We have focused on a rejuvenation behavior of recovery annealed Pd$_{42.5}$Cu$_{30}$Ni$_{7.5}$P$_{20}$ metallic glass. Specific heat measurement results revealed that only 33%, which is lower than that (44%) of a Zr$_{55}$Al$_{10}$Ni$_{5}$Cu$_{30}$ metallic glass, was recovered by annealing. This result indicates that the recovery of a Pd$_{42.5}$Cu$_{30}$Ni$_{7.5}$P$_{20}$ metallic glass is more difficult than the Zr-based alloy. The hardness measurement results obtained from the indentation test also supported this finding. The time dependence of the normalized storage modulus $E'/E_u$ at 0.8$T_g$ of both metallic glasses were successfully demonstrated by the KWW (Kohlrausch-Williams-Watts) equation, which means that the relaxation/rejuvenation behavior of each sample was well described by the free volume change. It also suggested that the distribution of relaxation modes of the Pd$_{42.5}$Cu$_{30}$Ni$_{7.5}$P$_{20}$ metallic glass is much narrower in a $\beta$-relaxation region. The normalized loss modulus $E'/E_u$ implied that two areas, one is in correlation to the free volume change and the other is not, are embedded in the intrinsic $\beta$-relaxation region and the lower rejuvenation ability in the Pd$_{42.5}$Cu$_{30}$Ni$_{7.5}$P$_{20}$ metallic glass may originate from a low volume fraction of the former area. The present study will provide the universal information for the research subject on the thermal rejuvenation in metallic glasses.

**Key words:**
Palladium-based metallic glass, Zirconium-based metallic glass, Recovery annealing, Rejuvenation, $\beta$-relaxation region

1 Introduction

Recently, structural rejuvenation has been intensively studied in the metallic glass fields and many methods have been proposed so far, such as plastic deformation$^{1-3)}$, elastostatic loading$^4)$, irradiation$^5)$ and so on. In particular, the high pressure torsion (HPT), which is classified in the plastic deformation method, is thought to be a promising technique to introduce the large amount of free volume into the glassy structure, and the maximum recovery amount of about 30% from the as-cast state on the Young’s modulus has been reported$^1)$. However, since this method is based on the way of an introduction of gigantic strain, the physical or mechanical damage of the glassy structure seems to be inevitable. Therefore, it is thought to be difficult to discuss the rejuvenation mechanism precisely or more in detail. Very recently, the cyclic cooling has attracted much attention in another way to attain the rejuvenation$^6)$. Unlike the mechanical way, this is just a thermal one, so it is easier to discuss the phenomenon. However, even though the relatively high recovery amount on the enthalpy of about ~40% from the as-cast state was reported, it is still unknown why such a drastic effect occurred in the glassy structure. Regardless of a thermal way, the real mechanism has not been clarified in detail.

Meanwhile, we have focused on the recovery annealing technique which is recognized as another thermal rejuvenation method$^{7,8)}$. Compared with others, this technique cannot recover metallic glasses so drastically, however it has many advantages like non-destructive, no shape change, homogeneous, isotropic, applicable to any samples and so on. Besides, this is based on annealing in the supercooled liquid region, and is not the extreme conditions as shown in the cyclic cooling. Therefore, we can easily and deeply discuss the real rejuvenation phenomenon only from the thermodynamic aspect. In our previous studies, we successfully observed the structural rejuvenation phenomenon in the Zr-based metallic glass$^{7,8)}$. However we still don’t know whether other glassy systems, especially for the fragile glass show the same kind of behavior. According to the reports by Ichitsubo et al.$^{9,10)}$, strong and fragile glasses show some different local structural features. They found that metallic glasses have the structural inhomogeneity in a micro structure level and two distinct regions, so called “Strongly bonded region (SBR)” and “Weakly bonded region (WBR)” exist in the glass matrix. They suggested that the volume fraction of these two regions seems to be different from each other in strong and fragile metallic glasses. More recently, Saida et al. reported the rejuvenation mechanism of the Zr$_{55}$Al$_{10}$Ni$_{5}$Cu$_{30}$ metallic glass and they figured out that the $\beta$-relaxation region, which is thought to be corresponding
to the WBR region, mainly relates to the recovery\(^0\). If so, the recovery behavior of the strong and fragile metallic glasses should be different from each other, though the clear difference has not been discussed yet. Therefore, it is of great interest to investigate the rejuvenation behavior of the fragile glass.

