Internal friction behaviours in $Zr_{57}Al_{10}Ni_{12.4}Cu_{15.6}Nb_5$ bulk metallic glass

Internal friction behaviours in $Zr_{57}Al_{10}Ni_{12.4}Cu_{15.6}Nb_5$ bulk metallic glass

Bo Zhang[1], Fang Qiu Zu[1], Kang Zhen[2], Jia Peng Shui[2] and Ping Wen[3]

[1] Department of Materials Science and Engineering, Hefei University of Technology,
Hefei 230009, People's Republic of China
[2] Laboratory of Internal Friction and Defects in Solids, Institute of Solid State Physics,
Chinese Academy of Sciences, Hefei 230031, People's Republic of China
[3] Institute of Physics, Chinese Academy of Sciences, Beijing 100039, People's Republic of China

Abstract

The internal friction patterns of $Zr_{57}Al_{10}Ni_{12.4}Cu_{15.6}Nb_5$ bulk metallic glass (BMG) were investigated with different frequencies and heating rates. An internal friction peak with extremely large magnitude is observed in the internal friction curves as a function of temperature (Q^{-1}–T curves). The internal friction peak was fitted by an equation $Q^{-1} = AX(T)/\eta$, where A is a constant, $X(T)$ is the fraction of the glass/supercooled liquid and the viscosity η obeys the Vogel–Fulcher–Tammann relation. We confirm that the internal friction peak originates from both of the glass transition and crystallization. The anomalous behaviours of the peak suggest that $Zr_{57}Al_{10}Ni_{12.4}Cu_{15.6}Nb_5$ BMG has a wide supercooled liquid region and the magnitude of the peak can be used to judge the glass forming ability (GFA) of the glass forming alloys. In addition, the internal friction technique proved to be a new powerful tool for studying structural relaxation and phase transition as well as the GFA of BMG.

1. Introduction

There has been long-standing interest in the internal friction behaviours of the melt-spun metallic glasses [1–4]; however, the studies of the structure and structural relaxation in the metallic glasses have been impeded by the inability to prepare bulk specimens of the conventional metallic glasses. Recently, multicomponent glass forming systems have been developed by the conventional casting process at a low cooling rate [5–9]. Although these bulk metallic glasses (BMGs) with a large three-dimensional size and wide supercooled liquid region offer new opportunities for investigating the physical properties of BMGs by various physical methods, no investigations of the internal friction behaviours in BMG have been

reported so far. Meanwhile, the nature of the glass transition and crystallization of metallic glasses remains unclear, because adequate experimental data concerning the glass transition and crystallization are lacking, and different methods lead to different results [10–16]. So exploring a new method for studying the nature of the glass transition and crystallization of BMG is highly necessary. Considering that internal friction is a structure-sensitive physical property and a powerful tool widely used to study structures and phase transitions in solids [17] as well as in conventional metallic glasses [1–4], we should reap benefits from investigating the structural relaxation and phase transition of BMG using the internal friction technique. On the other hand, the origin of the internal friction peak observed in the short region between the glass transition temperature (T_g) and the onset temperature of crystallization (T_x) in some conventional metallic glasses [1–4] is as yet a controversial. Some investigators [2] proposed a cluster model of the metallic glass to consider the mechanism associated with the peak, while other investigators [4] interpreted the peak as a simple result of the increase of internal friction in the supercooled liquid region above T_g and a following decrease due to crystallization. A final explanation of the origin of the peak should be reached if we are to understand the internal friction patterns of BMG and obtain more useful information about the glass and crystallization transitions.

