Ultrasound-Induced Structural Anomaly of Supercooled Liquid in Some Bulk Metallic Glasses

Tetsu Ichitsubo1-*, Eiichiro Matsubara1, Kazuhiro Anazawa1, Nobuyuki Nishiyama2, Satoshi Kai3 and Masahiko Hirao3

1 Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
2 RIMCOF Tohoku University Laboratory, R&D Institute of Metals and Composites for Future Industries, Sendai 980-8577, Japan
3 Graduate School of Engineering Science, Osaka University, Toyonaka 560-8531, Japan

We have studied the elastic and anelastic behavior of fully structural-relaxed Pd40Ni40P20 and Zr55Al10Ni5Cu10 bulk metallic glasses using high-frequency ultrasound vibrations at elevated temperature, and found that the structural anomaly is induced by ultrasound vibrations in a supercooled liquid region. The electromagnetic acoustic resonance and resonant ultrasound spectroscopy methods were employed to measure the resonant spectra and ultrasonic attenuation coefficients. When the glassy samples are subjected to sub/low-MHz ultrasound vibrations during heating process, the crystallization is accelerated around their glass transition temperatures, and with this abrupt structural change, irregular A-shaped internal friction peaks appear. From the standpoint of ultrasonic echography, the glass transition and crystallization temperatures are considerably lowered by ultrasound vibrations in the present measurements.

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1. Introduction

Various bulk metallic glasses in multicomponent systems that possess an excellent glass-forming ability have been discovered in the last decade.1-7 Their glass transitions have attracted much attention both in physical and practical aspects, and have been extensively investigated in terms of the specific heat capacity, elastic constants, viscosity, diffusion, etc.

The elastic constants are important for discussing the structural stability, because they provide the important physical information such as the Debye temperatures and the characteristics of the glass transitions. Several papers related with the elastic constants have appeared in various alloy systems.8-14 On the other hand, there are several studies on the low-frequency (~1 Hz) internal friction.15-17 It is well-known that the peak magnitude of internal friction Q-1 becomes higher when the measurement frequency f is lower: Q-1 ∝ T/ν (ν = dT/dt is the heating rate).16,17 Hence, there are only a few studies on the high-frequency anelastic properties around the glass transition temperature Tg.

Apart from interests in the physical properties of amorphous alloys, it is of importance to study the stability or instability of glassy structures under external fields (electric, magnetic or stress fields). Mizubayashi et al.18-24 have investigated effects of passing electric current on the structural relaxation and crystallization of some kinds of amorphous alloys, which shows that crystallization is very much accelerated by the electropulsing far below the normal crystallization temperature without the pulsing. Recently, elastic and anelastic properties of Zr55Al10Ni5Cu10(25) and Pd40Ni40P20(26) bulk metallic glasses around Tg have been studied with the electromagnetic acoustic resonance (EMAR) method within the frequency range of 300-1500 kHz. As shown in Fig. 1 (sample: Pd40Ni40P20), we see a notable change in resonance frequencies in the case of heat treatment with ultrasound vibrations (Tg in the figure was determined by DSC measurement with a rate of 0.333 K/s), and this drastic change is considered to be caused by nano-crystallization.20 Similarly, reduction of the glass transition and crystallization temperatures is also recognized in the ultrasound pulse-echo measurements for a Zr55Al10Ni5Cu30 metallic glass by Keryvin et al.(13) These indicate that the glassy state cannot be retained under high-frequency ultrasound vibrations in a supercooled liquid region (near/above Tg), that is, crystallization is accelerated by ultrasound vibrations. In this paper, we have performed ultrasonic measurements in fully structural-relaxed Pd40Ni40P20 and Zr55Al10Ni5Cu10 metallic glasses, and have also examined the possible effects concomitant with excitation of ultrasound vibrations.

2. Experimental

Alloy ingots of Pd40Ni40P20 (PNP) and Zr55Al10Ni5Cu30 (ZANC) (at%) bulk metallic glasses were used in this work. The details of the fabrication technique have been described in literature.2,4,10 Tg and Tc were determined by the differential scanning calorimeter (DSC) with the heating rate of 0.333 K/s. The samples for the ultrasonic measurements were machined into cylindrical shape. Table 1 shows the sample characteristics.

