Development of Full-field XRD (FFXRD) Imaging Method Realized in the Laboratory Using a Straight Polycapillary and in situ Observation of the Oxidation Process of Cu by Heat Treatment

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We developed a full-field X-ray diffraction (FFXRD) imaging method using a straight polycapillary realized in the laboratory that can obtain X-ray diffraction (XRD) images with a large area in a short time throughout the simple process without the synchrotron radiation facility. The FFXRD imaging instrument can obtain the XRD images of several millimeter sizes in several hundreds of seconds at each lattice plane. The positional resolution and the spatial resolution was improved by using a straight polycapillary with long type. The FFXRD imaging instrument was attached to the heat treatment system and Cu plate was heat-treated at 300°C. As an example of in situ monitoring of the change in the crystal structure distribution, a high-temperature oxidation process of Cu was observed. The XRD images of Cu, Cu₂O, and CuO at each lattice plane were obtained every hour. While the crystal structure distribution of Cu was reduced, the crystal structure distribution of Cu₂O and CuO were increased with the oxidation process of Cu by the heat treatment. The change of the crystal structure distribution near the surface by the oxidation process of Cu was confirmed. The XRD image obtained by the FFXRD imaging instrument was analyzed by micro-XRD measurements and confirmed that the FFXRD imaging instrument can accurately obtain the crystal structure distribution. In order to obtain the XRD image with a large area, the FFXRD imaging instrument that can be realized in the laboratory has advantages regarding the exposure time of X-rays and in situ analysis.

Keywords: X-ray imaging; X-ray diffraction; Polycapillary; In situ analysis

I. INTRODUCTION

Many kinds of analytical techniques concerned with the elemental composition and the crystal structure support the development of the industry. Along with the progress of nanomaterials and nanotechnologies, information of elements and crystal structures in micro and full-field area are more important. In particular, full-field analysis plays an important role in determining optimal analysis points. Various analytical methods have been developed by using X-rays that interact with substances such as transmission, scattering, reflection, and so on. For example, X-ray fluorescence (XRF) analysis of a nondestructive method enables the elemental analysis under atmospheric conditions [1, 2]. One of the characteristics is that X-ray imaging analysis called an XRF imaging method can obtain a two-dimen-
sional element distribution by using X-ray optics [3]. Recently, two kinds of XRF imaging methods have been studied. The first technique is known as a micro or nano X-ray beam scanning method [4–11]. The incident X-rays collected by X-ray focusing optics irradiate the sample. XRF from the sample is detected by a detector. The two-dimensional element distribution is constructed while scanning the incident X-rays on the sample. The second technique is known as a full-field method [12–15]. The incident X-rays irradiate the whole sample. XRF is detected in a short time by a two-dimensional detector, and the two-dimensional element distribution is constructed. The full-field method requires the X-ray optics that hold positional information of the sample to the two-dimensional detector.

Chemical reactions such as corrosions reacted on the surface are understood by obtaining the crystal structure in addition to elemental information. X-ray diffraction (XRD) imaging methods have been studied as well as the XRF imaging methods. Most of the XRD imaging methods are the scanning type called a micro-XRD imaging method. In synchrotron radiation facilities, the micro-XRD imaging methods are often used for obtaining a crystal structure distribution [16–19]. The spatial resolution reached the nanometer size [20–22], but the irradiation area of the incident X-rays was so small that takes a long time (several hours to several tens of hours) to obtain a crystal structure distribution with a large area about several millimeter sizes. To obtain the crystal structure distribution with a large area, a full-field XRD (FFXRD) imaging instrument using a two-dimensional detector was often used in the synchrotron radiation facilities [23–28]. Sakurai et al. reported the difference of the crystal structure distribution in TiO$_2$ [29]. However, the convenience of the synchrotron radiation facility has not been so good. The expedient of the FFXRD imaging instrument throughout the simple process that can be realized in the laboratory is required. In our previous study, a preliminary experiment of a FFXRD imaging instrument using a polycapillary half lens and a polycapillary plate was performed [30]. The intensity of the incident X-rays was insufficient, and the clear XRD images could not be obtained.

