Acta Cryst. (1986). A**42**, 14–19

X-ray Diffraction Profiles Described by Refined Analytical Functions

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(*Received* 28 *January* 1985; *accepted* 16 *July* 1985)

Abstract

The line profiles from a sample containing small spherical particles, non-uniform strain and instrumental broadening can be described exactly by using error functions with complex arguments. Consequently, the development by Houska & Smith [*J. Appl. Phys.* (1981). **52**, 748–754] has been revised in terms of these functions. This calculation has been extended, by the use of error functions with complex arguments, to include a more general distribution of particle size or column heights than that obtained from a single sphere. The latter extension is applied to profiles obtained from a partially stabilized zirconia wear debris. It is found, in this example, that a column-height variation coefficient that is greater than that from a single sphere gives a somewhat better fit of the experimental line profiles. We find that if the single-sphere model is used to fit the profiles the particle size and root-mean-square strain differ by about 12 and 5% respectively.

Introduction

Warren & Averbach (1950, 1952) developed an X-ray diffraction line-shape analysis that is applied to reflections from two or more orders of the same (*hkl*) planes to yield particle size and nonuniform strain information. Adler & Houska (1979) have simplified the Warren–Averbach treatment to analyse for two components of intrinsic strain present in thin films as well as the particle size. They demonstrated that the Fourier coefficients in the Warren–Averbach line-shape analysis can be interrelated with five parameters for two orders, which include two strain parameters, the average particle size and two instrumental parameters. The instrumental parameters are obtained separately by fitting data obtained from ideal samples to an analytical function that describes instrumental broadening. Analytical functions developed by Houska & Smith (1981) greatly reduced the computer time. An advantage of the latter approach is that useful results may be obtained even though entire profiles are not available. It is well known that the classical Warren–Averbach analysis (Warren, 1969) gives a hook effect, which may introduce considerable error in the final results if for one reason or another the full background is not obtained. This difficulty is eliminated through the use of analytical functions that are capable of describing the complete profile.

The authors have recently discovered that the development by Houska & Smith (1981) could have been carried out exactly with integrals leading to error functions with complex arrangements. This, combined with the new computer routine *MERRCZ* (IMSL, 1982), allows these complex functions to be generated with a high degree of precision. These two developments have inspired the first part of the present paper as well as an extension of the theory that allows the single-size-sphere model to be extended to include a variation in sphere size. To complete the calculations, both must be related to the column-length distribution found in the more conventional line-shape theory, which is described in the preceding paper.

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Theory

It has been shown that the profile shape from sputtered films or cold-worked materials is described by the integral (Houska & Smith, 1981)

$$P(h_3^o)/2N_3Y_o = \int_0^{3/2} [1 - u + (4/27)u^3] \times \exp - (\gamma u + \beta u^2) \cos 2\pi h_3^o u \, du \quad (1)$$

with the various terms given by

$$\gamma = 2\pi N_3(a_\gamma + \pi\langle\varepsilon_{1D}^2\rangle l^2),$$

$$\beta = \pi N_3^2(a_\beta^2 + 2\pi\langle\varepsilon_{1U}^2\rangle l^2),$$

where N_3 is the average number of cells in a statistically spherical grain, $\langle\varepsilon_{1D}^2\rangle$ and $\langle\varepsilon_{1U}^2\rangle$ are strain parameters with an *n*th neighbor dependence given by $\langle\varepsilon_u^2\rangle = \langle\varepsilon_{1D}^2\rangle/n + \langle\varepsilon_{1U}^2\rangle$. h_3^o is a scaled reciprocal-lattice variable in units of N_3/d_0 with d_0 = spacing for first-order 00*l* reflection. The parameters a_γ and a_β describe the shape of the instrumental broadening for each 00*l* reflection and, lastly, Y_o provides scaling along the intensity axis. Equation (1) is applicable to

