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X-ray Particle-Size Broadening

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Abstract

X-ray diffraction profiles and Fourier coefficients are given for particles distributed according to experimentally verified size distributions. Calculations are based upon the log normal distribution of sphere diameters and intercept lengths in addition to a normal distribution of column heights. It is found that the diffraction profile is not sensitive to the fine details of the distribution but rather the mean column height and the column-height variation coefficient. Errors in particle-size determinations will result from an improper choice of the variation coefficient. Two simplified models are given that describe the diffraction profiles for a large range of variation coefficients.

Introduction

Interest in the use of X-ray diffraction to obtain particle-size information can be traced to Scherrer (1918). Subsequent contributions were made by Stokes & Wilson (1942) and Warren & Averbach (1950, 1952). The early work made use of either the full width at half maximum or the integral breadth while the later works tended to make use of a Fourier analysis of the full diffraction profile. A complete list of contributors would cover several pages. Recently, Adler & Houska (1979) and Houska & Smith (1981) described procedures for obtaining particle size (and strain) for a spherical shape of average diameter, by using non-linear least-squares fitting routines. Again, profile information is required, although full profiles are not required.

There is very little literature that deals with the effect of different column-sized distributions upon the particle-size Fourier coefficients or on the shape of measured line profiles. A major goal of this paper is to assess the importance of the form of the column-height distribution on the Fourier coefficients and X-ray profiles.

Considerable experimental information is available on particle-size distributions from quantitative optical microscopy. This is based largely upon spherical grains in metallic systems (Saltykov, 1961). These data are generally best described by log normal size distributions. X-ray diffraction profiles are relateable to coherent subgrain distributions rather than grains and such determinations have been interpreted as an average distance between dislocations along the various crystallographic directions.

We will make use of the directly observed distributions obtained by microscopy and assume that the subgrains follow the same well known distributions. A log normal distribution of spheres has been found to be valid for many reactions in metallic systems (Saltykov, 1961) and will be applied here as one of the important functions. Recently, there has been an interest in the structure of films. Here, a normal distribution of columnar grains appears to be justified when the surface is irregular. If the subgrains are spherical, the X-ray diffraction profiles associated with small particle size requires the distribution of line intercepts for each spherical subgrain. This is directly relateable to the column distribution required in diffraction theory (Adler & Houska, 1979). The derivation of the column-height distribution from a grain-size distribution is readily obtained with a spherical shape. Only spherical and columnar subgrains are considered here.

Guinier (1963) notes, in an earlier paper, that it is not feasible to determine experimentally the shape of subgrains of non-uniform size, by using only one profile of the X-ray diffraction pattern. It will be seen later that the most readily available information from X-ray particle-size broadening is the average column length and the size-variation coefficient perpendicular to the reflecting planes and additional detail about particle shape is not readily obtainable from X-ray particle-size broadening.

Distribution functions

The empirically determined log normal distribution of grain sizes is applied to subgrain size. This is

$$P(\ln D)\,d(\ln D)=[(2\pi)^{1/2}\ln\sigma_g]^{-1}\times\exp\{-\tfrac{1}{2}[((\ln D-\ln D_g)/\ln\sigma_g)]^2\}\,d(\ln D) \quad (1)$$

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with a mean diameter of

$$\langle D\rangle = D_g \exp[\tfrac{1}{2}(\ln \sigma_g)^2]. \quad (2)$$

The most probable subgrain is $D_g \exp[-(\ln \sigma_g)^2]$ and D_g is the geometric mean defined as

$$D_g = \exp(\langle \ln D\rangle). \quad (2a)$$

Similarly, σ_g is the geometric standard deviation. The column-length distribution associated with (1) is readily derived by making use of the column-length distribution from a single sphere of diameter D:

$$\begin{aligned} p(L) &= 2L/D^2, \quad L \le D \\ p(L) &= 0, \quad L > D. \end{aligned} \quad (3)$$

By using relation (A-1) of Appendix A, the required distribution function is evaluated as

$$\begin{aligned} p(L)\,\mathrm{d}L = \{&L \exp[2(\ln \sigma_g)^2]/D_g^2\} \\ &\times \operatorname{erfc}\{2^{-1/2}[(\ln L - \ln D_g)/\ln \sigma_g \\ &+ 2 \ln \sigma_g]\}\,\mathrm{d}L. \end{aligned} \quad (4)$$

This gives an average chord length of

$$\langle L\rangle = \tfrac{2}{3} D_g \exp[\tfrac{1}{2}(\ln \sigma_g)^2] = \tfrac{2}{3}\langle D\rangle. \quad (5)$$

Equation (5) contains the same factor $(\frac{2}{3})$ that is obtained in calculating the average column length from a single sphere. From the relation $\langle L\rangle = \langle d\rangle N_3$ and $D_g = \langle d\rangle_{3D}$, where N_3 is the average column height and $\langle d\rangle$ is the average d spacing for the first order of the reflecting planes, and the substitution of (5) in (4), the probability distribution of column heights in terms of dimensionless distance j, $p(j)\,\mathrm{d}j (j = L/\langle d\rangle)$, becomes

$$\begin{aligned} p(j)\,\mathrm{d}j = &(4/9)(j/N_3^2) \exp[3(\ln \sigma_g)^2] \\ &\times \operatorname{erfc} 2^{-1/2}[(\ln j - \ln N_{3D})/\ln \sigma_g \\ &+ 2 \ln \sigma_g]\,\mathrm{d}j. \end{aligned} \quad (6)$$

