Development of in-house fast X-ray diffraction apparatus and its application to the supercooled liquid Pd$_{40}$Ni$_{10}$Cu$_{30}$P$_{20}$ alloy

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Abstract

A fast X-ray diffraction apparatus has been developed for obtaining the local structures of bulk metallic glasses at the supercooled liquid state by applying the Debye–Scherrer camera geometry in combination with a curved position sensitive proportional counter. This arrangement makes it possible to eliminate the time loss due to angular motion of a counter and to do a very short time X-ray measurement when using the conventional in-house X-ray source. The usefulness of this new apparatus was confirmed by obtaining the radial distribution functions of silicon powder and SiO$_2$ glass sample within one hundred seconds. Then, the short-range ordering structure of the supercooled liquid Pd$_{40}$Ni$_{10}$Cu$_{30}$P$_{20}$ alloy was observed as a function of time at 583 K. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Some Zr-based or Pd-based metallic glasses show wide supercooled liquid region [1,2] and their physical properties such as viscosity [3] and electrical resistivity [4] are found to change in this supercooled liquid state. Several reports such as packing densities [5], crystallization behavior of supercooled liquid [6,7], heat of mixing [8] and X-ray photoelectron spectroscopy analysis [9] have been available in order to reveal the origin of such particular behavior of these alloys. This includes the local structures of Zr [10–12], Fe [13,14] and Pd-based [15] bulk metallic glasses by the anomalous X-ray scattering (AXS) method. However, these results cannot provide any definite comment for the origin of their thermal stability, because of no information of their atomic structures at the supercooled liquid state. At the present time, structural studies of metallic glasses in the supercooled liquid state are limited to a sample that is quenched to room temperature after once it is annealed above the glass transition temperature [10,11].

A fast X-ray diffraction (XRD) apparatus has been developed using a synchrotron radiation source and some interesting results were obtained with respect to crystallization behavior [16] or structural evolution [17] of Zr-based bulk metallic glass in the supercooled liquid state. However, it is strongly requested from the limitation of beam time in a synchrotron radiation facility to develop a fast XRD apparatus in combination with the conventional in-house X-ray source. The purpose of this paper is to describe a fast XRD apparatus newly developed and the results on the structural evolution of Pd$_{40}$Ni$_{10}$Cu$_{30}$P$_{20}$ bulk metallic glass will be examined at 583 K as a function of time.

2. Experimental

The master alloy of Pd$_{40}$Ni$_{10}$Cu$_{30}$P$_{20}$ was prepared by induction melting a mixture of pure Ni and Cu metals and pre-alloyed Pd–P ingot in a purified argon atmosphere. From the master ingot, a Pd$_{40}$Ni$_{10}$Cu$_{30}$P$_{20}$ glass wire of about 0.2 mm diameter was produced. For X-ray measurements, it was sealed in a silica capillary of 0.3 mm diameter and 0.01 mm thick wall to keep its shape in annealing. Measurements in the supercooled liquid region were carried out at 583 K just above the glass transition temperature (572 K) [18].
A long experimental time, typically of several hours, is required for obtaining a whole intensity profile of non-crystalline systems such as liquids and glasses using the conventional X-ray apparatus. A part of the reasons could be attributed to the requirement for angular motion of a counter, so that we developed a fast XRD apparatus with no angular motion. Fig. 1 shows the schematic diagram of the experimental setup presently built. The basic concept of this fast XRD apparatus is based on the geometry of Debye–Scherrer camera coupled with the curved position sensitive proportional counter. The scattering intensity in the angular range up to 120° is simultaneously counted and accumulated through a multi-channel analyzer. Since no receiving slit is used in the geometry, this also contributes to the improvement of the counting rate of the scattering intensity from a sample. The camera radius is 250 mm and the angular resolution of about 3 mrad is obtained by keeping the diameter of a cylindrical sample less than 0.3 mm. This angular resolution is good enough for structural analysis of broad diffraction profile from non-crystalline materials and for identification of crystalline phases. Stainless steel plates of 0.5 mm thick were placed to cover incident and transmitted beams to exclude scattering from substances except for the sample. Air scattering was reduced by evacuating the chamber using a rotary pump.

In this work, an 18 kW rotating anode X-ray generator with molybdenum target is used as an X-ray source. Monochromatic X-ray beams were obtained by a graphite monochromator of 0002 reflection. Since the fluorescent radiation of nickel and copper is emitted from a Pd_{40}Ni_{10}Cu_{30}P_{20} sample, an iron foil of 0.02 mm thick is used for selective absorption of Ni and Cu fluorescence. In addition, an aluminum window of 0.2 mm thick of the chamber absorbs iron fluorescence emitted from the iron foil as a result of absorption of Ni and Cu fluorescence. By using these combined filters, the fluorescent radiation is diminished less than 0.4%, although about 60% of the original Mo Kα intensity is lost.

