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The Relations Between Three X-ray Scan Modes and their Applications*†

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Abstract

For the conventional Bragg-Brentano X-ray diffractometer, besides the θ and 2θ angles, an α angle, made by the incident X-ray beam and the sample surface, is introduced in this paper. This has made it possible to normalize three X-ray scan modes in terms of $\theta(\alpha)/2\theta$ and then to derive the corresponding equations of diffraction intensities and azimuthal angles of measured crystal planes based on asymmetrical Bragg reflection geometry, so that the intensity and the azimuth equations for many well known X-ray diffraction methods can be derived from them. Also a new X-ray method called sample-tilting X-ray diffraction (STD) has been developed for solving problems related to phase analysis. A discussion of the effective X-ray penetration depth for each X-ray method is included.

1. Introduction

A conventional Bragg-Brentano (B-B) X-ray diffractometer has two circles; the θ circle carrying the sample and the 2θ circle carrying the detector. In general, there are three scan modes: $\theta/2\theta$, 2θ and θ. It is convenient to use the function $\theta(\alpha)/2\theta$ to normalize three modes, where the parameter α is the angle made by the incident X-ray beam and the sample surface. Hence, we have $\theta(\alpha)/2\theta$, $\theta(\alpha_0)/2\theta$ and $\theta(\alpha)/2\theta_0$ corresponding to the above three scan modes, respectively, where the subscript 0 identifies a constant or an adjustable parameter during one scan process.

The purpose of this paper is to show the important effects of the α-angle introduction, to discuss the use of asymmetrical Bragg reflection geometry to normalize the characterization, for three scan modes, of the reflection intensities and the azimuthal angles of the observed crystal planes, and to show new areas of application of X-ray diffraction, solving problems of phase determination with non-destructive depth profiling and orientations of observed reflections.

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2. Basic equations

2.1. *Intensities*

As shown in Fig. 1, the area A which is illuminated by the incident X-ray beam in the Bragg-Brentano diffractometer is given by

$$A = A_0/\sin\alpha \tag{1}$$

where α is the angle between the incident X-ray beam and the sample surface and A_0 is the illuminated area when α is 90°.

The volume of material contributing to diffraction which is located at a depth x below the surface and is of thickness dx *is*

$$dv = A\,dx = (A_0/\sin\alpha)\,dx. \tag{2}$$

The intensity of the beam diffracted from this differential volume is (James, 1950)

$$dI \propto (A_0/\sin\alpha)\,dx \times \exp\{-\mu x[(1/\sin\alpha)+(1/\sin\beta)]\}P. \tag{3}$$

The observed intensity from a finite thickness, t, is obtained from (3) by integration:

$$I = C_{hkl}[\sin\beta/(\sin\alpha+\sin\beta)] \times (1-\exp\{-\mu t[(1/\sin\alpha)+(1/\sin\beta)]\})P. \tag{4}$$

For convenience, (4) is written as

$$I = J(\alpha, 2\theta, t)P. \tag{4'}$$

β is the angle between the diffracted beam and the sample surface $(=2\theta-\alpha)$, C_{hkl} is a constant for the given hkl reflection and includes the structure, multiplicity and Lp factors under the given experimental

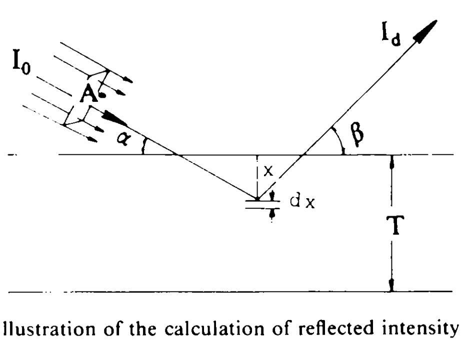

Fig. 1. Illustration of the calculation of reflected intensity from a flat sample in the case of asymmetrical Bragg reflection geometry.

