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A local structure change of bulk $Pd_{40}Ni_{40}P_{20}$ glass during full relaxation

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Abstract

The change in the amorphous structure of bulk $Pd_{40}Ni_{40}P_{20}$ glass during structural relaxation was examined by an anomalous X-ray scattering (AXS) experiment with energies near the Ni K-absorption edge. It was confirmed by differential scanning calorimetry that the sample reached a meta-stable state (a fully relaxed state) with an equilibrium free volume concentration after annealing for about 1×10^4 s at 563 K and 4×10^4 s at 557 K just below the glass transition temperature $T_g = 567$ K. The structural changes on the progression toward a fully relaxed state were examined in samples annealed for 1×10^3 and 2×10^4 s at 563 K (glass A), and for 3.2×10^3, 1×10^4 and 7×10^4 s at 557 K (glass B). The structural analysis revealed that the coordination number of Ni–Ni like atom pairs increased with annealing time and that of Ni–Pd, unlike atom pairs, decreased. Meanwhile, the coordination number N_{PNi} of P–Ni atom pairs and the nearest neighbor distance r_{PNi} did not show a remarkable variation. However, prolonged annealing of 7×10^4 s at 557 K induced a remarkable change in N_{PNi} and r_{PNi}.

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Keywords: Amorphous metals; Metallic glasses; Crystallization; Structure; X-rays

1. Introduction

The Pd–P based glass shows high resistance to crystallization and is reported to reach a fully relaxed state by prolonged annealing just below glass transition temperature [1,2]. The isothermal relaxation process in $Pd_{40}Ni_{40}P_{20}$ glass was investigated by Koerbugge et al. by means of Young's modulus [3]. They reported that chemical ordering occurs in an initial period of relaxational, and thereafter the quenched-in free volume starts to annihilate to the equilibrium level. It is interesting how the amorphous structure changes during relaxation toward a fully relaxed state. However, stable metallic glass is generally a multi-component system and it is difficult to examine the local amorphous structure. In addition, it is generally known that the change in the amorphous structure is very small during relaxation. Therefore, careful experiments and techniques are necessary to realize such a specific study. Schaal et al. found [4] from neutron diffraction experiments that the structural change of $Pd_{52}Ni_{32}P_{16}$ metallic glass is more remarkable in the second nearest topological order than that in the nearest neighbor correlation. They pointed out that the second peak in the radial distribution function was largely changed after relaxation. Egami et al. reported [5] that the structure of $Pd_{40}Ni_{40}P_{20}$ bulk glass is basically described by the dense random packed structure. However, the structural change during relaxation toward a fully relaxed state was not studied systematically. In a previous study [15], we showed that the structural change in a $Pd_{41}Ni_{41}Si_{18}$ amorphous alloy, pre-annealed just before crystallization, occurred in a way to increase the Ni–Ni like atom pairs, indicating micro-phase separation, by AXS near the Ni–K absorption edge. Since this alloy system did not show a clear glass transition and high thermal

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stability, it was difficult to further perform a systematic experiment of structural relaxation behavior. The high glass forming ability of $Pd_{40}Ni_{40}P_{20}$ glass, typically appearing at a small critical cooling rate of 0.16 K/s [6], enables us to prepare the bulk sample appropriate for X-ray diffraction experiment with high precision. The objective of present research is to clarify the local change in the amorphous structure of a $Pd_{40}Ni_{40}P_{20}$ glass toward a fully relaxed state by means of an Ni-AXS experiment. By the use of an Ni-AXS experiment, we can take out three atomic correlations, Ni–Ni, Ni–Pd and Ni–P, regarding Ni atom from six atomic correlations in a $Pd_{40}Ni_{40}P_{20}$ glass.