0108-7673/86/010014-06$01.50

symmetrical peaks. Highly symmetrical peaks can be obtained by use of a high-resolution diffractometer with a quartz monochromator, which eliminates the $K\alpha_2$ component of the $K\alpha$ doublet. In deriving (1), it was assumed that the distribution of column lengths in the subgrains can be represented by the distribution of column lengths in a sphere of the correct average diameter. The convolution of two strain distributions is used to describe the state of nonuniform microstrain in the sample. One is due to the strain distribution caused by dislocations and is represented by the term $\langle\varepsilon_{1D}^2\rangle$. The other distribution is related to long-range fluctuations, which cause variations in the uniform column strain from one subgrain to another, and is represented by the term $\langle\varepsilon_{1U}^2\rangle$. The instrumental function is obtained by setting the particle-size term

$$[1-u+\tfrac{4}{27}u^3]=1$$

and

$$\langle\varepsilon_{1D}^2\rangle=\langle\varepsilon_{1U}^2\rangle=0.$$

The major steps required to obtain the exact function are outlined by the equations that follow. Equation (1) is written as three integrals according to

$$\begin{aligned}P(h_3^o)/2N_3Y_o &= \int_0^{3/2}\exp-(\gamma u+\beta u^2)\cos 2\pi h_3^o u\,\mathrm{d}u\\ &\quad-(1/2\pi)\,\mathrm{d}/\mathrm{d}h_3^o\left[\int_0^{3/2}\exp-(\gamma u+\beta u^2)\times\sin 2\pi h_3^o u\,\mathrm{d}u\right]\\ &\quad-\tfrac{4}{27}(1/2\pi)^3\,\mathrm{d}^3/\mathrm{d}h_3^{o3}\left[\int_0^{3/2}\exp-(\gamma u+\beta u^2)\times\sin 2\pi h_3^o u\,\mathrm{d}u\right].\end{aligned}\quad(2)$$

The first integral can be related to standard forms given by Grobner & Hofreiter (1975, p. 109) if $x=\beta^{1/2}u+\gamma/2\beta^{1/2}$. With some algebraic and trigonometric manipulation, one arrives at terms involving standard integrals containing error functions with complex arguments, *i.e.*

$$\begin{aligned}&\int\exp(-x^2)\cos 2\pi h_3^o x/\beta^{1/2}\,\mathrm{d}x\\ &\quad=[\pi^{1/2}/\exp(\pi^2h_3^{o2}/\beta)]\\ &\qquad\times[\mathrm{erf}\,(x-i\pi h_3^o/\beta^{1/2})+\mathrm{erf}\,(x+i\pi h_3^o/\beta^{1/2})]\end{aligned}\quad(3)$$

and

$$\begin{aligned}&\int\exp\,(-x^2)\sin 2\pi h_3^o x/\beta^{1/2}\,\mathrm{d}x\\ &\quad=[-i\pi^{1/2}/\exp(\pi^2h_3^{o2}/\beta)]\\ &\qquad\times[\mathrm{erf}\,(x-i\pi h_3^o/\beta^{1/2})-\mathrm{erf}\,(x+i\pi h_3^o/\beta^{1/2})].\end{aligned}$$

Using these results and the error function complement $=1-\mathrm{erf}\,z$, we obtain

$$\begin{aligned}&\int_0^{3/2}\exp[-(\gamma u+\beta u^2)]\cos 2\pi h_3^o u\,\mathrm{d}u\\ &\quad=(\pi^{1/2}/2\beta^{1/2})\exp(-\pi^2h_3^{o2}/\beta)\exp(\gamma^2/4\beta)\\ &\qquad\times\{\mathrm{Re}\,[\exp(-i\pi h_3^o\gamma/\beta)\\ &\qquad\times\mathrm{erfc}\,(\gamma/2\beta^{1/2}-i\pi h_3^o/\beta^{1/2})]\\ &\qquad-\mathrm{Re}\,[\exp(-i\pi h_3^o\gamma/\beta^{1/2})\,\mathrm{erfc}\,(\gamma/2\beta^{1/2}\\ &\qquad+\tfrac{3}{2}\beta^{1/2}-i\pi h_3^o/\beta^{1/2})]\},\end{aligned}\quad(4)$$

which makes use of the real part of the term in the brackets.