The variation coefficient of the column-height distribution, V_c, which gives a measure of the spread of the distribution (Saltykov, 1961), is given by

$$V_c = [j^2 p(j)\,\mathrm{d}j - \langle j\rangle^2]^{1/2}/\langle j\rangle \quad (7)$$

or in this case

$$V_c = \tfrac{3}{2}\{\tfrac{1}{2} \exp[(\ln \sigma_g)^2] - (4/9)\}^{1/2}. \quad (8)$$

The cell-height distribution (6) is normalized and goes to the following limits as $\ln \sigma_g \to 0$:

$$p(j)\,\mathrm{d}j \begin{cases} = 2j/N_{3D}^2, & j \le N_{3D} \\ = 0, & j > N_{3D}. \end{cases} \quad (9)$$

This causes the log normal distribution to become a δ function localized at N_{3D} giving the column-height distribution from a single sphere. Also, the variation coefficient of (8) goes to the correct limit of 0·354 as $\ln \sigma_g \to 0$, which is the value for the column-height distribution from a single sphere.

If a normal distribution of columnar subgrains is assumed in the case of thin films with some surface irregularities, the distribution of column heights is given by

$$\begin{aligned} p(j)\,\mathrm{d}j = &[1/(2\pi)^{1/2}\sigma][2/\operatorname{erfc}(-N_{3G}/2^{1/2}\sigma)] \\ &\times \exp[-(j - N_{3G})^2/2\sigma^2]\,\mathrm{d}j, \end{aligned} \quad (10)$$

where N_{3G} is the most probable column height. It is required that $p(0)$ be zero, which occurs only if $N_{3G} \gg 2^{1/2}\sigma$. This condition was identically satisfied for the previously discussed log normal distribution. The average number of cells per column for the sample, N_3, is given by

$$\begin{aligned} N_3 = &N_{3G} + (2/\pi)^{1/2}\sigma \exp[-N_{3G}^2/2\sigma^2] \\ &\times [\operatorname{erfc}(-N_{3G}/2^{1/2}\sigma)]^{-1} \end{aligned} \quad (11)$$

and the variation coefficient, V_c, by

$$V_c = [\sigma^2/N_3^2 + N_{3G}/N_3 - 1]^{1/2}. \quad (12)$$

If $N_{3G}/2^{1/2}\sigma$ is reasonably large, say >2, then

$$\begin{aligned} N_3 &\simeq N_{3G} \\ V_c &\simeq \sigma/N_3. \end{aligned} \quad (13)$$

By substituting (11) in (10) and simplifying, one finds

$$p(j)\,\mathrm{d}j = (N_3 - N_{3G})/\sigma^2] \exp[jN_{3G}/\sigma^2 - j^2/2\sigma^2]\,\mathrm{d}j. \quad (14)$$

The cell-height distribution of (14) is normalized and goes to the limit

$$p(j)\,\mathrm{d}j = \delta(j - N_{3G})\,\mathrm{d}j \quad (15)$$

as $\sigma \to 0$. This causes the normal distribution to become a δ function localized at $j = N_{3G}$, giving columnar grains of height N_{3G}.

The column-height distribution associated with a normal distribution of diameters of statistically spherical subgrains is difficult and cumbersome to derive rigorously. Hence, an approximate treatment will be followed, which gives a more useable end result (Appendix B). Following this treatment, it can be shown that

$$\begin{aligned} p(j)\,\mathrm{d}j = &(4/9)(j/N_3^2) \exp[3\sigma'^2/N_{3G}^2] \\ &\times \operatorname{erfc} 2^{-1/2}[(j - N_{3G})/\sigma' + 2\sigma'/N_{3G}]\,\mathrm{d}j \end{aligned} \quad (16)$$

provided subgrain diameters are normally distributed by

$$\begin{aligned} &p(\ln D)\,\mathrm{d}(\ln D) \\ &= (2^{1/2}\pi\sigma')^{-1} \exp\{-\tfrac{1}{2}[(D - D_g)/\sigma']^2\}\,\mathrm{d}D, \end{aligned} \quad (17)$$

where $D_g = \langle d\rangle N_{3G}$, $\langle d\rangle$ being the average d spacing for the first order of the reflecting planes. Equations (16) and (17) are valid only if $N_{3G}/2^{1/2}\sigma$ is sufficiently large. The average number of cells per column, N_3, is given approximately by

$$N_3 \simeq \tfrac{2}{3} N_{3G} \exp\left[\tfrac{1}{2}\sigma'^2/N_{3G}^2\right] \quad (18)$$

and the variation coefficient, V_c, by

$$V_c \simeq \tfrac{3}{2}\{\tfrac{1}{2}\exp(\sigma'^2/N_{3G}^2) - 4/9\}^{1/2}. \quad (19)$$

The cell-height distribution described by (16) goes to the limit of the distribution from a single sphere of diameter D_g, as $\sigma' \to 0$.

