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Solid Argon Precipitation in a Metallic Glass: Does Free-Volume Help?

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We find that small particles (~ 1 nm) of solid argon are densely precipitated in a $\text{Pd}_{40}\text{Ni}_{20}\text{P}_{20}$ metallic glass matrix after argon ion-beam irradiation with an accelerating voltage of 4 keV. This is in sharp contrast to the case of noble-gas implantations into crystalline metals, for which high-energy beam (50–300 keV) has been essential to promote creations of precursor defects, such as voids or vacancy aggregates for initial confinements of noble-gas atoms. Therefore, the present low-energy implantation implies that the argon confinements have occurred at pre-existing low-density regions in the glass matrix, providing an important clue to phenomenological free-volume entities.

Keywords: Metallic Glass, Electron Microscopy, Microstructure

Noble-gas atoms exist as monoatomic molecule gas at ordinary temperature/pressure conditions, and generally cryogenic and/or high-pressure techniques are required to solidify these gases.[1] Interestingly, even at room temperature the noble gases form small solid precipitates when implanted into metals (e.g. aluminum) by ion-beam irradiations,[2–5] since the noble-gas elements are essentially inert and hence insoluble to the host matrix. These noble-gas precipitates are typically at nanometer dimensions and effectively stabilized by the relevant matrix cavity that acts as a high-pressure cell.[5] Namely, the host cavity provides a pseudo-high-pressure, P , yielded to balance with the surface tension γ of the matrix, described as $P = 4\gamma/d$ where d is a diameter of the spherical cavity (note that the pseudo-pressure originates from a shrinking force against the unit normal surface of the cavity, resulting in an effective internal pressure to the substances that are embedded into the cavity). This fact in turn indicates that local precursors to form such nanometer-scale cavity are essential for the noble-gas precipitations, and therefore high-energy ion-beam implantations with typical accelerating voltages 50–300 keV [2–5] have been commonly used to promote creations of voids or vacancy aggregates, which provide sufficient spaces for the initial condensation of noble-gas atoms. So

far Ne, Ar, Xe and Kr were indeed precipitated as solid particles in the crystalline metal of mostly aluminum, and these nanometer-scale solids were successfully probed by electron diffraction,[2–5] electron energy loss spectroscopy (EELS) [2] and high-resolution electron microscopy.[4,6–8] Note in particular that phase-contrast lattice imaging clearly showed up distinct fringes of the Xe precipitates grown epitaxially on the host aluminum lattice,[4] providing direct evidences about their crystalline order and even structural dynamics (e.g. coalescence behaviors [7]).

In the present paper, we describe that Ar atoms precipitate as disordered/amorphous solids in a metallic glass $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$, the feature of which has clearly emerged by utilizing the state-of-the-art scanning transmission electron microscopy (STEM) combined with EELS at the sub-nanometer scale. The remarkable fact is that the present Ar implantations have been achieved, for the first time, with significantly low-energy Ar ion-beam irradiations during conventional thin-specimen preparations for STEM (known as *ion-milling*; the present Ar solids have been accidentally discovered rather than a well-designed experiment). Consequently, the present results have significant implications on the pre-existing cavity/void precursors in the glass structure, providing a direct clue to phenomenological free-volume entities

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[9–11] whose realistic configurations/distributions are not fully understood yet.

Master alloys of nominal composition $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ were synthesized by arc melting pure metals and pre-sintered Pd-P alloy with B_2O_3 flux in a purified argon atmosphere. Ribbon specimens of metallic glass were produced by a single roller melt spinning method with the wheel rotating at a speed of approximately 40 m/s. Thin specimens for STEM observations were prepared by standard Ar ion-beam milling with an accelerating voltage of 4 keV, during which the Ar atom implantations were unexpectedly made to a total dose of approximately 2×10^{25} ions/m² (beam current 1.3×10^{-4} A, total milling time ~ 6 h). We used an aberration-corrected STEM (JEM-ARM200F) operated at an accelerating voltage of 200 kV, equipped with the EELS detector to carry out elemental mapping with a high-spatial resolution less than 0.2 nm.