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conditions, P is the peak profile function, 2θ is the diffraction angle, t is the film thickness or the effective X-ray penetration depth and μ is the linear absorption coefficient.

2.2. *Azimuthal angles*

As shown in Fig. 2, the azimuthal angle, φ_{hkl}, which is the angle between the sample surface and the observed lattice plane, is defined as

$$\varphi_{hkl} \equiv \theta_{hkl} - \alpha, \quad (5)$$

where θ_{hkl} is the Bragg angle of the given hkl reflection.

2.3. *Relationship between the X-ray penetration depth and the α angle*

If R_t represents the intensity ratio of penetration of X-rays in a thin film with thickness t to that of a thick film with $t \to \infty$, then

$$R_t = 1 - \exp\{-\mu t[(1/\sin\alpha) + (1/\sin\beta)]\}. \quad (6)$$

If, in the case of $R_t = 0.63$, the diffracted intensity is high enough to be detected, then, from (6),

$$t = (1/\mu)[\sin\alpha \sin\beta/(\sin\alpha + \sin\beta)]. \quad (7)$$

In the general case where $0 < R_t < 1$, (7) is expressed as

$$t = (c/\mu)[\sin\alpha \sin\beta/(\sin\alpha + \sin\beta)] \quad (7')$$

where

$$c = \ln(1 - R_t).$$

3. For the three scan modes

3.1. *$\theta(\alpha)/2\theta$ coupled scan mode*

(*a*) In the case of $\beta = \theta = \alpha$, (4), (5) and (7) become

$$I_c = (C_{hkl}/2)[1 - \exp(-2\mu t/\sin\theta)]P_c, \quad (8)$$

$$(\varphi_{hkl})_c = 0° \quad (9)$$

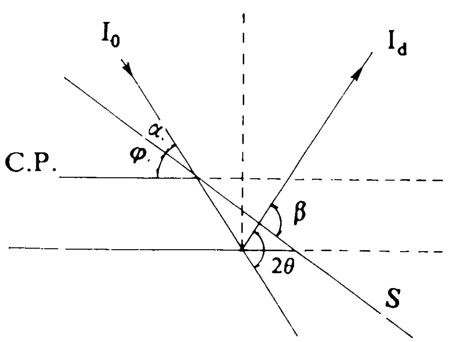

Fig. 2. Asymmetrical Bragg surface reflection geometry, where S is the sample surface, I_0 is the incident X-ray beam, I_d is the diffracted X-ray beam and C.P. is the observed crystal plane; $\alpha = \widehat{I_0S}$, $2\theta = \widehat{I_0I_d}$, $\beta = \widehat{I_dS}$ and $\varphi_{hkl} = \widehat{\text{C.P.S}}$.

and

$$t_c = \sin\theta/2\mu, \quad (10)$$

respectively, where the subscript c indicates that these expressions apply to conventional B-B X-ray diffraction (CBD) (Wilson, 1950). Equation (9) implies that the lattice planes of all reflections observed using the CBD method are parallel to the sample surface.

(*b*) In the case of $\alpha = \theta - \alpha_0$, $\beta = \theta + \alpha_0$, (4), (5) and (7) become

$$I_{mc} = J_{mc}(\theta - \alpha_0, 2\theta, t)P_{mc}, \quad (11)$$

$$(\varphi_{hkl})_{mc} = \alpha_0 \quad (12)$$

and

$$t_{mc} = (1/\mu) \times \{[\sin(\theta + \alpha_0)\sin(\theta - \alpha_0)] \times [\sin(\theta + \alpha_0) + \sin(\theta - \alpha_0)]^{-1}\}, \quad (13)$$

respectively, where α_0 is the small angle, in general less than 0.5°, between the incident X-ray beam and the original position of the sample; the subscript mc indicates that these expressions apply to a modified CBD (MCBD) method. This scan mode is similar to the above, *i.e.* θ: $2\theta = 1:2$. Owing to the small α, the X-ray penetration depth (13) is close to that with the CBD method [see (10)]. The MCBD method is ideally suited for the analysis of coatings on single-crystal substrates; reflections from the single-crystal substrate are effectively eliminated by the effect of orientation.

