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2.5.3. Instrumentation

2.5.3.1. *X-ray source and optics*

2.5.3.1.1. *Beam path in a diffractometer equipped with a 2D detector*

The Bragg–Brentano (B-B) parafocusing geometry is most commonly used in conventional X-ray diffractometers with a point detector (Cullity, 1978; Jenkins & Snyder, 1996). In the Bragg–Brentano geometry, the sample surface normal is always a bisector between the incident beam and the diffracted beam. A divergent incident beam hits the sample surface with an incident angle θ. The area of the irradiated region depends on the incident angle θ and the size of the divergence slit. The diffracted rays leave the sample at an angle 2θ, pass through the anti-scatter slit and receiving slit, and reach the point detector. Soller slits are used on both the primary side and secondary side to minimize the effects of axial divergence due to the line-focus beam. The primary line-focus beam sliced by the Soller slits can also be considered as an array of point beams parallel to the diffractometer planes. Each of these point beams will produce a diffraction cone from the sample. The overlap of all the diffraction cones will create a smeared diffraction peak. The Soller slits on the receiving side allow only those diffracted beams nearly parallel to the diffractometer plane to pass through, so the smearing effect is minimized. In another words, the so-called 'line-focus geometry' in conventional diffractometry is actually a superposition of many layers of 'spot-focus geometry'.

The beam path in a diffractometer equipped with a 2D detector is different from that in a conventional diffractometer in many respects (He & Preckwinkel, 2002). In a 2D-XRD system the whole or a large portion of the diffraction rings are measured simultaneously, and neither slits nor monochromator can be used between the sample and detector. Therefore, the X-ray source and optics for 2D-XRD systems have different requirements in terms of the beam spectral purity, divergence and beam cross-section profile. Fig. 2.5.9 shows the beam path in a 2D-XRD system with the θ–θ configuration. The geometry for the θ–2θ configuration is equivalent. The X-ray tube, monochromator and collimator assembly are all mounted on the primary side. The incident-beam assembly rotates about the instrument centre and makes an incident angle θ_1 to the sample surface. The first main axis is also called the θ_1 axis. The diffracted beams travel in all directions and some are intercepted by a 2D detector. The detector is mounted on the other main axis, θ_2. The detector position is determined by the sample-to-detector distance D and the detector swing angle α (= $\theta_1 + \theta_2$).

All the components and space between the focal spot of the X-ray tube and sample are collectively referred to as the primary beam path. The primary beam path in a 2D-XRD system is typically sheltered by optical components except between the exit of the collimator and the sample. The X-rays travelling through this open incident-beam path are scattered by the air with two adverse effects. One is the attenuation of the primary beam intensity. The more harmful effect is that the scattered X-rays travel in all directions and some reach the detector, as is shown by the dashed lines with arrows in Fig. 2.5.9. This air scatter introduces a background over the diffraction pattern. Weak diffraction patterns may be buried under the background. Obviously, the air scatter from the incident beam is significantly stronger than that from diffracted X-rays. The intensity of the air scatter from the incident beam is proportional to the length of the open incident-beam path. The effect of air scatter also depends on the wavelength of the X-rays. The longer the wavelength is, the more severe is the air scatter. The secondary beam path is the space between the sample and the 2D detector. The diffracted X-rays are also scattered by air and the diffraction pattern is both attenuated and blurred by the air scattering. In a conventional diffractometer, one can use an anti-scatter slit, diffracted-beam monochromator or detector Soller slits to remove most of the air scatter that is not travelling in the diffracted-beam direction. These measures cannot be used for a 2D-XRD system, which requires an open space between the sample and the 2D detector. Therefore, the open incident-beam path should be kept as small as possible. In order to reduce the air attenuation and air scatter of the incident beam, a helium-purged beam path or a vacuum beam path are sometimes used in a diffractometer. The air scatter from the diffracted X-rays is relatively weak and the effect depends on sample-to-detector distance. It is typically not necessary to take measures to remove air scatter from the diffracted X-rays between the sample and 2D detector if the sample-to-detector distance is 30 cm or less with Cu $K\alpha$ radiation. However, if the sample-to-detector distance is larger than 30 cm or longer-wavelength radiation, such as Co $K\alpha$ or Cr $K\alpha$, is used, it is then necessary to use an He beam path or vacuum beam path to reduce the air scatter.

