Crystallization Behavior of Thermally Rejuvenated Zr\textsubscript{50}Cu\textsubscript{40}Al\textsubscript{10} Metallic Glass

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The recovery annealing technique was used to clarify the crystallization behavior of a rejuvenated Zr\textsubscript{50}Cu\textsubscript{40}Al\textsubscript{10} metallic glass. Specific heat and thermal expansion measurements showed that the glassy states of fast cooled and recovery annealed samples are almost identical from the energetic and volumetric points of view. Dynamic mechanical analysis also suggested that their internal microstructures resemble each other. These results indicate that the glassy state and the structure can be controlled according to the final cooling conditions from the supercooled liquid region. However, a clear difference of the incubation time for crystallization was observed between the fast cooled and recovery annealed samples, implying that thermal accumulation seems to mostly correlate to the crystallization rather than to atomic diffusion through the newly created excess free volume in the rejuvenated sample. In addition, a transmission electron microscopy image of the sample, performed on double sets of the recovery annealing process, shows a precipitation of the crystalline phase with approximately 50 nm in diameter in the amorphous matrix. These results suggest that the recovery annealing independently leads to two different thermal paths, one towards structural rejuvenation and the other towards crystallization. The high-resolution transmission electron microscopy result of the recovery annealed sample indicates that these two regions co-exist in the amorphous matrix.

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1. Introduction

Recently, structural rejuvenation has attracted much attention from researchers owing to its great importance in the metallic glass fields. For instance, it has been reported that a change in ductility by the rejuvenation is exhibited compared with the as-cast and relaxed states\textsuperscript{1–5}). This result clearly indicates that the mechanical properties can be controlled by the rejuvenation. More recently, Meng et al. reported that a Zr-based metallic glass after high pressure torsion (HPT) showed distinct ductility and a recovery amount of \(-30\%\) on the Young’s modulus was attained compared with the as-cast sample\textsuperscript{5}).

While the rejuvenation has been intensively studied from the mechanical point of view, as described above, detailed discussions on the thermal aspects, especially the crystallization behavior, are still lacking. It is known that the rejuvenation is a process to result in an unstable glassy state and obtain a less dense random packing, while crystallization is a completely opposite process (i.e., toward stable and high density packing states) from the energetic and volumetric points of view. Hence, one would expect that the rejuvenation and crystallization are strongly correlated with each other. Indeed, Saida et al. have already reported that different nucleation and grain growth rates of nanoscale quasicrystals are observed in a Zr\textsubscript{65}Al\textsubscript{23}Ni\textsubscript{12}Cu\textsubscript{12.5}Pd\textsubscript{5} metallic glass with several relaxation states\textsuperscript{6}). This result clearly suggests that a certain relationship exists between the rejuvenation and crystallization behaviors. However, the discussions regarding the glassy state and the crystallization process of the rejuvenated metallic glass are still not sufficient. Most of the rejuvenation methods (e.g., high pressure torsion\textsuperscript{2,3}), shot peening\textsuperscript{4}), irradiation\textsuperscript{5}) and so forth) are based on a mechanical or physical damage inducing process (e.g., severe plastic strain, irradiation and so forth) to acquire a high rejuvenation amount. In short, a destruction of the initial glassy structure or a significant deformation (i.e., large change of shape) are always inevitable when these methods are applied. This may prevent a proper discussion on the rejuvenation. Actually, the rejuvenation effect by these methods are mostly non-isotropic (e.g., not the whole but just a part of the sample), which makes the situation more complex. Moreover, these methods can generally be applied only for a certain shaped sample, which limits an investigation in a multilateral manner. All these factors hide the real nature of rejuvenation, resulting in the difficulty for discussion with relation to the crystallization.

Meanwhile, we have focused on a thermal approach, especially a recovery annealing technique, to discuss the rejuvenation\textsuperscript{9,10}). This process is based on annealing a relaxed sample in a supercooled liquid region followed by rapid cooling. Unlike the mechanical paths, this is just a thermal path, namely it is non-destructive for the sample, so we can obtain a sound glassy structure even after the process. Since the glassy state should be fixed only by a thermodynamic function more easily and properly from a thermal viewpoint. In addition, we can eliminate the concern of a non-isotropic effect arising from a homogeneous process. Furthermore, this thermal rejuvenation process can be applied widely to any shaped samples such as rod, disk and ribbon.

