2.5. Two-dimensional powder diffraction

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2.5.1. Introduction

2.5.1.1. *The diffraction pattern measured by an area detector*

The diffracted X-rays from a polycrystalline or powder sample form a series of cones in three-dimensional space, since large numbers of crystals oriented randomly in the space are covered by the incident X-ray beam. Each diffraction cone corresponds to the diffraction from the same family of crystal planes in all the participating grains. The apex angles of cones are given by Bragg's law for the corresponding crystal interplanar *d*-spacing. A conventional X-ray powder-diffraction pattern is collected by scanning a point or linear detector along the 2θ angle. The diffraction pattern is displayed as scattering intensity *versus* 2θ angle (Klug & Alexander, 1974; Cullity, 1978; Warren, 1990; Jenkins & Snyder, 1996; Pecharsky & Zavalij, 2003). In recent years, use of two-dimensional (2D) detectors for powder diffraction has dramatically increased in academic and industrial research (Sulyanov *et al.*, 1994; Rudolf & Landes, 1994; He, 2003, 2009). When a 2D detector is used for X-ray powder diffraction, the diffraction cones are intercepted by the area detector and the X-ray intensity distribution on the sensing area is converted to an image-like diffraction pattern, also referred to as a frame. Since the diffraction pattern collected with a 2D detector is typically given as an intensity distribution over a two-dimensional region, so X-ray diffraction with a 2D detector is also referred to as two-dimensional X-ray diffraction (2D-XRD) or 2D powder diffraction. A 2D diffraction pattern contains far more information than a conventional diffraction pattern, and therefore demands a special data-collection strategy and data-evaluation algorithms. This chapter covers the basic concepts and recent progress in 2D-XRD theory and technologies, including geometry conventions, X-ray source and optics, 2D detectors, diffraction-data interpretation, and various applications, such as phase identification and texture, stress, crystallinity and crystallite-size analysis. The concepts and algorithms of this chapter apply to both laboratory and synchrotron diffractometers equipped with 2D detectors.

2.5.1.2. *Comparison between 2D-XRD and conventional XRD*

Fig. 2.5.1 is a schematic of X-ray diffraction from a powder (polycrystalline) sample. For simplicity, it shows only two diffraction cones; one represents forward diffraction ($2\theta \leq 90^\circ$) and one represents backward diffraction ($2\theta > 90^\circ$). The diffraction measurement in a conventional diffractometer is confined within a plane, here referred to as the diffractometer plane. A point (0D) detector makes a 2θ scan along a detection circle. If a line (1D) detector is used in the diffractometer, it will be mounted on the detection circle. Since the variations in the diffraction pattern in the direction (**Z**) perpendicular to the diffractometer plane are not considered in a conventional diffractometer, the X-ray beam is normally extended in the *Z* direction (line focus). Since the diffraction data out of the diffractometer plane are not detected, the structures in the material that are represented by the missing diffraction data will either be ignored, or extra sample rotation and time are needed to complete the measurement.

With a 2D detector, the diffraction measurement is no longer limited to the diffractometer plane. Depending on the detector size, the distance to the sample and the detector position, the whole or a large portion of the diffraction rings can be measured simultaneously. Diffraction patterns out of the diffractometer plane have for a long time been recorded using Debye–Scherrer cameras, so the diffraction rings are referred to as Debye rings. However, when a Debye–Scherrer camera is used, only the position of the arches in the 2θ direction and their relative intensities are measured for powder-diffraction analysis. The diffraction rings collected with a large 2D detector extend further in the 'vertical' direction and the intensity variation in the vertical direction is also used for data evaluation. Therefore, the terms 'diffraction cone' and 'diffraction ring' will be often be used in this chapter as alternatives to 'Debye cone' and 'Debye ring'.