For computational purposes, it is best to make use of a modified function related to the error function of a complex argument (see Abramowitz & Stegun, 1967, p. 297). This is given by

$$w(z)=\exp(-z^2)\,\mathrm{erfc}\,(-iz).\quad(5)$$

With this substitution, the first term of (2) is given by

$$\begin{aligned}&\int_0^{3/2}\exp-(\gamma u+\beta u^2)\cos 2\pi h_3^o u\,\mathrm{d}u\\ &\quad=(\pi^{1/2}/2\beta^{1/2})(\mathrm{Re}\,w(\pi h_3^o/\beta^{1/2}+i\gamma/2\beta^{1/2})\\ &\qquad-\exp[-\tfrac{9}{4}\beta-\tfrac{3}{2}\gamma]\\ &\qquad\times\{\cos 3\pi h_3^o\\ &\qquad\times\mathrm{Re}\,w[\pi h_3^o/\beta^{1/2}+i(\tfrac{3}{2}\beta^{1/2}+\gamma/2\beta^{1/2})]\\ &\qquad-\sin 3\pi h_3^o\\ &\qquad\times\mathrm{Im}\,w[\pi h_3^o/\beta^{1/2}+i(\tfrac{3}{2}\beta^{1/2}+\gamma/2\beta^{1/2})]\}).\end{aligned}\quad(6)$$

Similarly, one finds for the second integral of (2)

$$\begin{aligned}&\partial/\partial h_3^o\int_0^{3/2}\exp-(\gamma u+\beta u^2)\sin 2\pi h_3^o u\,\mathrm{d}u\\ &\quad=\partial/\partial h_3^o((\pi^{1/2}/2\beta^{1/2})[\mathrm{Im}\,w(\pi h_3^o/\beta^{1/2}+i\gamma/2\beta^{1/2})\\ &\qquad-\exp[-(\tfrac{9}{4})\beta-\tfrac{3}{2}\gamma]\\ &\qquad\times\{\cos 3\pi h_3^o\times\mathrm{Im}\,w[\pi h_3^o/\beta^{1/2}\\ &\qquad+i(\tfrac{3}{2}\beta^{1/2}+\gamma/2\beta^{1/2})]\\ &\qquad+\sin 3\pi h_3^o\times\mathrm{Re}\,w[\pi h_3^o/\beta^{1/2}\\ &\qquad+i(\tfrac{3}{2}\beta^{1/2}+\gamma/2\beta^{1/2})]]\}).\end{aligned}\quad(7)$$

The following relations are used in simplifying the derivatives of these complex functions:

$$w(iz'')=\exp(z''^2)\,\mathrm{erfc}\,z'';$$

with

$$z''=\begin{cases}\gamma/2\beta^{1/2}-i\pi h_3^o/\beta^{1/2}\\ \text{or}\\ \tfrac{3}{2}\beta^{1/2}+\gamma/2\beta^{1/2}-i\pi h_3^o/\beta^{1/2}\end{cases}$$

$$\partial/\partial h_3^o \operatorname{Im} w(z) = \pi/\beta^{-1/2}[-2\pi h_3^o/\beta^{-1/2} \operatorname{Im} w(z) - 2\times\begin{cases}(\gamma/2\beta^{1/2})\\ \text{or}\\ (\gamma/2\beta^{1/2}+\tfrac{3}{2}\beta^{1/2}\end{cases} \times \operatorname{Re} w(z) + 2\pi^{-1/2}];$$

$$\partial/\partial h_3^o \operatorname{Re} w(z) = \pi\beta^{-1/2}[-2\pi h_3^o/\beta^{-1/2} \operatorname{Re} w(z) + 2\times\begin{cases}(\gamma/2\beta^{1/2})\\ \text{or}\\ (\gamma/2\beta^{1/2}+\tfrac{3}{2}\beta^{1/2})\end{cases} \times \operatorname{Im} w(z)].$$

