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Reversible structural relaxation and crystallization of $Zr_{62}Al_8Ni_{13}Cu_{17}$ bulk metallic glass

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Abstract

The effect of pre-treatment above glass transition temperature (T_g) on the reversible structural relaxation in a $Zr_{62}Al_8Ni_{13}Cu_{17}$ bulk metallic glass at sub-T_g annealing has been investigated. It is found that the enthalpy relaxation can be well described by a stretched exponential function. A free-volume model can only qualitatively simulate the process of enthalpy recovery. Sub-T_g heat treatments after enthalpy recovery have almost no effect on the following crystallization, which can be accelerated when critical clusters are formed for a longer time annealing.

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1. Introduction

Bulk metallic glasses (BMGs), also called bulk amorphous alloys, are thermodynamically metastable and would transform into stable crystalline phases eventually upon heating. Prior to crystallization, a process for atoms gradually to approach their equilibrium sites in the amorphous phase is called structural relaxation. Equilibrium amorphous phase [1] is an ideal state of non-crystalline solids obtained at the Kauzmann temperature with the lowest energy and a unique configuration. Due to atomic rearrangements, mechanical, physical, and chemical properties of BMGs can be changed, e.g., sub-T_g annealing can cause some BMGs to be brittle [2], while some soft magnetic properties can be more preferable [3]. Usually, the more rapid cooling rate, the higher residual stress remains in an as-quenched amorphous alloy, and the further the sample is away from the equilibrium amorphous state. This should be removed before one can study the reversible structural relaxation in an amorphous phase.

Multi-component Zr-based BMGs [4] with high glass forming ability and wide supercooled liquid region can be prepared by conventional mold casting method at lower cooling rates, providing a suitable way to understand the nature of structural relaxation. It was reported that the structural relaxation of a Zr–Ti–Ni–Cu–Be (Vit 4) [5] below the calorimetric glass transition temperature could cause enthalpy to overshoot near the T_g temperature. Such enthalpy recovery was considered to compensate for the excess free volume annihilated during structural relaxation. In addition, Tool–Narayanaswamy–Moynihan (TNM) model [6,7] is also widely used to describe the structural relaxation based on the change in fictive temperature (T_f). T_f often represents the degree of departure from the equilibrium of a glass, because the free volume and excess enthalpy of the system are directly proportional to the

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fictive temperature. The free volume can be estimated by model calculations or by means of density measurements [8,9]. However, the relationship between the structural relaxation and the following crystallization is rarely studied. In this paper, we investigate the effect of different holding time in the supercooled liquid region of a Zr–Al–Ni–Cu BMG on the sub-T_g structural relaxation, and the difference in the following crystallization behaviors after enthalpy recovery. Both free volume model and cluster model are employed to describe the reversible structural relaxation.

2. Experimental

Pre-alloyed ingots with a nominal composition of $Zr_{62}Al_8Ni_{13}Cu_{17}$ (at.%) were prepared by arc melting under a Ti-gettered purified Ar atmosphere. High-purity elements of Zr, Al, Ni, and Cu with purities higher than 99.9% were used as raw materials. Each alloy ingot of about 3 g was remelted several times for improving the homogeneity, and then sucked into a water-cooled copper mold with cavity of 3 mm in diameter. The amorphous nature of resulting rods was verified by using an X-ray diffractometer (Philip X'Pert) with Cu-Kα radiation. A differential scanning calorimetry (Perkin–Elmer Pyris DSC) was used to investigate the isochronal and isothermal crystallization kinetics in Ar flow.