Additionally, the difference between the conventional metallic glasses and BMG in internal friction behaviours is of great importance for understanding the unique structural characteristics of BMG, which has close relation with the high glass forming ability (GFA) of BMG. This difference not only can provide critical information on the intrinsic structure of BMG, but also would suggest a new convenient tool for judging the GFA of the glass forming alloys. In this paper, the internal friction technique is applied to investigate the structural relaxation and structural alteration of the bulk $Zr_{57}Al_{10}Ni_{12.4}Cu_{15.6}Nb_5$ amorphous alloy in continuous heating and cooling processes. An internal friction peak with extremely large magnitude is observed in the Q^{-1}–T curves with a position between T_x and the temperature (T_p) for the exothermic peak of the differential scanning calorimeter (DSC) results. The measured internal friction peak was fitted by an equation $Q^{-1} = AX(T)/\eta$, where A is a constant, $X(T)$ is the fraction of the glass/supercooled liquid and the viscosity η obeys the Vogel–Fulcher–Tammann relation. We confirm that the internal friction peak results from both the glass transition and crystallization. The internal friction behaviours of the bulk $Zr_{57}Al_{10}Ni_{12.4}Cu_{15.6}Nb_5$ amorphous alloy during the glass transition reveal that $Zr_{57}Al_{10}Ni_{12.4}Cu_{15.6}Nb_5$ BMG has wide supercooled liquid region, which has a close relation with the GFA of BMG. Furthermore, the magnitude of the internal friction peak proves to be a convenient property for judging the GFA of the glass forming alloys.

2. Experimental details

The ingots of the glass with nominal compositions $Zr_{57}Al_{10}Ni_{12.4}Cu_{15.6}Nb_5$ were synthesized from a mixture of pure elements in an arc-melting furnace under a Ti-gettered Ar atmosphere. The bulk amorphous alloy with the dimensions of $2 \times 12 \times 50$ mm^3 was prepared by sucking the remelted alloy into the copper mould. The amorphous nature of the cast sample was verified using x-ray diffraction with Cu Kα radiation. The thermal properties of the alloy were also characterized using DSC in a Perkin-Elmer DSC 2C under a N$_2$ atmosphere with a heating rate of 2.5 K min^{-1}. Specimens with the dimensions of $1 \times 2 \times 50$ mm^3 used for the internal friction study were cut from the cast bulk. The internal friction measurement was performed at different frequencies and different heating rates using a conventional low-frequency inverted torsion pendulum controlled by the computer.
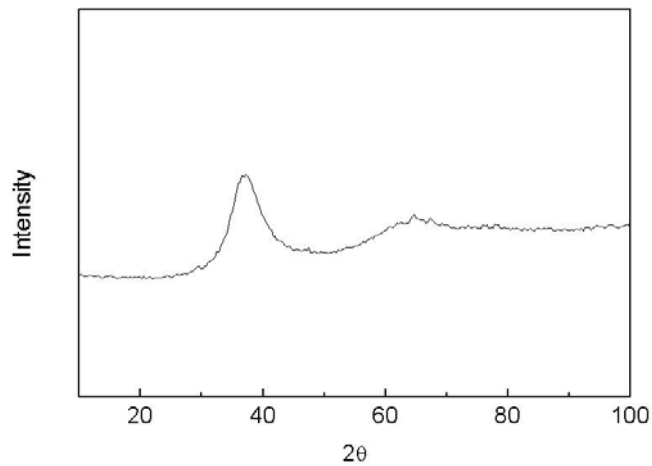
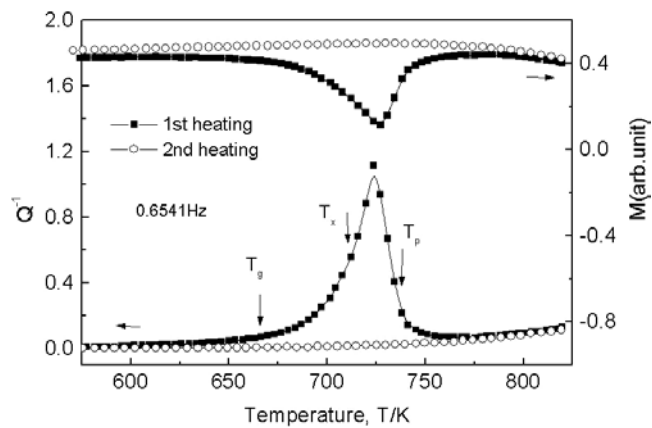**Figure 1.** The XRD pattern of $Zr_{57}Al_{10}Ni_{12.4}Cu_{15.6}Nb_5$ BMG.

