Micro-area X-ray diffractometry

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1. Introduction

X-ray diffractometry is a well-known method for analyzing samples of several tens of milligrams or more in weight or several millimeters or more in particle size. It is used to identify substances in a sample and to analyze crystal quality, crystal orientation, and residual stress. Recently, new requirements of the technology have arisen. These include the identification of substances present in trace amounts (less than 0.1 mg) resulting from multiple synthesis processes, identification of foreign substances or deposits of 100 μm or less in size, and microanalysis of orientation and stress in welded parts and deformation-processed areas. For these experiments, point detectors (i.e., scintillation counters) require long measurement times because of their low sensitivity coupled with the small signal. In some situations, an incorrect diffraction intensity ratio, resulting from the effect of coarse grains or particles, can make identification difficult. Combining a high-intensity X-ray source and a two-dimensional detector provides the increased diffracted X-ray intensity and detection sensitivity needed for rapid analysis, even for extremely small samples or sample analysis areas.

This report primarily discusses the use of the latest X-ray diffractometer to analyze trace substances and micro areas. It also discusses specific applications.

2. Overview of a micro-area X-ray diffractometer

A high-intensity X-ray source and a high-efficiency, high-sensitivity detector are needed to achieve and measure adequate diffracted X-ray intensity from trace substances and micro areas. Laboratory X-ray diffractometers capable of conducting these measurements consist of rotating anode X-ray generators, optical devices capable of focusing X-rays efficiently, and two-dimensional imaging plate (IP) or semiconductor detectors with large detection areas. Two representative systems are described below.

2.1. Dedicated micro-area X-ray diffractometer

The D/MAX RAPID II-CMF is an X-ray diffractometer with a curved IP designed specifically for micro-area analyses. As shown in Fig. 1, this system is equipped with a microfocus rotating anode X-ray generator that provides high intensity for micro-area analyses, and side-by-side laterally graded multilayer optics (confocal mirrors) to focus the beam[(1)]. The combination of these components results in much higher X-ray intensity than from conventional equipment. For example, the D/MAX RAPID II-CMF provides 80 times higher intensity than conventional equipment using a collimator with an inner diameter of 30 μm. Since the D/MAX RAPID II-CMF uses an IP detector and is capable of measuring a wide area simultaneously, Debye rings or Laue spots can be integrated. The system provides the X-ray intensity needed to identify substances, even with low diffracted X-ray intensity or coarse crystal grains.

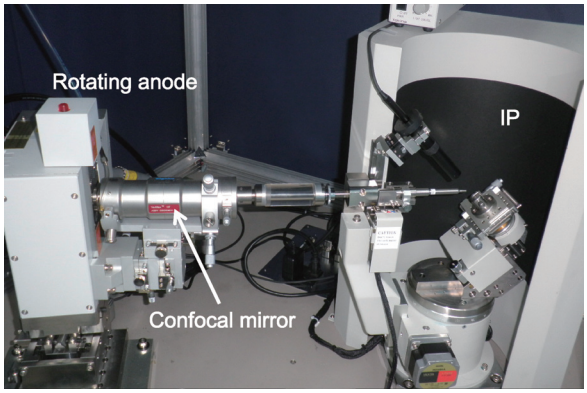

Fig. 1. D/MAX RAPID II-CMF X-ray diffractometer with curved IP.

Featuring a high-intensity incident X-ray source and a large-area two-dimensional detector, the D/MAX RAPID II-CMF can significantly reduce measurement times for micro-area X-ray diffractometry of regions as small as several tens of micrometers.

2.2. Micro-area X-ray diffractometer based on general-purpose equipment

In addition to the dedicated equipment described in Section 2.1, we can use a general-purpose X-ray diffractometer without major modifications to analyze trace substances and micro areas. Figure 2 shows an example of a micro-area analysis system configured using the SmartLab X-ray diffractometer.