In this study, we investigate the rejuvenation phenomenon on the well-known fragile glass of Pd\(_{42.5}\)Cu\(_{30}\)Ni\(_{7.5}\)P\(_{20}\)\(^{(3)}\), from the viewpoints of the rejuvenation ability in relation to the local structure by the specific heat and viscoelastic measurements. The final goal of the present work is to clarify the rejuvenation behavior of the Pd\(_{42.5}\)Cu\(_{30}\)Ni\(_{7.5}\)P\(_{20}\) metallic glass, comparing with that of the Zr\(_{50}\)Cu\(_{40}\)Al\(_{10}\) metallic glass.

2 Experimental methods

The ribbon with a cross section of \(-1.0\times0.02\) mm\(^2\) (as-spun), and the disk samples with a diameter of 3 mm, height of \(-1\) mm (as-cast) with a composition of Pd\(_{42.5}\)Cu\(_{30}\)Ni\(_{7.5}\)P\(_{20}\) were prepared by the melt spinning and copper mold casting techniques, respectively. The Zr\(_{50}\)Cu\(_{40}\)Al\(_{10}\) ribbon with a cross section of \(-0.8\times0.025\) mm\(^2\) (as-spun) and the disk samples with a diameter of 4, 5 mm and height of \(-1\) mm (as-cast) were also prepared for the reference by the melt spinning and tilt casting techniques, respectively. Thermal properties were examined with differential scanning calorimetry (DSC) (Perkin Elmer DSC8500) under a heating rate of 20 K/min. Both samples were annealed in an induction heating furnace. To prevent the oxidization during the annealing, the samples were wrapped with aluminum foil. In the present study, the two kinds of samples with different thermal histories were prepared. One is a “relaxed” sample, which was obtained by annealing the as-spun/cast glass at 1.05 T\(_g\) (i.e. 1.05 times higher than the glass transition temperature) for 2 min followed by slow cooling at 20 K/min. The other is a “recovery annealed” sample, in which the relaxed glass was annealed again at 1.05 T\(_g\) for 2 min followed by rapid cooling. The rapid cooling was performed by blowing He gas directly to the sample holder and the rate is estimated to be \(-200\) K/min for Pd\(_{42.5}\)Cu\(_{30}\)Ni\(_{7.5}\)P\(_{20}\) and \(-250\) K/min for Zr\(_{50}\)Cu\(_{40}\)Al\(_{10}\). The heating rate was set at 20 K/min for these processes. The specific heats of the as-spun/cast, relaxed and recovery annealed samples were measured by DSC with a heating rate of 20 K/min. The indentation test was conducted with a square pyramid shaped diamond indenter for each disk sample to investigate the rejuvenation phenomenon from the mechanical point of view. To remove the oxidation layer, mirror like polishing was performed on the surface of the sample in advance. The maximum applied load was 300 mN for Pd\(_{42.5}\)Cu\(_{30}\)Ni\(_{7.5}\)P\(_{20}\) and 100 mN for Zr\(_{50}\)Cu\(_{40}\)Al\(_{10}\). The loading, holding at the maximum load and unloading times were set at 10 s. The viscoelastic properties such as the normalized loss modulus \(E''/E_\alpha\) and the normalized storage modulus \(E'/E_\alpha\) were measured with dynamic mechanical analysis (DMA) under isochronal and isothermal modes, respectively. The isochronal measurement was conducted under a heating rate of 5 K/min and a frequency of 1 Hz. For the Pd\(_{42.5}\)Cu\(_{30}\)Ni\(_{7.5}\)P\(_{20}\) metallic glass, the \(E''/E_\alpha\) measurement of the heat treated sample (annealed at 458 K for 7 hours for the relaxed sample) was also carried out to analyze the \(\beta\)-relaxation behavior. The isothermal measurement was performed under a frequency of 1 Hz at 458 K for the Pd\(_{42.5}\)Cu\(_{30}\)Ni\(_{7.5}\)P\(_{20}\) metallic glass and at 585 K for the Zr\(_{50}\)Cu\(_{40}\)Al\(_{10}\) metallic glass. These annealing temperatures are corresponding to \(-0.8T_g\) for each alloy. All the viscoelastic measurements were conducted with ribbon samples under tensile mode with a fixed strain amplitude of \(\varepsilon=0.05\%\).