Figure 2. The internal friction (Q^{-1}) and modulus (M) of $Zr_{57}Al_{10}Ni_{12.4}Cu_{15.6}Nb_5$ BMG as a function of temperature, for the rate 2 K min^{-1} during the first and second heating processes. T_g, T_x and T_p correspond to the results of the DSC.

3. Results and discussion

Figure 1 shows the x-ray diffraction pattern taken from the transverse cross-section (the surface of 2×50 mm^2) of the quenched specimen. The pattern consists only of a broad peak and there are no diffraction peaks corresponding to crystalline phases. Figure 2 shows the changing patterns of the internal friction (denoted as $Q^{-1} = \tan \Phi$) and shear modulus (M) as a function of temperature (T) (Q^{-1}–T and M–T curves) from 575 to about 825 K with 0.6541 Hz for a heating rate of 2 K min^{-1}. An obvious peak occurs at 723 K in the Q^{-1}–T curve. Internal friction and modulus change in opposite directions and the internal friction peak corresponds approximately to the modulus minimum. In order to get more detailed information about the peak, further experiments were done with different frequencies and heating rates. Figure 3 presents the Q^{-1}–T curves for the heating rate of 2 K min^{-1} with the frequencies of 0.5022, 1.0045 and 2.0089 Hz. The position of the peak does not alter with the frequencies, but the
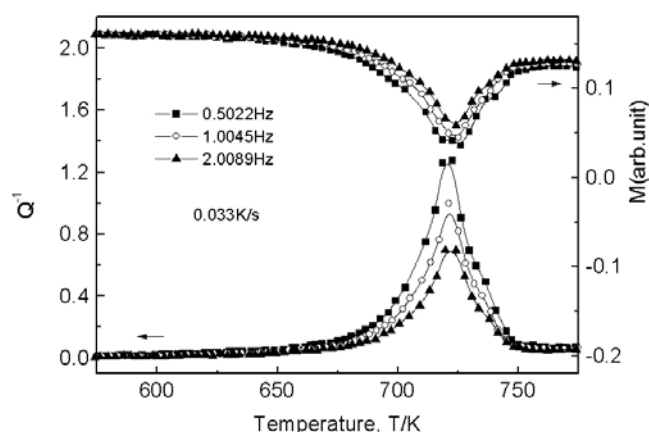
Figure 3. Q^{-1}–T and M–T curves with different frequencies, for a heating rate of 2 K min^{-1}.
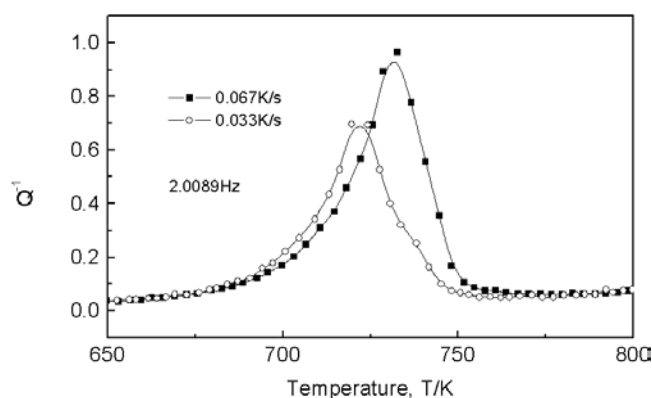

Figure 4. Q^{-1}–T curves for different heating rates.