3. Results

Fig. 1 shows the DSC scan of an as-quenched $Zr_{62}Al_8Ni_{13}Cu_{17}$ sample at a heating rate of 40 K/min. Here 40 K/min was chosen to heat and cool the samples in DSC during the whole experiments if without special mention. It is found that the glass transition temperature T_g of this alloy is about 665 K and the onset temperature of crystallization T_x about 745 K, and thus the supercooled liquid region, $\Delta T_x = T_g - T_x$, is about 80 K for this alloy. The inset is an isothermal DSC curve when this BMG annealed at a T_h temperature of 703 K in the supercooled liquid region, which shows the incubation time t_0 is about 7.65 min before crystallization. To study reversible structural relaxation, heat treatments were carried out in DSC. Samples were first scanned (100 k/min) to $T_h = 703$ K above T_g and held for 3 and 5 min shorter than the incubation time, and then cooled to 298 K. This treatment could reduce the effect of irreversible structural relaxation [10], i.e., the internal stress and excess free volume formed during rapid quenching and to reach a relatively-defined starting state. The sample was reheated (100 k/min) to a pre-selected temperature ($T_a = 633$ K), at which it was annealed for different periods of t_a. When the sample was cooled to 298 K again, the second scan was carried out immediately to T_h. This second DSC scan shows the enthalpy recovery caused by annealing at T_a for different times. Finally, the third scan was performed to heat sample from 298 to 823 K. Using the data below 703 K as the baseline, enthalpy recovery could be estimated and the data above 703 K could be used to investigate the change in crystallization.

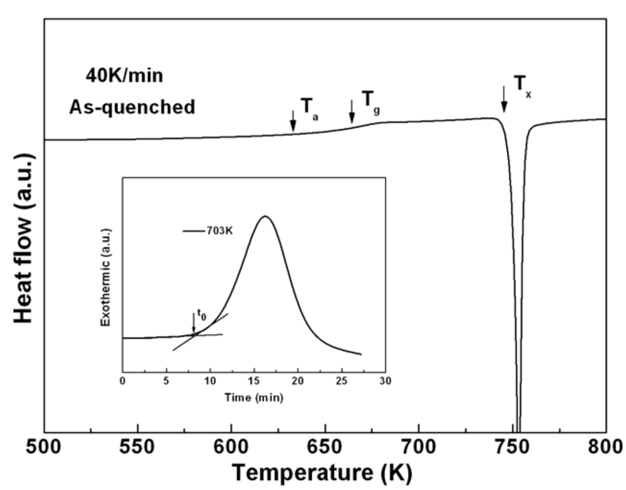

Fig. 1. DSC trace of as-quenched $Zr_{62}Al_8Ni_{13}Cu_{17}$ BMG at a heating rate of 40 K/min and inset is an isothermal DSC curve by holding the temperature at 703 K in the supercooled liquid region.

Fig. 2 shows enthalpy recovery upon different annealing times at $T_a = 633$ K, in which Fig. 2(a) is for the samples pre-treated at 703 K for 3 min and Fig. 2(b) is at 703 K for 5 min. Usually the time dependence of $\Delta H_{T_a}(t)$ at a given temperature can be well fitted by stretched exponential relaxation function [11]

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

where $\Delta H_{T_a}^{eq}$ is the equilibrium value of enthalpy at the annealing temperature T_a, t is the annealing time and τ is the characteristic structural relaxation time, β is the Kohlrausch exponent whose value is between zero and unity, reflecting a broad distribution of Debye relaxation times. By fitting the data of enthalpy vs. annealing time with Eq. (1), the values of fitting parameters were obtained that $\Delta H_{T_a}^{eq} = 358$ kJ/mol, $\tau = 1514$ s, $\beta = 0.61$ for 703 K–3 min pre-treated samples and 261 kJ/mol, 586 s, 0.84 for 703 K–5 min pre-treated samples, also listed in Fig. 3.

According to the free-volume model [12–14], the melt of an alloy contains a certain amount of free volume x_{eq} at its equilibrium state. After quenching a melt, atomic configurations could be frozen to some extent and no longer reach their equilibrium states with decreasing temperature. Since the free volume in this 'frozen' structure has no possibility to be annihilated, an excess free volume remains in the glass. Upon sub-T_g annealing, the excess free volume can be annihilated out of the glass. When the sample is reheated to a high temperature above T_g, the lost free volume would be recreated. This is the reason that an overshoot of enthalpy recovery near the T_g temperature appears, as observed in Fig. 2. The free volume vs.