These relations lead one to the result

$$\begin{aligned}
&-(1/2\pi)\,\partial/\partial h_3^o \int_0^{3/2} \exp-(\gamma u+\beta u^2)\sin 2\pi h_3^o u\,du\\
&=(\pi^{1/2}/2\beta^{1/2})(\beta^{-1/2}(\gamma/2\beta^{1/2})\operatorname{Re} w(z)\\
&\quad+\beta^{-1/2}(\pi h_3^o/\beta^{-1/2}\operatorname{Im} w(z)-\beta^{-1/2}\pi^{-1/2}\\
&\quad-\exp[-\tfrac{9}{4}\beta-\tfrac{3}{2}\gamma]\\
&\quad\times\{[-\tfrac{3}{2}\cos 3\pi h_3^o+\beta^{-1/2}(\pi h_3^o\beta^{-1/2})\sin 3\pi h_3^o\\
&\quad+\beta^{-1/2}(\gamma/2\beta^{1/2}+\tfrac{3}{2}\beta^{1/2})\cos 3\pi h_3^o]\operatorname{Re} w(z')\\
&\quad+(\tfrac{3}{2}\sin 3\pi h_3^o+\beta^{-1/2}(\pi h_3^o\beta^{-1/2})\cos 3\pi h_3^o\\
&\quad-\beta^{-1/2}(\gamma/2\beta^{1/2}+\tfrac{3}{2}\beta^{1/2})\sin 3\pi h_3^o)\operatorname{Im} w(z')\\
&\quad-\beta^{-1/2}\pi^{-1/2}\cos 3\pi h_3^o\}),
\end{aligned}\tag{8}$$

where

$$\begin{aligned}
z&=\pi h_3^o/\beta^{-1/2}+i\gamma/2\beta^{1/2};\\
z'&=\pi h_3^o\beta^{-1/2}+i(\gamma/2\beta^{1/2}+\tfrac{3}{2}\beta^{1/2}).
\end{aligned}\tag{8'}$$

The evaluation of the third integral in (2) leads to a lengthier expression, which will not be given here since the general approach is illustrated in taking the first derivative. The final equation can be written in the following simple form:

$$\begin{aligned}
&P'(h_3^o)/2N_3Y_o\\
&=\int_0^{3/2}[1-u+\tfrac{4}{27}u^3]\exp-(\gamma u+\beta u^2)\cos 2\pi h_3^o u\,du
\end{aligned}\tag{9}$$

$$=(\pi^{1/2}/2\beta^{1/2})\{[A_1(\beta,x,y)\operatorname{Re} w(z)+A_2(\beta,x,y) \times\operatorname{Im} w(z)+A_3(\beta,x,y)\pi^{-1/2}]-\text{FLC}\},$$

where

$$x=\pi h_3^o\beta^{-1/2};\qquad y=\gamma/2\beta^{1/2};\qquad y'=\gamma/2\beta^{1/2}+\tfrac{3}{2}\beta^{1/2};$$

and

$$\begin{aligned}
A_1(\beta,x,y)&=1-y\beta^{-1/2}[-1+(4/27\beta)(\tfrac{3}{2}+y^2-3x^2)];\\
A_2(\beta,x,y)&=-x\beta^{-1/2}[-1+(4/27\beta)(\tfrac{3}{2}-x^2+3y^2)];\\
A_3(\beta,x,y)&=\beta^{-1/2}[-1+(4/27\beta)(1-x^2+y^2)];\\
B_1(\beta,x,y')&=(1/3\beta)(1-2x^2+2y'^2)\\
&\quad-(4y'/27\beta^{3/2})(\tfrac{3}{2}+y'^2-3x^2);\\
B_2(\beta,x,y')&=(4/3\beta)xy'-(4x/27\beta^{3/2})(\tfrac{3}{2}-x^2+3y'^2);\\
B_3(\beta,x,y')&=-(2/3\beta)y'+(4/27\beta^{3/2})(1-x^2+y'^2);\\
B_4(\beta,x,y')&=-(2/3\beta)x+(8/27\beta^{3/2})xy'.
\end{aligned}$$

FLC (finite limit correction)

$$\begin{aligned}
&=\exp[-\tfrac{9}{4}\beta-\tfrac{3}{2}\gamma]\{(\operatorname{Re} w(z')\cos 3\pi h_3^o\\
&\quad-\operatorname{Im} w(z')\sin 3\pi h_3^o)B_1(\beta,x,y')\\
&\quad+[\operatorname{Re} w(z')\sin 3\pi h_3^o+\operatorname{Im} w(z')\cos 3\pi h_3^o]\\
&\quad\times B_2(\beta,x,y')+\pi^{-1/2}\cos 3\pi h_3^o B_3(\beta,x,y')\\
&\quad+\pi^{-1/2}\sin 3\pi h_3^o B_4(\beta,x,y')\}.
\end{aligned}$$

