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Journal of Non-Crystalline Solids 354 (2008) 1780–1785

JOURNAL OF NON-CRYSTALLINE SOLIDS

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Stabilization of metallic glass studied by internal friction measurement

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Received 4 November 2006
Available online 1 October 2007

Abstract

The internal friction Q^{-1} and the oscillation frequency f of Zr–Ti–Cu–Ni–Be metallic glass specimens were measured using an inverted torsion pendulum with the free decay method. A single-roller melt-spinning apparatus was used for preparing the specimens. Isothermal annealing near the glass transition temperature T_g was performed to investigate the stabilization of the specimens. Q^{-1} decreased with annealing time t due to the stabilization. Q^{-1}-vs-t was measured at various annealing temperatures T_a, and the values of relaxation time τ for the stabilization process were determined. The dependence of τ on T_a showed that the hydrodynamic behavior represented by the Vogel–Tammann–Fulcher form and the hopping behavior represented by the Arrhenius form were observed in high- and low-temperature regions, respectively. The crossover of the two behaviors was seen at a temperature near and somewhat higher than T_g. The result was discussed on the basis of the viscoelastic relaxation in glassy materials.

PACS: 62.40.+i; 61.43.Fs; 61.43.Dq; 64.60.My

Keywords: Amorphous materials; Metallic glasses; Internal friction; Isothermal annealing; Glass transition

1. Introduction

In a glass-forming process, a material in the liquid state is cooled to the supercooled state instead of the crystalline state, and to the glassy state at the glass transition temperature T_g. The supercooled state is a quasi-stable liquid state, and the glassy state is a frozen-in liquid and is not a stable state. The energies of both states are higher than that of the crystal, and they are apt to change to more stable states. Their composing atoms can rather easily move and relaxations due to the motions frequently occur [1]. When such "stabilization" occurs we can obtain useful knowledge on the glass-forming materials by observing the phenomenon [1]. We are interested in mechanical relaxations in glassy materials, especially near T_g. The motivation is to understand the characteristics of glassy state and the glass transition phenomenon.

In the present study a kind of metallic glasses (MG) called the bulk metallic glasses (BMG) is chosen as the test material. BMG alloys have high glass-forming ability (GFA). Namely, such alloys can be glasses even when they are cooled rather slowly. Interest in these materials is increasing because of their scientific and technological importance [2–5]. BMGs provide an adequate prototype for studying various properties of glassy materials. Further, BMGs have wide supercooled range, and are convenient for studying the properties of glass-forming materials in this state. Note that BMG is just a name of the group of glasses with high GFA, and their properties have widely been studied using bulk, ribbon, and wire specimens.

In order to study the mechanical relaxations in materials measurements of internal friction (IF) can conveniently be used, since this quantity is sensitive to the internal state of materials. We already used the measurement method for various BMGs [6–9], and we recognized the convenience of the method. In the present study, IF of a Zr-base

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0022-3093/$ - see front matter
doi:10.1016/j.jnoncrysol.2007.08.054

BMG was measured in a low frequency range. Isothermal annealing experiments were carried out at various temperatures near T_g, the decrease of IF with time was observed, and the relaxation time for the process was determined. The present article is a more precise report following the preliminary one [10].

2. Experimental methods

The specimen material adopted is the alloy $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$, which is one of BMGs with highest GFA. The method of preparing the specimens is as follows. A mother alloy ingot of the alloy composition is produced by melting together appropriate amounts of constituent elements in an arc-melting furnace under an argon atmosphere. The mother alloy is melt-quenched with a single-roller melt-spinning apparatus in an argon atmosphere (4000 Pa) to produce a glassy ribbon sample of about 30 μm in thickness, 1 mm in width, and several m in length. The melt-spinning speed is in the range of 2600–5200 m/s. From the long ribbon a number of specimens about 50 mm in length are obtained for the experiment. The differential scanning calorimetry (DSC) is used to determine the values of the glass transition temperature T_g and the crystallization temperature T_x. The conventional graphical method is adopted for determining T_g. Namely, the specimen temperature is increased with the standard heating rate of 10 K/min, the heat evolution curve is recorded as a function of temperature, the background at low temperatures and the rapid rise near T_g are extrapolated, and T_g is determined as the intercept of the two extrapolations. About the T_x value, when several crystallization peaks appear, the lowest-temperature peak position is adopted as T_x. The determined values are: $T_g = 621.8$ K and $T_x = 712.9$ K.