Figure 1(a) shows the high-angle annular dark-field (HAADF)-STEM image, where a large number of dark particles with an average diameter of ~ 1 nm are formed in the $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ glass matrix. Since the HAADF provides significantly enhanced atomic-number-dependent contrast [12] (Z-contrast), at first glance one may intuitively attribute the dark particles to be possibly phosphides if concerning only the constituent elements of Pd ($Z = 46$), Ni ($Z = 28$) and P ($Z = 15$). Note that these particles are hardly detectable by phase-contrast imaging (Figure 1(b)), and no distinct lattice fringes were observed at any places both in the phase-contrast and Z-contrast atomic-resolution images, as exemplified in Figure 1(b) and 1(c), respectively. Unambiguous identification of the particles comes uniquely from the high-spatial resolution EELS, which performs simultaneous acquisitions

of spectrum at each probe position during ADF imaging with STEM, generating a data-cube composed of ADF intensity map (x, y) and energy-loss spectrum (ΔE) dimensions. By summing up the spectra obtained at the dark particle positions, a distinct peak showing the presence of Ar ($L_{2,3}$ -edge: ~ 245 eV) clearly emerges in the reconstructed spectrum in Figure 2(a), while such an Ar peak becomes remarkably weak for the spectrum reconstructed using all the spectra in the entire scanned area. Details of the element distributions are confirmed in the reconstructed maps in Figure 2(b), where it is immediately noticed that the Ar enrichment indeed occurs at the dark particles in the corresponding ADF image. We here note that the other elements become reasonably deficient in the particles; the constituent elements of Pd, Ni and P (Figure 2(b)) and even the impurity oxygen (Supplementary Material, Figure S1) tend to be rejected from the particles, as confirmed by their positive cross-correlation with reference to the ADF intensity map, even though the correlations appear to be very weak (diffuse) for Ni and P owing to their insufficient signal-to-noise ratio (similar weak-correlation feature is also seen for Fe in Figure S1). On the basis of these facts, the dark particles in the HAADF image (Figure 1(a)) are evidently identified as pure Ar precipitates. It was confirmed that no particles were observed when the thin specimen is prepared not by Ar ion-milling but by electrochemical polishing, or when the very thin edge of whiskers in the as-solidified ribbon is directly used for STEM observations.

Stabilization of the present Ar precipitates in the metallic glass matrix can be understood by the pseudo-high-pressure scenario described earlier. Given the particle diameter $d \sim 1.1$ nm (Figure 1(a)) and assuming γ of the $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ glass as being 1.0 N/m (this is

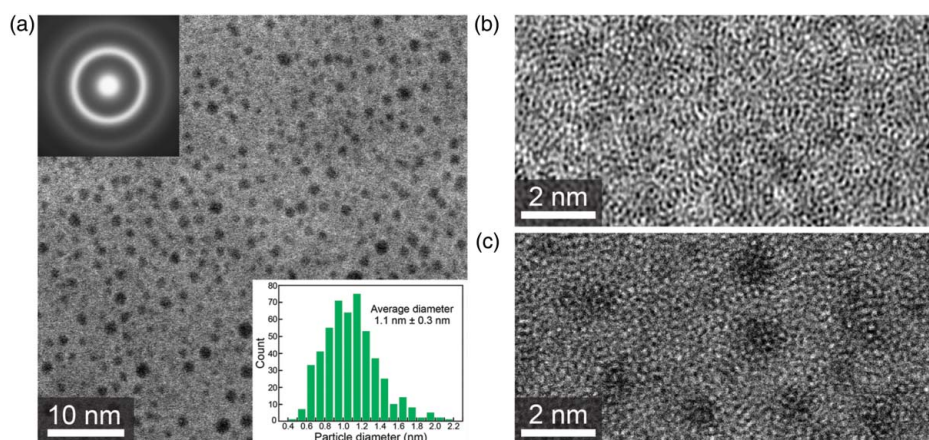


Figure 1. (a) HAADF-STEM image of a $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ metallic glass irradiated by 4 keV Ar ion-beam, commonly used for a standard ion-milling for thin-specimen preparations. Inner angle of the annular detector was set to be 70 mrad, which is sufficiently large to achieve the chemical-sensitive Z-contrast condition. Histogram of dark-particle size is constructed from ~ 500 particles, evaluating an averaged diameter of 1.1 ± 0.3 nm. Extra peaks are hardly observed in the corresponding electron diffraction pattern, which merely shows halo rings of a $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ amorphous structure. Atomic-resolution (b) phase-contrast and (c) Z-contrast images of the Ar-irradiated $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ glass. Specimen thickness of the observed region was estimated to be approximately 18 ± 2 nm based on the EELS log-ratio method.

