Stabilization of metallic glass by isochronal and isothermal annealing treatments

2007 J. Phys.: Condens. Matter 19 205147

(http://iopscience.iop.org/0953-8984/19/20/205147)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **19** (2007) 205147 (7pp) doi:10.1088/0953-8984/19/20/205147

Stabilization of metallic glass by isochronal and isothermal annealing treatments

Y Hiki[1], M Tanahashi[2], R Tamura[2], S Takeuchi[2] and H Takahashi[3]

[1] Tokyo Institute of Technology, 39-3-303 Motoyoyogi, Shibuya-ku, Tokyo 151-0062, Japan
[2] Tokyo University of Science, Noda, Chiba 278-8510, Japan
[3] Ibaraki University, Nakanarusawa, Hitachi 316-0033, Japan

Received 2 February 2007
Published 25 April 2007
Online at stacks.iop.org/JPhysCM/19/205147

Abstract

The internal friction (IF) of a Zr–Ti–Cu–Ni–Be metallic glass was measured using an inverted torsion pendulum with the free decay method. A single-roller melt-spinning apparatus was used for preparing the specimens. In the isochronal annealing experiment, specimens in different states were prepared by annealing, and the temperature dependence of the IF was measured from room temperature up to the crystallization temperature T_x. The glass attained a stabilized state under a long-time annealing near and below the glass transition temperature T_g. IF peaks always appeared near and below T_x, while an anomaly was observed clearly near T_g only in the stabilized state. A differential scanning calorimetry experiment was carried out for the same specimens, and the results showed the same characteristics. The isothermal annealing experiment revealed that the stabilization was a relaxation process, and how long a time was required for reaching the stabilized state. The essential features of glass-forming materials could be clearly observed when the specimens were in the stabilized state.

1. Introduction

In a glass-forming material, the energies of the supercooled state and the glassy state are higher than those of the crystal, and both states are apt to change to more stable ones. Such a phenomenon is called 'stabilization', which frequently occurs in various kinds of glasses [1]. The observation of the stabilization process is useful for studying the characteristics of various kinds of glasses. The stabilization phenomenon can be studied experimentally using various kinds of measuring methods.

In the present study a kind of bulk metallic glasses (BMG) is chosen as the test material. BMG alloys have high glass-forming ability (GFA), namely, the alloys can be glasses even when they are cooled rather slowly. There are a variety of BMG alloys composed of various kinds of elements, and interest in these glasses is increasing because of their scientific and

technological importance [2–5]. It is interesting and important to study the stabilization phenomenon in BMGs.

For studying the stabilization phenomenon, the method of internal friction (IF) measurement can usefully be used since the quantity is sensitive to the internal state of materials. The measurement method was used by us for BMGs for investigating their characteristics [6–9]. Meanwhile, the method of differential scanning calorimetry (DSC) can also usefully be adopted for studying the internal state of materials.

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 a BMG with high GFA. The specimens were prepared 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 metres in length. The melt-spinning speed is 2600–5200 m s^{-1}. From the long ribbon, specimens about 50 mm in length are obtained for the IF measurement. The amorphous state of the specimen is checked by the x-ray diffraction measurement.

The IF measurement is performed using an inverted torsion pendulum with the free decay method. A ribbon sample of the metallic glass with gauge length 10–20 mm is used. The amplitude of the damping oscillation is optically detected. Three cycles of oscillation with frequency f are used for evaluating the value of internal friction Q^{-1}. The values of f and Q^{-1} are automatically measured and recorded. Usually the measurement frequency adopted is 0.2–0.3 Hz, and the maximum shear strain is of the order of 10^{-5}.

The DSC measurement is performed by using Rigaku DSC-8230 apparatus. In the measurement the same ribbon specimens as in the IF measurement are used. The measurement is carried out in an argon gas flow. A preliminary experiment for determining the calorimetric glass transition temperature T_g and the crystallization temperature T_x is performed, and the result is analysed by the conventional method [2–5]. Namely, the specimen temperature is increased with the standard heating rate of 10 K min^{-1}, 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 at the T_x value, when several crystallization peaks appear, the lowest temperature peak position is adopted as T_x. The values thus determined are: $T_g = 621.8$ K and $T_x = 712.9$ K.

3. Results and discussion

3.1. IF experiment—isochronal annealing

The specimen was annealed at various temperatures for a definite time, and the temperature dependences of the internal friction and the measurement frequency were determined. 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^{-1} was adopted in the measurement, and the data sampling was every 3 K. A new specimen was used for each measurement. Figure 1 shows the temperature dependences of the internal friction Q^{-1} and the squared frequency f^2 for specimens in different states. The f^2 value is proportional to the shear modulus G of the material. Here the relation between G and f^2 is given: $G = 3lI\pi^2 f^2[(Q^{-1})^2 + 4]/[b^3(h - 0.63b)]$, where l, b, and h are the length, the thickness, and the width of the specimen, and I is the moment of inertia. In the usual case $(Q^{-1})^2 \ll 4$, and the relation $f^2 \propto G$ is a good approximation.