Many ordinary X-ray powder diffractometers use line focusing. For micro-area analyses, the beam must be constricted and shaped into a point using slits or a collimator. In many cases, this reduces X-ray intensity to levels too low for effective analysis. The SmartLab incorporates an optical device (CBO-f) to convert the line focus to a point focus. This results in X-ray intensity about 40 to 50 times higher than that achieved if the X-ray beam is collimated to the same focus size with slits. Additionally, using a PILATUS 100K/R high-speed two-

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dimensional X-ray detector, the SmartLab can measure in fixed mode (exposures are performed with the detector at a fixed position) or scan mode (TDI [Time Delayed Integration] mode). Adding an *in situ* measurement attachment enables rapid measurements of change in the crystal structure of a sample with phase transition, as well as analysis of thin film samples.

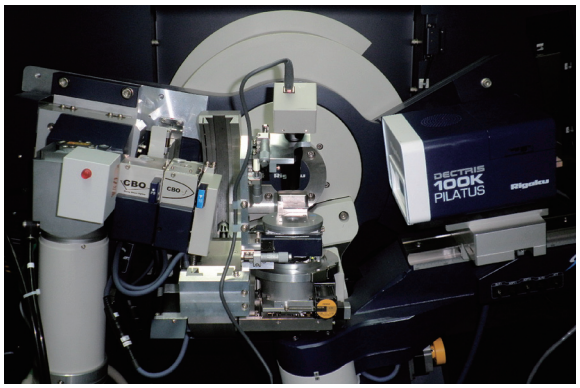


Fig. 2. SmartLab X-ray diffractometer.

3. Example: Using the D/MAX RAPID II-CMF

The D/MAX RAPID II-CMF incorporates a large-area imaging plate that allows it to integrate diffracted X-rays even with low diffraction intensities due to small sample amounts, or when the Debye rings appear spotty due to coarse crystal grains. Additionally, the detection area is large and measurements can be performed near $2\theta=0°$, making all-direction transmission measurements possible and facilitating the analysis of samples with orientation. Presented below are some examples of analyses that draw on these advantages of the D/MAX RAPID II-CMF.

3.1. Analysis of extremely small paint flakes

When a traffic accident occurs, investigators examine the physical evidence left at the accident site to try to understand what happened. The physical evidence in these cases is often present in trace quantities. This underscores the importance of being able to rapidly analyze such evidence.

Figure 3 shows a paint flake found at an accident site together with the analysis results. To analyze the material composition, which requires that we direct X-rays onto a specific location on the paint flake measuring approximately 150 μm, we used a collimator with an inner diameter of 10 μm. With an X-ray exposure time of 10 minutes, we obtained the two-dimensional image shown in Fig. 3. We converted this image into angle and intensity data and performed qualitative analysis, identifying TiO_2 (rutile) and $BaSO_4$ as pigment components (Fig. 4). Even such small samples can be quickly analyzed.

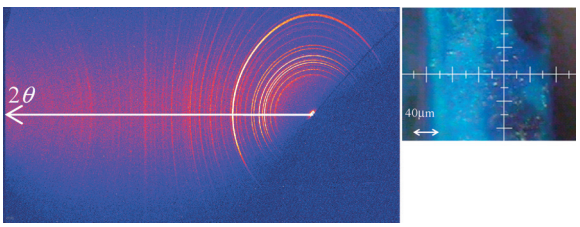


Fig. 3. Measurement position on paint flake and the two-dimensional image obtained