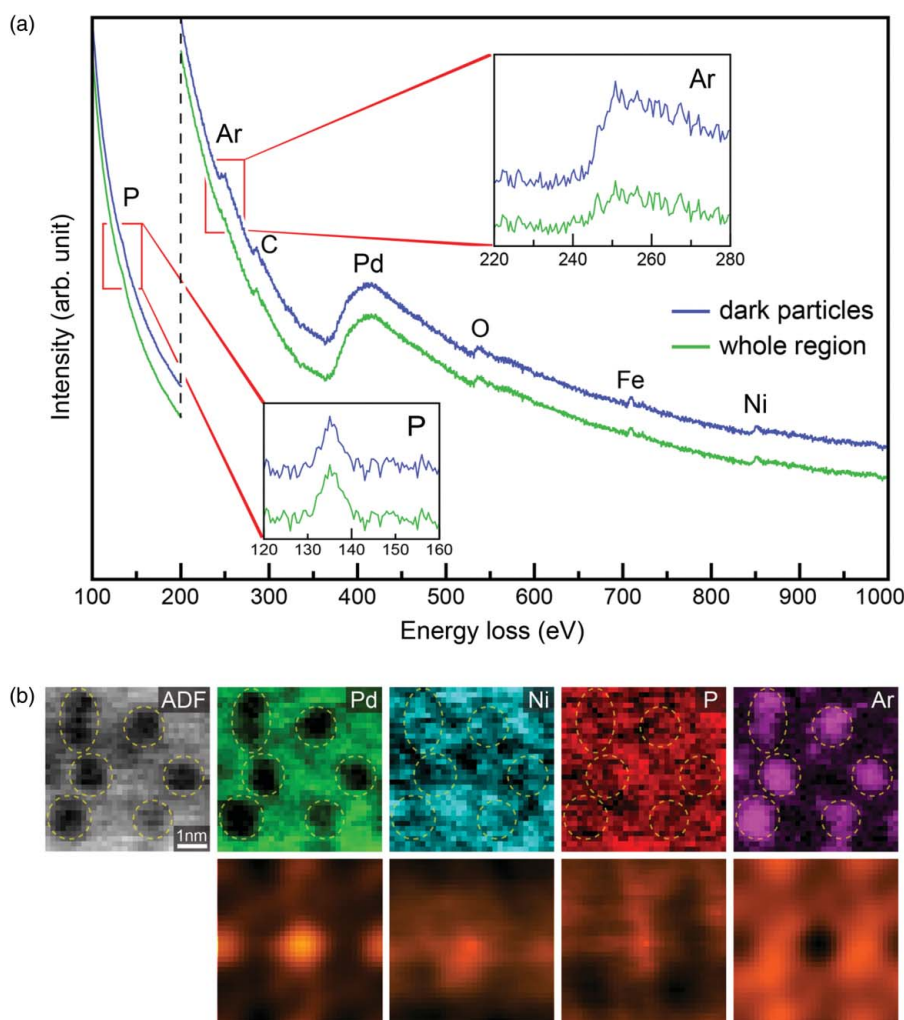


Figure 2. STEM-EELS analysis of the dark particles in Figure 1(a). Spectra and the corresponding ADF image (detector inner angle; ~ 20 mrad) were simultaneously obtained using the electron probe approximately 0.2 nm in diameter with a current of ~ 0.2 nA (~ 5.0 nA/nm²), scanned over the 5.5×5.5 nm (32×32 pixel) area with a speed of 0.1 s/pixel. Multivariate statistical analysis using MSA software (HREM Research Inc.) was applied for the obtained spectra to reduce the noise effectively. (a) Reconstructed EEL spectra; shown in blue is obtained by summing 161 spectra taken at the dark-particle regions in the ADF image, while green is a summation of all the 1024 spectra in the whole scanned region (intensities are normalized for comparison). Enlarged peaks are inserted for P and Ar, after removing the background according to conventional power-law function extrapolations. Carbon originates from contaminations during scanning the electron beam, and oxygen and iron are involved as impurities in the present specimen. (b) Reconstructed element maps of Pd, Ni, P and Ar. Cross-correlation maps with reference to the ADF image are shown at the bottom, showing distinct positive/negative correlations between ADF intensity and Pd/Ar map. Maps of the impurity elements are shown in the Supplementary Material, Figure S1.