height of the peak decreases with the frequency increasing. Figure 4 shows the Q^{-1}–T curves of 2.0089 Hz at the heating rates of 2 and 4 K min^{-1}. The peak temperature is raised from 723 to 728 K, and the peak height from 0.76 to 0.97 as the heating rate (dT/dt) was changed from 2 to 4 K min^{-1}. These features are perfectly in accordance with those of the first-order phase transitions in crystalline solids, which have been theoretically interpreted by Delorme and Belko models [18], leading to the same conclusion: $Q_p^{-1} = K(dT/dt)/\omega$, where K is a constant for a given material, and ω equals $2\pi f$. Figure 5 shows the linear relation between Q_p^{-1} (the magnitude of the internal friction peak) and $(dT/dt)/f$, which suggests a first-order phase transition around the peak temperature. From these results we assume that the peak is associated with crystallization. As shown in figure 2, the internal friction peak occurs at 723 K during the first heating process, while it has disappeared in the second heating process, indicating obviously that the peak is irreversible and the quenched specimen was completely crystallized during the first run. However, more detailed inspection reveals that the internal friction peak has two anomalous phenomena which are scarcely observed in the conventional phase transition of crystalline solids [17]. First, the magnitude of the internal friction peak is as large as 1.5, about two orders larger than that of the conventional phase transition of crystalline solids [17]. Second, the peak is much less symmetric: the left side of the peak from
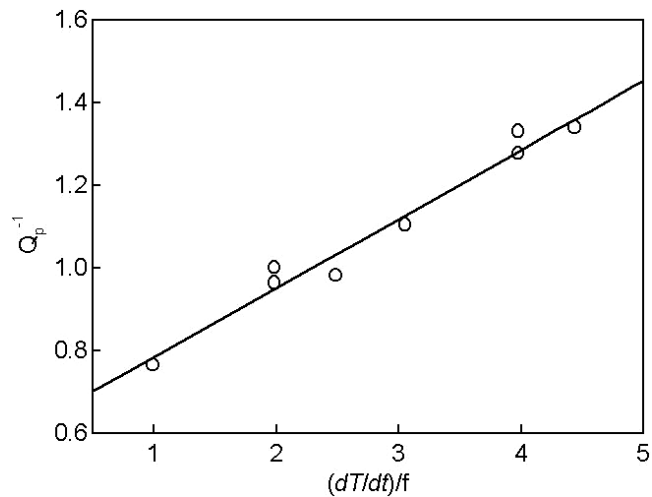
Figure 5. The relationship between the magnitude of the peak (Q_p^{-1}) and $(dT/dt)/f$.
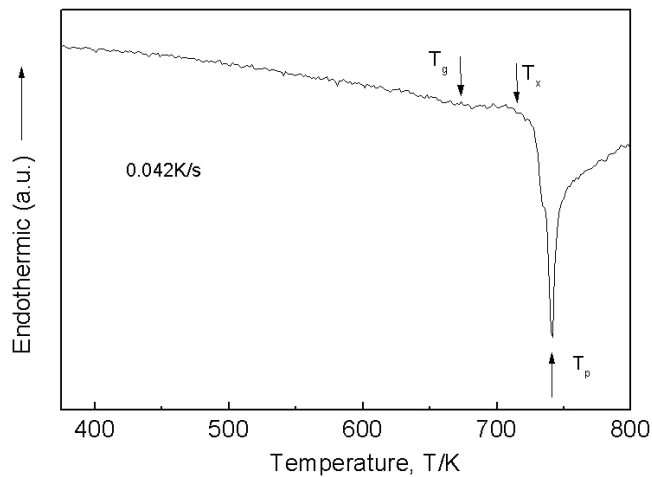

Figure 6. DSC results for $Zr_{57}Al_{10}Ni_{12.4}Cu_{15.6}Nb_5$ BMG, for a heating rate of 2.5 K min^{-1}.

623 to 723 K is much broader than the right one from 723 to 753 K; that is, the right side of the peak seems rather steeper than the left.