Particle-size Fourier coefficient and line shape

The diffracted X-ray intensity from a sample with only small particle-size broadening is given by the Fourier series (Warren, 1969)

$$P'(h_3) = Y_o\left\{1 + 2\sum_{n=1}^{\infty} A_n^s \cos[2\pi n(h_3 - l)]\right\}, \quad (20)$$

where h_3 is the reciprocal-space variable given by $h_3 = 2\langle d\rangle \sin\theta/\lambda$, Y_o is a scaling parameter, and the integer l translates the origin of the h_3 axis to the peak maximum of the $00l$ reflection. A_n^s is the particle-size coefficient. Equation (20) can be written in an equivalent integral form (Guinier, 1963):

$$P'(h_3)/2N_3 = Y_o \int A_n^s \cos 2\pi h_3^o u \, du, \quad (21)$$

where $h_3^o = N_3(h_3 - l)$ and $u = n/N_3$. The particle-size coefficient, A_n^s, can be written in terms of the column-height distribution, $p(j)$ (Warren, 1969):

$$A_n^s = (1/N_3)\int_{j=|n|}^{\infty} (j - |n|)p(j)\, dj. \quad (22)$$

By differentiating (22), one can show (Warren, 1969) that

$$dA_n^s/dn|_{n=0} = -1/N_3 \quad \text{and} \quad d^2A_n^s/dn^2 = p(n)/N_3. \quad (23a)$$

The integral breadth of a reflection, defined as the ratio of the peak area to the peak maximum, has been shown by Warren (1969) to be

$$\beta(2\theta) = \lambda/L\cos\theta, \quad (23b)$$

where λ is the wavelength, θ is the Bragg angle and L, an effective dimension perpendicular to the reflecting planes, is given by Warren (1969) and extended here to include the variation coefficient V_c:

$$L = \langle n^2\rangle/\langle n\rangle = N_3(1 + V_c^2). \quad (23c)$$

From (23a), (23b) and (23c), a determination of the slope of the particle-size coefficient at $n = 0$ along with the integral breadth can be used to determine the average column height as well as the variation coefficient of the column-height distribution, perpendicular to the reflecting planes.

From (23a), it is evident that the second derivative of the particle-size coefficient gives the column-height distribution. Simple physical reasoning requires that $p(0) = 0$, a condition that sometimes is ignored. The particle-size coefficient for those distributions previously discussed can be determined by using (22). The results of such calculations are listed below:

$$\begin{aligned}
A_n^s(SL) = {} & \tfrac{1}{2}\,\text{erfc}\, 2^{-1/2}[(\ln n - \ln N_{3D})/\ln\sigma_g - \ln\sigma_g] \\
& - \tfrac{1}{2}(n/N_3)\,\text{erfc}\, 2^{-1/2}[(\ln n - \ln N_{3D})/\ln\sigma_g] \\
& + (2/27)(n^3/N_3^3)\exp[3(\ln\sigma_g)^2] \\
& \times \text{erfc}\, 2^{-1/2}[(\ln n - \ln N_{3D})/\ln\sigma_g + 2\ln\sigma_g] \\
A_n^s(CN) = {} & [N_3\,\text{erfc}(-N_{3G}/2^{1/2}\sigma)]^{-1} \\
& \times\{(2/\pi)^{1/2}\sigma \times \exp[-(n - N_{3G})^2/2\sigma^2] \\
& + (N_{3G} - n)\,\text{erfc}\,(n - N_{3G})/2^{1/2}\sigma]\} \\
A_n^s(SN) \simeq {} & \tfrac{1}{2}\,\text{erfc}\, 2^{-1/2}[(n - N_{3G})/\sigma' - \sigma'/N_{3G}] \\
& - \tfrac{1}{2}(n/N_3)\,\text{erfc}\, 2^{-1/2}[(n - N_{3G})/\sigma'] \\
& + (2/27)(n^3/N_3^3)\exp[3\sigma'^2/N_{3G}^2] \\
& \times \text{erfc}\, 2^{-1/2}[(n - N_{3G})/\sigma' + 2\sigma'/N_{3G}],
\end{aligned} \quad (24)$$

where $A_n^s(SL)$ is the particle-size Fourier coefficient for a log normal distribution of spherical grains, $A_n^s(CN)$ is the Fourier coefficient for a normal distribution of column heights and $A_n^s(SN)$ is the Fourier coefficient for a normal distribution of spherical grains. The Fourier coefficients can be checked for consistency in two ways: (i) by checking for their limiting values as their respective distribution width parameters tend to zero and (ii) by verifying that equations (23a) are identically satisfied. Both coefficients, $A_n^s(SL)$ and $A_n^s(SN)$, tend to the correct limit of the Fourier coefficient, deriveable from a column-height distribution from a single sphere (Adler & Houska, 1979) as $\ln\sigma_g$ and σ' tend to zero, *i.e.* as $\ln\sigma_g \to 0$ or $\sigma' \to 0$

$$A_n^s(SL) = A_n^s(SN)\begin{cases} = 1 - n/N_3 + \tfrac{4}{27}n^3/N_3^3, & n \le \tfrac{3}{2}N_3 \\ = 0, & n > \tfrac{3}{2}N_3. \end{cases} \quad (25)$$

Similarly, as $\sigma \to 0$, the Fourier coefficient $A_n^s(CN)$ tends to the limit of the Fourier coefficient derivable from a single column height (Warren, 1969), *i.e.* $\sigma \to 0$,

$$A_n^s(CN)\begin{cases} = 1 - n/N_3, & n \le N_3 \\ = 0, & n > N_3. \end{cases} \quad (26)$$

All three Fourier coefficients, $A_n^s(SL)$, $A_n^s(CN)$, $A_n^s(SN)$, can be shown to satisfy (23a) though the approximation $N_{3G}/2\sigma^{1/2'}$ is large must be made use of in the case of $A_n^s(SN)$.

