1. Introduction

The assessment study of solid matter can be done in various ways, one of which is X-ray diffraction. X-ray diffraction techniques give information about the structure of solids, that is, the arrangement of the atoms that compose the solid.

Among various assessment methods the X-ray diffraction method is commonly used because it permits nondestructive structure analysis, although it is relatively low in sensitivity. The types of information this method can provide are:

1. The kinds of materials that compose a solid (qualitative analysis).
2. The quantities of materials that compose the solid (quantitative analysis).
3. The quantities of materials that are crystallized (crystallinity).
4. The amount of stress present in the solid (residual stress).
5. The size of crystallites that compose the solid (crystallite size).
6. Average orientation of crystallites that compose the solid (texture).

As tools for analysis, X-ray diffraction equipment may be classified by sample forms into those for the polycrystal method (powder method), those for the single crystal method, and those for the amorphous method. Likewise, according to the way of detecting X-rays, they may be classified into those for the photographic method using film and those for the counter method using a photon counter. X-ray cameras play a major role for the photographic method and so do X-ray diffractometers for the counter method. The latter devices are being widely utilized jointly with various attachments.

Fig. 1 shows X-ray diffraction equipment as classified by sample forms.

In the past, because of its rather low sensitivity, the X-ray diffraction technique was not actively used, in particular, for surface analysis and micro area analysis. In recent years, however, in order to upgrade the sensitivity, efforts have been made to improve the measuring optical systems, detectors, and X-ray sources. This has resulted in its increasing use for the assessment study of solids.

In micro area X-ray diffraction techniques, the PSPC (position sensitive proportional counter) is used to simultaneously detect diffracted rays generated at different angular positions in the shortest possible time. X-ray information is efficiently obtained from micro areas down to 0.01 mm in diameter. Also, in thin film X-ray diffraction techniques, X-ray incidence is made at a minimum angle to the sample surface so as to get as much information as possible on the surface. Further, in the thin film study, a monochromator is used to improve the peak-to-background ratio [1].

Described below are the aforementioned X-ray diffraction techniques (1) through (6).

2. Processing of X-ray Diffraction Data

It is necessary to correctly read the intensity and position of diffracted rays from X-ray diffraction data obtained by measurement with a diffractometer. While various methods are available for this purpose, computer processing is now prevalent.

2.1 Background Subtraction

The background must be removed when attempting to correctly read the intensities of diffracted rays from X-ray diffraction data. The background is caused by fluorescent X-rays emitted from the sample, scattered X-rays from amorphous substances in the sample, and so on.

There are different ways of removing the background. Sonneveld et al. [2] used measured values at every 20 points (e.g. point n) as the first approxi-
Figure 1: Classification of X-ray diffraction equipment according to sample forms.
mation of the background. But in view of a likelihood that some of the selected points fall on diffraction lines, they conceived sample $P_i$ ($i = 2, 3, \ldots, n - 1$) at point $n - 2$ by removing both ends in order to achieve a better approximation. In this case, calculation of $(m_{i-1} + P_{i+1})/2$ is to be made, and if $P_i > m_i$, then $P_i$ should be replaced with $m_i$.

A smooth curve can be obtained by repeating the above procedure several times and sequentially connecting each point. This curve is regarded as the background and is to be subtracted from the measurement data. If the background changes forming a curve as shown in Fig. 2(b) instead of changing almost linearly in terms of $2\theta$, then $P_i > m_i + C$ may be used to replace the formula $P_i > m_i$.

There is R. P. Goehner’s [3] method as another method along with other pertinent ones which have been devised according to the memory size and speed of computers to be used.

2.2 Detection of Peak Position and Its Measurement

Various methods are available for peak position determination as well. What is frequently used is one by means of a quadratic differential curve of the measurement data [4], [5], [6]. (See Fig. 3.) The quadratic differential method is advantageous in that it allows peak detection even in the case of raw data as well as in the case of a peak overlapped with another peak at its shoulder, thus making its detection difficult by the linear differential method.