In our previous studies, we successfully observed the rejuvenation phenomenon and clarified its mechanism\textsuperscript{9,10}). In the present study, we attempt to investigate the detailed crystallization behavior of the rejuvenated glass. Generally, the crystallization process of metallic glass is known to be governed by atomic diffusion. Qiao et al. reported that the crystallization mechanism of metallic glass under an isothermal annealing condition was well described by the Johnson-Mehl-Avrami models, and they revealed from the Avrami exponent that the crystallization was mainly a diffusion-controlled type\textsuperscript{11}). Gallino et al. also suggested that the crystallization was controlled by the diffusion of the midsize atoms\textsuperscript{12}). They measured the apparent activation energies of...
primary crystallization and finally concluded that the atomic
mobilities controlled the process. As described here, many
reports have shown that atomic diffusion is one of the major
factors to determine the crystallization behavior. Hence, it is
readily assumed that the higher the free volume, the easier
the sample will be crystallized, because the atomic diffusion
appears to be more preferred through the atomic moving
space. However, these details have not yet been confirmed.
There is a case where the as-cast sample, which is thought to
have a higher free volume, shows much higher resistance
compared with the heat treated (relaxed) sample, suggesting
that containing a higher free volume does not always explain
the ease for crystallization. This fact suggests that their rela-
tionship cannot be easily explained. Therefore, it is worth
discussing the origin of crystallization and the relationship
to the free volume. Since our rejuvenation method can intro-
duce the free volume into the sample with heat treatment,
the crystallization nature of the metallic glass can be clari-
fied through an investigation of the behavior of a rejuvenated
sample.
For this purpose, we prepared Zr-based metallic glass
samples with almost the same cooling path from the super-
cooled liquid region, where they are initially produced by a
different thermal history. We also discussed the mutual rela-
tionship between the crystallization behavior and the rejuve-
nated glassy state through several thermal analysis and TEM
observations.

2. Experimental Procedures
An alloy ingot with a nominal composition of
\( \text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10} \) was prepared by arc melting in an argon atmo-
sphere. The alloy was re-melted several times to ensure ho-
mogeneity. The rod and disk samples with a diameter of
4 mm, and heights of approximately 8 mm and 1 mm, re-
spectively, were prepared by cutting the glassy alloy ob-
tained by tilt casting. The rod was for the thermal expansion
measurements while the disk was for the specific heat mea-
surement, incubation time measurement and internal struc-
ture observation. The ribbon samples with a cross section of
\(-0.8 \times 0.025 \text{ mm}^2\) were also prepared by the melt spin-
ing technique. The thermal properties of each sample were
examined by differential scanning calorimetry (DSC) under
a heating rate of 0.33 K/s (glass transition temperature
\( T_g \approx 702 \text{ K} \), crystallization temperature \( T_c \approx 784 \text{ K} \), super-
cooled liquid region \( \Delta T_c \approx 82 \text{ K} \)). All of the samples were annealed in a DSC or induction heating furnace. To prevent
the possible oxidation during annealing, the samples were
wrapped with an aluminum pan or foil. In the present study,
three kinds of samples with different thermal histories were
prepared. One was the “fast cooled” sample; the as-cast sam-
ples were annealed at 740 K for 2 min followed by rapid cool-
ing at \(-4.17 \text{ K/s} \). Here, the annealing temperature of 740 K
corresponded to 1.05 times higher than the \( T_g \). Another was
the “relaxed” sample; the as-cast sample was annealed at
740 K for 2 min followed by slow cooling at 0.17 or 0.33 K/s.
The third was the “recovery annealed” sample; the
relaxed sample (740 K–2 min–0.17 or 0.33 K/s cooling) was
annealed again at 740 K for 2 min, then cooled with a
higher cooling rate of \(-4.17 \text{ K/s} \). For all heating processes,
the rate was set at 0.33 K/s. It should be noted that the cool-
ning rates of the fast cooled and recovery annealed samples
were intentionally unified to enable discussion of the glassy
state more easily. The specific heat of each disk sample was
measured with DSC under a heating rate of 0.33 K/s. The
linear thermal expansion coefficient was measured for each
sample. An applied load of 15 cN and a heating rate of
0.083 K/s were selected. The viscoelastic properties, such as
the normalized loss modulus \( E'/E_u \), where \( E' \) is a loss mod-
ulus and \( E_u \) is an unrelaxed storage modulus which is as-
sumed to be almost equal to the storage modulus \( E' \) at room
temperature, were also measured by dynamic mechanical
analysis (DMA) using ribbon samples. The heating rate and
frequency were 0.083 K/s and 1 Hz, respectively. To investi-
gate the crystallization behavior, the incubation time was
measured with isothermal DSC at 720, 730, 740, and 750 K.
Moreover, a “double sets recovery annealed” sample, which
was annealed twice with the two sets of conditions of
740 K–2 min–0.33 K/s cooling and 740 K–2 min–
\(-4.17 \text{ K/s} \), was prepared in advance and its micro-
structure was observed by transmission electron microscopy
(TEM). The detailed local structure of the fast cooled, re-
axed and recovery annealed samples were also observed by
high-resolution transmission electron microscopy (HRTEM)
with an aberration corrector.