determined for the high-temperature liquid [13] and hence may differ somewhat from the precise γ value of the room-temperature glass), the internal pressure provided by the relevant matrix cavity is estimated to be approximately 3.6 GPa, which is sufficiently beyond the critical pressure for Ar solidification at room temperature (about 1.15 GPa,[1] which can be yielded by the cavity size up to $d \sim 3.5$ nm with $\gamma \sim 1.0$ N/m). In fact, in Figure 1(a) there are no particles larger than this maximum size. It should be noted that the present Ar solid precipitates are not distinctly crystalline but significantly disordered or amorphous, as in the following reasons. Suppose that

the Ar particles form face-centered-cubic (*fcc*) structure under a high pressure,[1] the lattice parameter is expected to be about $a = 0.48$ nm with the pseudo-pressure of 3.6 GPa. Then, the relevant diffraction peaks and/or the occasional *fcc* lattice fringes should be observed; though, neither of these appears both in the diffraction pattern (Figure 1(a)) and the high-resolution images (Figure 1(b) and 1(c)). Besides, the Ar precipitates may well reveal faceted morphology if having distinct crystalline order;[14] this is evidently not consistent with the spherical morphology of the present precipitates (Figure 1(a)). These considerations lead to a conclusion

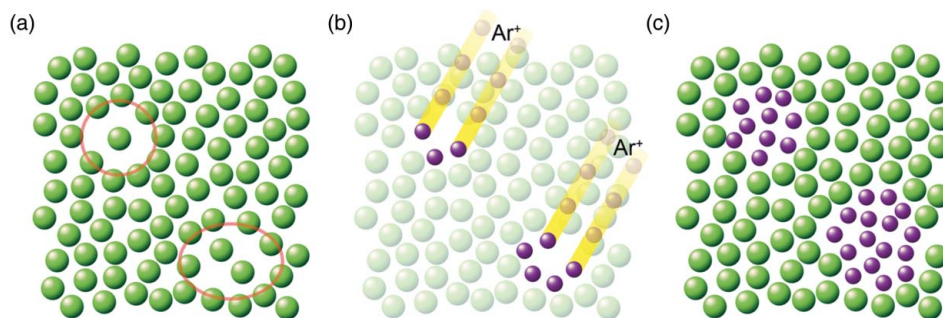


Figure 3. Schematic illustrations of an effective Ar trapping at ‘free-volume’ in the metallic glass matrix. The free-volume structure is represented as local low-density configurations (a), where the primary confinements of Ar atoms are achieved (b) and finally small Ar solids precipitate as being stabilized by nanometer-scale cavities (c).

that the structure of the present Ar precipitates is highly disordered or amorphous. Perhaps this may naturally be expected from the fact that the present particles are embedded in an amorphous matrix. Remember that there are at most 50–60 Ar atoms contained in the particles as small as 1 nm in diameter (under nearly dense-packing conditions), and more than half of the constituent atoms are exposed to the particle surface and directly attached to the host atoms of the amorphous matrix. In such a specific condition, the Ar atoms in the particles may take the form of amorphous as an energy-minimized configuration. The icosahedral clusters,[15] e.g. so-called as Mackay-type,[16] may also be favored so as to fit the spherical morphology. Unfortunately, further details of the Ar atom configurations within the particles are hardly determined by the present experiments. It is also noteworthy that the embedded Ar atoms could be a rather fluid state (i.e. less dense condition), and hence the noble-gas precipitates were frequently referred to as ‘bubbles’.[4] In fact, Ne in the crystalline Al matrix was likely to be of fluid state since there were no distinct diffraction peaks,[2] and Xe precipitates in Al crystals behaved fluidly with partial crystalline order at the particle/matrix interfaces.[8]

Occurrence of the present Ar precipitations with the remarkably low-energy ion-beam implantations gives significant implications in terms of local structures of a metallic glass. As mentioned earlier, noble-gas precipitations in crystalline metals essentially require the high-energy ion-beam (50–300 keV) irradiations in order to generate precursory defects of voids or vacancy aggregates, to which the noble-gas atoms are primarily confined. The present accelerating voltage of 4 keV is far below by 1–2 orders of magnitude for promoting such internal voids in the matrix, suggesting that the Ar precipitation has occurred at pre-existing void-like low-density regions in the glass. Such local low-density zones are believed to be intrinsically involved in the glass structures, known as ‘free-volume’ that had been originally introduced as a phenomenological entity to understand thermodynamic [9,10] and mechanical [11] behaviors of