3 Results

3.1 Rejuvenation Ability of Pd\(_{42.5}\)Cu\(_{30}\)Ni\(_{7.5}\)P\(_{20}\) Metallic Glass

Figure 1(a) shows specific heat measurement results of the Pd\(_{42.5}\)Cu\(_{30}\)Ni\(_{7.5}\)P\(_{20}\) metallic glass in the as-spun, relaxed and recovery annealed states. All of them show a drastic increase of the specific heat around 560 K, which is
Rejuvenation Behavior and New Classification of β-relaxation Region in Pd-based Metallic Glass

The obtained relaxation enthalpies were \( \Delta H_{\text{as-(spin, cast)}} \) and \( \Delta H_{\text{recovered}} \) and recovery annealed, \( \Delta H_{\text{recovered}} \) samples were obtained by the following equations:

\[
\Delta H_{\text{as-(spin, cast)}} = \int_{T_R}^{T_{\text{gast}}} (C_p^{\text{relaxed}} - C_p^{\text{as-(spin, cast)}}) dT
\]

\[
\Delta H_{\text{recovered}} = \int_{T_R}^{T_{\text{gast}}} (C_p^{\text{relaxed}} - C_p^{\text{recovered}}) dT
\]

Here, \( T_R \) is a room temperature, \( C_p^{\text{relaxed}}, C_p^{\text{as-(spin, cast)}}, \) and \( C_p^{\text{recovered}} \) are specific heats of the relaxed, as-(spin, cast), and recovery annealed samples, respectively. This value is corresponding to the surrounded area of the two curves (relaxed - as-(spin, cast) or recovered) as shown in Fig. 1(a).

\( \Delta H_{\text{as-(spin, cast)}} \) of the Pd\(_{42.5}\)Cu\(_{30}\)Ni\(_{7.5}\)P\(_{20}\) metallic glass is calculated to be 9.7 J/g, while the relaxation enthalpy decreases by recovery into 3.2 J/g. Here, we derived the recovery amount by the following equation:

\[
\text{Recovery amount(\%)} = \frac{\Delta H_{\text{recovered}}}{\Delta H_{\text{as-(spin, cast)}}} \times 100
\]

From this Eq. (2), it is calculated to be 33% in the Pd\(_{42.5}\)Cu\(_{30}\)Ni\(_{7.5}\)P\(_{20}\) metallic glass. To validate its data, the recovery amount of the disk samples was also investigated. The obtained relaxation enthalpies were \( \Delta H_{\text{as-(spin, cast)}} \) = 8.2 J/g and \( \Delta H_{\text{recovered}} \) = 2.5 J/g, both of the values were lower than that of the ribbon samples. This might be due to the lower cooling rate of the cast sample than the ribbon sample. Nevertheless, the calculated recovery amount was 30% which was closer to the ribbon data of 33%, indicating that the derived value was appropriated for the Pd\(_{42.5}\)Cu\(_{30}\)Ni\(_{7.5}\)P\(_{20}\) metallic glass. In the same way, the obtained enthalpies of each state and the calculated recovery amount for the Zr\(_{50}\)Cu\(_{40}\)Al\(_{10}\) metallic glass are \( \Delta H_{\text{as-(spin, cast)}} \) = 11.6 J/g, \( \Delta H_{\text{recovered}} \) = 5.1 J/g, 44%, respectively. From these results, it is obvious that the recovery amount of the Pd\(_{42.5}\)Cu\(_{30}\)Ni\(_{7.5}\)P\(_{20}\) metallic glass (33%) is significantly lower than that (44%) in the Zr\(_{50}\)Cu\(_{40}\)Al\(_{10}\) metallic glass.