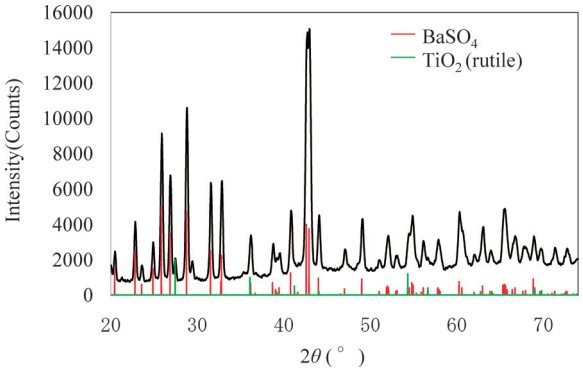
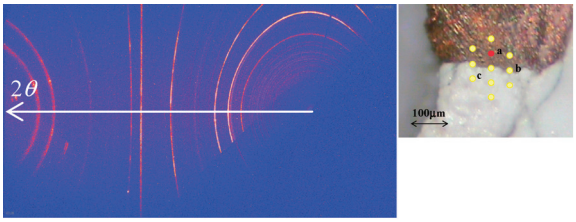


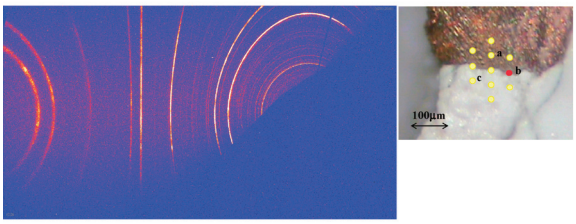
Fig. 4. Paint film identification result.

3.2. Analysis of printed circuit board

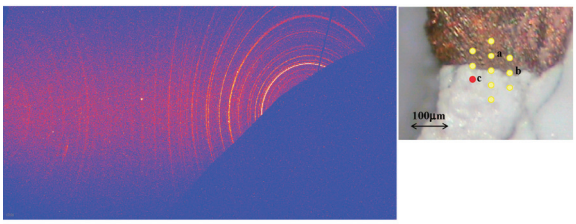
Electronic components such as circuit boards generally consist of very small parts. The performance of an electronic component can be evaluated efficiently by obtaining information on each component part. We used an X–Y stage for automatic mapping measurements of the base material and coating section of a circuit board. The irradiated field at each measurement point was approximately 30 μm, and the exposure time was one minute. As Fig. 5 clearly shows, we can readily and



(1) Measurement point a (base material section)



(2) Measurement point b (border between base material section and coating section)



(3) Measurement point c (coating section)

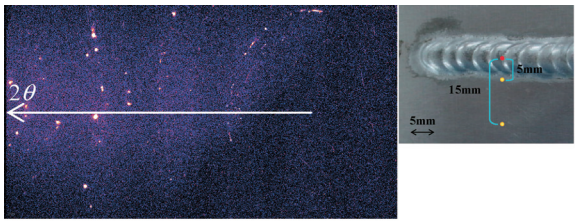
Fig. 5. Measurement positions on a circuit board and the two-dimensional images obtained.

quickly identify differences in conditions for different sections, including the exposed base material, the border of the coating section, and the coating section.

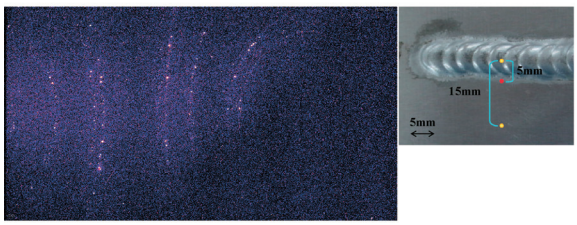
3.3. Analysis of change in size of crystal grains due to welding

Metal welding causes the growth of crystal grains in the welded section. The D/MAX RAPID II-CMF is ideal for analyzing differences in the size of crystal grains in a welded area. We performed bead welding on a 5182 aluminum board. Using a 10 μm collimator, we then analyzed measurement points *a*, *b*, and *c* near the welded section shown in Fig. 6, and observed the changes in grain size.