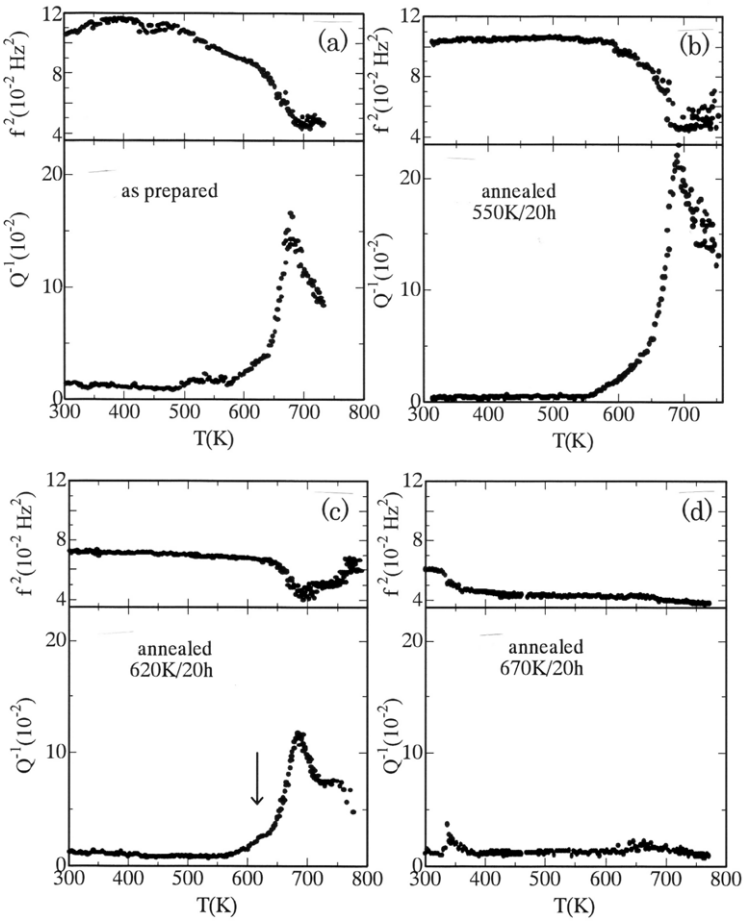

Figure 1. Temperature dependences of the internal friction Q^{-1} and squared frequency f^2 for Zr–Ti–Cu–Ni–Be metallic glass in different states (a)–(d).

The characteristics of the results obtained are compiled in the following.

(a) *As prepared:* At lower temperatures, the Q^{-1} value is not much varied with temperature but is somewhat scattered. As the temperature is increased, Q^{-1} increases gradually and then rapidly. A peak appears at a temperature T_p near and somewhat below T_x. The peak can be associated with the phase transition of the crystallization. We call the peak the 'crystallization peak'. Meanwhile, the value of f^2 shows a dip near the Q^{-1} peak.

(b) *Annealed at 550 K for 20 h:* Upon the annealing the low temperature Q^{-1} value is decreased and the scatter of the value is diminished. The height of the high temperature Q^{-1} peak is enhanced, and the shape of the peak becomes diffusive, namely, the scatter of the value at high temperature side is noticeable.

(c) *Annealed at 620 K for 20 h:* The Q^{-1} value changes 'regularly' with temperature. Namely, the low temperature Q^{-1} value is almost constant and not much scattered. The value gradually and then rapidly increases with temperature. The increase looks very smooth. Clear multiple-peak behaviour can be seen in the crystallization region, which is often

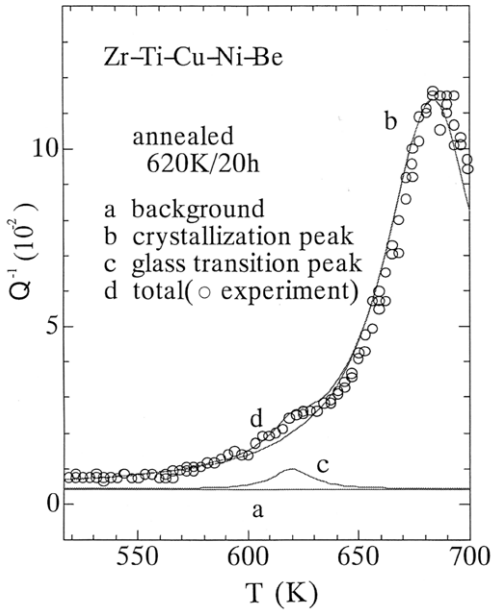

Figure 2. Temperature dependence of Q^{-1} showing glass transition and crystallization peaks. The result of the analysis taking a Lorentzian line shape for the peaks is shown.

observed in some of BMGs [2, 3]. A very slight anomaly (slope change) can be seen near T_g as indicated by the arrow in the figure. The f^2 value also regularly changes with temperature in accordance with the change of Q^{-1} value.