To measure the resonance frequencies and ultrasonic attenuation coefficients, we have used EMAR27,28 and the resonant ultrasound spectroscopy (RUS)29 techniques. For the attenuation-coefficient measurements and high-temperature in-situ measurements, the former technique was used because the resonance vibrations can be excited in a non-contact manner by the Lorentz forces caused by the interaction between eddy current and a static magnetic field, which enables us to measure accurate internal friction without effects of couplant etc.
The resonance frequencies $f_r$ ($\omega_r = 2\pi f_r$) of the cylindrical samples were measured in sub/low-MHz frequency range. The EMAR measurements were performed in the $B_2g^{-1}$ (shear) resonance mode. The ultrasonic-attenuation coefficients were measured by the free-decay method; the attenuation coefficient $\alpha_t$ (unit: $s^{-1}$) was determined by fitting $\exp(-\alpha_t t)$ to the amplitude decay with time, and the internal friction was obtained by $Q^{-1} = \alpha_t / 2\pi f_r$. The resonance frequencies were detected by sweeping frequency in a step of 0.1 kHz; at each frequency, a burst-wave packet of $\sim 10^{-4}$ s was injected into the samples.

The high-temperature EMAR measurements were performed in a vacuum of $10^{-3}$ Pa.

Prior to the high-temperature EMAR measurements, to attain a fully structurally-relaxed state, the samples were heated over $T_g$ with a heating rate of 0.333 K/s (without ultrasound vibration), and kept at about $T_g + 20$ K (597 K for Pd$_{40}$Ni$_{40}$P$_{20}$ and 700 K for Zr$_{55}$Al$_{10}$Ni$_{5}$Cu$_{30}$) for 2 h and cooled down to room temperature. Hereafter they are called post-annealed samples. Subsequently, we measured $T$-behavior of the resonance frequency $f_r$ and the internal friction $Q^{-1}$ with the EMAR technique using these post-annealed samples. The samples after heat treatments under ultrasonic vibrations are called post-US samples.

3. Results

Figure 2 shows the results of the in-situ EMAR measurements; the upper part of the figure shows the thermal history (measurement time versus temperature), and the lower part shows $T$-dependence of $f_r$ and $Q^{-1}$ in the heating and cooling processes, in which the numbers and arrows indicate the heat-treatment procedure. It is noticeable that remarkable change (jump) in the resonance frequency appears around $T_g$.

Fig. 1 Resonance-frequency shifts after heat treatments with or without ultrasound vibrations for a Pd$_{40}$Ni$_{40}$P$_{20}$ sample. (a) shows the heat treatment procedure, (b) and (c) show the resonant-ultrasound-spectroscopy (RUS) spectra. Shifts of the resonance frequencies for the sample annealed without ultrasound vibrations are about 2–3% of those for the as-cast samples, whereas those for the sample annealed under vibrations are about 20%. The samples were heated up to above $T_g + 20$ K with a heating rate of 0.333 K/s in both cases.

Table 1 Typical sample dimensions, densities, $T_g$ and $T_x$ determined by the DSC measurements with a heating rate of 0.333 K/s.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diameter</th>
<th>Length</th>
<th>Density</th>
<th>$T_g$</th>
<th>$T_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd$<em>{40}$Ni$</em>{40}$P$_{20}$</td>
<td>3.046</td>
<td>2.172</td>
<td>9123</td>
<td>577</td>
<td>662</td>
</tr>
<tr>
<td>Zr$<em>{55}$Al$</em>{10}$Ni$<em>{5}$Cu$</em>{30}$</td>
<td>3.024</td>
<td>2.397</td>
<td>6703</td>
<td>680</td>
<td>770</td>
</tr>
</tbody>
</table>