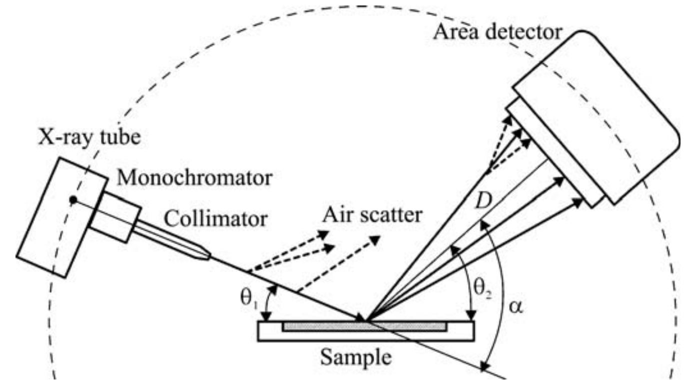

Figure 2.5.9
X-ray beam path in a two-dimensional X-ray diffraction system.

2.5.3.1.2. *Liouville's theorem*

Liouville's theorem can be used to describe the nature of the X-ray source, the X-ray optics and the coupling of the source and optics (Arndt, 1990). Liouville's theorem can be stated in a variety of ways, but for X-ray optics the best known form is

$$S_1\alpha = S_2\beta, \tag{2.5.14}$$

where S_1 is the effective size of the X-ray source and α is the capture angle determined by the effective size of the X-ray optics and the distance between the source and optics. S_2 is the size of the image focus. β is the convergence angle of the X-ray beam from the optics, which is also determined by the effective size of the X-ray optics and the distance between the optics and the image focus. The β angle is also called the crossfire of the X-ray beam. S_2 and β are typically determined by experimental requirements such as beam size and divergence. Therefore, the product $S_1\alpha$ is also determined by experimental conditions. In another expression of Liouville's theorem, the space volume containing the X-ray photons cannot be reduced with time along the trajectories of the system. Therefore, the brilliance of an X-ray source cannot be increased by optics, but may be reduced because of the loss of X-ray photons passing through the optics. In practice, no optics can have 100% reflectivity or transmission.

Considering this, Liouville's theorem given in equation (2.5.14) should be expressed as

$$S_1\alpha \le S_2\beta. \qquad (2.5.15)$$

This states that the product of the divergence and image size can be equal to or greater than the product of the capture angle and source size. If the X-ray source is a point with zero area, the focus image from focusing optics or the cross section of a parallel beam can be any chosen size. For focusing optics, the source size must be considerably smaller than the output beam size in order to achieve a gain in flux. In this case, the flux gain is from the increased capture angle. For parallel optics, the divergence angle β is infinitely small by definition, so it is necessary to use an X-ray source as small as possible to achieve a parallel beam. Focusing optics have an advantage over parallel optics in terms of beam flux. Using an X-ray beam with a divergence much smaller than the mosaicity of the specimen crystal does not improve the resolution, but does sacrifice diffraction intensity. For many X-ray diffraction applications with polycrystalline materials, a large crossfire is acceptable as long as the diffraction peaks concerned can be resolved. The improved peak profile and counting statistics can most often compensate for the peak broadening due to large crossfire.

2.5.3.1.3. *X-ray source*

A variety of X-ray sources, from sealed X-ray tubes and rotating-anode generators to synchrotron radiation, can be used for 2D powder diffraction. The history and principles of X-ray generation can be found in many references (Klug & Alexander, 1974; Cullity, 1978). The X-ray beam intensity depends on the X-ray optics, the focal-spot brightness and the focal-spot profile. The focal-spot brightness is determined by the maximum target loading per unit area of the focal spot, also referred to as the specific loading. A microfocus sealed tube (Bloomer & Arndt, 1999; Wiesmann *et al.*, 2007), which has a very small focal spot size (10–50 µm), can deliver a brilliance as much as one to two orders of magnitude higher than a conventional fine-focus sealed tube. The tube, which is also called a 'microsource', is typically air cooled because the X-ray generator power is less than 50 W. The X-ray optics for a microsource, either a multilayer mirror or a polycapillary, are typically mounted very close to the focal spot so as to maximize the gain on the capture angle. A microsource is highly suitable for 2D-XRD because of its spot focus and high brilliance.