2.5.1.3. *Advantages of two-dimensional X-ray diffraction*

A 2D diffraction frame contains far more information than a diffraction pattern measured using a conventional diffraction system with a point detector or a linear position-sensitive detector. In addition to the significantly higher data-collection speed, the intensity and 2θ variation along the diffraction rings can reveal abundant structural information typically not available from a conventional diffraction pattern. Fig. 2.5.2 shows a 2D pattern collected from a battery component containing multiple layers of different phases. Some diffraction rings have strong intensity variation due to preferred orientation, and the spotty diffraction rings are from a phase that contains large crystal grains. It is apparent that different diffraction-ring patterns are from different phases. 2D-XRD analyses commonly performed on polycrystalline materials include phase identification, quantitative phase analysis, preferred-orientation quantification and characterization of residual stresses.

Phase identification (phase ID) can be done by integration in a selected 2θ range along the diffraction rings (Hammersley *et al.*,

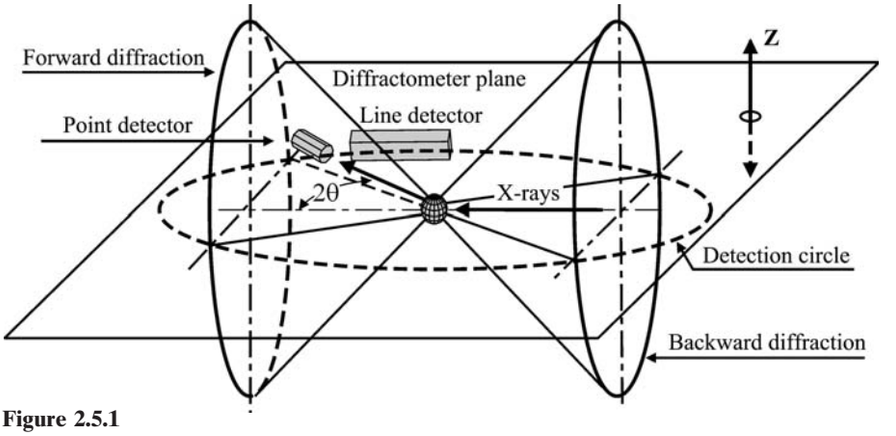

Figure 2.5.1
Diffraction patterns in 3D space from a powder sample and the diffractometer plane.

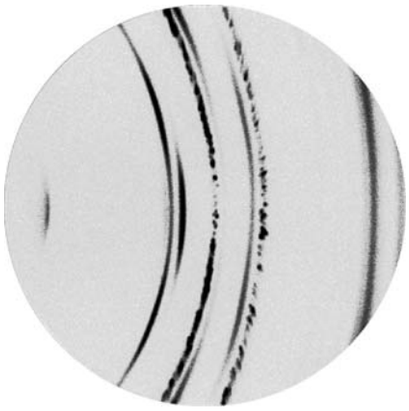

Figure 2.5.2
Diffraction pattern from a battery component containing multiple layers.

1996; Rodriguez-Navarro, 2006). The integrated data give better intensity and statistics for phase ID and quantitative analysis, especially for those samples with texture or large grain sizes, or where the sample is small. Then the integrated diffraction profiles can be analysed with existing algorithms and methods: profile fitting with conventional peak shapes and fundamental parameters, quantification of phases, and lattice-parameter indexing and refinement. The results can be used to search and match to entries in a powder-diffraction database, typically the Powder Diffraction File.

Texture measurement with 2D-XRD is extremely fast compared to measurement using a point or linear detector. The area detector collects texture data and background values simultaneously for multiple poles and multiple directions. Owing to the high measurement speed, pole figures can be measured at very fine steps, allowing detection of very sharp textures (Smith & Ortega, 1993; Bunge & Klein, 1996; He, 2009).

Stress measurement with 2D-XRD is based on a direct relationship between the stress tensor and distortion of the diffraction cones. Since the whole or a part of the diffraction ring is used for stress calculation, 2D-XRD can measure stress with high sensitivity, high speed and high accuracy (He & Smith, 1997; He, 2000). It is highly suitable for samples containing large crystals and textures. Simultaneous measurement of stress and texture is also possible, since 2D data contain both stress and texture information.