3.2. *$\theta(\alpha_0)/2\theta$ scan mode*

In the case of the $\theta(\alpha_0)/2\theta$ scan mode, the θ circle for the sample is fixed at the α_0 angle with respect to the incident X-ray beam, and the 2θ circle for the detector is rotated, thus (4), (5) and (7) become

$$I = J(\alpha_0, 2\theta, t)P, \quad (14)$$

$$\varphi_{hkl} = \theta_{hkl} - \alpha_0 \quad (15)$$

and

$$t = (1/\mu)[\sin\alpha_0 \sin\beta/(\sin\alpha_0 + \sin\beta)], \quad (16)$$

respectively. In this mode, the term θ has a double meaning: (i) θ ($= \theta_0 = \alpha_0$) represents the stationary sample position; (ii) θ represents the Bragg angle of the observed reflection; in this case, $\theta = (2\theta)/2$, where 2θ represents the position of the detector.

It is known from (15) that the azimuthal angles of the observed lattice planes are not equal to zero except for $\alpha_0 = \theta_{hkl}$.

There are three special X-ray diffraction methods depending on the α_0 angle.

(*a*) In the case where $0.6 \leq \alpha_0 \leq 1°$, there is the grazing-angle X-ray diffraction (GAD) method

(Segmuller, 1987). The X-ray penetration depth from (16) becomes

$$t \simeq \alpha_0/\mu \qquad (17)$$

when $\sin \alpha_0 \ll \sin \beta$.

(*b*) In the case where $1 \leq \alpha_0 \leq 10°$, thin-film diffractometry (TFD) is performed using the thin-film diffractometer with parallel X-ray beam optics (Katayama & Shimizu, 1988).

(*c*) In the case where $0.6° \leq \alpha_0 \leq \theta_{hkl}$, there is the sample-tilting X-ray diffraction (STD) method (Cong, Ou Yang, Yu & Zhao, 1991), which has been performed by the authors on the conventional B-B X-ray diffractometer with divergent X-ray optics. The X-ray penetration depth can be expressed by

$$t_s = (1/\mu)[\sin \alpha_0 \sin \beta/(\sin \alpha_0 + \sin \beta)], \qquad (16')$$

where $\beta = 2\theta - \alpha_0$ and $0.6° \leq \alpha_0 \leq \theta_{hkl}$ for Cu $K\alpha$ radiation.

Equation (16′) is in the same form as (16). Therefore, the STD method can in some ways be used for the same purposes as the GAD and TFD methods.

For the STD method, two important points must be noted. First, the effective X-ray penetration depth can be adjusted by changing the value of α_0 [see (16) or (16′)]. So it is reasonable to say that phase analysis with non-destructive depth profiling can be performed by the STD technique. Second, the azimuthal angles of the observed crystal planes can be found for a sample with preferred orientation [see (15)].

3.3. $\theta(\theta)/2\theta_0$ *scan mode*

In the case of the $\theta(\theta)/2\theta_0$ scan mode, a rocking curve is obtained for the given *hkl* reflection. Then (4), (5) and (7) become

$$I_a = J_a(\alpha, 2\theta_{hkl}, t)P_a, \qquad (18)$$

$$(\varphi_{hkl})_a = \theta_{hkl} - \theta \qquad (19)$$

and

$$t_a = (1/\mu)[\sin \alpha \sin \beta/(\sin \alpha + \sin \beta)], \qquad (20)$$

respectively, where $\alpha = \theta$, $\beta = 2\theta_{hkl} - \alpha$, $2\theta_{hkl}$ is the diffraction angle for the *hkl* reflection and the subscript *a* indicates that these expressions apply to the angular dispersion analysis (ADA) for a given rocking curve.