(d) *Annealed at 670 K for 20 h:* The Q^{-1} behaviour becomes non-regular. Namely, the high temperature peak becomes ambiguous, and an unexpected small peak appears at a lower temperature. This result may possibly indicate that a partial crystallization, which is often observed in some of BMGs [2, 3], occurs in the material through long-time annealing at a temperature above T_g and below T_x.

We consider that the regular internal friction behaviour in case (c) corresponds to the well stabilized glassy state of the material. In order to stabilize the present material the long-time annealing at a temperature slightly below T_g seems to be most effective.

Here, the anomaly in the Q^{-1} value near T_g observed in case (c) is considered. The anomaly can clearly be seen in Q^{-1} versus T and not so clearly in f versus T, and only the former data are considered here. The enlarged Q^{-1} versus T data in the higher temperature region are reproduced in figure 2. The data are fitted to a combination of the constant background loss (a), the crystallization peak (b), and the glass transition peak (c). A glass transition peak is anticipated to really exist near the anomaly. The background loss is assumed to be temperature independent. In the present case, most of the loss is due to the instrumental loss in the measurement, and the loss is far larger than the temperature dependent, such as viscoelastic, loss. It is further assumed that the two peaks are represented by the Lorentzian line shape:

$$Q^{-1} = Aw/[4(T - T_0)^2 + w^2], \tag{1}$$

where A is a constant, w is the halfwidth of the peak, T_0 is the peak position, namely, T_g or T_p. The parameter-fitted results are shown in the figure, and the fitting seems to be acceptable. The

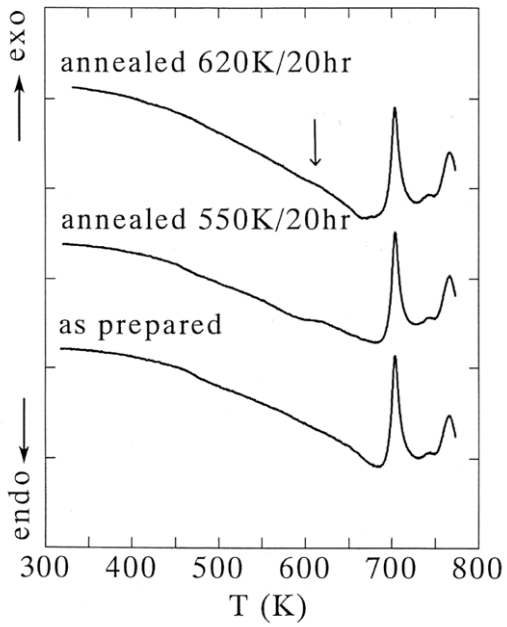

Figure 3. Results of DSC measurement for specimens in different states. Multiple crystallization peaks appear in all specimens, and a slope change representing the glass transition can be seen for the stabilized specimen.

obtained numerical results are $T_g \sim 620$ K, $T_p \sim 685$ K. It is noted here that the determined peak positions are not much changed even when the effect of the temperature-dependent loss is not so negligibly small. The determined value of T_g is very close to that obtained from the DSC measurement (621.8 K). Thus we can really recognize that the glass transition peak really exists in the IF data. Meanwhile, the determined value of T_p is lower than T_x obtained from the DSC measurement (712.9 K), as has been expected. We are mainly concerned with the glass transition, not the crystallization, and the important point is the following. In some glassy materials, the glass transition IF peak is too faint to be observed, but the peak can be detected using the method of analysis as developed here.

3.2. DSC experiment

The DSC experiments were carried out for the same material in different states, and the results were as shown in figure 3. The weight of the ribbon specimen used was 26.5 mg. The heating rate was selected as 1 K min^{-1} in accordance with that used in the IF measurement. The characteristic multiple-peak behaviour representing the crystallization is clearly seen in all specimens in different states. Meanwhile, the characteristic behaviour of the glass transition, namely the slope change of the curve, can be seen near 620 K in the stabilized specimen as indicated by the arrow. Thus, using the DSC method we can again observe clearly the existence of the glass transition in the case of the stabilized state. The apparent glass transition temperature depends on the heating rate since the transition is a relaxation phenomenon, and thus the same heating rate has been used both in the DSC and IF measurements for comparing the results.