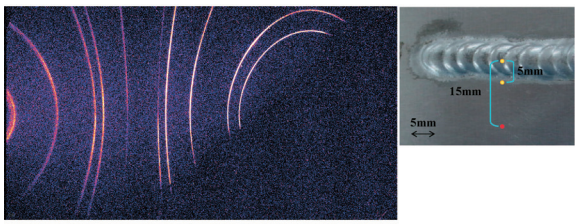
Located at the center of the welded section, measurement point *a* was subjected to the greatest amount of heat. The Debye ring in the obtained two-dimensional image appeared spotty, indicating that the number of crystals contributing to diffraction was very small. Measurement point *b* was located 5 mm from the center of the welded section. Although the Debye ring in the diffraction image also appeared spotty, more spots were observed here than at point *a*. Measurement point *c* was located 15 mm from the center of the welded section and was therefore least affected by welding heat. The Debye ring in the corresponding image appeared ring-shaped, indicating that an adequate number of crystals contributed to diffraction. In short, the Debye ring was spottier the closer the measurement point was to the center of the welded section, which means fewer crystals contributed to diffraction. Fewer crystal grains contributing to diffraction with the same field of view implies that the grains in that area are larger. In this way, we can easily confirm that the crystal grains grew in size when heat was applied.



(1) Measurement point a (center of the welded section)



(2) Measurement point b (5 mm from center of the welded section)

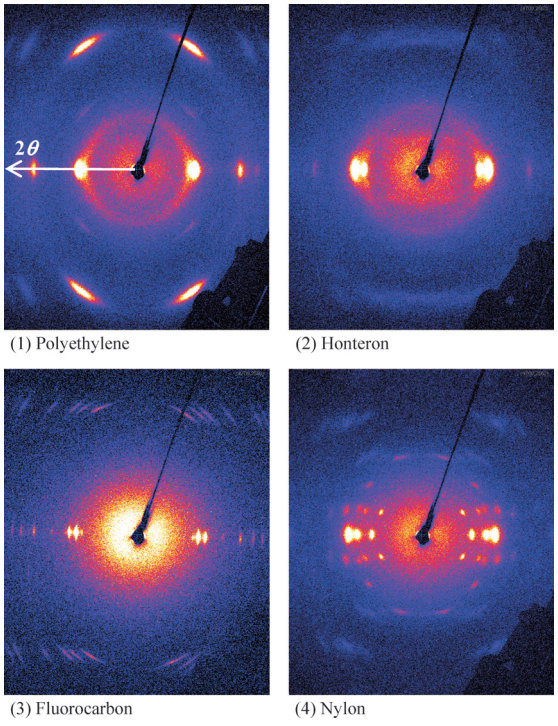


(3) Measurement point c (15 mm from center of the welded section)

Fig. 6. Measurement positions on 5182 aluminum board and the two-dimensional images obtained.

3.4. Analysis of crystal quality and orientation in microfilament

To analyze polymer filaments by conventional measurement methods, we generally need to bundle multiple filaments. Since the filaments can't be aligned perfectly along the same axis when bundled, the profile obtained can vary from case to case. Ideally, we would analyze single filaments; however, a single filament is extremely thin and generates very low diffraction intensity. Using a collimator with an inner diameter of 10 μm, we analyzed single filaments, each with a diameter of approximately 20 μm, and examined the differences from sample to sample. The exposure time was five minutes. Figure 7 shows two-dimensional images obtained from polyethylene, Honteron, fluorocarbon, and nylon filaments. Even a single filament sample quickly generated a two-dimensional image, allowing ready examination of crystal quality and orientation.



(1) Polyethylene (2) Honteron

(3) Fluorocarbon (4) Nylon

Fig. 7. Two-dimensional images obtained from polymer filaments.

3.5. Pole figure measurement of Cu wire

Conventional pole figure measurement methods, typically the Schultz method, are not suited to measurements of extremely small or curved samples. With the Schultz method, the sample is moved in the tilt direction (α) and the rotation direction (β) at a certain

2θ position to plot a pole figure. Small α angles result in wide X-ray beam widths. In the case of a Cu wire (see Fig. 8) with a diameter of 125 μm, accurate intensity distribution cannot be obtained for various reasons, including the shift of the angle position resulting from eccentricity errors and X-ray beams extending beyond the sample. By arranging multiple filaments next to each other, we can minimize the effects of eccentricity and keep the X-ray beam from extending beyond the sample to some extent. Obviously, this requires more than one filament. The D/MAX RAPID II-CMF can perform measurements using a 10 μm collimator. The area irradiated by the X-ray beam is free of the effects of curvature and pole figure measurements can be performed while keeping the X-ray beam from extending beyond the sample.