3. Results
Figure 1 shows the specific heat measurement results of
the fast cooled, relaxed and recovery annealed samples. A
clear endothermic reaction, corresponding to a glass tran-
sition, is observed at around 700 K in each curve. The peaks
around 720 K, which correspond to enthalpy relaxation, are
also observed in all curves. In the case of the fast-cooled
sample, the curve follows almost the same path as that of the
relaxed sample up to 600 K; however, it deviates below the
line of the relaxed state at higher temperature. The enthalpy
relaxation of the fast-cooled sample is less than that of the
relaxed sample, indicating that the former seems to be the
less relaxed state compared with the latter\(^{13,14}\). These differ-
cences observed in the specific heat curves of the fast cooled
and relaxed samples upon heating may arise from differing
cooling paths from the supercooled liquid region.
Accordingly, at the higher cooling rate, more of the glass
adopts the less relaxed state. Interestingly, the curve of the
recovery annealed sample almost overlapped with that of the
fast-cooled sample. To compare the enthalpy of relaxation of
the fast cooled and recovery annealed samples, we calcu-
lated \( \Delta H_{\text{Fast cooled/Recovery annealed}} \) from the following equation:

\[
\Delta H_{\text{Fast cooled/Recovery annealed}} = \int (C_p_{\text{Relaxed}} - C_p_{\text{Fast cooled/Recovery annealed}})dT
\]  

(1)

where \( C_p_{\text{Relaxed}}, C_p_{\text{Fast cooled}}, C_p_{\text{Recovery annealed}} \) are the specific
heats of the relaxed, fast cooled and recovery annealed sam-
ples, respectively. These values can be derived from the area
between the two curves (relaxed – fast cooled or recovery annealed), as shown in the
figure. The \( \Delta H_{\text{Fast cooled}} \) was calculated to be 3.4 \text{ J/g}, while
\( \Delta H_{\text{Recovery annealed}} \) was 2.8 \text{ J/g}. This result suggests that the
amount of heat released from these two states during the measurement is almost the same. It should be noted that these are obviously prepared with different thermal histories, namely, the recovery annealed sample has an extra heat treatment (740 K–2 min–0.33 K/s) compared with the fast-cooled sample; however, they show almost the same thermal heat release behavior upon heating. This reveals that the cooling rate from the supercooled liquid region determines the subsequent glassy state.

Figure 2 shows the apparent linear expansion coefficient of each sample. As can be seen from the relaxed sample (740 K–2 min–0.17 K/s cooling), the curve did not follow the other two curves of the fast cooled and recovery annealed samples above 510 K. The value of the apparent linear expansion coefficient of the relaxed sample was almost constant from 550 K to 650 K, and then increased significantly. Unlike the curves of the fast cooled and recovery annealed states, a structural relaxation could not be clearly observed during the heating of the relaxed sample, resulting in an absence of a decrease of the apparent linear expansion coefficient in that temperature range\textsuperscript{15}. From this almost constant range, we calculated the linear expansion coefficient and 1.3 × 10\textsuperscript{-5}/K was obtained for the Zr\textsubscript{50}Cu\textsubscript{40}Al\textsubscript{10} metallic glass. This value is relatively close to that of 1.1 × 10\textsuperscript{-5}/K for the Zr\textsubscript{55}Al\textsubscript{10}Ni\textsubscript{5}Cu\textsubscript{30} metallic glass reported elsewhere\textsuperscript{16}, suggesting that our data seems to be appropriate. The increase of the apparent linear expansion coefficient observed around 700 K corresponds to the onset of the glass transition, where the excess free volume is introduced into the system with a volume expansion. The most important point is that the curves of the fast cooled and recovery annealed samples trace almost the same track, as observed from the specific heat curves. We calculated the uniaxial thermal expansion rate $\Delta L / L_{\text{Fast cooled}} / \text{Recovery annealed}$ using the following equation:

$$\Delta L / L_{\text{Fast cooled}} / \text{Recovery annealed} = \int (\alpha_{\text{Relaxed}} - \alpha_{\text{Fast cooled}} / \text{Recovery annealed}) \,dT$$

where $\alpha_{\text{Relaxed}}$, $\alpha_{\text{Fast cooled}}$, and $\alpha_{\text{Recovery annealed}}$ are the apparent linear expansion coefficients of the relaxed, fast cooled and recovery annealed samples, respectively. The $\Delta L / L_{\text{Fast cooled}}$ was calculated to be 2.2 × 10\textsuperscript{-4}, and $\Delta L / L_{\text{Recovery annealed}}$ was 2.0 × 10\textsuperscript{-4}, indicating that the temperature dependence of their thermal expansion rates was almost the same during the heating. This supports our insight that the glassy state could be determined mostly by the final cooling rate from the supercooled liquid region.

From these specific and thermal expansion measurements, we successfully confirmed that the glassy states of the fast cooled and recovery annealed samples were nearly the same from the energetic and volumetric points of view. It is very important to determine how these metallic glasses crystallize upon heating. If a glassy state is almost the same by unifying the final cooling rate from the supercooled liquid region, the crystallization behaviors should also be approximately the same.

Figure 3 shows the time-temperature-transformation (TTT) diagrams of the relaxed, fast cooled and recovery annealed samples. Here, the incubation time was determined by the onset of crystallization during the isothermal DSC. Table 1 summarizes the incubation times of each sample at several holding temperatures. Although a slight difference was observed between the relaxed and fast-cooled samples, namely, the incubation time for the relaxed sample was slightly shorter than that of the fast-cooled sample at 750 K, the TTT curves were similar. This arose from almost the same thermal path, that is, both samples were heated once from the as-cast state (only the cooling process was different), leading to the very slight difference in the incubation time. However, the TTT curve of the recovery annealed sam-
Table 1 Incubation time for crystallization of the relaxed, fast cooled and recovery annealed samples.

<table>
<thead>
<tr>
<th>Temperature $T$ (K)</th>
<th>Relaxed</th>
<th>Fast cooled</th>
<th>Recovery annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>720</td>
<td>50</td>
<td>50</td>
<td>42</td>
</tr>
<tr>
<td>730</td>
<td>20</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>740</td>
<td>7.5</td>
<td>7.5</td>
<td>5.3</td>
</tr>
<tr>
<td>750</td>
<td>2.5</td>
<td>2.7</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Discussion

As described above, the glassy states of the fast cooled and recovery annealed samples were similar from the energetic and volumetric points of view. Meanwhile, the isothermal DSC results indicated that their crystallization behaviors were different and the crystallization was more likely to occur for the recovery annealed glass than the fast-cooled sample. Here, we consider the crystallization process of the recovery annealed glass by assuming two cases as follows. The first case is that the rejuvenation and crystallization proceed in the same place at different times, i.e., they occur in a time sequence (Fig. 4 (i)). The rejuvenation occurs by the recovery annealing and at the same time, some amounts of free volume is introduced into the amorphous matrix. The atomic diffusions become more activated than before owing to the adequate space from the newly created excess free volume. Finally, atomic rearrangement, that is, ordering, starts in the area containing the excess free volume, which results in crystallization. In contrast, the other case is that the rejuvenation and crystallization occur simultaneously at a different place, i.e., they occur concurrently, see Fig. 4 (ii). In this case, the correlation between rejuvenation and crystallization would be weaker. Here, it is assumed that the crystallization proceeds constantly by a thermal accumulation during the heat treatment; however, it is almost independent on the excess free volume area that was newly created during the rejuvenation.