the glass. Although realistic features of the free-volume are not fully understood, yet its structural concept can be schematically represented as in Figure 3(a). Suppose that most of the relevant zones have been used for Ar confinements, the random distributions of the particles (Figure 1(a)) may well trace an initial distribution of the free-volume in the specimen. Given that the penetration depth of the implanted Ar atoms is about 8 nm (calculated by Monte-Carlo simulation [17] with the present accelerating voltage 4 keV; details are described in Supplementary Material, Figure S2), the number density (ND) of the Ar particles is estimated to be about $\sim 1.0 \times 10^{-2} \text{ nm}^{-3}$. This might be comparable with a typical ND of the free-volume zone in the glass; i.e. ND is only reported for the polymer glass to be a order of $\sim 1.0 \text{ nm}^{-3}$, [14] according to which ND of the metallic glass can be estimated as being a order of 10^{-1} – 10^{-2} nm^{-3} if simply weighted by their relevant total free-volume ratio ($\sim 10\%$ [14] and $\sim 0.1\%$ [18,19] for polymer and metallic glasses, respectively. Note that for these glasses, mean volume of one free-volume (v_f [9]) is reasonably assumed to be roughly in a same order of magnitude). As for the comparison of their total free-volumes, the volume fraction of the Ar particles (V_{Ar}) may overestimate the pre-existing total free-volume (V_{fv}), since V_{Ar} is a consequence of initial confinements and subsequent growth of the Ar precipitates; see Figure 3. The latter stage indeed involves expanding the original free-volume regions into cavities, which is perhaps accomplished by subsequent assembling of intrinsic vacancies. Although a precise value of V_{fv} cannot be deduced from V_{Ar} , it is nevertheless noteworthy that V_{Ar} is estimated to be about $\sim 0.8\%$ based on the present particle distributions (Figure 1(a)), the value of which is reasonably comparable with $V_{fv} \sim 0.3\%$ reported for the Pd-based bulky glass phases [18,19] (note that V_{fv} of the present rapidly cooled ribbon should be larger than that of the bulky glass prepared by slow-cooling; therefore, the true V_{fv} of the present specimen can even be closer to the present V_{Ar}). To test further the idea of an effective Ar trapping at free-volume zones in the $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ glass, we check possible