If the X-rays used for diffraction have a wavelength slightly shorter than the K absorption edge of the sample material, a significant amount of fluorescent radiation is produced, which spreads over the diffraction pattern as a high background. In a conventional diffractometer with a point detector, the fluorescent background can be mostly removed by either a receiving monochromator mounted in front of the detector or by using a point detector with sufficient energy resolution. However, it is impossible to add a monochromator in front of a 2D detector and most area detectors have insufficient energy resolution. In order to avoid intense fluorescence, the wavelength of the X-ray-tube $K\alpha$ line should either be longer than the K absorption edge of the sample or far away from the K absorption edge. For example, Cu $K\alpha$ should not be used for samples containing significant amounts of the elements iron or cobalt. Since the $K\alpha$ line of an element cannot excite fluorescence of the same element, it is safe to use an anode of the same metallic element as the sample if the X-ray tube is available, for instance Co $K\alpha$ for Co samples. In general, intense fluorescence is produced when the atomic number of the anode material is 2, 3, or 4 larger than that of an element in the sample. When the sample contains Co, Fe or Mn (or Ni or Cu), the use of Cu $K\alpha$ radiation should be avoided; similarly, one should avoid using Co $K\alpha$ radiation if the sample contains Mn, Cr or V, and avoid using Cr $K\alpha$ radiation if the sample contains Ti, Sc or Ca. The effect is reduced when the atomic-number difference increases.

2.5.3.1.4. *X-ray optics*

The function of the X-ray optics is to condition the primary X-ray beam into the required wavelength, beam focus size, beam profile and divergence. Since the secondary beam path in a 2D-XRD system is an open space, almost all X-ray optics components are on the primary side. The X-ray optics components commonly used for 2D-XRD systems include a β-filter, a crystal monochromator, a pinhole collimator, cross-coupled multilayer mirrors, a Montel mirror, a polycapillary and a monocapillary. Detailed descriptions of these optic devices can be found in Chapter 2.1. In principle, the cross-sectional shape of the X-ray beam used in a 2D diffraction system should be small and round. In data-analysis algorithms, the beam size is typically considered to be a point. In practice, the beam cross section can be either round, square or another shape with a limited size. Such an X-ray beam is typically collimated or conditioned by the X-ray optics in two perpendicular directions, so that the X-ray optics used for the point beam are often called 'two-dimensional X-ray optics'.

A pinhole collimator is normally used to control the beam size and divergence in addition to other optic devices. The choice of beam size is often a trade-off between intensity and the ability to illuminate small regions or resolve closely spaced sample features. Smaller beam sizes, such as 50 µm and 100 µm, are preferred for microdiffraction and large beam sizes, such as 0.5 mm or 1 mm, are typically used for quantitative analysis, or texture or crystallinity measurements. In the case of quantitative analysis and texture measurements, using too small a collimator can actually be a detriment, causing poor grain-sampling statistics. The smaller the collimator, the longer the data-collection time. The beam divergence is typically determined by both the collimator and the coupling optic device. Lower divergence is typically associated with a long beam path. At the same time, the beam flux is inversely proportional to the square of the distance between the source and the sample. There are two main factors determining the length of the primary beam path: the first is the required distance for collimating the beam into the required divergence, the second is the space required for the primary X-ray optics, the sample stage and the detector. On the condition that the above two factors are satisfied, the primary X-ray beam path should be kept as short as possible.

2.5.3.2. *2D detector*

Two-dimensional (2D) detectors, also referred to as area detectors, are the core of 2D-XRD. The advances in area-detector technologies have inspired applications both in X-ray imaging and X-ray diffraction. A 2D detector contains a two-dimensional array of detection elements which typically have identical shape, size and characteristics. A 2D detector can simultaneously measure both dimensions of the two-dimensional distribution of the diffracted X-rays. Therefore, a 2D detector may also be referred to as an X-ray camera or imager. There are many technologies for area detectors (Arndt, 1986; Krause & Phillips, 1992; Eatough *et al.*, 1997; Giomatartis, 1998; Westbrook,