To determine the line shape, from small particle size with the three different kinds of size distributions, the Fourier integral of (21) must be evaluated using the three different forms of the Fourier coefficient, $A_n^s(SL)$, $A_n^s(CN)$ and $A_n^s(SN)$. $A_n^s(SL)$ cannot be transformed analytically and a fast Fourier transform routine must be used. The line profile derived from $A_n^s(SL)$ is denoted by $\Phi(SL)$. An exact Fourier transform can be obtained from $A_n^s(SN)$ giving the following complicated expression:

$$\begin{aligned}\Phi(SN) &= P'(h_3)/N_3^2Y_o\\ &= \operatorname{erfc}(-y)\{x^{-2}+\tfrac{8}{9}\exp[3/2y^2]x^{-4}\}\\ &\quad+\operatorname{Re} w(z)\exp[-y^2]\\ &\quad\times\{x^{-2}-y''^2+\exp[3/2y^2](-\tfrac{8}{9}x^{-4}+\tfrac{4}{9}x^{-2}y'^2\\ &\quad-\tfrac{4}{9}x^{-2}y''^2+\tfrac{4}{27}x^2y''^6)\}+\operatorname{Im} w(z)\exp[-y^2]\\ &\quad\times\{x^{-1}-y'x^{-1}+\exp[3/2y^2]\\ &\quad\times(\tfrac{8}{9}x^{-3}y'+\tfrac{4}{27}x^{-1}y'^3-\tfrac{4}{9}x^{-1}y'y''^2-\tfrac{4}{9}xy''^4y')\}\\ &\quad+\{\exp[-y^2+3/2y^2]/(2\pi^{1/2})\}\\ &\quad\times\{\tfrac{8}{9}x^{-2}y'y''+\tfrac{16}{27}y'y''^3\},\end{aligned} \tag{27}$$

where $x=2\pi h_3^o$, $y=N_{3D}/2\sigma'^{1/2}$, $y'=N_{3D}/N_3$, $y''=\sigma'/N_3$, $z=2\pi^{1/2}h_3^o\sigma'/N_3-iN_{3D}/2\sigma'^{1/2}$, $w(z)=e^{-z^2}\times\operatorname{erfc}(-iz)$ (Abramowitz & Stegun, 1965) and Re and Im denote real and imaginary parts, respectively. Once again, taking the limit of $\Phi(SN)$ as $\sigma'\to 0$,

$$\begin{aligned}\Phi(SN) &= [9/8(\pi h_{o3})^2]\{1+\sin^2\pi h_{o3}/(\pi h_{o3})^2\\ &\quad\times[1-2\pi h_{o3}\cot(\pi h_{o3})]\}\end{aligned} \tag{28}$$

gives a result identical to the X-ray line shape from a spherical subgrain of average column height, N_3. Here, h_{o3} is equal to $\frac{3}{2}h_3^o=\frac{3}{2}N_3h_3$. The IMSL (1982) routine *MERRCZ* can be used to generate the values of the function $w(z)$, which is related to the error function complement of a complex argument (Abramowitz & Stegun, 1965). Likewise the Fourier coefficient $A_n^s(CN)$ can be transformed analytically and the resulting line shape is given by

$$\begin{aligned}\Phi(CN) &= P'(h_3)/N_3^2Y_o\\ &= 4/(2\pi h_3^o)^{-2}\{1-[\exp(-u_0^2)/\operatorname{erfc}(-u_0)\}\\ &\quad\times\operatorname{Re} w(\pi h_3^o/u_1-iu_0)\},\end{aligned} \tag{29}$$

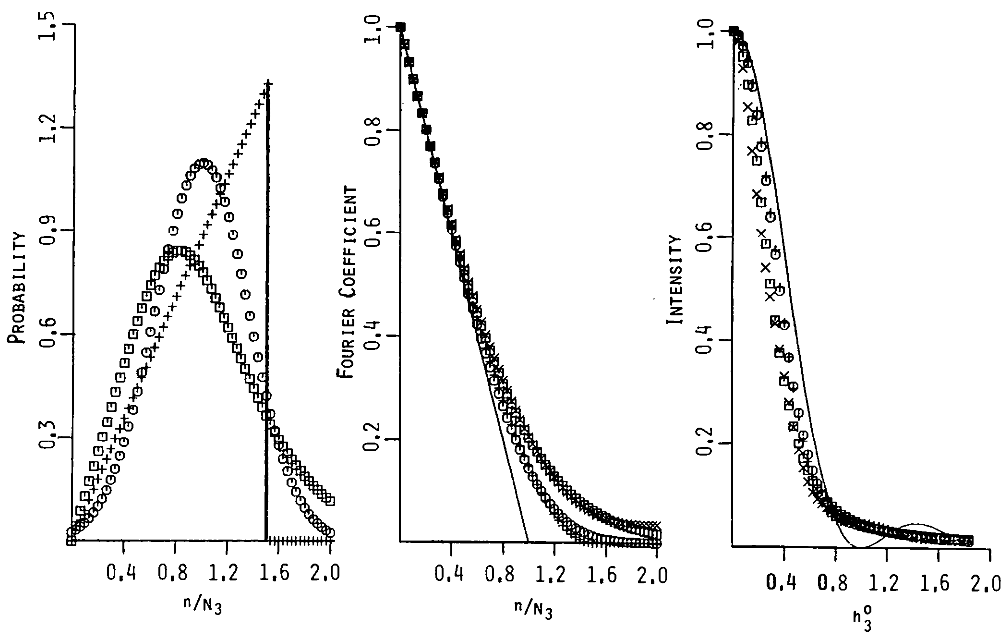
where $u_0=N_{3G}/(2\sigma^{1/2})$, $u_1=N_3/(2\sigma^{1/2})$. As the parameter $\sigma\to 0$, the resulting line shape tends to the well known limiting value

$$\Phi(CN)=\sin^2\pi h_3^o/(\pi h_3^o)^2, \tag{30}$$

which is the X-ray line shape from a single crystal of constant column height, N_3.