Before we start the discussion on which type of process, namely "atomic diffusion through the newly created excess free volume" or "thermal accumulation", mainly governs the crystallization of the rejuvenated sample, we first will consider the internal structure of the samples with a similar glassy state, i.e., fast cooled and recovery annealed samples. To investigate their microstructures, we conducted the viscoelastic measurement, as shown in Fig. 5 (the data of the relaxed sample is also included as a reference). The horizontal axis is normalized by $T_p$, which is the peak temperature of the obtained loss modulus at 1 Hz. Although a slight difference is observed at around 0.8$T_p$, it is obvious that these curves trace almost identical paths compared with that of the relaxed sample, indicating that their structures resemble each other. If the crystallization is only governed by the atomic diffusion through the newly created excess free volume, the behaviors of the fast cooled and recovery annealed samples should be almost identical, since their microstructures are similar. However, as shown in Fig. 3, the isothermal DSC results clearly show that the incubation times for these two samples are quite different, suggesting that the real crystallization nature of the recovery annealed sample would be weakly affected by the atomic diffusion through the newly created excess free volume.

To consider the effect of thermal accumulation, we investigated whether the crystallization was enhanced by repeated recovery annealing. Figure 6 shows the TEM observations of the samples in the single (a) and double (b) sets of the recovery annealing process. Here, the double sets of the process mean the recovery annealing was performed twice. No clear contrast can be observed for the single process (a) whereas a distinct contrast, corresponding to the crystalline phase, was observed by repeating the recovery annealing, as shown in (b). As can be seen, several crystalline particles with approx-
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approximately 50 nm in diameter were precipitated in the matrix. Hence, we can confirm that the crystallization certainly occurs with increasing the number of times for the recovery annealing process and the thermal accumulation definitely assists the progress of crystallization. The same phenomenon was observed for the Pd22.5Cu30Ni27.5P20 metallic glass (not shown here), which is known to have a higher resistance to the crystallization than Zr50Cu40Al10, suggesting that the enhancement of crystallization by thermal accumulation might be universal for metallic glass systems. This process also well explains why the as-cast sample was the most difficult to crystallize of all the others, as mentioned in the Introduction section. The as-cast sample does not undergo any heat treatment, which leads to a high resistance to the crystallization.

To investigate the crystallization process further, we conducted the HRTEM observations of the three samples, as shown in Fig. 7. From the image of both the relaxed and fast-cooled samples (Fig. 7(a) and (b), respectively), the typical salt-and-pepper like pattern can be seen, indicating that the structure kept the single amorphous state. The fast Fourier transform (FFT) of the image also confirmed the amorphous structure. These results are consistent with the TTT investigation. However, the faint contrast can be barely seen in the recovery annealed sample (Fig. 7(c)). The size of the region was too small to be detected from the normal TEM image (see Fig. 6(a)). It is generally known that the critical radius where nuclei become an embryo is around $r_c \sim 1$ nm$^{17}$, and the area size of the present study is around 5 nm. Therefore, the area would be recognized as the initial stage of crystallization. Since the rejuvenation is surely observed in the recovery annealed sample, as proved by the specific heat and thermal expansion measurements, our result suggests that both regions, the thermally stable and less stable areas, can exist at the same time.

From these results, we conclude that even if the glassy state seems to be similar, the crystallization behavior can be totally different and it is influenced mostly by the thermal accumulation rather than the atomic diffusion through the newly created excess free volume. Moreover, it is evident that the rejuvenation and crystallization, which are known to be opposite phenomena from the energetic and volumetric points of view, can exist simultaneously in the amorphous matrix.

Although the crystallization behavior of the recovery annealed sample becomes clear, the most important question as to why the fast cooled and recovery annealed samples exhibit the different crystallization behaviors still remains. Here, we propose that the crystallization presented in this study is too small (i.e., early stage) to significantly influence the remaining amorphous structure. Although a few ordering areas can be observed, as shown in Fig. 7(c), most of the microstructure still consists of a glassy structure, as evidenced by Fig. 6(a). Therefore, the rejuvenation and crystallization are proposed to be almost independent of each other in the early stage of crystallization. In such cases, crystallization can be negligible and, as the remaining glass experienced the same cooling path, it shows similar glassy features macroscopically. This is the reason why almost the same behaviors, although the dynamic mechanical analysis shows a slight difference, are observed in the fast cooled and recovery annealed samples from the specific heat and thermal expansion measurements. However, when the crystallization starts, such ordering/crystalline area cannot be ignored even though it is small and on the microscopic scale. In contrast, this local ordering plays an important role in enhancing the crystallization. Therefore, the shorter incubation time for crystallization in the recovery annealed sample compared with the fast-cooled sample is seen in the isothermal DSC.