The SiC heater was placed 3 mm away from a sample to heat efficiently and to avoid scattering from the heater itself. Temperature of the heater was controlled with a thermocouple placed under the heater. The temperature of the sample was calibrated by monitoring the difference between the heater temperature and the temperature monitored by another thermocouple sealed in the capillary. With this method, the sample temperature was controlled within ±3 K.

Measured intensity profile includes the scattering intensity from silica capillary as well as Pd_{40}Ni_{10}Cu_{30}P_{20} sample. Thus, apart from the XRD measurement of the sample, an XRD measurement of the capillary alone was also made for the corrections of absorption and scattering from the capillary [19]. The scattering intensity of Pd_{40}Ni_{10}Cu_{30}P_{20} wire was converted to electron units per atom with the generalized Krogh–Moe–Norman method [20] using the X-ray atomic scattering factors, including the anomalous dispersion terms. The Compton scattering was corrected by the theoretical value [21]. Then, the interference function and radial distribution function (RDF) were computed. The details of data processing are described elsewhere [20,22].

3. Results and discussion

In order to test the capability of the newly developed XRD system for structural analysis of various materials, the measurements were performed for a silicon powder sample as a reference. Fig. 2 shows the intensity profile of silicon powder measured for 500 s. The resultant RDFs are
given in Fig. 3 and the dotted line corresponds to the calculated one using a least squares analysis to fit the experimental data. The small peaks at the left-hand side of the first peak should be considered to be ghost mainly arising from the truncation effect in Fourier transformation, as described by Warren [23]. The structural parameters of 10 coordination shells in near neighbors are summarized in Table 1 and overall agreement with those of the ideal case with diamond structure ($a = 0.5431$ nm) [24] is clearly obtained. As shown in Fig. 3 and Table 1, the experimental uncertainty mainly arising from the function effect in the Fourier transformation is known to be affected, more or less, by a summation of several pair correlation tails and their enhancement. However, it is stressed here that overall agreement for 10 coordination shells is rather good.

Furthermore, we also carried out the measurements of a SiO$_2$ glass rod of 0.35 mm in diameter in order to get an additional proof for capability of the new XRD system. Fig. 4 shows the interference functions $Q/(Q)$ of a SiO$_2$ glass sample obtained in four cases varying the experiment time from 10 to 300 s.

The resultant RDFs are given in Fig. 5. Of course there are differences in detail. It would be likely that the results of Figs. 4 and 5 are rather surprisingly good, because the essential structural features of SiO$_2$ glass are recognized in both the interference function and RDF even in case of the experimental time of 10 s. Nevertheless, it may be safely said that the minimum time required for the present SiO$_2$ sample is 100 s, because of the convergence detected in the first three correlation of Si–O, O–O and Si–Si pairs (see Fig. 5). It should also be stressed that this minimum time is much shorter than that required for the conventional angular scan method, even if we consider its variation depending on a sample composition and other experimental conditions.

The present XRD apparatus also covers the wave vector of $Q$ up to 150 nm$^{-1}$ which is wide enough to obtain a sufficiently resolved RDF. The interference refining method is widely used for estimating the short-range order parameters in non-crystalline materials. This method is based on the characteristic structural features of SiO$_2$ glass; the

![Fig. 2. X-ray diffraction profiles of silicon powder measured for 500 s.](image)

![Fig. 3. RDF of silicon powder calculated from the results of Fig. 2.](image)

![Fig. 4. Interference functions of SiO$_2$ glass measured in four cases varying the experimental times from 10 to 300 s.](image)

![Table 1](image)

|                  | Present work | Ideal case |
|------------------|--------------|------------|
| $r$ (nm)         |              |            |
| Si–Si            | 0.231 ± 0.003| 0.235      |
| Si–Si            | 0.385 ± 0.001| 0.384      |
| Si–Si            | 0.451 ± 0.002| 0.450      |
| Si–Si            | 0.550 ± 0.013| 0.543      |
| Si–Si            | 0.594 ± 0.003| 0.592      |
| Si–Si            | 0.665 ± 0.002| 0.665      |
| Si–Si            | 0.705 ± 0.003| 0.706      |
| Si–Si            | 0.768 ± 0.003| 0.768      |
| Si–Si            | 0.803 ± 0.002| 0.803      |
| Si–Si            | 0.858 ± 0.003| 0.859      |
contrast between the narrow distribution of local ordering and a complete loss of positional correlation at the longer distance [25]. For convenience, the calculated results are shown by dotted line in Fig. 4, in the 300 s case as an example. The structural parameters of atomic distances and coordination numbers obtained by this refining method are listed in Table 2 together with the conventional $\theta$–2$\theta$ XRD results [26].