Simplified models

In Fig. 1, the different column-height distributions along with their particle-size Fourier coefficients and line shapes are plotted. For all the distributions, the average column height, N_3, was kept a constant at 150. The variation coefficient of the log normal distribution of subgrain diameters, normal distribution of



(a) (b) (c)

Fig. 1. Computer simulations of (*a*) the different column-height distributions along with (*b*) their particle-size Fourier coefficients and (*c*) line shapes. Solid line-single column height ($V_c=0$), ⏀-Gaussian distribution of column heights ($V_c=0{\cdot}354$), +-spherical subgrain ($V_c=0{\cdot}354$), ⊞-log normal distribution of spherical subgrains ($V_c=0{\cdot}52$), ×-Gaussian distribution of spherical subgrains ($V_c=0{\cdot}52$).

subgrain diameters and the normal distribution of column heights, was kept constant, with a value of 0·354. Notice that the variation coefficient of the column-height distribution would be greater than the variation coefficient of the diameters of spherical subgrains, since the spherical shape itself provides some spread to the column-height distribution. For example, a variation coefficient of 0·354 in the diameter distributions gives a variation coefficient of approximately 0·52 in the column-height distribution. Experimental data on metallic systems (Saltykov, 1961) indicate that the variation coefficient of the distribution of diameters of grains lies in the range 0·10–0·60. Taking these values as the limit, then the variation coefficient of the column-height distribution should lie approximately in the range 0·10–0·80.

From Fig. 1, it is evident that as the variation coefficient of the column-height distribution increases, the particle-size coefficient deviates from a straight-line behavior (corresponding to a single column height) more and more, and the line shape becomes sharper near the peak position and asymptotic to an h_3^{-2}-type behavior at the tail portion of the peak. It is also clear that the two most important parameters of the column-height distribution, which determine the particle-size coefficient and line shape, are the average column height N_3 and the variation coefficient, V_c. For example, a normal distribution of column heights with average column height N_3 and variation coefficient 0·354 gives an almost identical behavior for the particle-size coefficient and line shape when compared with the spherical distribution that has a variation coefficient of 0·354 (see Fig. 1). The differences in line shape and particle-size coefficient that can be attributed to third- and higher-order moments of the column-height distribution are almost insignificant, probably within the statistical accuracy of the diffraction data. The process of double integration of the column-height distribution to obtain the particle-size coefficient essentially smooths out any fine detail that might exist in the distribution functions and reduces the importance of the higher-order moments of the column-height distribution.

In Fig. 2, the column-height distributions along with their line shape and particle-size Fourier coefficients for a log normal distribution of spherical subgrains, a sphere and a single column height are plotted. The average column height was kept constant for all the three cases. The variation coefficient of column heights of the log normal distribution was fixed at 0·707. The variation coefficient for a sphere and a single column height are 0·354 and 0 respectively. Both the line shapes and the particle-size coefficients show marked differences, illustrating the importance of variation coefficient on the line shape and the particle-size coefficient. The half width from the line shape of the log normal distribution is less than half the half width from the line shape of a single column height.

Owing to the above considerations, in X-ray line-shape analysis, the modeling of particle-size broadening should be such that it incorporates both the average column height N_3 and the variation coefficient V_c. The exact shape of the probability

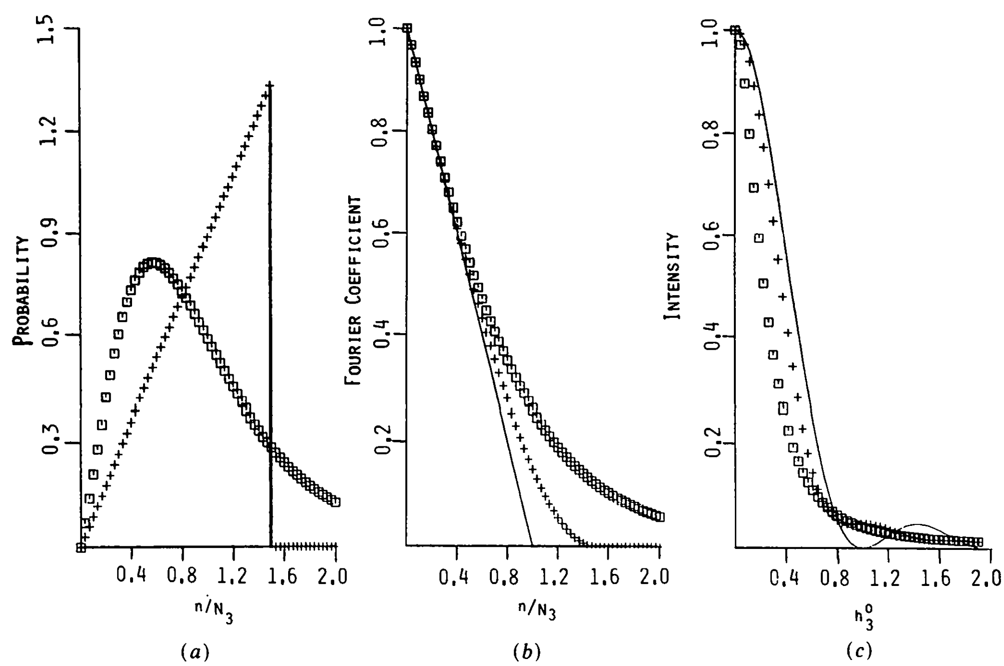


Fig. 2. Computer simulation of (*a*) the column-height distributions, (*b*) particle-size Fourier coefficients and (*c*) line shapes from a log normal distribution of spherical subgrains (□), a spherical subgrain (+) and a single column height (solid line). $V_c = 0{\cdot}707$ for the log normal distribution, 0·354 for the spherical subgrain and 0 for the single column height.