Figure 2(a) shows load-displacement curves in the Pd\(_{42.5}\)Cu\(_{30}\)Ni\(_{7.5}\)P\(_{20}\) metallic glass obtained by the indentation test. The average maximum depth during 10 times of the measurements of the as-cast and the relaxed samples are 1614 (±1%) and 1593 (±1%) nm, respectively, while the recovery annealed one is 1597 (±1.1%) nm. The Martens hardness of each sample, which can be derived from the attained maximum depth, is 4258 (±1.8%), 4362 (±1.8%) and 4344 (±1.9%) N/mm\(^2\) in the as-cast, relaxed and recovery annealed states, respectively. Figure 2(b) shows load-displacement curves in the Zr\(_{50}\)Cu\(_{40}\)Al\(_{10}\) metallic glass. The calculated Martens hardness of the as-cast, relaxed and recovery annealed states are 3900 (±3.7%), 4326 (±1.5%) and 4121 (±1.9%) N/mm\(^2\). From the mechanical point of views, only 17% is rejuvenated for the Pd\(_{42.5}\)Cu\(_{30}\)Ni\(_{7.5}\)P\(_{20}\) metallic glass while it is 48% for the Zr\(_{50}\)Cu\(_{40}\)Al\(_{10}\) one.
rejuvenate than the Zr$_{50}$Cu$_{40}$Al$_{10}$ metallic glass by the present thermal and mechanical measurements.

### 3.2 Viscoelastic Measurements to Predict Internal Structure

#### 3.2.1 Isochronal Mode

As described above, it is proved that the recovery amount of the Pd$_{42.5}$Cu$_{30}$Ni$_7.5$P$_{20}$ metallic glass is lower than that of the Zr$_{50}$Cu$_{40}$Al$_{10}$ metallic glass. Then, one would expect that this may originally come from the differences of the respective intrinsic glassy structure. To investigate why the Pd$_{42.5}$Cu$_{30}$Ni$_7.5$P$_{20}$ metallic glass is more difficult to rejuvenate, we performed the viscoelastic measurement to predict each internal glassy structure and tried to clarify the origin of their differences. Figure 3(a) shows temperature dependence of the normalized loss modulus $E''/E_0$ of the Pd$_{42.5}$Cu$_{30}$Ni$_7.5$P$_{20}$ metallic glass in the as-spun, relaxed and recovery annealed states under 1 Hz. Here, $E_0$ is the storage modulus at room temperature and it is approximately $7.6 \times 10^9$ Pa in the Pd$_{42.5}$Cu$_{30}$Ni$_7.5$P$_{20}$ metallic glass. The clear shoulder peak of the signal around 460 K, which is corresponding to the $\beta$-relaxation, is observed in the curve of the as-spun sample. The intensity of the peak decreases in the relaxed sample. This result indicates that the relaxation is involved in the $\beta$-relaxation region. Furthermore, it is found that the value of the normalized loss modulus of the recovery annealed sample from 400 K to 575 K was slightly larger than that of the relaxed one. This meant that the $\beta$-relaxation region recovered through annealing. These tendencies can be also seen in the data of Zr$_{50}$Cu$_{40}$Al$_{10}$ metallic glass as shown in Figure 3(b). As mentioned in the introduction section, Saida et al. have already reported that the $\beta$-relaxation region mainly relates to the recovery in the Zr$_{40}$Al$_{10}$Ni$_{40}$Cu$_{20}$ metallic glass$^3).$ Though the $\alpha$-relaxation peak cannot be obtained for the Pd$_{42.5}$Cu$_{30}$Ni$_7.5$P$_{20}$ metallic glass in the present study (i.e. too fragile to keep the shape at $T_g$ during the test), we can demonstrate the same mechanism, namely, the rejuvenation phenomenon strongly correlates to a change in the atomic configuration in the $\beta$-relaxation region. However, unlike the Zr-based metallic glass, it should be noted that the $\beta$-relaxation signal of the Pd$_{42.5}$Cu$_{30}$Ni$_7.5$P$_{20}$ metallic glass still remains clearly even in the relaxed sample (It was denoted as “remained peak” in Fig. 4). From this result, one could suggest that the relaxation is incomplete and still proceed by further annealing. Then, we conducted the isothermal heat treatment for the Pd$_{42.5}$Cu$_{30}$Ni$_7.5$P$_{20}$ metallic glass relaxed sample at $-0.8T_g$ for 7 hours with the aim of investigating the change in the signal. Figure 4 shows the normalized loss modulus $E''/E_0$ of the relaxed and heat treated samples (annealed at 458 K for 7 hours for the relaxed sample) for Pd$_{42.5}$Cu$_{30}$Ni$_7.5$P$_{20}$ metallic glass.