The resonance frequencies $f_r$ ($= \omega_r / 2\pi$; $\omega_r$ is the resonance angular frequency) of the cylindrical samples were measured in sub/low-MHz frequency range. The EMAR measurements were performed in the $B_2g^{-1}$ (shear) resonance mode. The ultrasonic-attenuation coefficients were measured by the free-decay method; the attenuation coefficient $\alpha_t$ (unit: $s^{-1}$) was determined by fitting $\exp(-\alpha_t t)$ to the amplitude decay with time, and the internal friction was obtained by $Q^{-1} = \alpha_t / 2\pi f_r$. The resonance frequencies were detected by sweeping frequency in a step of 0.1 kHz; at each frequency, a burst-wave packet of $\sim 10^{-4}$ s was injected into the samples.

Fig. 2 Temperature dependence of the resonance frequency and the internal friction of the shear vibration ($B_2g^{-1}$) mode in the heating and cooling processes.
spectra. Since the elastic modulus, which were derived from the resonance frequency constants and modulus changes after respective heat treatments, the square of resonance frequencies starts to increase simultaneously. If the softening and jump positions in the $f_r$ decreases (i.e., elastic softening occurs) rapidly around $0.9T_g$, and $Q^{-1}$ starts to increase simultaneously. If the softening and jump positions in the $f_r$ curves are redefined as the glass transition temperature $T_g^{(US)}$ and crystallization temperature under ultrasound vibrations $T_x^{(US)}$, $T_g^{(US)} \approx 530 \text{ K}$ and $T_x^{(US)} \approx 580 \text{ K}$ for Pd$_{50}$Ni$_{30}$P$_{20}$, and $T_g^{(US)} \approx 625 \text{ K}$ and $T_x^{(US)} \approx 675 \text{ K}$ for Zr$_{55}$Al$_{10}$Ni$_{30}$Cu$_{5}$. They are tabulated in Table 3.

In our DSC measurements, we checked that $T_g$ decreases with decrease in heating rate, and $T_x$ is virtually insensitive to heating rates. Consequently, we can regard that the use of ultrasound vibrations considerably lowers $T_g$ as well as $T_x$.

Figure 3 shows the RUS spectra measured at room temperature for (a) the as-cast sample, (b) the post-annealed samples without vibrations, and (c) post-US samples after the 4th process in the EMAR measurements. Shifts of the resonance frequencies for the post-annealed samples are about 2-3% of those for the as-cast samples. Such small changes are considered to be caused by structural relaxation. It is considered that at this stage crystallization hardly occurs.

For the US-vibration samples, however, all the resonance frequencies drastically increase compared with the others. Figure 4 shows X-ray diffraction (XRD) profiles after the heat treatments. It is found that the post-annealed samples are in the amorphous state (Fig. 4(b)). The profiles for the post-US samples indicate that they are partially nano-crystallized (Fig. 4(c)). Thus, rapid crystallization takes place under ultrasound vibrations at the temperatures around $T_g$ (see Table 3).

In the EMAR measurement, the eddy current is induced on the sample surface and the magnetic field (~0.2 T) is applied. These influences on the rapid crystallization have been examined using a Zr$_{55}$Al$_{10}$Ni$_{30}$Cu$_{5}$ sample with RUS at room temperature. The RUS spectrum for an as-cast sample is shown in Fig. 5(a). The heat treatment under a magnetic field does not cause the significant shifts, and subsequent heat treatment with the only eddy current does not cause such large shifts either, as it is seen in Figs. 5(b) and (c), respectively. These small changes are explained by the structural relaxation, for example, as is shown in Fig. 1(b). The ultrasound vibrations (caused by eddy current and magnetic field) obviously induce a drastic change in Fig. 5(d).

