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ANOMALOUS TEMPERATURE DEPENDENCE OF SOUND VELOCITY IN $Zr_{50}Cu_{40}Al_{10}$ WITH DIFFERENT EXCESS FREE VOLUME

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Abstract. Temperature dependence of the mechanical resonance frequency f_m of ultrasonic wave in as-quenched and annealed $Zr_{50}Al_{10}Cu_{40}$ metallic glasses was measured from room temperature to liquid nitrogen temperature. The mechanical resonance of longitudinal wave for the as-quenched sample disappeared in lower temperature below 200 K. The resonance was restored at about 240K with increasing temperature. A hysteresis was observed in temperature dependence of f_m. The qualitatively similar behaviors were observed also for transverse wave. The phenomena for the annealed samples are different from ones for the as-quenched one. The excess free volume may cause anomalous temperature dependence of f_m.

1. INTRODUCTION

Recently it has been reported that metallic glasses prepared by rapid solidification contain an excess quenched-in free volume (hereafter, this is abbreviated to excess free volume.) and the higher the cooling rate, the more the excess free volume increases [1]. When the metallic glass is annealed at a temperature below a glass transition temperature T_g, a structure relaxation is caused by decrease of excess free volume [2,3].

In order to estimate the temperature dependence of mechanical properties such as the Young's modulus E and the Poisson's ratio ν aiming at application of metallic glasses to cryogenic machine, and to examine the relative change of mechanical properties of $Zr_{50}Cu_{40}Al_{10}$ between an as-quenched sample and an annealed one, we measured temperature dependence of the mechanical resonance frequency f_m of ultrasonic wave in low temperature below room temperature.

2. EXPERIMENTAL PROCEDURES

The metallic glasses were prepared by a technique of tilt melt casting. The details of the sample preparation have been described elsewhere [4]. One ingot of metallic glass was cut into two samples, one was used as an as-quenched sample (AP-3), and the other was annealed at T=673K (<T_g=711K) for 1 hour and used as an annealed sample (AT-3). The mass density of the sample was measured by the Archimedes method using a shaped rod sample.

The wave length λ_m of ultrasonic wave in a mechanical resonance is related to the sample length along the wave propagation direction L by $L=m\lambda_m/2$, where m is an integer indicating the resonance

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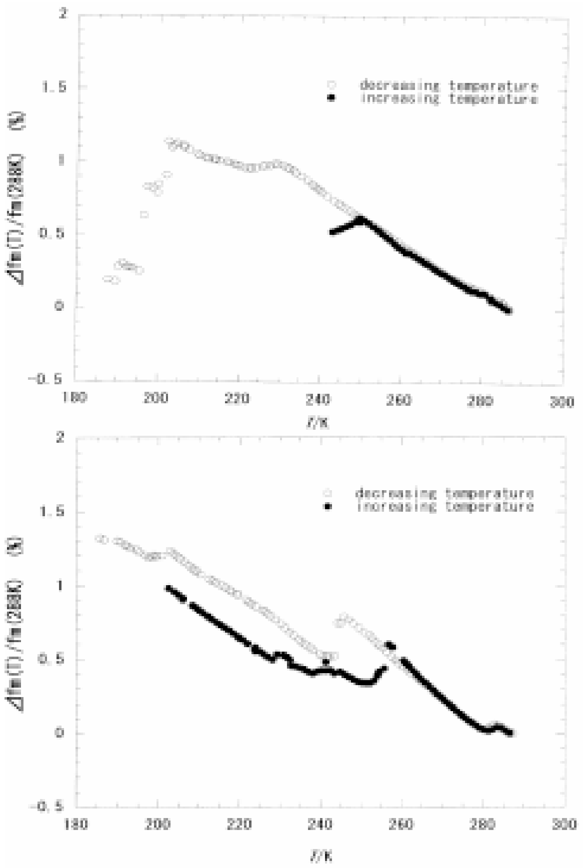

Fig.1. Temperature dependence of the change rate of $f_m(T)$ of longitudinal ultrasonic wave, $\Delta f_m(T)/f_m(288K) \equiv [f_m(T) - f_m(288K)]/f_m(288K)$, (a) for AP-3 and (b) for AT-3.

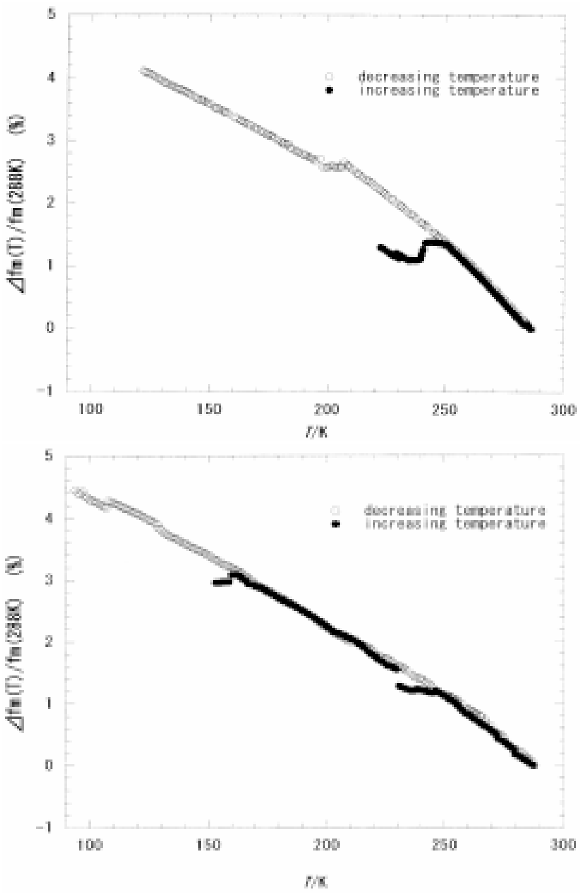

Fig. 2. Temperature dependence of the change rate of $f_m(T)$ of transverse ultrasonic wave, $\Delta f_m(T)/f_m(288K)$, (a) for AP-3 and (b) for AT-3.