#### 3.2.2 Isothermal Mode

To investigate the details of the $\beta$-relaxation behavior of the Pd$_{42.5}$Cu$_{30}$Ni$_7.5$P$_{20}$ metallic glass, we performed the viscoelastic measurement in the isothermal mode at 0.8$T_g$. Since the temperature of 0.8$T_g$ is much lower...
for the α-relaxation, only the β-relaxation should be considered in the experiment, which enables us to clarify the behavior.

During the isothermal heat treatment below \( T_0 \), the structural relaxation occurs and the free volume decreases with annealing time. The time dependence of the free volume change during the relaxation has already reported by Spaepen et al. and it is called "Flow defect model" as described below\(^{(12,13)}\):

\[
\frac{dc_f}{dt} = -k_i(c_f - c_{eq})
\]

(3)

where \( c_f \) and \( c_{eq} \) are the concentration of the free volume at a certain time and at an equilibrium state, respectively. \( k_i \) is a reaction rate. During the process, the physical value also changes with time and the following equation can be derived.

\[
\frac{A(t)}{A_0} = 1 + \frac{A_{eq}}{A_0} - 1\left(1 - \exp\left[-\frac{t}{\tau}\right]\right)
\]

(4)

Here, \( A \) is a certain physical value (e.g. viscosity\(^{(14)}\), density\(^{(15)}\) etc.), \( t (= t/\tau) \) is a relaxation time. In the present study, we chose the storage modulus \( E'(t) \) as the physical value \( A \). Generally, the distribution of the relaxation time is considered in the Eq. (4), and so, the following KWW type equation can be finally obtained:

\[
\frac{E'(t)}{E_0} = 1 + \frac{E_{eq}}{E_0} - 1\left(1 - \exp\left[-\frac{t}{\tau}\right]^\beta\right)
\]

(5)

where \( E_0, E_{eq} \) are the storage modulus at 0 sec and the equilibrium state, respectively. \( \beta \) (0<\( \beta \)≤1) is a stretched exponential parameter which represents the distribution of the relaxation time.