Concentrations of crystalline phases can be measured faster and more accurately with data analysis over 2D frames, especially for samples with an anisotropic distribution of crystallite orientations and/or amorphous content. The amorphous region can be defined by the user to consist of regions with no Bragg peaks, or the amorphous region can be defined with the crystalline region included when the crystalline region and the amorphous region overlap.

Microdiffraction data are collected with speed and accuracy. Collection of X-ray diffraction data from small sample amounts or small sample areas has always been a slow process because of limited beam intensity. The 2D detector captures whole or a large portion of the diffraction rings, so spotty, textured or weak diffraction data can be integrated over the selected diffraction rings (Winter & Squires, 1995; Bergese *et al.*, 2001; Tissot, 2003; Bhuvanesh & Reibenspies, 2003; He, 2004). The point beam used for microdiffraction allows diffraction mapping with fine space resolution, even on a curved surface (Allahkarami & Hanan, 2011).

Data can be collected from thin-film samples containing a mixture of single-crystal and polycrystalline layers with random orientation distributions, and highly textured layers, with all the features appearing simultaneously in diffraction frames (Dickerson *et al.*, 2002; He, 2006). The pole figures from different layers and the substrate can be overlapped to reveal the orientation relationships. The use of a 2D detector can dramatically speed up the data collection for reciprocal-space mapping on an in-plane reciprocal-lattice point (Schmidbauer *et al.*, 2008).

Because of the penetrating power of the X-ray beam, fast nondestructive data collection and the abundant information about atomic structure, two-dimensional X-ray diffraction can be used to screen a library of materials with high speed and high accuracy. Two-dimensional X-ray diffraction systems dedicated for combinatorial screening are widely used in the pharmaceutical industry for drug discovery and process analysis (Klein *et al.*, 1998; He *et al.*, 2001).

Forensic science and archaeology have benefited from using two-dimensional X-ray diffraction for identifying materials and structures from small specimens (Kugler, 2003; Bontempi *et al.*, 2008). It is nondestructive and does not require special sample treatment, so the original evidence or sample can be preserved. Two-dimensional diffraction patterns contain abundant information and are easy to observe and explain in the courtroom.

2.5.2. Fundamentals

A conventional powder-diffraction pattern is displayed as the scattering intensity *versus* scattering angle 2θ or d-spacing. A 2D-XRD pattern contains the scattering-intensity distribution as a function of two orthogonal dimensions. One dimension can be expressed in 2θ, which can be interpreted by Bragg's law. The distribution in the dimension orthogonal to 2θ contains additional information, such as the orientation distribution, strain states, and crystallite-size and -shape distribution. In order to understand and analyse 2D diffraction data, new geometry conventions and algorithms are introduced. The geometry conventions and algorithms used for 2D-XRD should also be consistent with conventional XRD, so that many existing concepts and algorithms are still valid when 2D diffraction data are used.

The geometry of a 2D-XRD system can be explained using three distinguishable and interrelated geometry spaces, each defined by a set of parameters (He, 2003). The three geometry spaces are the diffraction space, detector space and sample space. The laboratory coordinate system $\mathbf{X}_L$, $\mathbf{Y}_L$, $\mathbf{Z}_L$ is the basis of all three spaces. Although the three spaces are interrelated, the definitions and corresponding parameters should not be confused. Except for a few parameters introduced specifically for 2D-XRD, many of these parameters are used in conventional X-ray diffraction systems. Therefore, the same definitions are maintained for consistency. The three-circle goniometer in Eulerian geometry is the most commonly used, and all the algorithms for data interpretation and analysis in this chapter are based on Eulerian geometry. The algorithms can be developed for the geometries of other types (such as kappa) by following the same strategies.

2.5.2.1. *Diffraction space and laboratory coordinates*

2.5.2.1.1. *Diffraction cones in laboratory coordinates*

Fig. 2.5.3(a) describes the geometric definition of diffraction cones in the laboratory coordinate system $\mathbf{X}_L$, $\mathbf{Y}_L$, $\mathbf{Z}_L$. The laboratory coordinate system is a Cartesian coordinate system.