distribution of column heights is not that critical. Use of the spherical distribution for particle-size modeling assumes that the variation coefficient of the column-height distribution is fixed at 0·354. In order to remove this restriction, two models are suggested: one treating the range 0–0·57 of V_c and the second treating the range 0·36–0·70 of V_c. For $V_c > 0{\cdot}707$, more complicated models are required such as the log normal distribution of spherical grains. However, the limit 0·70 is not expected to represent a true restriction.

Model I. $0 \leq V_c \leq 3^{-1/2}$

The column-height distribution is assumed to be rectangular and can be written as

$$p(j)\,\mathrm{d}j \begin{cases} = (2\times 3^{1/2} V_c N_3)^{-1}\,\mathrm{d}j, \\ \quad \times N_3(1-3^{1/2}V_c) < j < N_3(1+3^{1/2}V_c) \\ = 0, \quad \text{otherwise} \end{cases} \tag{31}$$

such that $V_c < 3^{-1/2}$.

Here V_c is the variation coefficient of the column-height distribution and N_3 is the average column height. The particle-size coefficient and line shape become simple for the probability distribution of (31) and are given by

$$(A_n^s)^{\mathrm{I}} \begin{cases} = 1 - n/N_3, \; 0 \leq n \leq N_3(1-3^{1/2}V_c) \\ = \dfrac{(1+3^{1/2}V_c)^2}{4\times 3^{1/2}V_c} - \dfrac{n}{N_3}\dfrac{1+3^{1/2}V_c}{2\times 3^{1/2}V_c} \\ \quad + \dfrac{n^2}{N_3^2}\dfrac{1}{4\times 3^{1/2}V_c}, \\ \quad N_3(1-3^{1/2}V_c) \leq n \leq N_3(1+3^{1/2}V_c) \\ = 0, \quad \text{otherwise} \end{cases} \tag{32}$$

and

$$P_{\mathrm{I}}'(h_3)/N_3^2 Y_o = 2(2\pi h_3^o)^{-2} - (2/3^{1/2}V_c)(2\pi h_3^o)^{-3} \times \sin 2\times 3^{1/2} V_c \pi h_3^o \cos 2\pi h_3^o. \tag{33}$$

As $V_c \to 0$, (33) tends to the correct limit of the line shape from a single crystal of uniform column height N_3, given by (30).

Model II. $8^{-1/2} \leq V_c \leq 2^{-1/2}$

The subgrain is assumed to be spherical in shape and a rectangular diameter distribution is assumed for the subgrains. The column-height distribution from such an assumption can be calculated as (see Appendix *A*)

$$p(j)\,\mathrm{d}j \begin{cases} = \frac{8}{9}(j/N_3^2)(1-3V_g^2), \\ \quad 0 \leq j < \frac{3}{2}N_3(1-3^{1/2}V_g) \\ = (2/3\times 3^{1/2} N_3 V_g) \\ \quad - [4j/9(1+3^{1/2}V_g)3^{1/2}V_g N_3^2], \\ \quad \frac{3}{2}N_3(1-3^{1/2}V_g) \leq j \leq \frac{3}{2}N_3(1+3^{1/2}V_g) \\ = 0, \quad \text{otherwise,} \end{cases} \tag{34}$$

and $0 \leq V_g \leq 3^{-1/2}$.

Here, N_3 is the average column height and V_g is the variation coefficient of the original subgrain diameter distribution. The variation coefficient of the column-height distribution can be shown to be equal to

$$V_c = \tfrac{3}{2}\{(1+V_g^2)/2 - 4/9\}^{1/2}. \tag{35}$$

The particle-size coefficient and line shape can be calculated as

$$(A_n^s)^{\mathrm{II}} \begin{cases} = 1 - n/N_3 + (4/27)[1/(1-3V_g^2)] \\ \quad \times (n^3/N_3^3), \\ \quad 0 \leq n \leq \frac{3}{2}N_3(1-3^{1/2}V_g) \\ = \dfrac{1}{4}\dfrac{(1+3^{1/2}V_g)^2}{3^{1/2}V_g} - \dfrac{1}{2}\dfrac{1+3^{1/2}V_g}{3^{1/2}V_g}\dfrac{n}{N_3} \\ \quad + \dfrac{1}{3\times 3^{1/2}V_g}\dfrac{n^2}{N_3^2} \\ \quad - \dfrac{2}{27}\dfrac{1}{(1+3^{1/2}V_g)3^{1/2}V_g}\dfrac{n^3}{N_3^3}, \\ \quad \frac{3}{2}N_3(1-3^{1/2}V_g) \leq n \leq \frac{3}{2}N_3(1+3^{1/2}V_g) \\ = 0, \quad \text{otherwise,} \end{cases} \tag{36}$$

and

$$\frac{P_{\mathrm{II}}'(h_3)}{N_3^2 Y_o} = 2(2\pi h_3^o)^{-2} + 32[9(2\pi h_3^o)^4]^{-1} \times (1-3V_g^2)^{-1} \sin^2 \pi h_{o3}(1-3^{1/2}V_g) - 16[9(2\pi h_3^o)^4]^{-1}[3^{1/2}V_g(1+3^{1/2}V_g)]^{-1} \times \sin 2\times 3^{1/2} V_g \pi h_{o3} \sin 2\pi h_{o3}. \tag{37}$$

As $V_g \to 0$, (37) tends to the correct limit of the line shape from a spherical subgrain of average column height, N_3, given by (28).