In order to interpret these anomalies, DSC measurement was carried out. Figure 6 shows the DSC result for a heating rate of 2.5 K min^{-1}. The glass transition temperature (T_g), the onset temperature of crystallization (T_x) and the exothermic peak temperature of crystallization (T_p) are around 663, 712 and 740 K, respectively. The wide supercooled liquid region, $\Delta T = T_x - T_g$, is as large as 49 K at 2.5 K min^{-1}, indicating the high thermal stability and large GFA of $Zr_{57}Al_{10}Ni_{12.4}Cu_{15.6}Nb_5$ alloy. Considering the small deviation between the two heating rates of 2 and 2.5 K min^{-1}, T_g, T_x and T_p were marked on the Q^{-1}–T curve (figure 2). T_g is located just at the bottom of the left side of the internal friction peak, which demonstrates that our results from DSC are in good accordance with those based on internal friction in respect of T_g. The modulus decrease resulting from the material softening
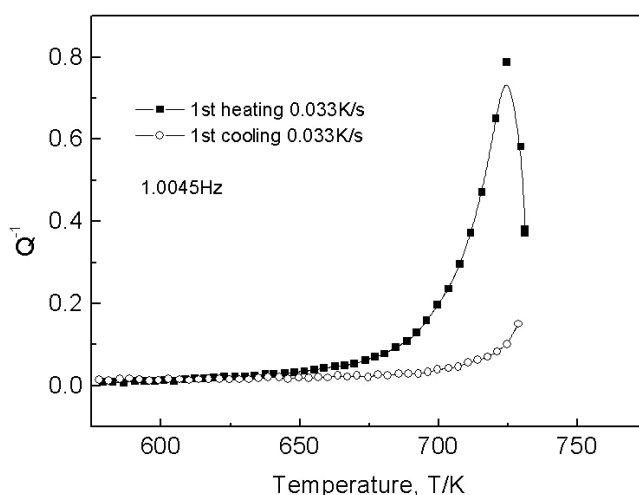
Figure 7. Q^{-1}–T curves for the first run. The quenched specimen was heated to 460 °C at 2 K min^{-1}, then cooled down at the same rate.

accompanying the rise of internal friction shows that the transition from the glassy state to the supercooled liquid state has taken place. However, it should be noted that T_x locates at a certain position about 10 K lower than the internal friction peak temperature and the temperature of the internal friction peak does not correspond to that of DSC (T_p), but is just between T_x and T_p. There is no doubt that the occurrence of the internal friction peak is ascribable to both the glass transition and crystallization. Sinning [4] has discussed the origin of such a peak for conventional metallic glasses and he interpreted it as a simple result of a drastic, monotonic increase of internal friction in the supercooled liquid and a following decrease due to crystallization. In his opinion, crystallization causes the decrease of internal friction and the internal friction peak temperature should correspond well with T_x. However, our experimental results show that T_x is on the left of the internal friction peak and the Sinning's proposal seems to disagree with this. To obtain a better understanding of the origin of the internal friction peak, the internal friction of the partially crystallized specimen was also measured. Figure 7 presents the results of the first run for the quenched specimen which was only heated up to 733 K before the peak ended. The peak is also observed at 723 K for a heating rate of 2 K min^{-1}, but no peak is seen on cooling down. Figure 8 shows the Q^{-1}–T curves of the second run and the third heating. A small internal friction peak in the second heating process occurs at about 738 K which is very near to T_p (740 K; see figure 6), indicating that this small peak mainly results from crystallization and that the value of the internal friction does not decrease monotonically with the process of crystallization.