In this study, we developed a FFXRD imaging method realized in the laboratory using a straight polycapillary and a two-dimensional detector with a 9-kW X-ray tube that can obtain XRD images. The crystal structure distribution with a large area can be clearly confirmed throughout the simple process with an enough intensity of the X-rays. Analytical performance and in situ monitoring of the oxidation process of Cu combined with the heat treatment system will be shown. Then, the validity of the FFXRD imaging instrument was shown by comparison with micro-XRD measurements. The FFXRD imaging method was shown to be superior in terms of a large analysis area, a short exposure time of the X-rays, and in situ analysis.

II. EXPERIMENTAL

A. FFXRD imaging instrument

Figure 1 shows a photograph of the FFXRD imaging instrument which was based on SmartLab (Rigaku, Japan) for obtaining XRD images with a large area and was adopted the reflection type for measuring the surface of the bulk sample instead of the transmission type. The X-ray tube with a Cu target was operated at 45 kV and 200 mA (9 kW). The incident X-rays were monochromatized to a Cu K$_\alpha$ line by multilayer films. Two rotation arms operate the X-ray tube and a two-dimensional detector for maintaining the Bragg’s rule (the $\theta-2\theta$ condition) shown in Eq. (1).

$$2d \sin \theta = n\lambda$$  \hspace{1cm} (1)

The diffracted X-rays, which hold positional information of the sample by a two-dimensional Soller slit or a straight polycapillary, were detected by a two-dimensional detector (HyPix-3000, Rigaku), and XRD images including the crys-

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**Figure 1:** A photograph of the FFXRD imaging instrument.
tal structure distribution were constructed. HyPix-3000 (pixel size: 100 μm × 100 μm, detection area: 3000 cm², quantum efficiency: 99% at Cu Kα) had a large detection area and was suitable for the FFXRD imaging method. Additionally, attaching the heating system to the sample stage enabled an in situ analysis during the heat treatment process. Figure 2 and Table 1 show schematic diagrams and specifications of the two-dimensional Soller slit and the straight polycapillary. The two-dimensional Soller slit was composed of horizontal and vertical slits (pixel size: 698 μm × 138 μm) as indicated in Figure 2(a) and Table 1(a). The straight polycapillary had a honeycomb structure which was composed of a lot of glass capillaries [Figure 2(b)], and the diffracted X-rays from the sample were collimated. The channel diameter and the pixel size have the same meaning, and the pixel size of the straight polycapillary was 10 μm in diameter [Table 1(b)]. The diffracted X-rays through the straight polycapillary were limited to 6 mm, which corresponded to the effective diameter of the X-ray slit. Therefore, the obtained XRD images were circular in shape with the diameter of 6 mm.

B. Evaluation of the positional and spatial resolutions

The pixel size and the capillary length affect the positional resolution and the spatial resolution. The positional resolution caused by the difference in the pixel size between the two-dimensional Soller slit and the straight polycapillary was evaluated. Figure 3 shows a photograph of two pieces of the Al plates which were attached to a Si wafer with a ~500-μm gap in between. The XRD image of the Al plates holding positional information was acquired using the two-dimensional Soller slit and a long-type straight polycapillary. The incidence angle was 5°, and the diffraction angle of 2θ was adjusted to the Al (200) and (220) peaks. The exposure time of the X-rays was 300 s.

The spatial resolution of the FFXRD imaging instrument was evaluated by using short and long types of the straight polycapillary, whose dimensions are indicated in Table 1(b). The samples were Al and Cu plates. The incidence angle was 5°, and the diffraction angle of 2θ was adjusted to the Al (220) and Cu (200) diffraction peaks. The exposure time of the X-rays was 60 s. A half of the detection area was hidden by a Pb plate, and the edge of the XRD image was used for evaluating the spatial resolution. The difference of the spatial resolutions by the short and long straight polycapillary was compared.

C. In situ XRD imaging of oxidation process of Cu plate with heat treatment

The oxidation process during the heat treatment was ob-

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<th>Table 1: Specifications of (a) a two-dimensional Soller slit and (b) a straight polycapillary (short and long type).</th>
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<td>(a) Two-dimensional Soller slit</td>
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<td>Horizontal slit space</td>
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<td>Vertical slit space</td>
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<td>Pixel size</td>
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<td>Horizontal slit</td>
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<td>Vertical slit</td>
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<td>Enclosure area</td>
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<td>(b) Straight polycapillary</td>
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<td>Channel diameter</td>
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<td>Effective diameter</td>
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<td>Capillary length</td>
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Figure 2: Schematic diagrams of (a) a two-dimensional Soller slit and (b) a straight polycapillary.