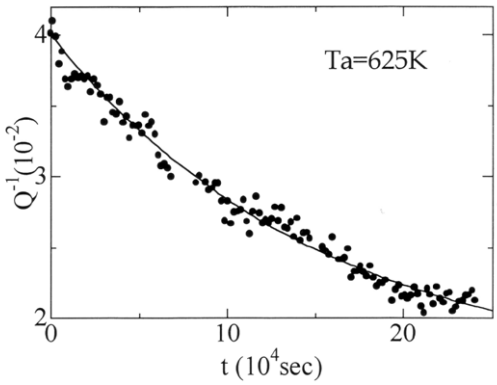

Figure 4. Result of isothermal annealing measurement showing time change of Q^{-1}. The solid curve shows result of analysis based on a relaxation process.

3.3. IF experiment—isothermal annealing

The as-prepared specimen was annealed at a constant temperature T_a, and the changes of IF with time t were observed. Figure 4 shows an example of the results. The decrease in Q^{-1} is considered to represent the stabilization process through the isothermal annealing. Let $Q^{-1} = Q^{-1}(0)$ at $t = 0$, and from this value Q^{-1} monotonically decreases with t. For considering this stabilization process, a relaxation with a single relaxation time is taken into account here. Q^{-1} versus t can be represented as [1]

$$Q^{-1}(t) = Q^{-1}(\infty) + [Q^{-1}(0) - Q^{-1}(\infty)] \exp(-t/\tau), \tag{2}$$

where $Q^{-1}(0)$ and $Q^{-1}(\infty)$ represent the initial and the final (equilibrium) values of Q^{-1}, respectively, and τ is the relaxation time for the stabilization process. By adopting the experimental value of $Q^{-1}(0)$ and adjusting the values of $Q^{-1}(\infty)$ and τ, equation (2) is fitted to the experimental data. The curve in the figure represents the result of the numerical fit. The result of the fit seems to be acceptable.

The above analysis shows that the stabilization is realized through a relaxation process and permits one to determine the time required for obtaining a stabilized state at temperature close to T_g. Related numerical results are given in the following: $Q^{-1}(0) = 4.0 \times 10^{-2}$, $Q^{-1}(\infty) = 1.6 \times 10^{-2}$, $\tau = 15.1 \times 10^4$ s. From figure 4 we obtain the value Q^{-1} (20 h) $= 3.1 \times 10^{-2}$. Thus the Q^{-1} value is decreased by about 40% of the stabilization value, $Q^{-1}(0) - Q^{-1}(\infty)$, through 20 h annealing at $T_a = 625$ K. The annealing time is still not so long as for obtaining full stabilization, but can be enough for a practical purpose of obtaining a rather well stabilized specimen state.

The isothermal annealing experiments were further performed at several annealing temperatures in the range of $T_a = 615$–695 K, namely, near and below or above T_g. The relaxation time τ was determined as a function of temperature. The results obtained were interesting, but details have been given in another article [10].

4. Conclusion

Through an isochronal annealing experiment, using the internal friction measurement, it is shown that the metallic glass currently studied can be well stabilized in the glassy and supercooled regions by a prolonged annealing near and below the glass transition temperature.

Annealing at lower temperature is not effective for obtaining the stabilized state, while annealing at higher temperature results in partial crystallization and the glassy state is partly destroyed. The same features can also be found using the DSC measurement. Through the isothermal internal friction measurement, the stabilization is shown to be a relaxation process, the relaxation time is determined, and the annealing time for obtaining the stabilized state is estimated.

It is considered that for the stabilized state we can experimentally investigate the essential features of glass-forming materials well, since every parasitic unstable anomaly has been eliminated from the materials. Furthermore, the observation of the stabilization process is useful for studying the characteristics of the glass-forming materials.

References

[1] Gutzow I and Schmelzer J 1995 *The Vitreous State* (Berlin: Springer)
[2] Johnson W L 1996 *Mater. Sci. Forum* **225–227** 35
[3] Johnson W L 1999 *MRS Bull.* **24** 42
[4] Inoue A 1995 *Mater. Trans. JIM* **36** 866
[5] Inoue A 2000 *Acta Mater.* **48** 279
[6] Hiki Y, Yagi T, Aida A and Takeuchi S 2003 *J. Alloys Compounds* **355** 42
[7] Hiki Y 2004 *Mater. Sci. Eng.* A **370** 253
[8] Hiki Y, Yagi T, Aida T and Takeuchi S 2004 *Mater. Sci. Eng.* A **370** 302
[9] Hiki Y, Aida T and Takeuchi S 2004 *Proc. 3rd Int. Symp. on Slow Dynamics in Complex Systems* (New York: American Institute of Physics) p 661
[10] Hiki Y, Tanahashi M and Takeuchi S 2006 *Mater. Sci. Eng.* A **442** 287