The markers in Fig. 5(a) show experimental data of the \( E'(t)/E_0 \) of the Pd\(_{42.5}\)Cu\(_{30}\)Ni\(_{7.5}\)P\(_{20}\) metallic glass. As can be seen here, the increasing ratio of the \( E'(t)/E_0 \) is more significant for the as-spun sample and the value is almost 1.06 around 15000 sec. On the other hand, for the relaxed and recovery annealed samples, the values are about 1.02 and 1.04 at the same period. The fitting curves derived from the Eq. (5) are also inserted in Fig. 5(a). As shown in the figure, the experimental data can be well fitted by using three parameters, \( E_{eq}/E_0, \tau \) and \( \beta \), indicating that the relaxation behavior of each sample is described by the free volume change. Accordingly, the classical free volume theory governs their behavior. In the same way, the data of the Zr\(_{50}\)Cu\(_{40}\)Al\(_{10}\) metallic glass was also shown in Fig. 5(b). Table 1 shows obtained fitting parameters of each sample. For the Zr\(_{50}\)Cu\(_{40}\)Al\(_{10}\) metallic glass, \( E_{eq}/E_0 \) for the as-cast, relaxed and recovery annealed states are 1.21, 1.05, 1.12, respectively. As can be seen, an abrupt change is observed in the Zr\(_{50}\)Cu\(_{40}\)Al\(_{10}\) metallic glass. Whereas the change is small, in which they are 1.08, 1.04 and 1.06 for the three states, respectively, in the Pd\(_{42.5}\)Cu\(_{30}\)Ni\(_{7.5}\)P\(_{20}\) metallic glass. The same tendency can be observed for the relaxation time. These results suggested that the Pd\(_{42.5}\)Cu\(_{30}\)Ni\(_{7.5}\)P\(_{20}\) metallic glass is more weakly dependent on the free volume change in the β-relaxation region than the Zr\(_{50}\)Cu\(_{40}\)Al\(_{10}\) metallic glass. Furthermore, the stretched exponential parameter \( \beta \) of the as-spun Pd\(_{42.5}\)Cu\(_{30}\)Ni\(_{7.5}\)P\(_{20}\) metallic glass is 0.89 which is larger than that (0.64) of the Zr\(_{50}\)Cu\(_{40}\)Al\(_{10}\) metallic glass. This means that the distribution of the relaxation mode in the β-relaxation.
region is initially much narrower in the Pd$_{42.5}$Cu$_{30}$Ni$_{7.5}$P$_{20}$ metallic glass, and it is nearly 1 for the relaxed and recovery annealed samples (i.e. the relaxation mode is almost saturated after annealing). Nevertheless, as already mentioned in the isochronal viscoelastic measurement result, the shoulder peak of the $E''/E_0$ around the $\beta$-relaxation region still remains in the relaxed and heat treated samples (see Fig. 4), and that is more significant than a Zr$_{50}$Cu$_{40}$Al$_{10}$ metallic glass in the relaxed state (see Fig. 3).