The measurement of IF is carried out using a torsion pendulum with ribbon samples. In this case the deformation of the sample is of the pure shear mode. The apparatus is a conventional inverted torsion pendulum and the free decay method is adopted. Gauge length of the sample is 10–20 mm. The amplitude of the damping oscillation is optically detected, and three cycles of oscillation with frequency f are used for evaluating the value of internal friction Q^{-1}. The maximum amplitude of the shear strain in the specimen is around 10^{-5}. In the present experiment the change with time of IF during an isothermal annealing is measured for studying the stabilization phenomenon. For that purpose the ribbon specimen seems to be adaptable since thermal and mechanical responses of the specimen are quite rapid.

3. Results and analysis

In order to overlook the characteristics of IF in the present material, temperature dependent behavior is firstly shown. The measurement was performed from room temperature, through T_g, and up to or somewhat above T_x. A heating rate of 1 K/min was adopted, and the data sampling was made in every 3 K. Fig. 1 shows examples of the temperature dependences of internal friction Q^{-1}, and squared frequency f^2 which is proportional to the shear modulus of the material. The features of results are as follows.

(a) Annealed at 620 K for 20 h: The data show the regular feature of well-stabilized specimen annealed for a long time at a temperature near and below T_g. The overall Q^{-1} values of the specimen have been much reduced compared with the as-prepared specimen [10]. The low-temperature value is almost constant and not much scattered. The value gradually and then rapidly increases with temperature very smoothly. Clear multiple-peak behavior is seen in the crystallization region, which is often observed in BMGs [2,3]. A slight anomaly (slope change) can be seen near T_g as indicated by an arrow in the figure. The value of f^2 also regularly changes with temperature in accordance with the change of Q^{-1}.

(b) Annealed at 670 K for 20 h: The Q^{-1} behavior becomes rather irregular. The high-temperature peak becomes ambiguous, and an unexpected small peak

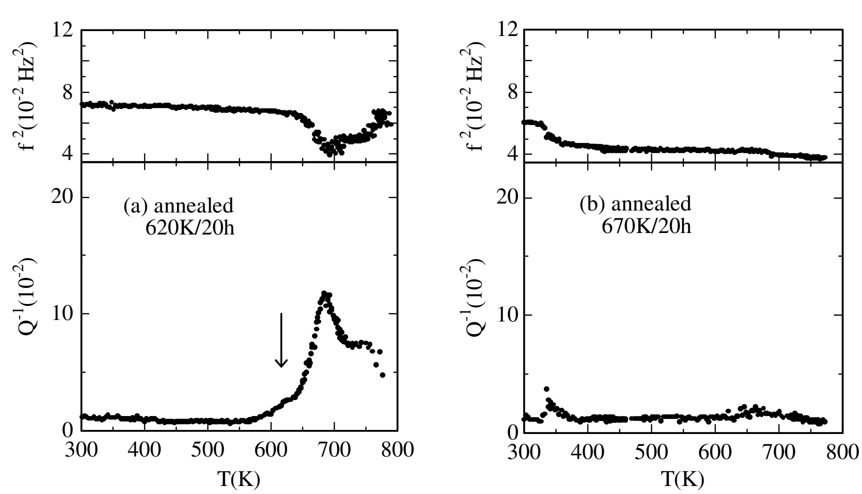

Fig. 1. Temperature dependences of internal friction Q^{-1} and squared frequency f^2 in different states after different annealing.