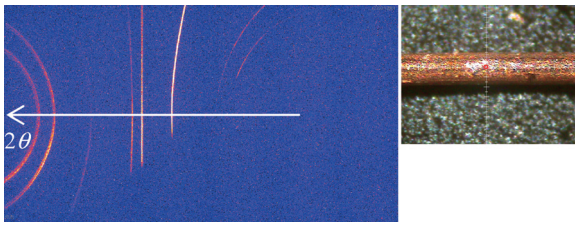


Fig. 8. Measurement position on Cu wire and the two-dimensional image obtained.

With the conventional method, the sample is moved in the α and β directions at the 2θ position of each plane index. By comparison, a two-dimensional detector measures the entire periphery of the sample in the in-plane direction because it can obtain the intensity distribution in the α direction all at once. Thus, it can provide a pole figure (see Fig. 9) from multiple two-dimensional images and create multiple pole figures in a single step without changing the incident angles for each plane index. The two-dimensional detector offers several

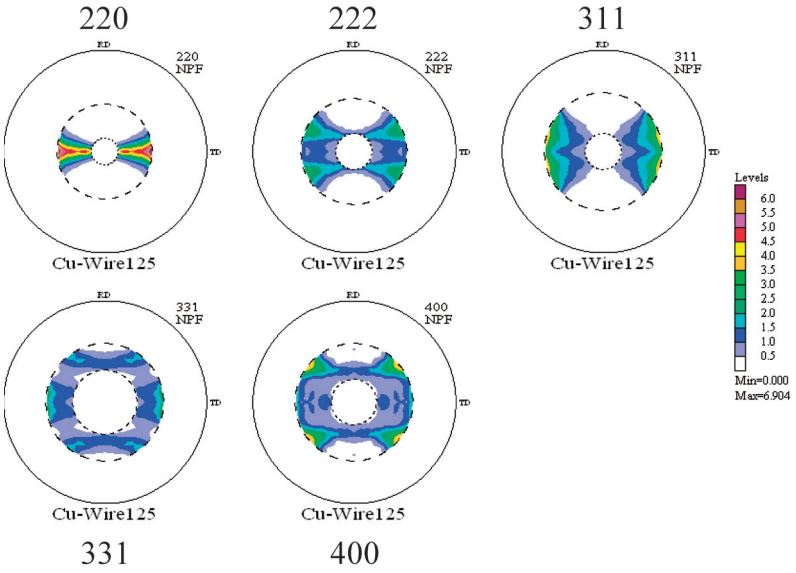


Fig. 9. Pole figures of Cu 220, 222, 311, 331, 400 (after defocus correction).