3.4. *The relationship between STD and ADA*

Both STD and ADA resulted from asymmetrical Bragg reflection geometry, *i.e.* $\beta \neq \alpha$. Combining (14), (15) and (16′) with (18), (19) and (20), respectively, we obtain

$$I_s = I_a, \qquad (21)$$

$$(\varphi_{hkl})_s = (\varphi_{hkl})_a \qquad (22)$$

and

$$t_s = t_a, \qquad (23)$$

when $\alpha = \alpha_0$ for (18)-(20) and $2\theta = 2\theta_{hkl}$ for (14)-(16).

Equations (21)-(23) are important for calculating the X-ray penetration depth *versus* the α-angle values, which may be used in X-ray diffraction analysis with the STD method, detailed elsewhere.

4. Transmitted reflection

A limitation of the surface reflection methods is that, when φ in (5) is greater than θ_{hkl}, the diffracted beam does not emerge from the front surface of the specimen. In this case, the specimen must be made sufficiently thin for the X-rays to be transmitted through it. Equation (3) is changed accordingly and then the transmitted reflection intensity is given from (3) by integration:

$$I = C_{hkl}[\sin \beta/(\sin \alpha_0 - \sin \beta)] \times [\exp(-\mu T/\sin \alpha_0) - \exp(-\mu T/\sin \beta)]P, \qquad (24)$$

where $\beta = \alpha_0 - 2\theta$, T is the whole thickness of thin

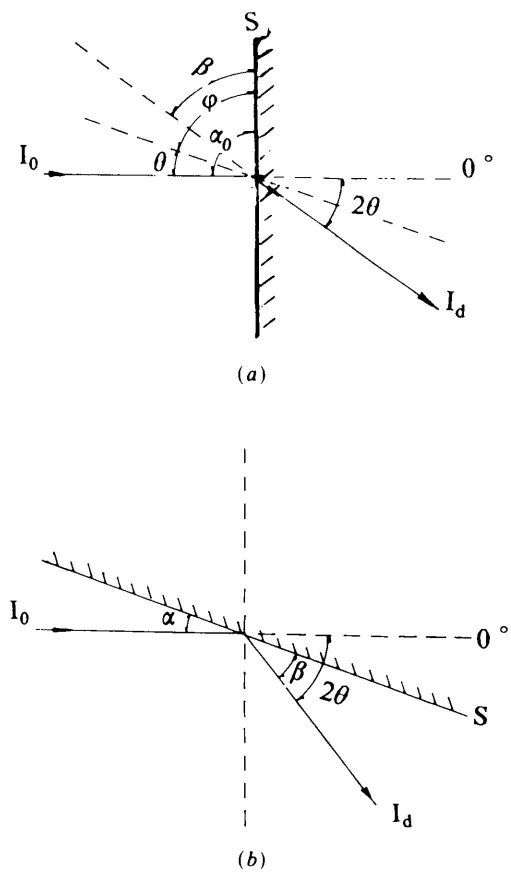

Fig. 3. The geometrical arrangements of specimens with respect to X-ray sources and counters for diffractometry with (*a*) transmitted reflection and (*b*) surface reflection as in Fig. 2.