Fig. 3 illustrates the line shape and particle-size coefficient from models I and II, for a variation coefficient, V_c, of 0·50, as compared with the line shape and particle-size coefficient from a log normal distribution of spherical grains with the same variation coefficient. The three column-height distributions are also plotted. The discrepancies among the three particle-size coefficients and among the three line shapes are minimal, even though the original column-height distributions show marked differences. The differences in the line shape are minimal even at the tail portion of the peaks where the percent differences are greatest. The simple form of the particle-size coefficients from (32) and (36) can be very useful in X-ray line-shape analysis, because particle-size broadening can be introduced by multiplication with the strain coefficients. This provides the required mathematical convolution, which is treated in the following paper.

Discussion

X-ray particle-size broadening is determined by the column-height distribution, perpendicular to the reflecting planes. The two parameters of the distribution that most affect the line shape are the average column height, N_3, and the variation coefficient of the column height distribution, V_c. Different combinations of subgrain shape and size distribution can give identical column-height distributions, thereby making a determination of shape impossible from a single profile. In principle, the column-height distribution perpendicular to the reflecting planes can be determined, although realistically only the first- and second-order moments of the distribution can be obtained experimentally. The average column height, N_3, determined from the peak half width using the Scherrer equation (Scherrer, 1918) can be in error by more than 50%, for large values of V_c. It gives the best results as $V_c \to 0$. A determination of the particle-size coefficient for different values of n would give the column-height distribution, unambiguously. But, the particle-size-coefficient determination is prone to large errors at low and high n values (Warren, 1969). The frequently made assumption of a Cauchy shape for particle-size broadening (de Keijser, Langford, Mittemeijer & Vogels, 1982) is incorrect, since the true shape continuously varies with V_c, with a more Cauchy-like behavior at larger values of V_c. Non-linear least-squares fitting procedures can be used to determine the two parameters of the column-height distribution very accurately when other kinds of specimen broadening exist. This method is superior to the Fourier analysis technique when the full diffraction profile is not available (Houska & Smith, 1981). Furthermore, the availability of analytical forms allows one to obtain that background correction that minimizes the misfit error. This procedure is not available in conventional integral breadth measurements. Finally, particle-size broadening and non-uniform strain broadening can be separated very easily, by non-linear least-squares fitting of two orders of an *hkl* reflection.

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APPENDIX *A*

The column-length distribution from a single sphere of diameter D is given by (3). The column-length distribution, from a distribution of subgrain diameters, $p(D)\,\mathrm{d}D$ is given by (Adler & Houska, 1979)

$$p(L)\,\mathrm{d}L = 2L\int_L^\infty p(D)\,\mathrm{d}D/D^2. \qquad (A\text{-}1)$$

If the subgrain diameter distribution is log normal in character, then the column-length distribution can be calculated as

$$p(L)\,\mathrm{d}L = 2L\int_L^\infty (2^{1/2}\pi\ln\sigma_g)^{-1} \times \exp\{-\tfrac{1}{2}[(\ln D - \ln D_g)/\ln\sigma_g]^2\}D^{-3}\,\mathrm{d}D. \qquad (A\text{-}2)$$

Integration of (A-2) by parts produces the column length distribution, as given by equation (A-1). Similarly, for a rectangular distribution of subgrain