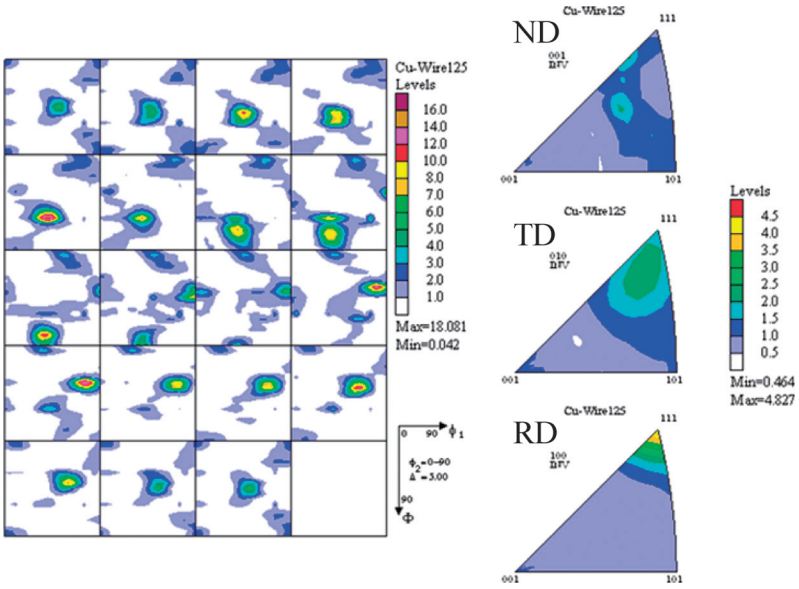


Fig. 10. Crystal orientation distribution figure and inverse pole figure (rolling direction [111]).

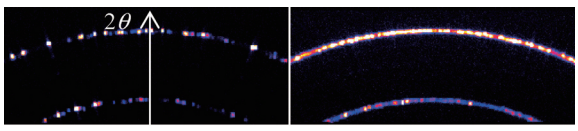
clear advantages for pole figure measurements. We analyzed the pole figures obtained for the crystallite ODF (Orientation Distribution Function) and obtained the primary and secondary orientations, as shown in Fig. 10. Recent advances have made it possible to calculate each orientation using the volume fraction for quantitative processing. This is done by fitting the full width at half maximum (expressed in Eulerian angles) of the pole in the crystalline orientation distribution figure[2]. The intensity is attenuated at higher rates toward the outer edge of the pole figure due to defocusing at the location irradiated. Therefore, to calculate volume fractions correctly, we need to perform corrections based on a random sample (e.g., a powder).

4. Example: Using SmartLab

A general-purpose device, the SmartLab is also capable of measuring trace sample amounts and micro areas by using a point conversion device and PILATUS 100K/R two-dimensional detector. Additionally, we can switch the detector measurement mode to fixed mode or TDI mode depending on the purpose of the measurement. In fixed mode, the center of the detector is set to a certain 2θ angle during exposure. In TDI mode, the detector scans the same way a one-dimensional detector does, and the diffraction intensity values obtained at different 2θ angles are integrated.

Figure 11 shows two-dimensional images of quartz sand with a crystal grain size of 50 μm obtained in fixed mode and in TDI mode. In fixed mode, the Debye rings appear spotty due to coarse particle size, but we can still obtain information within a certain angle range with a short exposure. In TDI mode, we can reduce the effects of coarse particle size and obtain a seamless image. This makes fixed mode better for measurements of fast structural changes, such as *in situ* measurements, and TDI mode better for experiments to obtain profiles with a wide angle range, such as qualitative and quantitative analyses.

The next few sections discuss examples of *in situ* and residual stress measurements in fixed mode and reciprocal space map measurement in TDI mode.



(1) Fixed mode (2) TDI mode

Fig. 11. Two-dimensional images of quartz sand obtained in fixed mode and TDI mode.

4.1. *In situ* measurement of a medicinal product

We can mount an attachment on the sample section of the SmartLab for *in situ* measurements. Figure 12 shows an XRD-DSC measurement device that can be used to simultaneously obtain information on crystal structure and thermal change from a certain sample.

Figure 13 shows the DSC curve for terfenadine, an anti-allergic agent, during heating. We performed

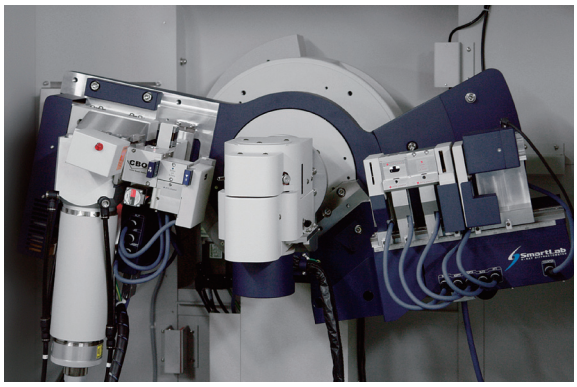


Fig. 12. SmartLab with XRD-DSC attachment.

