2. INSTRUMENTATION AND SAMPLE PREPARATION

centre. The 2θ shift in the segment is averaged. The segment size $\Delta\gamma$ should be sufficient to produce a smooth diffraction profile, but not so large as to introduce too much smearing. For data frames containing high pixel counts, the integration segment can be small, *e.g.* $\Delta\gamma \leq 2°$, and still have a smooth profile for each segment. For data frames having low pixel counts, for example the frames collected from a micron-sized area, from a sample with large grains or with a short data-collection time, it is critical to choose a sufficiently large segment size. The segment size can be determined by observing the smoothness of the integrated profile.

Peak evaluation in each segment can be done using the same algorithm used in the conventional method. The corrections to the integrated profiles are performed before or during the peak evaluation. Absorption correction eliminates the influence of the irradiated area and the diffraction geometry on the measured intensity distribution. The absorption for a given material and radiation level depends on the incident angle to the sample and the reflected angle from the sample. For 2D-XRD, the reflected angle is a function of γ for each frame. The polarization effect is also a function of γ. Therefore, the correction for polarization and absorption should be applied to the frame before integration. (Details of these corrections were discussed in Section 2.5.4.3.4.) The polarization and absorption correction is not always necessary if the error caused by absorption can be tolerated for the application, or if the data-collection strategy involves only ψ and φ scans.

In most cases, $K\alpha$ radiation is used for stress measurement, in which case the weighted average wavelength of $K\alpha_1$ and $K\alpha_2$ radiation is used in the calculations. For samples with a broad peak width, diffraction of $K\alpha_1$ and $K\alpha_2$ radiation is merged together as a single peak profile, and the profile can be evaluated as if there is a single $K\alpha$ line without introducing much error to the measured d-spacing. For samples with a relatively narrow peak width, the diffraction profile shows strong asymmetry or may even reveal two peaks corresponding to the $K\alpha_1$ and $K\alpha_2$ lines, especially at high 2θ angles. In this case the profile fitting should include contributions from both the $K\alpha_1$ and $K\alpha_2$ lines. It is common practice to use the peak position from the $K\alpha_1$ line and the $K\alpha_1$ wavelength to calculate the d-spacing after $K\alpha_2$ stripping.

Background correction is necessary if there is a strong background or the peak-evaluation algorithms are sensitive to the background, such as in $K\alpha_2$ stripping, peak fitting, and peak-intensity and integrated-intensity evaluations. Background correction is performed by subtracting a linear intensity distribution based on the background intensities at the lower 2θ side and the higher 2θ side of the diffraction peak. The background region should be sufficiently far from the 2θ peak so that the correction will not truncate the diffraction profile. The 2θ ranges of the low background and high background should be determined based on the width of the 2θ peak and available background in the profile. Based on a normal distribution, a 2θ range of 2 times the FWHM covers 98% of the peak intensity, and 3 times the FWHM covers more than 99.9%, so the background intensity should be determined at more than 1 to 1.5 times the FWHM away from the peak position. The background correction can be neglected for a profile with a low background or if the error caused by the background is tolerable for the application. The peak position can be evaluated by various methods, such as gravity, sliding gravity, and profile fitting by parabolic, pseudo-Voigt or Pearson-VII functions (Lu, 1996; Sprauel & Michaud, 2002).

2.5.4.3.6. *Stress calculation*

The final data set after integration and peak evaluation should contain many data points describing the diffraction-ring shape for all collected frames. Each measured data point contains three goniometer angles (ω, ψ, φ) and the diffraction-ring position (γ, 2θ). The peak intensity or integrated intensity of the diffraction profile is another value to be determined and may be used in the stress calculation. In most cases the number of data points is more than the number of unknown stress components, so a linear least-squares method can be used to calculate the stresses. In a general least-squares regression, the residual for the ith data point is defined as

$$r_i = y_i - \hat{y}_i, \tag{2.5.86}$$

where y_i is the observed response value, $\hat{y}_i$ is the fitted response value and r_i is the residual, which is defined as the difference between the observed value and the fitted value. The summed square of residuals is given by