The experimental results shown in figures 7 and 8 indicate again that the internal friction peak for the thorough heating process is attributable to both the glass and crystallization transitions. However, it is difficult to consider their contributions to the measured internal friction peak separately because of crystallization which has already taken place before the end of the glass transition. The case where crystallization occurs in the region of the glass transition can be demonstrated by the results of DSC (figure 6), which shows that there is no obvious interval between the end point of the glass transition and the onset of crystallization (T_x). The similar result that nanocrystallization was observed in the region of the glass transition in bulk amorphous Zr–Ti(Nb)–Cu–Ni–Al alloys by SANS and TEM has been reported [19].
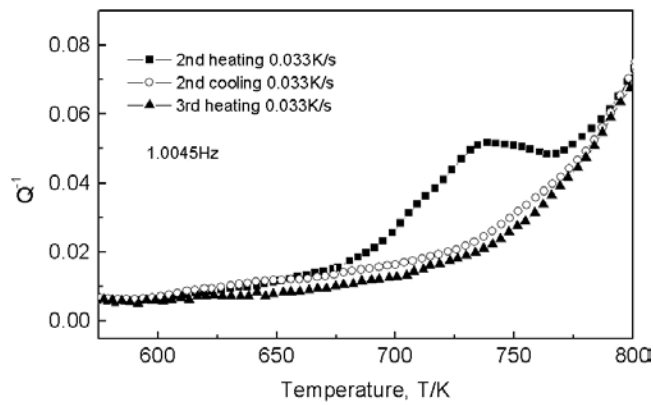
Figure 8. Q^{-1}–T curves for the second run and the third heating at 2 K min^{-1} after the first run.
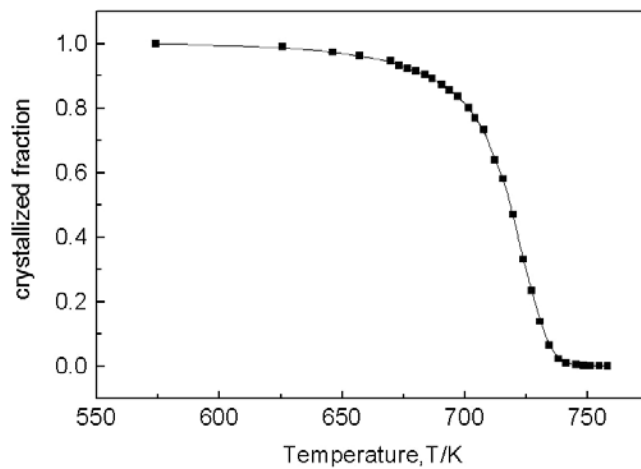

Figure 9. The crystalline fraction pattern as a function of temperature.

Sinning has deduced that near the glass transition the internal friction of the system on which measurements were performed can be approximately written as $Q^{-1} \propto 1/\eta$, where η is the viscosity of the supercooled liquid [20]. However, below T_x, the contribution of crystallization to internal friction cannot be neglected. Therefore, we propose an improved equation to describe the measured internal friction during the glass transition and crystallization:

$$Q^{-1} = AX(T)/\eta, \tag{1}$$

where A is the constant, $X(T)$ is the fraction of the glass/supercooled liquid and η is the viscosity of the material. This equation assumes that η is effectively infinite both for the glass at low temperatures and the crystalline phase. The crystallized fraction is shown in figure 9, which was obtained by integrating the crystallization peak (shown in figure 2) and dividing the integral by the total area of the peak. As shown in figure 9, $X(T) = 1$ at low temperatures (below 623 K), and $X(T) = 0$ after crystallization (above 753 K). For viscosity η, an activation equation could be used [21]:
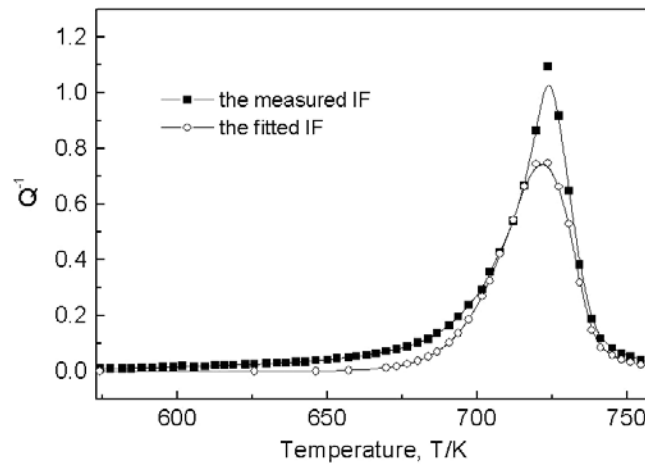
$$\eta = \eta_0 \exp(D/T) \tag{2}$$