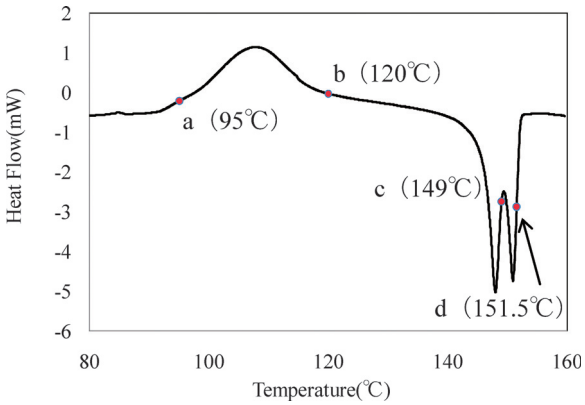


Fig. 13. DSC curve of terfenadine (in heating process).

exposures at 10-second intervals in fixed mode while heating at a rate of 2°C/min, observing changes in the crystal structure resulting from the temperature change. Two-dimensional images in Fig. 14 were obtained at the temperatures *a, b, c,* and *d* shown in Fig. 13. Figure 14 shows that terfenadine, which is in an amorphous state at room temperature (a), crystallizes (b) through an exothermal reaction at about 110°C. However, crystal phase I (c) melts due to the first endothermic reaction, and crystal phase II (d) melts due to the next endothermic reaction. This clearly shows that crystal phase I and crystal phase II crystallize nearly simultaneously at temperature (b). Setting the PILATUS to fixed mode reduces exposure time, increases

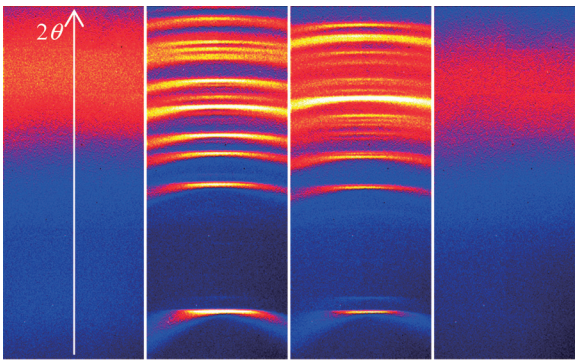


Fig. 14. Two-dimensional images obtained at different temperatures.

diffracted X-ray detection sensitivity, and improves counting efficiency. Even if multiple reactions occur in the sample within a narrow temperature range, information on crystal structures before and after the reactions are easily obtained.

4.2. Measurement of residual stress in a formed container

Residual stress in a metal significantly affects the material's fatigue strength and fractures. In particular, residual stress measurements on the surface of a metallic material are used to evaluate the strength of the material. Demand has risen for residual stress measurements of micro areas, such as welded sections and deformation-processed sections (e.g., sections where a deep drawing process is performed). We performed residual stress measurements on the highest part of a projecting section of a formed aluminum container. Since processed products such as this container have curved surfaces, a wide beam always produces errors in the stress value. We must reduce the beam size based on the curvature factor. The result of our analysis shows a pronounced texture in the formed aluminum container. No Debye rings were detected at certain ψ angles (Fig. 15). In such cases, using a two-dimensional detector in residual stress measurements makes it possible to use not just the conventional $\sin^2\psi$ method, but also the two-dimensional stress analysis (2D method) based on the shape of the Debye ring obtained[3]. With the 2D method, even if areas exist in which no peaks are detected, we can calculate the stress values of $\sigma 11$ and $\sigma 22$ using other directional components and Debye ring distortion. Our analysis results show the stress values (see Table 1 and Fig. 16) along the different directions of the formed aluminum container.