2. Experimental procedure

A master alloy with the nominal composition of $Pd_{40}Ni_{40}P_{20}$ was prepared by sintering elements and homogenizing the melt at 1370 K for 20 h in an evacuated silica tube. The alloy was further flux-treated at 1370 K with a B_2O_3 in a silica tube for 72 h. Two bulk glass rods (*A* and *B*) with the same nominal composition were made by quenching fluxed molten alloy, approximately 11 mm in diameter and 30 mm in length, into cooled water. A piece of bulk glass was used to prepare the ribbon sample with a cross section of about 2.0×0.04 mm^2 by melt spinning technique. The amorphous nature of the sample was checked by X-ray diffraction and differential scanning calorimetry (DSC). The structural relaxation process was investigated by thermal analysis with a Perkin Elmer Pyris 1 DSC. Seven bulk glass plates, approximately $10 \times 22 \times 1$ mm^3, were cut from different glass rods. The isothermal relaxation process was examined at both 563 and 557 K for glass plates. A normal scattering experiment with X-ray energy (17.5 keV) near Mo Kα radiation, and an anomalous X-ray scattering (AXS) experiment just under the Ni–K absorption edge (8.3317 keV) was performed with a strong radiation source in the Photon Factory at the High Energy Accelerator Research Organization in Tsukuba. The details of the AXS experiment were reported elsewhere [7]. The density of bulk glass necessary for the structure analysis was measured by Archimedes's method using toluene as a working fluid. The density of the bulk sample was 9.405 and 9.409 g/cm^3 at room temperature for glass A and glass B in as-quenched state. After reaching a fully relaxed state, density changed to 9.415 and 9.418 g/cm^3 at room temperature, respectively. However, variation is the order of 0.1 in the unit of 1 nm^{-3} and is almost negligible, so we used the density of the fully relaxed sample for annealed samples.

3. Diffraction theory

The environmental radial distribution function $RDF_{Ni}(r)$ is given as Eq. (1)

$$RDF_{Ni}(r) = 4\pi r^2\rho_0 + \frac{2}{\pi}\int Q\Delta i(Q)\sin(rQ)\mathrm{d}Q, \tag{1}$$

where ρ_0 is the mean number density of the sample. The environmental interference function $\Delta i(Q)$ is defined as Eq. (2) [7] using the partial structure factor $S_{Nij}(Q)$ as shown below:

$$\Delta i(Q) = \frac{\{I_{coh}(Q,E_{far}) - \langle f^2(Q,E_{far})\rangle\} - \{I_{coh}(Q,E_{near}) - \langle f^2(Q,E_{near})\rangle\}}{C_{Ni}\{f'_{Ni}(E_{far}) - f'_{Ni}(E_{near})\}W(Q)}, \tag{2}$$

where $W(Q) = \sum_j^3 C_j \Re e\{f_j(Q,E_{far}) + f_j(Q,E_{near})\}$. The function $f_j(Q,E) = f_0(Q) + f'(E) + \mathrm{i}f''(E)$ is the atomic scattering factor of *i*-element and anomalous dispersion terms f' and f'' are the correction to normal scattering, where i is the imaginary unit. Parameters used in the calculation are summarized in Table 1.

4. Results

The DSC scan indicated that the glass transition temperature T_g is approximately 576 K with a heating rate of 0.67 K/s. The DSC experiment exhibited that the absorption peak height in the DSC curve appearing on glass transition increased with time, and it saturated after annealing for about $t_f = 1 \times 10^4$ s at 563 K and 4×10^4 s at 557 K. This result shows that the quenched-in free volume reached an equilibrium concentration [8] and is referred to as the fully relaxed state. Fig. 1 shows $Qi_{as}(Q)$ for the normal scattering experiment of as-quenched samples (glass A) and the difference $\Delta Qi(Q) = Qi_{an}(Q) - Qi_{as}(Q)$ between as-quenched glass and one relaxed at 563 K (glass A) and 557 K (glass B). The relaxation for a relatively short time, 1×10^3 s at 563 K and 3.2×10^3 s at 557 K, shows a change in $\Delta Qi(Q)$ similar to previous reports [9,10,15], appearing typically in the first peak behavior that the intensity of as-quenched $Qi(Q)$ decreases in a lower Q side of peak and increases in a higher Q side of peak. This means that the atomic correlation at a longer distance disappears and one at a shorter distance increases during relaxation. However, the sample annealed for 1×10^4 s at 557 K, relatively close to a fully relaxed state at 557 K, shows a change in $\Delta Qi(Q)$ unreported so far. To examine, in detail, the local structure change during isothermal relaxation, the AXS experiment was performed near the Ni–K absorption

Table 1
Anomalous dispersion terms used in calculation of $RDF_{Ni}(r)$

Energy	f'_{Pd}	f''_{Pd}	f'_{Ni}	f''_{Ni}	f'_P	f''_P
Ni far-edge 8.0317 keV	−0.0718	3.950	−3.000	0.511	0.284	0.437
Ni near-edge 8.3067 keV	−0.0881	3730	−5.480	0.481	0.274	0.408
Near Mo Kα 17.5000 keV	−1.185	1.005	0.287	1.110	0.0900	0.0943