### Table 2

<table>
<thead>
<tr>
<th>Modulus</th>
<th>As-cast</th>
<th>Pd$<em>{50}$Ni$</em>{30}$P$_{20}$</th>
<th>Post-annealed</th>
<th>Post-US</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_{II}$</td>
<td>224</td>
<td>231 (3.13%)</td>
<td>250 (11.6%)</td>
<td></td>
</tr>
<tr>
<td>$c_{II}$</td>
<td>36.7</td>
<td>38.1 (3.81%)</td>
<td>49.4 (34.6%)</td>
<td></td>
</tr>
<tr>
<td>$E$</td>
<td>103</td>
<td>107 (3.88%)</td>
<td>136 (32.0%)</td>
<td></td>
</tr>
<tr>
<td>$B$</td>
<td>175</td>
<td>180 (2.86%)</td>
<td>185 (5.71%)</td>
<td></td>
</tr>
</tbody>
</table>

### Table 3

<table>
<thead>
<tr>
<th>Modulus</th>
<th>As-cast</th>
<th>Zr$<em>{55}$Al$</em>{10}$Ni$<em>{30}$Cu$</em>{5}$</th>
<th>Post-annealed</th>
<th>Post-US</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_{II}$</td>
<td>153</td>
<td>155 (1.31%)</td>
<td>156 (2.00%)</td>
<td></td>
</tr>
<tr>
<td>$c_{II}$</td>
<td>32.4</td>
<td>33.7 (4.01%)</td>
<td>36.3 (12.0%)</td>
<td></td>
</tr>
<tr>
<td>$B$</td>
<td>88.4</td>
<td>91.7 (3.73%)</td>
<td>98.3 (11.2%)</td>
<td></td>
</tr>
<tr>
<td>$B$</td>
<td>110</td>
<td>110 (0.00%)</td>
<td>111 (0.91%)</td>
<td></td>
</tr>
</tbody>
</table>

### Table 3 Elastic softening temperature $T_g^{(US)}$ and rapid crystallization temperature $T_x^{(US)}$ for fully structural-relaxed (post-annealed) samples after annealed at $T_g + 20 \text{ K}$ for 2 h.

<table>
<thead>
<tr>
<th></th>
<th>$T_g + 20$</th>
<th>$T_g^{(US)}$</th>
<th>$T_x^{(US)}$</th>
<th>$\Delta T_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd$<em>{50}$Ni$</em>{30}$P$_{20}$</td>
<td>597 K</td>
<td>530 K</td>
<td>580 K</td>
<td>50 K</td>
</tr>
<tr>
<td>Zr$<em>{55}$Al$</em>{10}$Ni$<em>{30}$Cu$</em>{5}$</td>
<td>700 K</td>
<td>625 K</td>
<td>675 K</td>
<td>50 K</td>
</tr>
</tbody>
</table>
4. Discussions

In the present study, we clearly observed elastic softening below $T_g$ and drastic jump of elastic constants due to crystallization at much lower $T_x$ under ultrasound vibrations. Thus, we regarded these temperatures as $T_{g(US)}$ and $T_{x(US)}$, as we explained above. Since the elastic constants usually increase accompanied with crystallization and there are broad crystallization peaks in the XRD profiles of Fig. 4, it is natural that the jump position in $T$-dependence curve of the resonance frequencies is redefined as the crystallization temperature under ultrasound vibrations. In contrast, the definition of the glass transition temperature is rather unclear, because the structure of atomic configuration changes gradually and continuously in the “glassy solid $\leftrightarrow$ supercooled liquid” transition. When a glassy solid changes into a viscoelastic supercooled liquid state, the elastic constants would soften, that is, their temperature derivative would change. From the viewpoint of the elastic constants, it is not totally wrong to redefine the elastic softening temperature as $T_{g(US)}$. It is intriguing that $T_{g(US)}$ is far below $T_{g(DSC)}$ and the rapid crystallization takes place considerably low temperatures.