4 Discussion

4.1 New Classification of $\beta$-relaxation Region in Pd$_{42.5}$Cu$_{30}$Ni$_{7.5}$P$_{20}$ Metallic Glass

To explain the discrepancy as mentioned in the end of the session 3.2.2, we newly classify the $\beta$-relaxation region in the Pd$_{42.5}$Cu$_{30}$Ni$_{7.5}$P$_{20}$ metallic glass into two areas as illustrated in Fig. 6. As the figure shows, we divided the region in terms of whether the rejuvenation is occurred or not. Since we discussed the phenomenon by using the recovery annealing process, which follows only by the thermodynamic rule, then our classification can be readily interpreted as whether the area is concerned with the thermodynamic free volume change $\Delta v_f$. In short, one is an area where it has a potential to annihilate/introduce the free volume thermally (Fig. 6 1) and the other does not (Fig. 6 2). The change of $E''/E_0$ between the as-spun, relaxed and recovery annealed states in Fig. 3(a) is mainly attributed to the former area while the remained peak around 460 K seems to be contributed by the latter area. This assumption also explains why the relaxation mode in the $\beta$-relaxation region is initially narrow in the Pd$_{42.5}$Cu$_{30}$Ni$_{7.5}$P$_{20}$ metallic glass regardless of the clear peak remained in the $E''/E_0$. As can be seen in Fig. 5(a), the time dependence of the $E''/E_0$ is well expressed by the Eq. (5), which is originally based on the free volume theory, and so, we can regard the change of $E''/E_0$ as the free volume contribution terms. Namely, the results of isothermal measurement are reflected by the characteristics of the former area, and the contribution of the latter area does not concern directly. It can be considered that the volume fraction of the former area is low, which leads to the large stretched exponential parameter $\beta$ even in the as-spun sample. In the case of the Zr$_{50}$Cu$_{40}$Al$_{10}$ metallic glass, the remained peak of $E''/E_0$ cannot be observed as clear as that of the Pd$_{42.5}$Cu$_{30}$Ni$_{7.5}$P$_{20}$ metallic glass in the relaxed state. It indicates that such a distinctive area does not exist and the $\beta$-relaxation region consists mostly of the free volume correlated area, resulting in the drastic change of $E_{aq}/E_0$, $\tau$ and $\beta$. As described here, our assumption consistently demonstrates the $\beta$-relaxation behavior in the Zr$_{50}$Cu$_{40}$Al$_{10}$ metallic glass as well.

Therefore, it was concluded that the volume fraction of the free volume correlated area is initially low in the $\beta$-relaxation region in the Pd$_{42.5}$Cu$_{30}$Ni$_{7.5}$P$_{20}$ metallic glass and that makes the relaxation and rejuvenation more difficult to occur through the thermal treatment. The distinct $\beta$-relaxation signal observed in the isochronal viscoelastic measurement tends to suppose that the relaxation/rejuvenation is easy to occur, but it should be noted that their phenomena are only dependent on the free volume correlated area. In case of the Pd$_{42.5}$Cu$_{30}$Ni$_{7.5}$P$_{20}$ metallic glass, the area independent on the free volume change also exists in the region. It is tentatively predicted that the area seems to be associated with a peculiar local glassy structure in the Pd$_{42.5}$Cu$_{30}$Ni$_{7.5}$P$_{20}$ metallic glass.

In the previous studies, $\beta$-relaxation behaviors of the Pd-Cu-Ni-P systems have already been discussed. Pelletier et al. suggested that the $\beta$-relaxation signal observed in the Pd$_{40}$Cu$_{27}$Ni$_{10}$P$_{20}$ metallic glass is attributed to the strong atomic bonding between metallic (Pd, Ni, Cu) and non-metallic (P) atoms$^{[18]}$. More recently, Yu et al. reported the chemical influence on the $\beta$-relaxation region of the Pd$_{40}$(Cu$_{17}$Ni$_{13}$)$_{60}$P$_{20}$ system$^{[17,18]}$ and found that the addition of Cu promotes $\beta$-relaxation region. They finally concluded that the similarly large negative enthalpy of mixing leads to
the pronounced β-relaxation. Park et al. investigated the local atomic configurational differences between the Pd_{40}Cu_{30}Ni_{10}P_{20} and Pd_{40}Ni_{40}P_{20} metallic glasses by using anomalous X-ray scattering measurement\(^{(19)}\). They revealed that the Pd_{40}Cu_{30}Ni_{10}P_{20} metallic glass exhibits a particular structural feature around Cu, namely, tetragonal dodecahedral packing, which is different from the typical prismatic packing of metal atoms for the Pd_{40}Ni_{40}P_{20} metallic glass. According to the dynamic mechanical analysis results from Yu et al., the former shows more distinct β-relaxation signal than the latter. This may suggest that the tetragonal dodecahedral packing in Pd-Cu-Ni-P metallic glasses, including Pd_{42.5}Cu_{30}Ni_{7.5}P_{20} alloy system, might play an important role in the β-relaxation signal. Also, it is interesting to note that the β-relaxation signal of Pd_{40}Ni_{40}P_{20} and Zr-Cu-Al metallic glasses are more alike with each other\(^{(7)},^{(18)}\). It suggests that, though the fundamental local structure are totally different (i.e. the former exhibits prismatic packing while the latter shows icosahevron like packing), β-relaxation signal might be annihilated by heat treatment even in the Pd_{40}Ni_{40}P_{20} metallic glass.