Considering all these factors, the newly developed XRD system basically works well and its usefulness is not over-emphasized by obtaining the local structures of silicon powder and SiO$_2$ glass in a very short time measurement.

The fast XRD apparatus was applied to the Pd$_{60}$Ni$_{15}$Cu$_{35}$P$_{20}$ metallic glass sample when heating up to 583 K just above its glass transition temperature of 572 K and was kept isothermally at this temperature during measurements. According to Nishiyama et al. [27], the supercooled liquid state of this particular alloy glass is found to be kept at this temperature for a few 10,000 s. Thus, a whole intensity profile was obtained by accumulating counts for 200 s. Fig. 6 shows the intensity profiles of the Pd$_{60}$Ni$_{15}$Cu$_{35}$P$_{20}$ as a function of annealing time. The numerical values for time described in Fig. 6 is the beginning time of each measurement after the sample temperature reaches 583 K. Some small peaks attributed to Pd$_{13}$P$_2$ and Ni$_4$P crystalline phases are detected in the profile for 29,092 s. It may be worth mentioning that the onset time for finding crystalline phases in this work agrees well with the value reported by Nishiyama et al. [27]. No distinct difference is observed between the intensity profile in the supercooled liquid state and that for the as-quenched one. The interference functions were calculated from these intensity profiles and the RDFs were obtained. The RDF results in near neighbor region are given in Fig. 7.

Since the RDF for multi-component non-crystalline system includes many atomic pair correlations, 10 atomic pairs such as Pd–Pd, Pd–Ni and Pd–Cu, etc. in the present case, it is extremely difficult to draw any definite comment from the conventional RDF data alone. For example, a small variation might be possible at some atomic pairs owing to the relaxation in the supercooled liquid state. However, it is likely that no significant change occurs in the local structure.

![Image](image_url)

**Table 2**

| Coordination numbers, $N$, and atomic distances, $r$, for a SiO$_2$ glass sample together with those obtained by the conventional $\theta$–2$\theta$ XRD method [26] |
|---|---|---|---|
| Present work | Conventional $\theta$–2$\theta$ XRD method |
| $r$ (nm) | $N$ | $r$ (nm) | $N$ |
| Si–O | 0.160 ± 0.001 | 4.1 ± 0.1 | 0.161 ± 0.002 | 3.9 ± 0.2 |
| O–Si | 0.160 ± 0.001 | 2.0 ± 0.1 | 0.161 ± 0.002 | 2.0 ± 0.2 |
| O–O | 0.265 ± 0.001 | 6.1 ± 0.3 | 0.265 ± 0.002 | 6.1 ± 0.3 |
| Si–Si | 0.308 ± 0.001 | 4.2 ± 0.2 | 0.309 ± 0.002 | 4.0 ± 0.2 |

![Image](image_url)

**Fig. 7.** Annealing time dependence RDFs of Pd$_{60}$Ni$_{15}$Cu$_{35}$P$_{20}$ metallic glass alloy at 583 K. (a) Comparison between as-quenched state and supercooled liquid one. (b) Comparison between as-quenched state and long time annealed one which include some crystalline precipitates.
of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ metallic glass in the supercooled liquid state, because we cannot detect any significant change in RDF obtained from the sample annealing at least, within 25,507 s (see Fig. 7(a)). On the other hand, some change attributed to the precipitation of a certain crystalline phase is quite likely to start in this alloy glass, because the first peak which corresponds to the atomic distances of $\text{Pd}–\text{Pd}$ pairs (0.28 nm) becomes distinct (see Fig. 7(b)) when comparing the results of a long time annealing with the as-quenched case. This variation may be related to the certain atomic rearrangement for inducing the precipitation of $\text{Pd}_{3}\text{P}$ crystalline phase [27], although some further experiments should be required.

4. Concluding remarks

A fast XRD apparatus has been developed by introducing the Debye–Scherrer camera geometry coupled with a curved position sensitive proportional counter. This new apparatus makes possible a short time X-ray measurement for crystalline and non-crystalline materials when using the conventional in-house X-ray source. The capability of this new XRD system was demonstrated by obtaining the RDF data for silicon powder and $\text{SiO}_2$ glass with sufficient reliability.

The in situ observation of structural evolution of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ metallic glass in the supercooled liquid was successfully carried out. No significant difference is observed in the local structures between the supercooled liquid state and the as-quenched one. This clearly suggests that the structure of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ metallic glass is quite stable in the supercooled liquid state before crystallization. Thus, it would be very interesting to extend the present fast XRD apparatus to other metastable substances in order to obtain information about thermal stability or phase transformation.

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