Figure 3: A photograph of two pieces of the Al plates on the Si wafer for evaluating the positional resolution.
served by using the Cu plate. The temperature of the heat treatment was 300°C under the atmospheric pressure. The diffraction angle of 2θ was adjusted to the lattice plane of Cu, Cu2O, and CuO. The XRD images were obtained at the heat treatment times of 0 h, 1 h, and 2 h. The exposure time of the X-rays was 300 s. The surface of the Cu plate was oxidized by heat treatment. The crystal structure distribution of Cu, Cu2O, and CuO were changed. Simultaneously, the XRD profile was obtained. The incidence angle was 5°, and the angle range of 2θ was varied from 25° to 100° with a 0.01° step. The penetration depth of the incident X-rays was about 2 μm.

D. Comparison between micro-XRD and FF-XRD imaging instruments

Micro-XRD analysis confirmed that the crystal structure distribution of the XRD image was accurate. The sample was the Cu plate which was heated at 300°C for 2 h. The diffraction angle was adjusted to the Cu (111) peak, and the XRD image was obtained by using the FFXRD imaging instrument. The incidence angle was 5°, and the exposure time of X-rays was 300 s. Then, the micro-XRD analysis was performed. The incident X-rays were focused to 100 μm in diameter by a mono-capillary. The incidence angle was 5°, and the angle range of 2θ was varied from 20° to 100° with a 0.01° step. The total measurement time of the micro-XRD analysis was 90 min.

III. RESULTS AND DISCUSSION

A. Positional and spatial resolutions

Figure 4 shows XRD images of Al (200) and Al (220) using the two-dimensional Soller slit and the straight polycapillary. The XRD images using the straight polycapillary [Figure 4 (b, d)] are less noisy and more clearly than those using the two-dimensional Soller slit [Figure 4 (a, c)]. The size of the XRD image was the same as the actual sample size. The Al plates were affected by the orientation. The crystal structure distribution was difference for each lattice plane. Therefore, the straight polycapillary is superior to the two-dimensional Soller slit for the positional resolution and is suitable for the FFXRD imaging instrument.

Figure 5 shows an analytical process to determine the spatial resolution. Firstly, a line analysis was carried out along the line indicated by a blue arrow in Figure 5(a). The line analysis gave the experimental plots as shown in Figure 5(b). Secondly, plots of the XRD intensities were fitted with a sigmoid curve (blue). Finally, a differential curve of the fitted sigmoid curve (orange) was obtained. The spatial resolution was defined as a full width at half maximum (FWHM) of the differential curve. Table 2 shows the spatial resolutions by using the short and long types of the straight polycapillary. The resolution of the long type is better than the short one. This is because the capillary length is so long that the incident X-rays to the straight polycapillary from a wide-angle are attenuated and the spread of the X-rays is reduced. Furthermore, the spatial resolution depends on the channel diameter and the distance of the optical system (between the straight polycapillary and the two-dimensional detector). The X-rays through the straight polycapillary spread with the critical total reflection angle in the capillary.

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<th>Short type</th>
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<tr>
<td>Al (220)</td>
<td>827 μm</td>
<td>594 μm</td>
</tr>
<tr>
<td>Cu (200)</td>
<td>794 μm</td>
<td>575 μm</td>
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Figure 5: (a) The XRD image of Al (220) and (b) the line analysis fitted sigmoid curve (blue) for calculation (orange) of the spatial resolution.

Table 2: The spatial resolution using the straight polycapillary of Al (220) and Cu (200) with short and long types.
As the distance of the optical system is long, the value of the spatial resolution is increased. In this study, the straight polycapillary had a channel diameter of 10 μm, however, the theoretical spatial resolution calculated considering the distance of the optical system and the capillary length is several hundreds of micrometers. The values of the spatial resolution shown in Table 2 are appropriate, although the theoretical and experimental values are slightly different. In the following experiment, the straight polycapillary of long type was used.