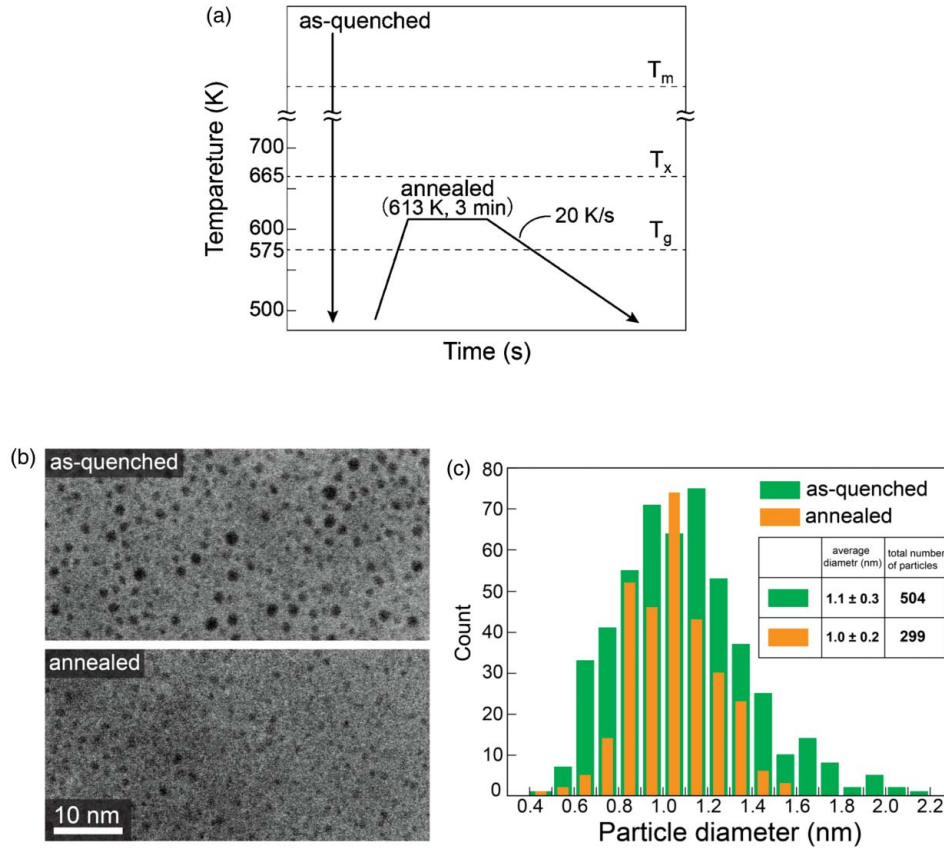


Figure 4. (a) Subsequent heating–cooling cycle applied to the as-quenched $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ ribbon specimen. Specimen is heated above glass transition temperature ($T_g \sim 575$ K) up to 613 K (supercooled liquid state), holding there for 3 min, followed by cooling with 20 K/s. (b) HAADF-STEM images of as-quenched (part of Figure 1(a)) and subsequently annealed $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ glass specimens. (c) Histogram of dark-particle size in the annealed specimen (yellow) is constructed from ~ 300 particles, evaluating an averaged diameter of 1.0 ± 0.2 nm. Histogram for the as-quenched specimen (green; same as that inserted in Figure 1(a)) is also shown for comparison.

changes of the Ar precipitation behaviors after the subsequent heating–cooling cycle across glass transition (T_g , Figure 4(a)), during which reductions of the free-volume take place due to a slower cooling (20 K/s) than the original fast-cooling (approximately $\sim 10^{4-5}$ K/s) during the melt spinning solidification. As confirmed in Figure 4(b) and 4(c), it is evident that the total number of the distinct Ar particles is reasonably decreased after the heating–cooling treatment across T_g ; the ND and the volume fraction become about $5.8 \times 10^{-3} \text{ nm}^{-3}$ and 0.4%, respectively. This reasonably supports a validity of the idea that the Ar precipitations have occurred at the free-volume zones in the glass.

We find that the Ar precipitations by low-energy ion-beam irradiation do not occur for all the metallic glasses; e.g. preliminary observations show that there are no Ar precipitates in some of the Zr-based metallic glasses (e.g. $\text{Zr}_{70}\text{Ni}_{30}$ and $\text{Zr}_{70}\text{Cu}_{30}$) irradiated by the same Ar ion-beam as the present condition. This suggests that, although a further study is necessary, local variations of the free-volume structures are perhaps substantially different between the present Pd–Ni–P and the

Zr-based glass phases. Regarding the issue, we note an implicative fact that they reveal remarkably different relaxation behaviors. A secondary relaxation with low activation energy (~ 1.0 eV), referred to as slow- β type,[20] is distinctly observed for the Pd–Ni–P glasses [21] (‘fragile’ type [22]), while the Zr-based glasses reveal predominantly the common α type relaxation (glass transition) driven by higher activation energy of 5–10 eV (‘strong’ type,[23] though accompanying weak β relaxation signs that are almost buried in the relevant α relaxation peak tails). Therefore, it may be presumed that the cavities necessary for the Ar confinements have grown at the local slow- β relaxation centers, where the atoms are reasonably mobile via vacancy-mediated diffusion jumps [24] that can be activated by ion bombardments (the activation energy of the slow- β relaxation for the present $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ glass is determined to be about 1.47 eV, as described in Supplementary Material, Figure S3). For such low-energy relaxation events, the relevant free-volume zone is likely to possess sufficiently sparse atomic configurations. Existence of such local configurations is in fact suggested as ‘holes’ [25] in the

Pd₅₂Ni₃₂P₁₆ glass, and the related high atomic mobility regions (weakly-bonded soft regions) are also confirmed in terms of a microstructural heterogeneity [26] in the Pd_{42.5}Ni_{7.5}Cu₃₀P₂₀ glass. In case that the critical ion-beam energy for the noble-gas confinements is turned out to be very sensitive to slight local density differences (i.e. different pore structural types), energy-variable ion-beam irradiations may be possibly used as an effective probe for tracing the free-volume variations [25,27] responsible for the different relaxation events of the metallic glass. By combining with the positron annihilation technique, it provides an interesting testing ground for elucidating details of the realistic free-volume features in various metallic glasses [28].

Supplementary online material. A more detailed information on experiments is available at <http://dx.doi.org/10.1080/21663831.2013.869270>.

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