Figure 10. The measured and the fitted internal friction patterns as a function of temperature. The peak at 0.6541 Hz in figure 2 is fitted by equation (5) with a constant $A = 6.79 \times 10^{-16}$ Pa s, a parameter $D = 20.83$ and a VFT temperature $T_0 = 400$ K.

or

$$\eta = \eta_0 \exp(DT_0/(T - T_0)). \tag{3}$$

From the equations (1) and (2) or (3),

$$Q^{-1} = AX(T)/(\eta_0 \exp(D/T)), \tag{4}$$

or

$$Q^{-1} = AX(T)/(\eta_0 \exp(DT_0/(T - T_0))). \tag{5}$$

Here, η_0 is set as 4×10^{-5} Pa s (see [22]). The measured internal friction peak with 0.6541 Hz shown in figure 2 can be fitted by equation (5) with a constant $A = 6.79 \times 10^{-16}$ Pa s, a parameter $D = 20.83$ and a VFT temperature $T_0 = 400$ K. Figure 10 presents the measured and the fitted internal friction curves as a function of temperature from 573 to 758 K. It is very interesting that our VFT temperature is close to that of Busch and Johnson [22], who found the VFT temperature 372 K for $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ BMG by viscosity measurement in the supercooled liquid region.

Since the measured internal friction peak can be fitted numerically by equation (5), it is not difficult to understand the two anomalies of the peak mentioned before. Near T_g, the crystallized fraction decreases slowly while the viscosity of the material under measurement decreases sharply, so the internal friction increases quickly. At T_x, the rate of decrease of the fraction $X(T)$ is still smaller than that of the viscosity of the system, and at T_p (the exothermic temperature of the DSC trace), the rate of decrease of the fraction $X(T)$ is much larger than that of the viscosity of the system; therefore, it is believed that the rate of decrease of the fraction $X(T)$ equals that of the viscosity of the system at a certain temperature between T_x and T_p, which corresponds to the peak temperature of the measured internal friction curves. After crystallization (at about 753 K), $X(T)$ equals zero, so the end of the internal friction peak coincides with the end of the sharp crystallization peak in the DSC trace (figure 6). From equation (5), the conclusion can be derived that the lower viscosity of the system under measurement without crystallization corresponds to the higher internal friction. Therefore, the extremely large magnitude of the observed internal friction peak originates from the high

thermal stability with respect to crystallization. The change of internal friction in figure 4 can also be explained, since at high heating rate the system can be heated further without crystallizing. In this case the system can be observed in a state of lower viscosity, corresponding to higher internal friction.

Another important conclusion deduced from our experiments is that the internal friction technique can be used as a convenient method for judging the GFA of metallic glasses. The supercooled liquid region (ΔT) is used widely as a criterion for judging the GFA of the glass forming alloys: the larger ΔT, the larger the GFA [23]. From the above results that the supercooled liquid plays a very important role in the formation of the extremely large internal friction peak, it is therefore confirmed that the magnitude of the internal friction peak of the quenched specimen also shows the GFA of the metallic glass under measurement. A principle can be derived: the higher the internal friction peak, the larger the GFA of metallic glasses. This is supported by the fact that the magnitude (1.5) of the internal friction peak of $Zr_{57}Al_{10}Ni_{12.4}Cu_{15.6}Nb_5$ BMG is about one order larger than those of thin ribbons of amorphous $Pd_{80}Si_{20}(0.2)$ [1], $Ni_{74}P_{16}B_6Al_4(0.13)$ [24], $Pd_{77.5}Cu_6Si_{16.5}(0.15)$ [2] and $Pd_{77.5}Ni_6Si_{16.5}(0.16)$ [25].