It has already been suggested that the initial stage of the crystallization of the metallic glass may proceed by reflecting the structural fluctuation of the glassy structure$^{18-20}$. Hirata et al. reported that metallic glass initially shows a local fluctuation in the internal structure including an ordered area of 1–2 nm in size$^{18}$. Although the volume fraction of the ordered area is estimated to be low, at most 20%$^{21}$, they concluded that the area can be thought to play an important role in the early stage of crystallization. Ichisubo et al. also reported that the microstructure of a partially crystallized area was observed in the Pd-based metallic glass with use of ultrasonic annealing below or near the glass transition temper-
perature\textsuperscript{19}. They used the resonance effect to enhance the atomic motions in the $\beta$-relaxation region and they finally confirmed that crystallization can proceed through the structural heterogeneity.

As already mentioned above, we successfully observed the two kinds of different areas (i.e., one is an ordered area, which finally results in the crystallization, while the other is a rejuvenated area (see Fig. 4 (ii))) through the recovery annealing. This result supports the crystallization process that was previously suggested. Namely, the two kinds of different areas we observed may originate from the intrinsic heterogeneity of the internal glassy structure. Through the overall annealing, the ordered area is enhanced and proceeds towards crystallization (i.e. thermal accumulation), whereas through the final rapid cooling, the other area is rejuvenated. Our results show that the fluctuation certainly exists in the initial amorphous matrix and we successfully separated the matrix into two areas (i.e., the rejuvenated and crystallization regions) independently through the recovery annealing technique. Additionally, we clarified that the newly created excess free volume has little do with the crystallization behavior, while thermal accumulation, which contains ordering/diffusion, strongly affects the initial crystallization.

An uncertain issue that remains is which area (representatively, $\alpha$-relaxation, $\beta$-relaxation regions) is mostly associated with the origin of the crystallization. Figure 5 clearly suggests that rejuvenation mainly arises from the recovery of the $\beta$-relaxation region. It is still unclear whether the faint difference observed in the normalized loss modulus $E''/E_0$ of the fast cooled and recovery annealed samples at 0.8$T_p$ relates to the initial crystallization of the recovery annealed samples. Further research to determine where the crystallization initially starts should be conducted.

It should be mentioned that even now, the nature of the crystallization of metallic glasses (e.g., what is the largest trigger for the crystallization? Where is the starting point of ordering/crystallization in the glassy matrix? In which area does the thermal history mostly accumulate? etc.) has not been clarified. However, our present results surely provide a hint towards clarifying the underlying questions and provide universal information for the research subject on amorphous or glassy materials.

5. Conclusions

The present study was undertaken to investigate the crystallization behavior and mechanism of rejuvenated Zr$_{55}$Cu$_{40}$Al$_{10}$ metallic glass by thermal analysis and TEM observations. The specific heat and thermal expansion measurements suggest that the energy and volume states of the fast cooled and recovery annealed samples are similar, while both samples experience the same final cooling rate from the supercooled liquid region but a different thermal history. The dynamic mechanical analysis almost supports the results from the structural point of view. However, the incubation time for crystallization of the recovery annealed sample is much shorter than that of the fast-cooled sample. This result indicates that it is not the atomic diffusion through the excess free volume newly created during the rejuvenation but rather the thermal accumulation that strongly affects the crystallization for the rejuvenated sample. TEM observation of the sample after the double sets of the recovery annealing process undoubtedly supports this result. We confirm that the rejuvenation (i.e., disordering, being unstable) and crystallization (i.e., ordering, being stable) areas can exist at spatially different places in the amorphous matrix based on the HRTEM results. Our findings provide beneficial information to answer the underlying questions concerning the crystallization of random atomic configuration systems.

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