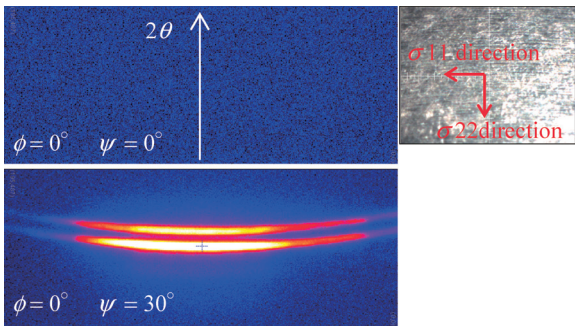


Fig. 15. Formed aluminum container and the two-dimensional image obtained.

Table 1. Residual stress values obtained by the 2D method.

Direction	Residual stress value (MPa)
σ11	177±32
σ22	136±28
σ12	11±9

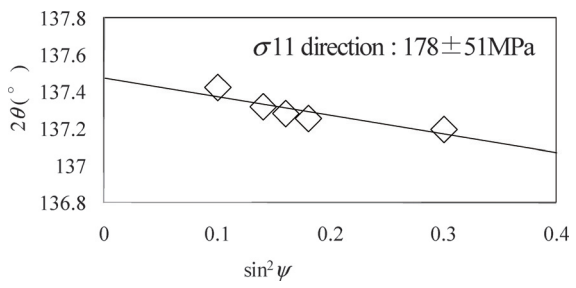


Fig. 16. Residual stress values obtained by the $\sin^2\psi$ method.

4.3. Reciprocal space map measurement of an oriented film

From the results of high-speed reciprocal space mapping measurements of a thin film sample obtained based on the characteristics of TDI mode, we can examine orientation in a thin film sample. Figure 17 shows a reciprocal lattice image obtained from (Pb, La)TiO_3/Pt/Si. We can obtain a reciprocal lattice image for a wide area within 10 minutes. The wide dynamic range of the PILATUS makes it possible to measure a wide range of X-rays simultaneously, from the high intensity of a direct beam or diffraction from a Si substrate to extremely weak diffracted X-rays, such as those from (Pb, La)TiO_3 002/200. In extended reciprocal space map measurements using a scintillation counter (a point detector), one measurement axis (χ or 2θ) is fixed and the other axis is scanned. This means each measurement takes a very long time. In contrast, a two-dimensional detector can obtain a reciprocal space map very quickly, since it acquires information along the χ direction in a single step through the $2\theta/\theta$ measurement. Hence, a two-dimensional detector reduces the time required to analyze crystal orientation and the degree of preferred orientation in a thin film sample.

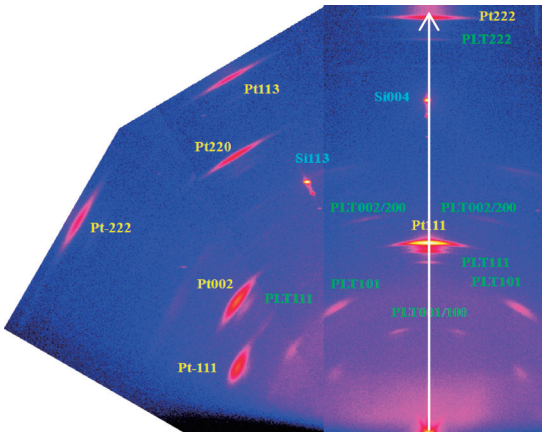


Fig. 17. Reciprocal lattice image obtained from (Pb, La)TiO_3/Pt/Si.

5. Summary

In response to the demand for rapid analysis of specific sample locations, the examples of analysis introduced in this paper present various techniques for measuring trace sample amounts and micro areas. Using a two-dimensional detector together with a rotating anode X-ray generator and a focusing device enables

rapid high intensity measurement, which in turn makes it possible to resolve various issues that could not be analyzed before. For these measurements, users can select from among dedicated micro-area X-ray diffractometers or general-purpose devices on which suitable focusing devices and detectors are installed, based on the specific purpose of the measurement.

References

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