A role of ultrasound vibrations in the rapid crystallization is considered below. In vibration motion, the elastic strain energy and kinetic energy are converted to each other from moment to moment, and we may consider that their sum is constant as far as the influences of frictions are neglected. We here consider the maximum strain energy as a representative of the ultrasound energy. The elastic strain is given by

\[ \epsilon = \frac{A}{\lambda}, \]

where $A$ is the vibration amplitude, and $\lambda$ is the wavelength, being of the order 1–10 mm for sub/low-MHz frequency range. When $A$ is assumed to be of the order 1–10 nm, we obtain

\[ \epsilon = 10^{-5} \sim 10^{-6}. \]

The strain energy by ultrasound vibrations is estimated to be

\[ \mathcal{E}_{US} = \frac{M}{V} \epsilon, \]

where $\mathcal{E}_{US}$ is the total strain energy, $V$ is the atomic volume, and $M$ is the elastic modulus. On the other hand, thermal energy per atom, $k_B T$, at 500–700 K approximates about $10^{-20}$ J/atom. Thus, the strain energy by the ultrasound vibration is infinitesimally small compared with the thermal energy. Therefore, the ultrasound-induced crystallization cannot be explained by assistance to thermal agitation of atoms.

The anomaly that ultrasound vibrations accelerate crystallization around the glass transition temperature is considered to be caused by a certain resonance phenomenon. There are two possible causes. As one scenario, it is considered that a certain collective motion is excited by ultrasound vibrations of a specific frequency range, the vibration amplitude becomes larger in a supercooled liquid above $T_g$, which...
finally leads to the rapid crystallization. Further investigation about the cluster unit associated with the collective motion is needed to make clear its possibility. On the other hand, we consider that the anomaly is attributed to irregular jump of individual atom induced by ultrasound vibrations. Prior to the rapid crystallization around $T_g$, the $\Delta$-shaped internal-friction peak appears. If $T_g$ is assumed to be the peak temperature of $Q^{-1}$ \(\text{i.e., } \omega T \sim 1 \text{ at } T_g\), the relaxation time $\tau(T_g)$ is of the order $10^{-7}$ s. From the viewpoint of the measurement frequencies and the order of relaxation time, it seems that the increase of $Q^{-1}$ below $T_g$ is attributed to atom movements with thermal activation.

We here focus on the possibility of irregular jumps induced by ultrasound vibrations. If assuming a phenomenon similar to Snoek relaxation, the elastic interaction energy caused by the oscillation is of the order $\Omega M \epsilon \sim 10^{-22} - 10^{-23}$ J/atom, and such jumps of atoms can be realized. The interatomic potential would be easily changed by the ultrasound strain $\epsilon$, because the interatomic-potential minima in an amorphous phase are not as rigid as those in a crystal lattice. It seems that the increase of $Q^{-1}$ for sub/low-MHz frequency vibrations is attributed to atom movements with thermal activation, whose jump frequency is probably comparable to the frequency of the interatomic-potential change caused by the ultrasound strain $\epsilon$. In such a situation, the atoms would move into the more favorable sites caused by $\epsilon$, being different from the ordinary. Such a change of the usual atomic configuration will accelerate the further change of interatomic-potential of surrounding atoms. Accumulation of these irreversible atomic jumps changes the original glass phase and deteriorates the thermal/structural stability.

If the presented phenomenon is caused by a certain resonance of the external force, the frequency dependence should appear. Namely, too low frequency or high frequency vibrations would not induce this phenomenon. In fact, low frequency (\~{}300–600 Hz)\(^3\) and high frequency (\~{}5 MHz)\(^6\) measurements have shown that no discontinuous change occurs in the $T$-dependence of elastic constants. In contrast, echography using sub-MHz (\~{}350 kHz) vibrations have shown that the glass transition and crystallization temperature are considerably lower compared with those determined by the DSC measurements.\(^{13}\)

5. Conclusions

In conclusions, we have studied the ultrasound-vibration effects on fully structural-relaxed glassy states of $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_{23}\text{Cu}_{12}$ and $\text{Pd}_{30}\text{Ni}_{40}\text{P}_{30}$ bulk metallic glasses. In the heat treatment under ultrasound vibrations, the resonance frequencies change drastically around $T_g$ and the internal friction increases approaching $T_g$ and it drops near above $T_g$. When the characteristic temperatures $T_g$ and $T_c$ are defined using ultrasonic measurements, these are considerably lowered compared with those determined by thermal measurements.

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REFERENCES