Additionally, it is of great importance to note that the signal is clearly observed in the viscoelastic measurement. Yet, two broad weak exothermic peaks can be seen around 400 and 540 K, which are thought to be derived from the chemical short range ordering (CSRO) process and structural relaxation near \(T_g\) suggested by previous report\(^{(20)}\). The corresponding peak is not remarkably detected in the specific heat measurement (see Figs. 1(a) and 3(a)). This indicates that the remained peak cannot be seen clearly by the heat treatment but can appear intensively by applying the periodic external stress. Therefore, it is suggested that the area independent on the free volume change is recognized as the “mechanically activated area” while the other is corresponding to the “thermally activated area”. Actually, Pelletier et al. have already referred to the symptom of the “mechanically activated area” in the Pd_{42.5}Cu_{30}Ni_{7.5}P_{20} metallic glass\(^{(16)}\). They argued that when a periodic stress is applied, the cluster units can be oriented in the stress field and a relaxation phenomenon can occur at an appropriate frequency in a β-relaxation region. They also mentioned that the phenomenon presents the similarity with the Snoek effect observed in certain crystalline materials. Though the slight difference exists against their view, namely, in our model, β-relaxation region consists of not only the mechanically activated area but also thermally activated area, the similarity is clearly observed in each study.

The latest relaxation studies revealed that the β-relaxation can be regarded as the ‘cage-breaking’ events and the α-relaxation is a consequence of the percolation of the events\(^{(21)}\). Each ‘cage-breaking’ event is defined as the activation of the loosely bonded region caged within their elastic surroundings. From this viewpoint, one could expect that the cage structure in the β-relaxation region of the Pd-Cu-Ni-P metallic glass is so strong that only a weakly part can be responded to the heat treatment, which is corresponding to the “thermally activated area”. On the other hand, the framework of the cage is too strong to break only by the heat treatment but is activated by an external mechanical stimulation, that is “mechanically activated area”. The origin of the newly defined area is still unknown (e.g. Are there any relationship between the local atomic configuration and the cage structure? / the mechanically activated area?). However, our findings will provide the beneficial information for rejuvenation studies.

### 5 Conclusions

We discussed the details of rejuvenation behavior of the Pd_{42.5}Cu_{30}Ni_{7.5}P_{20} metallic glass by using the as-spun/cast, relaxed and recovery annealed samples. It was revealed that the Pd_{42.5}Cu_{30}Ni_{7.5}P_{20} metallic glass is more difficult to rejuvenate than the Zr_{65}Cu_{27}Ni_{10} metallic glass. The results of viscoelastic measurement indicated that the β-relaxation peak of the Pd_{42.5}Cu_{30}Ni_{7.5}P_{20} metallic glass still remains clearly even in the relaxed state, suggesting that there is another region embedded in the β-relaxation region. Then, we newly classified the region into two areas for the Pd_{42.5}Cu_{30}Ni_{7.5}P_{20} metallic glass in terms of rejuvenation. One is in correlation to the free volume annihilation and introduction by annealing (i.e. thermally activated area) and the other is not (i.e. independent on the free volume change, mechanically activated area). We concluded that the lower rejuvenation ability of the Pd_{42.5}Cu_{30}Ni_{7.5}P_{20} metallic glass may come from a low volume fraction of the former area. Also, it was predicted that the region independent on the free volume change arises from the peculiar local structure. The present study can help to solve the recent important question of “what governs the rejuvenation behavior” and may provide the universal information for the research subject on the thermal rejuvenation in metallic glasses.

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