$$S = \sum_{i=1}^{n} r_i^2 = \sum_{i=1}^{n} (y_i - \hat{y}_i)^2, \tag{2.5.87}$$

where n is the number of data points and S is the sum-of-squares error to be minimized in the least-squares regression. For stress calculation, the observed response value is the measured strain at each data point,

$$y_i = \ln\left(\frac{\sin\theta_0}{\sin\theta_i}\right), \tag{2.5.88}$$

and the fitted response value is given by the fundamental equation as

$$\hat{y}_i = p_{11}\sigma_{11} + p_{12}\sigma_{12} + p_{22}\sigma_{22} + p_{13}\sigma_{13} + p_{23}\sigma_{23} + p_{33}\sigma_{33} + p_{\mathrm{ph}}\sigma_{\mathrm{ph}}, \tag{2.5.89}$$

where all possible stress components and stress coefficients are listed as a generalized linear equation. Since the response-value function is a linear equation of unknown stress components, the least-squares problem can be solved by a linear least-squares regression. In order to reduce the impact of texture, large grains or weak diffraction on the results of the stress determination, the standard error of profile fitting and the integrated intensity of each profile may be introduced as a weight factor for the least-squares regression (He, 2009).

2.5.4.3.7. *Comparison between the 2D method and the conventional method*

Stress measurement on a polycrystalline material by X-ray diffraction is based on the strain measurements in a single or in several sample orientations. Each measured strain is calculated from the average d-spacing of specific lattice planes {hkl} over many crystallites (grains). A larger number of contributing crystallites gives better accuracy and sampling statistics (also referred to as particle statistics). The sampling statistics are determined by both the crystal structure and the instrumentation. The instrument window is mainly determined by the divergence of the incident X-ray beam. Lattice-plane families with high multiplicity will also effectively improve the sampling statistics. The number of contributing crystallites measured by a conventional diffractometer is limited by the sizes and divergences of the incident and diffracted beams to the point detector. In a two-
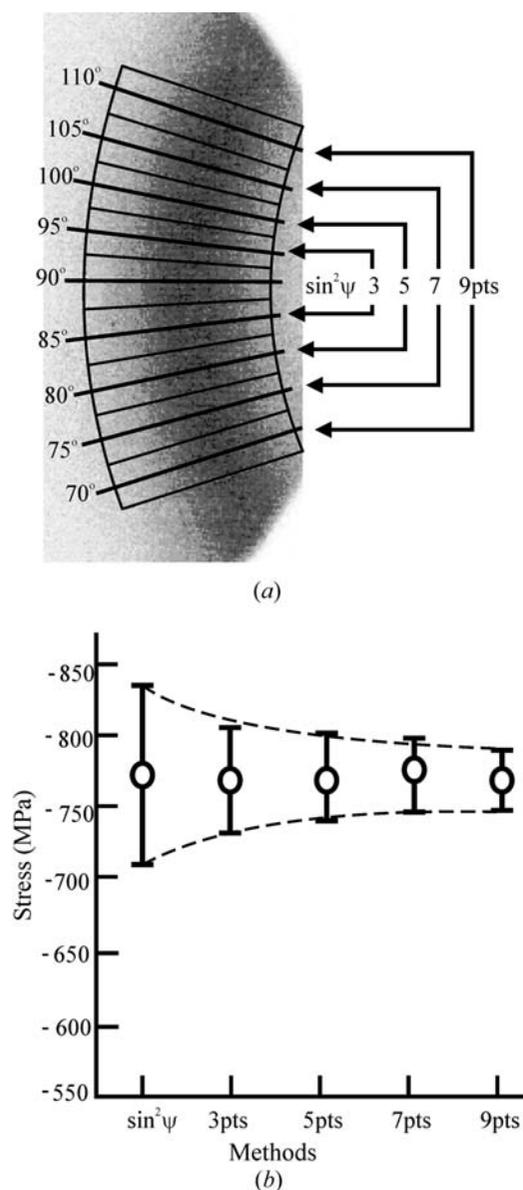
Figure 2.5.27
Stress calculation with the 2D method and the $\sin^2 \psi$ method: (*a*) nine data points (abbreviated as pts) on the diffraction ring; (*b*) measured stress and standard deviation by different methods.

dimensional diffraction system, more crystallites can contribute to the diffraction because of the larger γ range.