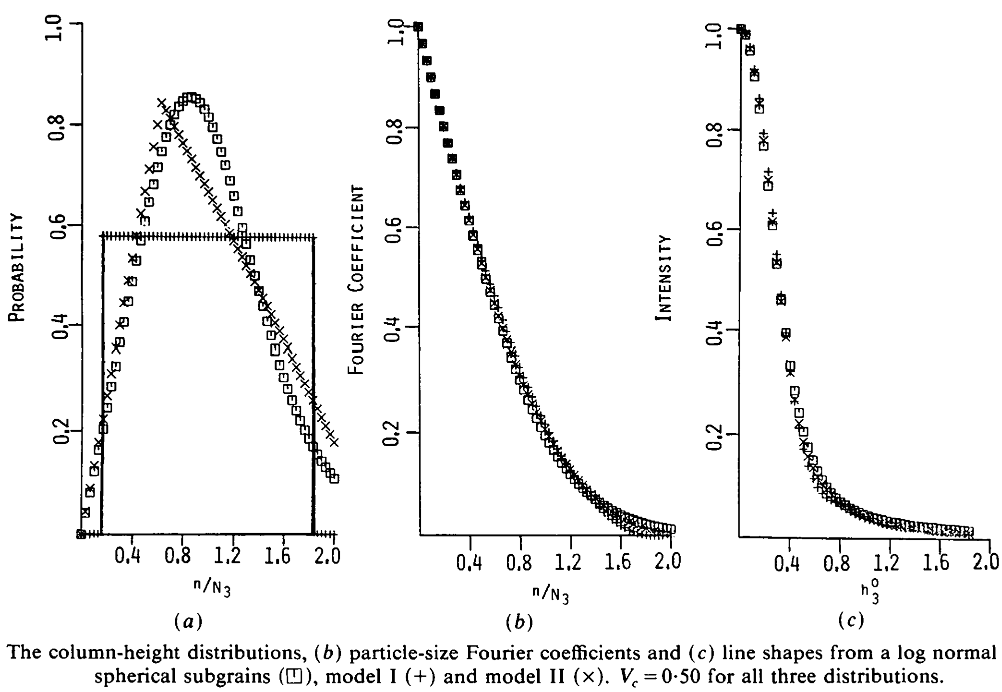

Fig. 3. (a) The column-height distributions, (b) particle-size Fourier coefficients and (c) line shapes from a log normal distribution of spherical subgrains (□), model I (+) and model II (×). $V_c = 0{\cdot}50$ for all three distributions.

diameters, the column height distribution is equal to

$$p(j)\,dj \begin{cases} = 2j \int_{\frac{3}{2}N_3(1-3^{1/2}V_g)}^{\frac{3}{2}N_3(1+3^{1/2}V_g)} (3\times 3^{1/2} V_g N_3)^{-1} D^{-2}\, dD, \\ \quad 0 \le j \le \frac{3}{2}N_3(1-3^{1/2}V_g) \\ = 2j \int_{j}^{\frac{3}{2}N_3(1+3^{1/2}V_g)} (3\times 3^{1/2} V_g N_3)^{-1} D^{-2}\, dD, \\ \quad \frac{3}{2}N_3(1-3^{1/2}V_g) \le j \le \frac{3}{2}N_3(1+3^{1/2}V_g) \\ = 0, \quad j > \frac{3}{2}N_3(1+3^{1/2}V_g). \end{cases}$$

APPENDIX *B*

Column-height distribution from a normal distribution of subgrain diameters is derived here using an approximate treatment. Initially the log normal distribution of diameters is approximated by a normal distribution of diameters. A log normal distribution of diameters can be written as

$$p(\ln D)\, d(\ln D) = (2^{1/2}\pi \ln \sigma_g)^{-1} \times \exp\{-\tfrac{1}{2}[(\ln D - \ln D_g)/\ln \sigma_g]^2\}\, d(\ln D). \quad (B\text{-}1)$$

$\ln D$ can be approximated as

$$\begin{aligned} \ln D &= \ln[D_g + (D - D_g)] \\ &\simeq \ln D_g - 2(D-D_g)/[2D_g + (D-D_g)] \\ &\simeq \ln D_g + (D-D_g)/D_g. \end{aligned} \quad (B\text{-}2)$$

Also, $\ln \sigma_g$ can be approximated as

$$\ln \sigma_g = \ln[1 + (\sigma_g - 1)] \simeq \sigma_g - 1. \quad (B\text{-}3)$$

From (B-2),

$$\begin{aligned} d(\ln D) &= d(\ln D - \ln D_g) \simeq d[(D-D_g)/D_g] \\ &= D_g^{-1}\, dD. \end{aligned} \quad (B\text{-}4)$$

Substituting (B-4), (B-3), (B-2) in (B-1) and writing $D_g(\sigma_g - 1)$ as σ', one can approximate $p(\ln D)\, d(\ln D)$ as

$$p(\ln D)\, d(\ln D) = (2^{1/2}\pi\sigma')^{-1} \exp\{-\tfrac{1}{2}[(D-D_g)/\sigma']^2\}\, dD, \quad (B\text{-}5)$$

which demonstrates that the linear approximations (B-2), (B-3), (B-4) lead to the normal distribution. Note that (B-5) is valid only for small values of $\ln \sigma_g$ or for large values of D_g/σ'. The column-height distribution for a log normal distribution of subgrain diameters is known from (6):

$$p(j)\, dj = (4/9) j N_3^{-2} \exp[3(\ln \sigma_g)^2] \times \operatorname{erfc} 2^{-1/2}[(\ln j - \ln N_{3D})/\ln \sigma_g + 2 \ln \sigma_g]\, dj.$$

With the approximations of (B-2), (B-3), (B-4) in (6), the following equation is obtained for the probability distribution of column heights:

$$p(j)\, dj = (4/9) j N_3^{-2} \exp[3\sigma'^2/N_{3G}^2] \times \operatorname{erfc} 2^{-1/2}(j - N_{3G}/\sigma' + 2\sigma'/N_{3G})\, dj, \quad (B\text{-}6)$$

where $N_{3G} = D_g/\langle d \rangle$. By making the same approximations as for (B-2), (B-3), (B-4) in the particle-size coefficient for a log normal distribution of subgrain diameters, $A_n^s(\mathrm{SL})$, the particle-size coefficient, $A_n^s(\mathrm{SN})$ can be shown to be equal to

$$\begin{aligned} A_n^s(\mathrm{SN}) \simeq\ & \tfrac{1}{2} \operatorname{erfc} 2^{-1/2}(n - N_{3G})/\sigma' - \sigma'/N_{3G}] \\ & - \tfrac{1}{2}(n/N_3) \operatorname{erfc} 2^{-1/2}(n - N_{3G})/\sigma'] \\ & + (2/27)(n^3/N_3^3) \exp[3\sigma'^2/N_{3G}^2] \\ & \times \operatorname{erfc} 2^{-1/2}(n - N_{3G})/\sigma' + 2\sigma'/N_{3G}]. \end{aligned} \quad (B\text{-}7)$$

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