In conclusion, an internal friction peak with anomalously high magnitude is observed in the Q^{-1}–T curves of the $Zr_{57}Al_{10}Ni_{12.4}Cu_{15.6}Nb_5$ BMG. The internal friction peak is not located at the temperature T_p corresponding to the exothermic peak of DSC, but between T_x and T_p. We confirm that the internal friction peak originates from both the glass transition and crystallization. The measured internal friction peak was fitted by an equation $Q^{-1} = AX(T)/\eta$, where A is a constant, $X(T)$ is the fraction of the glass/supercooled liquid and the viscosity η obeys the Vogel–Fulcher–Tammann relation. The anomalous features of the internal friction peak suggest that the $Zr_{57}Al_{10}Ni_{12.4}Cu_{15.6}Nb_5$ BMG has a wide supercooled liquid region. The magnitude of the internal friction peak can be used as a convenient indication for judging the GFA of metallic glass forming alloys. Also, the internal friction technique proved to be a useful approach for investigating the structural transition of BMG.

Acknowledgment

References

[1] Mo Chi-mei, Shui Jiapeng and He Yizhen 1981 *J. Physique Coll.* **42** C5 523
[2] He Yizhen and Li Xiao-guang 1987 *Phys. Status Solidi* a **99** 115
[3] Chen H S and Morito N 1985 *J. Non-Cryst. Solids* **72** 287
[4] Sinning H-R 1989 *J. Non-Cryst. Solids* **110** 195
[5] Inoue A, Zhang T and Masumoto T 1989 *Mater. Trans. JIM* **30** 722
[6] Inoue A, Zhang T and Masumoto T 1990 *Mater. Trans. JIM* **31** 425
[7] Peker A and Johnson W L 1993 *Appl. Phys. Lett.* **63** 2342
[8] Inoue A, Zhang T, Nishiyama N, Ohoa K and Masumoto T 1993 *Mater. Trans. JIM* **34** 1234
[9] Nishiyama N and Inoue A 1996 *Mater. Trans. JIM* **37** 1531
[10] Wang W H, Li L L, Pan M X and Wang R J 2001 *Phys. Rev.* B **63** 052204
[11] Jecht H J 1995 *Mater. Trans. JIM* **36** 777
[12] Löffler J F and Johnson W J 2000 *Appl. Phys. Lett.* **76** 3394
[13] Busch R, Kim Y J, Johnson W L, Rusison A J, Rhim W K and Isheim D 1995 *Appl. Phys. Lett.* **66** 3111
[14] Haruyama O, Kimura H, Inoue A and Nishiyama N 2000 *Appl. Phys. Lett.* **76** 2026
[15] Wang L M, Wang W H, Wang R J, Zhan Z J, Dai D Y, Sun L L and Wang W K 2000 *Appl. Phys. Lett.* **77** 1147
[16] Bakke E, Busch R and Johnson W J 2000 *Appl. Phys. Lett.* **67** 3260

[17] Nowick A S and Berry B S 1972 *Anelastic Relaxation in Crystalline Solids* (New York: Academic)
[18] Belko V N, Darinskii B M, Postnikov V S and Sharshakov I M 1969 *Fiz. Met. Metalloved.* **27** 141
    Delorme J F and Gobin P F 1973 *Metaux* **573** 185
[19] Löffler J F, Bossuyt S, Glade S C, Johnson W L, Wagner W and Thiyagarajan P 2000 *Appl. Phys. Lett.* **77** 525
[20] Sinning H R and Haessner F 1987 **93** 53
[21] Köster U, Meinhardt J, Roos S and Liebertz H 1996 *Appl. Phys. Lett.* **69** 179
[22] Busch R and Johnson W J 1998 *Appl. Phys. Lett.* **72** 2695
[23] Inoue A, Zhang T and Masumoto T 1993 *J. Non-Cryst. Solids.* **156** 473
[24] Li Xiao-guang and He Yizhen 1986 *Phys. Status Solidi* a **95** 467
[25] Yue Lanping and He Yizhen 1988 *J. Non-Cryst. Solids.* **105** 33