Fig. 2 Background determination. (a) When background is roughly a straight line. (b) When background has some curvature.

Fig. 3 Peak detection and positional determination with linear and quadratic curves.

Fig. 4 Example of qualitative analysis result.
3. General X-ray Diffraction Techniques

3.1 Qualitative Analysis

This analytical procedure is the so-called search-match of X-ray diffraction data, such that the diffraction pattern of an unknown sample is measured and is compared with already known standard patterns (JCPDS cards) to obtain an identification.

When the unknown sample consists of a single material, its qualitative analysis is rather simple. When it is a mixture, on the other hand, the analysis requires high-level skills because of the many diffraction present. A variety of combinations of standard patterns should be taken into account. To cope with the situation, an attempt to carry out search-match with a computer was initiated in the 1960s, and improvements have been made year after year. The present-day search-match has gone so far as to include a search of the complete JCPDS files, comprising over 48,000 patterns.

3.2 Quantitative Analysis

This procedure estimates the quantity of the analyte material by taking advantage of the fact that the peak heights in an X-ray diffraction pattern are proportional to the quantities of materials that compose a solid.

In quantitative analysis by X-ray diffraction, the mean mass absorption coefficient depends on the difference in the quantity ratio of material, resulting in a difference in the diffracted ray intensity. It is important, therefore, to correct for absorption due to the material. Quantitative analysis techniques are classified according to differences in the absorption correction.

Quantitative analysis may be made in two ways; one is the internal standard method designed to mix a known quantity of material into an unknown sample, and the other is the external standard method designed for separate measurement without mixing. Although the external standard method is preferable for quantitative analysis, errors are liable to occur in this method. For this reason, the internal standard method is more often used.

3.3 Crystallinity

In X-ray diffraction data a pattern due to a crystalline material and a pattern due to an amorphous material may overlap with each other. They differ as shown in Fig. 6.

While various methods are available for the determination of crystallinity, they are basically the same. That is, they employ a way of examining the degree of crystallinity from a ratio between the

![Fig. 5 Difference in calibration curve due to absorption coefficient.](image)

![Fig. 6 When crystalline material and amorphous material are mixed together.](image)
pattern area of the crystalline material and that of the amorphous material. There is such a case, however, as with graphite, for instance, where the position of its diffraction line will vary depending on the degree of crystalline properties. This is also referred to as crystallinity.

3.4 Residual Stress

When force is applied solid matter within its elastic limit, it will be deformed in proportion to the magnitude of the force. In other words, the crystal lattice interplanar spacing (d-value) of the material will change. This distortion is uniform and it should be distinguished from nonuniform distortion referred to in Fig. 7.

When changes in the diffraction angle (2θ) are examined by varying the angle ψ formed by the normal to the sample plane and that to the lattice plane, the stress value can be obtained by using the following equation.

$$\sigma = -\frac{E}{2(1+v)} \cdot \cot \theta_0 \cdot \frac{\pi}{180} \cdot \frac{\partial (2\theta)}{\partial (\sin^2 \phi)}$$

where

- $\sigma$: Stress (kg/mm$^2$)
- $E$: Young’s module (kg/mm$^2$)
- $v$: Poisson’s ratio
- $\theta_0$: Standard Bragg angle
- $K$: Constant determined by material and measurement wavelength (called a stress constant)

The optical system of the stress measuring system should be selected according to the shape of the object for measurement and the stress measuring direction.

3.5 Crystallite Size

The peak width in an X-ray diffraction pattern is related to the size of crystallites that compose the material.

Besides minuteness of the crystallite, nonuniform distortion of the crystallite (Fig. 7) is another factor that causes broadening of the peak width. Accordingly, the size of the average crystallite can be determined by measuring the peak width. Scherrer’s equation and Hall’s equation are often used for calculations of the crystallite size.