flat specimen, and the azimuthal angle is given by

$$\varphi_{hkl} = \alpha_0 - \theta_{hkl}, \qquad (25)$$

with a limitation of

$$\alpha_0 > 2\theta_{hkl} \qquad (26)$$

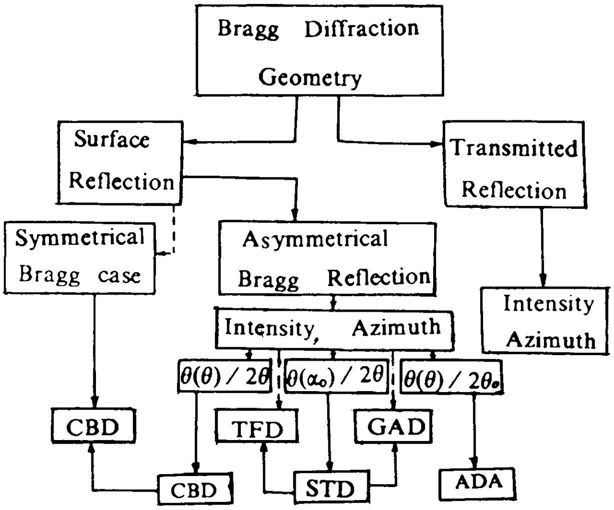

Fig. 4. Block diagram showing X-ray diffraction methods.

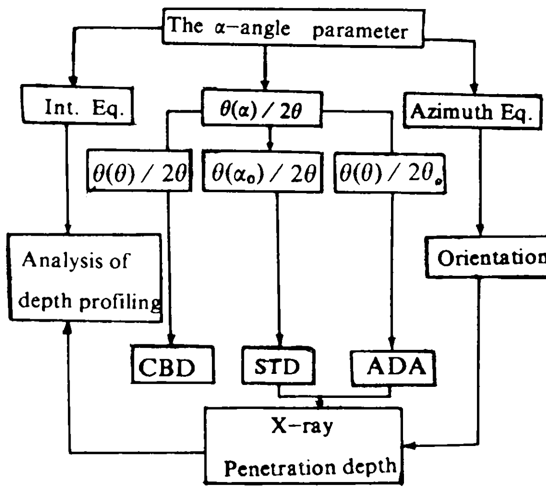

Fig. 5. Block diagram showing the effect of the α-angle parameter.

for the STD case. It is convenient if (25) is written as

$$\alpha_0 = \varphi_{hkl} + \theta_{hkl}, \qquad (25')$$

especially when $\varphi_{hkl} = 90°$; $\alpha_0 = \theta_{hkl} + 90°$.

5. Concluding remarks

The geometrical arrangements of specimens with respect to X-ray sources and counters for diffractometry with transmitted and surface reflection are shown in Figs. 3(a) and (b), respectively.

For uniform samples, in the surface reflection cases, one has

$$0° \le \varphi_{hkl} < \theta_{hkl} \qquad (27)$$

and

$$\varphi_{hkl} = \theta_{hkl} - \alpha_0, \qquad (15)$$

with a limitation of $2\theta_{hkl} > \alpha_0$; in the transmitted reflection cases,

$$\theta_{hkl} < \varphi_{hkl} \le 180° \qquad (28)$$

and

$$\alpha_0 = \varphi_{hkl} + \theta_{hkl}, \qquad (25)$$

with a limitation of $2\theta_{hkl} < \alpha_0$.

A summary of the Bragg X-ray diffraction methods described in the present paper is given in Fig. 4, where the dotted lines indicate well known methods and the solid lines indicate methods described in detail in this paper.

Fig. 5 shows the effects of the α-angle parameter introduced in this study. Owing to the introduction of this parameter, it has been possible to normalize the characterization of the diffracted intensities, azimuthal angles and X-ray penetration depths for three X-ray scan modes. These are helpful in characterizing a variety of the well known X-ray diffraction methods such as CBD, MCBD, GAD and TFD, in opening new areas of application, such as STD and ADA and in showing the relationships between them.

References

CONG, Q. Z., OU YANG, M. A., YU, D. Y. & ZHAO, J. Z. (1991). *J. Solid Lubrication*, **11**, 135–142. (In Chinese.)

JAMES, R. W. (1950). *The Optical Principles of the Diffraction of X-rays*, p. 44. London: Bell.

KATAYAMA, M. & SHIMIZU, M. (1988). *Adv. X-ray Anal.* **19**, 281–291.

SEGMULLER, A. (1987). *Thin Solid Films*, **154**, 32–42.

WILSON, A. J. C. (1950). *J. Sci. Instrum.* **27**, 321–325.