order [5]. Since V_s is related to f_m as $V_s = \lambda_m \times f_m$, we obtain $V_s = 2L(f_m/m)$. The ultrasonic velocity $V_s(T)$ at a temperature T is estimated from plots of f_m vs. m. Furthemore, the change of f_m, Δf_m is represented by

$$\frac{\Delta f_m(T)}{f_m(T_0)} = \frac{\Delta V_s(T)}{V_s(T_0)} - \frac{\Delta L(T)}{L(T_0)}. \tag{1}$$

Here, T_o is the temperature at a starting point. The longitudinal and the transverse ultrasonic velocities V_l and V_t are related to elastic constants c_{11} and c_{44} as $\rho V_l^2(T) = c_{11}(T)$ and $\rho V_t^2(T) = c_{44}(T)$, respectively, where ρ is the mass density of the sample. In the case that the second term in Eq. (1) is negligibly small compared with the first term, the change of $V_s(T)$ can be considered proportional to the change of $f_m(T)$. From the temperature dependence of c_{11} and c_{44}, the temperature dependence of c_{12}, E and ν are estimated. Such mechanical properties in low temperature can be clarified.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The amorphous state of the samples was confirmed by X-ray diffraction [6]. An excess free volume ratio FV is estimated by

$$FV = \frac{\rho_P^{-1} - \rho_T^{-1}}{\rho_P^{-1}} \times 100, \tag{2}$$

where, ρ_P and ρ_T are the mass density of AP-3 and the one of AT-3, respectively. The value of FV is 0.425 for AP-1 [6], and 0.133 for AP-3.

At first, the measurement system was checked using a single-crystalline bismuth, which has no structure instability in low temperature region. The longitudinal sound wave propagated along three fold symmetry axis. Any abnormal behavior in temperature dependence of $f_m(T)$ was not observed [6].

The temperature dependence of f_m of longitudinal wave in AP-3 and AT-3 was shown in Figs. 1a and 1b, respectively. The temperature dependence of f_m in AP-3 has a plateau from 230 to 220K with decreasing temperature, f_m decreased abruptly from 202K and the resonance signal became too small to be detected just below this temperature. This suggests that sound wave is absorbed largely or reflected in the sample. When the temperature was increased, the resonance restored at 242K and $f_m(T)$ coincided with the data with decreasing temperature from 250K. Namely, a kind of hysteresis is observed on the round trip of temperature dependence of $f_m(T)$. In the case of AT-3, the signal was restored from lower temperature compared with AP-3 with increasing temperature and a clear hysteresis was observed. Next, the same measurements were carried out using transverse wave. The results are shown in Fig. 2. The mechanical resonance in AP-3 survived to lower temperature in the process of decreasing temperature. The signal in AT-3 appeared at lower temperature and the hysteresis is scarcely observed. These results were similar to ones reported by us [6].

Since one of the changes in amorphous materials by annealing is a change of the excess free volume [2,3], this may cause above anomalies. Since the size of free volume is an order of atomic size, the space occupied by such defects is negligibly small compared with the wave length of ultrasonic wave, which is an order of 0.1 mm for 10 MHz. In order to explain the macroscopic effect of excess free volume to c_{11} and c_{44}, any long range order of change must happen in amorphous structure. At present it is not clear how the excess free volumes reduced by annealing are related to the hysteresis of $f_m(T)$. Annealing causes the increase of resonance frequency with decreasing temperature. From these data, mechanical properties in low temperature are estimated.

REFERENCES

[1] Y. Yokoyama, Y. Akeno, T. Yamasaki, P. K. Liaw, R. A. Buchanan and A. Inoue // *Mater. Trans., JIM* **46** (2005) 2755.

[2] K. Hajlaoui, T. Benameur, G. Vaughan and A.R. Yavari // *Scripta Materialia* **51** (2004) 843.

[3] A. R. Yavari, M. Tonegaru, N. Lupu, A. Inoue, E. Matsubara, G. Vaughan, A. Kvick and W.J. Botta // *Mater. Res. Symp., Proc. Vol*. **806** (2004) 203.

[4] Y. Yokoyama, H. Inoue, K. Fukaura and A. Inoue // *Mater. Trans.* **43** (2002) 575.

[5] D. I. Bolef and J. G. Miller, In: *Physical Acoustics*, ed. by W. P. Mason and R. N. Thurston (Academic Press, New York, 1971) vol. VIII, p. 95.

[6] T. Fukami, A. Nunbu, M. Fukatani, D. Okai, Y. Akeno, Y. Yokoyama, T. Yamasaki, and A. Inoue // *Materials Science Forum* **539-543** (2007) 2100.