. From the kinetic point of view [28], the energy barrier $\Delta G^*$ of the transition from one glassy state to another state at a given pressure $P$ can be expressed by

$$\Delta G*(T,P) = \frac{16\pi\gamma^3 (V_m^{a_2})}{3\left[P(V_m^{a_1} - V_m^{a_2}) - (\Delta G^{a_1\to a_2} + E_e)\right]^2} \quad (1)$$

where $\gamma$ is the interfacial energy, $V_m^{a_1}$ and $V_m^{a_2}$ the molar volumes of the $a_1$ and $a_2$ glassy states, $\Delta G^{a_1\to a_2}(T,P)$ the molar free energy change for the transformation from $a_1$ glassy state to $a_2$ glassy state, and $E_e$ the elastic energy induced by the volume change during the transformation [29], which can be expressed as

$$E_e = \frac{E\varepsilon^2 V_m^{a_2}}{2} \quad (2)$$

where $E$ is the Young's modulus and $\varepsilon = (V_m^{a_1} - V_m^{a_2})/3V_m^{a_2}$.

For $(Fe_{0.71}Dy_{0.05}B_{0.24})_{96}Nb_4$ MG, $E \approx 200$ GPa, $V_m^{a_2} = 6.94 \times 10^{-6}$ $m^3$/mol, and $V_m^{a_1} = 6.85 \times 10^{-6}$ $m^3$/mol. Therefore, the elastic strain energy is obtained as $E_e = 3014$ J/mol. Meanwhile, the interfacial energy $\gamma$ of $(Fe_{0.71}Dy_{0.05}B_{0.24})_{96}Nb_4$ MG is about 1.5 J/$m^2$ [30,31]. Thus, the energy barrier $\Delta G^*$ can be calculated from Eq. (1) by setting the load to zero,

$$\Delta G^* = \frac{2.652 \times 10^{11}}{(\Delta G^{a_1\to a_2} + 3014)^2} \text{ kJ/mol} \quad (3)$$

From Kissinger equation $\ln(\Phi/T_{inf}^2) = -E_a/RT_{inf} + C$ [32], here $\Phi$ is the heating rate, $R$ the gas constant, C the constant, and $E_a$ the overall activation energy for $a_1$ to $a_2$ glassy transformation at $P = 0$,