An example of a stress calculation is provided by the measurement of the residual stress on the end surface of a carbon steel roller. One of the seven frames taken with an ω scan is shown in Fig. 2.5.27(*a*). The (211) ring covering the γ range 67.5 to 112.5° was used for stress analysis. First, the frame data were integrated along γ with an interval of $\Delta\gamma = 5°$. A total of nine diffraction profiles were obtained from γ integration. The peak position 2θ for each γ angle was then obtained by fitting the profile with a Pearson-VII function. A total of 63 data points can be obtained from the seven frames. The data points at $\gamma = 90°$ from seven frames, a typical data set for an ω diffractometer, were used to calculate the stress with the conventional $\sin^2 \psi$ method. In order to compare the gain from having increased data points with the 2D method, the stress was calculated from 3, 5, 7 and 9 data points on each frame. The results from the conventional $\sin^2 \psi$ method and the 2D method are compared in Fig. 2.5.27(*b*). The measured residual stress is compressive and the stress values from different methods agree very well. With the data taken from the same measurement (seven frames), the 2D

method gives a lower standard error and the error decreases with increasing number of data points from the diffraction ring.

2.5.4.4. *Quantitative analysis*

2.5.4.4.1. *Crystallinity*

The crystallinity of a material influences many of its characteristics, including mechanical strength, opacity and thermal properties. Crystallinity measurement provides valuable information for both materials research and quality control in materials processing. The diffraction pattern from a material containing both amorphous and crystalline solids has a broad feature from the amorphous phase and sharp peaks from the crystalline phase. The weight percentage of the crystalline phases in a material containing both crystalline and amorphous phases can be determined by X-ray diffraction (Chung & Scott, 1973; Alexander, 1985; Murthy & Barton, 2000; Kasai & Kakudo, 2005). Assuming that the X-ray scattering intensity from each phase in such a material is proportional to its weight percentage, and that the scattering intensities from all phases can be measured within a given 2θ range, the per cent crystallinity is given by

$$x_{\text{pc}} = 100\% \frac{I_{\text{crystal}}}{I_{\text{crystal}} + I_{\text{amorphous}}}, \qquad (2.5.90)$$

where x_{pc} is the per cent crystallinity, I_{crystal} is the integrated intensity of all crystalline peaks and $I_{\text{amorphous}}$ is the integrated intensity of the amorphous scattering. The accuracy of the measured per cent crystallinity depends on the integrated diffraction profile. Since most crystalline samples have a preferred orientation, it is very difficult to obtain a consistent measurement of crystallinity with a conventional diffractometer. Fig. 2.5.28 shows a 2D diffraction frame collected from an oriented polycrystalline sample. The diffraction is in transmission mode with the X-ray beam perpendicular to the plate sample surface. Fig. 2.5.28(*a*) shows a diffraction profile integrated from a horizontal region analogous to a profile collected with a conventional diffractometer. Only one peak from the crystalline phase can be observed in the profile. It is also possible that a different peak or no peak is measured if the sample is loaded in other orientations. Fig. 2.5.28(*b*) is the diffraction profile integrated from the region covering all peaks from the crystalline phase over almost all azimuthal angles. A total of four peaks from the crystalline phase are observed. This shows that a 2D-XRD system can measure per cent crystallinity more accurately and with more consistent results (Pople *et al.*, 1997; Bruker, 2000) than a conventional system.

2.5.4.4.2. *Crystallite size*

The size of the crystallites in a polycrystalline material has a significant effect on many of its properties, such as its thermal, mechanical, electrical, magnetic and chemical properties. X-ray diffraction has been used for crystallite-size measurement for many years. Most methods are based on diffraction-line broadening and line-profile analysis (Wilson, 1971; Klug & Alexander, 1974; Ungár, 2000). Another approach to crystallite-size measurement is based on the spotty diffraction rings collected with two-dimensional detectors when a small X-ray beam is used (Cullity, 1978; He, 2009). Line-profile analysis is based on the diffraction profile in the 2θ direction, while crystallite-size analysis with a spotty 2D diffraction pattern is based on the diffraction profile in the γ direction. The latter may be referred to as γ-profile analysis.