B. Crystal structure distribution during oxidation process of Cu plate by heat treatment

Figure 6 shows XRD profiles at each heat treatment time [(a) 0 h, (b) 1 h, and (c) 2 h]. The XRD intensity of Cu is reduced in contrast to the increasing XRD intensity of Cu₂O and CuO, indicating that oxidation of Cu proceeds. The oxidation reaction of Cu at 300°C is expected to follow chemical equations in Eqs. (2) and (3) with a thermodynamically preferential formation of Cu₂O according to the Ellingham diagram [31–33].

\[4Cu + O_2 \rightarrow 2Cu_2O \quad (2)\]
\[2Cu + O_2 \rightarrow 2CuO \quad (3)\]

The XRD profile shows the average composition on the surface of the sample. Then, the XRD images were obtained to investigate the oxidation process of Cu as the crystal structure distribution. Figure 7 shows the XRD images of (a) Cu, (b) Cu₂O, and (c) CuO at the heat treatment times of 0 h, 1 h, and 2 h. Figure 7(a) shows the crystal structure distribution of Cu at each lattice plane. For example, Cu (111), which distributes in the central part of the detection area at 0 h and moves to the upper and left parts of the detection area at 2 h. With prolongation of the heat treatment time, the surface of the sample is oxidized to Cu₂O and CuO, and the crystal structure distribution of Cu is reduced. The crystal structure distributions of Cu₂O and CuO spread through the whole around the lower part of the detection area. The XRD intensity from Cu₂O is higher than that from CuO. The Cu plate was affected by the orientation, and the heat treatment was not provided uniformly. Figure 7 shows that Cu oxidation preferentially proceeds according to Eq. (2) [31]. The change of the crystal structure during the oxidation process
of Cu can be observed in a large area of the surface by using the FFXRD imaging instrument.

C. Evaluation of the validity of the XRD image by micro-XRD analysis

Figure 8(a) shows the XRD image of Cu (111) after heat treatment at 300°C for 2 h, and Figure 8(b) shows the XRD profile using a micro-XRD analysis. The analysis was carried out at the points where the XRD intensities were high (1) and low (2), as indicated in Figure 8(a). The analytical point 1 does not give intense diffraction peaks, whereas the XRD profile from the analytical point 2 shows a strong diffraction peak of Cu (111). Therefore, the results of the XRD image and the micro-XRD analysis correspond to each other, and the validity of the XRD images using the FFXRD imaging instrument is confirmed. Furthermore, if the XRD image of the same area (30 mm^2) as the FFXRD imaging instrument is obtained using the micro-XRD imaging instrument, the total measurement time will be about 4000 h using the incident X-rays with a diameter of 100 μm because it takes 90 min to measure one point by the micro-XRD analysis. Although the FFXRD imaging instrument can obtain the XRD images in several hundreds of seconds at each lattice plane, the FFXRD imaging instrument is a useful X-ray imaging method for measuring the crystal structure distribution with a large area.

IV. CONCLUSIONS

We developed a FFXRD imaging method realized in the laboratory using a straight polycapillary that can obtain the XRD image with a large area (the diameter of 6 mm) in several hundreds of seconds throughout the simple process. The FFXRD imaging instrument for obtaining the crystal structure distribution with a large area on the surface of the sample was developed and the analytical performance was evaluated. The positional resolution and the spatial resolution were improved by using a straight polycapillary of a long type. Then, the FFXRD imaging instrument was attached to the heat treatment system and in situ monitoring of the oxidation process of Cu at 300°C was performed. The crystal structure distributions of Cu, Cu_2O, and CuO at each lattice plane were obtained. With prolongation of the heat treatment time, the distribution of Cu is reduced while those of Cu_2O and CuO are extended. In the observation of the oxidation process of Cu, the result of the XRD profile is equivalent to the XRD images. Additionally, the XRD image obtained by the FFXRD imaging instrument was measured by the micro-XRD analysis. The difference of the intensity in the XRD image and the analysis of micro-XRD were corresponded. The validity of the analysis using the FFXRD imaging instrument was proved. To obtain the XRD image with a large area, the FFXRD imaging instrument that can be realized in the laboratory has advantages regarding the exposure time of the X-rays and the in situ analysis. In future analyses, the improvement of the FFXRD imaging method by advanced X-ray optics and a two-dimensional detector is expected.

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References


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