(Method by Scherrer)

$$D = \frac{K \cdot \lambda}{\beta \cos \theta}$$

where

- $\lambda$: X-ray wavelength for measurement (Å)
- $\beta$: Breadth of diffracted rays due to the crystallite size (rad)
- $\theta$: Bragg angle of diffracted rays
- $K$: Constant (which differs depending on $\beta$ and D constants)

(Method by Hall)

$$\beta = \frac{\lambda}{\epsilon \cos \theta} + 2\eta \tan \theta$$

$$\frac{\beta \cos \theta}{\lambda} = 2\eta + \frac{1}{\epsilon}$$

where

- $\beta_1$: Integral width of the breadth of diffracted rays due to the crystallite size (rad)
- $\beta_2$: Integral width of nonuniform distortion $\eta$, the relation with the nonuniform distortion is: $\beta_1 = 2 \tan \theta$
- $\epsilon$: Crystallite size (rad)
The gradient of a straight line obtained by plotting $\beta \cos \theta / \lambda$ and $\sin \theta / \lambda$ on the Y-axis and X-axis respectively, is $2\eta$. The point of intersection with the Y-axis is $1/\varepsilon$. From this, calculation can be made by separating the ununiform distortion $\eta$ and the crystallite size from each other.

3.6 Texture

When the crystal orientation of matter that composes a solid is random, the resultant Debye rings will be uniform, as shown in Fig. 11 (a), (b), (c). If, on the other hand, the crystal orientation is in a particular direction, an arc shape will result instead of a ring, as shown in Fig. 11 (d). Such a state is referred to as preferred orientation.

Sometimes there are cases in which preferred orientation is specifically given to utilize texture in order to improve the characteristics of solid materials. The device to measure the state of this texture is a pole figure diffractometer attachment.

4. Assessment of Materials by X-Ray Diffraction Techniques

The aforementioned items 3.1 through 3.6 serve as basic assessment methods to examine the state and quality of solid matter. By way of example, one of the methods used for analysis of the mechanical behaviors of materials is shown in Fig. 13.

5. Other X-ray Diffraction Techniques for Material Assessment

The above descriptions have been made centered on bulk analysis. In general X-ray diffraction techniques there are certain systems in which the X-

![Fig. 9 Example of residual stress calculation result.](image)

RESULTS OF STRESS ANALYSIS
PEAK POSITION : CENTER OF FWHM
STRESS = -0.36 kg/mm/mm
SIGMA RELIABILITY = +0.04 kg/mm/mm

![Fig. 10 Particle size and crystallite size.](image)

![Fig. 11 Observation of Debye rings in polycrystals: $\alpha$-Fe (211).](image)
Ray optics, detector and X-ray source are specifically designed for particular applications, such as:

- Thin film X-ray diffraction method [1]
- X-ray surface diffraction method [7]
- Cone scanning type microdiffractometer
- Curved PSPC type microdiffractometer (PSPC/MDG)
- Small angle scattering measurement method etc.

These methods are aimed at surface analysis, micro area analysis and the like. In any case the existence of preferred orientation must be taken into account.

Because the number of crystallites that contribute to diffraction is lessened in the case of micro area X-ray diffraction techniques, this may cause discontinuous Debye rings. For the purpose of getting a measurement result with high reproducibility by eliminating this drawback, rotation or oscillation is applied to the sample during measurement. Three axes \( \omega \), \( \chi \) and \( \theta \) are available as the axis of these movements, and they can be run independently or simultaneously to perform the desired rotation or oscillation.

The small angle scattering measurement method deals with diffuse scattering caused in the vicinity of
the incident X-ray direction as well as Bragg reflections in case of exceedingly large lattice interplanar spacing. It deals also with a phenomenon that diffraction due to long periodicity is observed when the crystalline properties and the amorphous properties are arranged periodically in fiber samples. These are utilized for particle size measurement, long-periodicity measurement, and so on.

6. Conclusion

In recent years, higher-intensity X-ray sources have become available, such as synchrotron radiation X-rays from an electron storage ring and X-rays from a high-power rotating anode X-ray generator. Moreover, the improvement and progress in measurement methods now make it possible to conduct structure analysis of micro area objects for measurement under various conditions by X-ray diffraction techniques.
References