Equation (9) is symmetric with respect to the variable h_3^o. This can be verified by noting that A_1, A_3, B_1, B_3 are even functions of h_3^o, A_2, B_2, B_4 are odd functions of h_3^o and that

$$w(-z)=\overline{w(z)},$$

i.e.

$$\operatorname{Re} w(-z)=\operatorname{Re} w(z)$$

and

$$\operatorname{Im} w(-z)=-\operatorname{Im} w(z).$$

The instrumental broadening function may be obtained by taking the limit of large particle size and zero strain leaving only a_γ and a_β to determine the line broadening. This also represents a convolution between Cauchy and Gaussian profiles

$$g_I(h_3)=Y_o\operatorname{Re} w(\pi h_3/a_\beta+ia_\gamma/a_\beta).\tag{10}$$

In this case, h_3 is the usual variable in reciprocal space. Equation (10) was obtained by Langford (1978) with an approximate treatment of particle-size broadening. However, applying (10) for a full strain-particle-size analysis instead of (9) is risky, because it is based upon an unrealistic particle-size distribution.

In the previous paper, it was found that both the average column height, N_3, and the variation coefficient of the column-height distribution, V_c, can be incorporated into the expression for the particle-size profile. The variation coefficient of the column-height distribution may not always be equal to the variation coefficient of the spherical distribution, 0·354. In order to remove this restriction, two overlapping models were suggested, model I treats the range $0\le V_c\le 0{\cdot}57$ while model II treats the range $0{\cdot}36\le$

$V_c \le 0{\cdot}70$. For model I, the profile shape with strain and instrumental broadening is described by two integrals based upon a rectangular distribution of columns

$$P(h_3^o)/2N_3Y_o = \int_0^{1-3^{1/2}V_c} (1-u)\exp-(\gamma u+\beta u^2) \times \cos 2\pi h_3^o u\, du + (1/4\times 3^{1/2}V_c) \times \int_{1-3^{1/2}V_c}^{1+3^{1/2}V_c} [(1+3^{1/2}V_c)^2 - 2u(1+3^{1/2}V_c)+u^2] \times \exp-(\gamma u+\beta u^2)\times \cos 2\pi h_3^o u\, du, \quad (11)$$

where V_c is the variation coefficient for columns. The integrals in (11) are of a form already considered and one obtains

$$P(h_3^o)/2N_3Y_o = (\pi^{1/2}/2\beta^{1/2})\{(1+y\beta^{-1/2})\,\mathrm{Re}\, w(z) + x\beta^{-1/2}\,\mathrm{Im}\, w(z) - \beta^{-1/2}\pi^{-1/2} - \mathrm{FLC}' - \mathrm{FLC}''\}, \quad (12)$$

where

$$x=\pi h_3^o\beta^{-1/2};\qquad y=\gamma/2\beta^{1/2};$$
$$y'=\gamma/2\beta^{1/2}+(1-3^{1/2}V_c)\beta^{1/2};$$
$$y''=(\gamma/2\beta^{1/2})+(1+3^{1/2}V_c)\beta^{1/2};$$
$$z=x+iy;\qquad z'=x+iy';\qquad z''=x+iy''$$

and

$$\mathrm{FLC}' = \exp-\beta(1-3^{1/2}V_c)^2-\gamma(1-3^{1/2}V_c) \times\{[\mathrm{Re}\, w(z')\cos 2\pi h_3^o(1-3^{1/2}V_c) - \mathrm{Im}\, w(z')\sin 2\pi h_3^o(1-3^{1/2}V_c)] \times[-(1/8\times 3^{1/2}V_c\beta)(1-2x^2+2y'^2)] + [\mathrm{Re}\, w(z')\sin 2\pi h_3^o(1-3^{1/2}V_c) + \mathrm{Im}\, w(z')\cos 2\pi h_3^o(1-3^{1/2}V_c)] \times[-(1/2\times 3^{1/2}V_c\beta)xy'] + \pi^{-1/2}(y'/4\times 3^{1/2}V_c\beta) \times\cos 2\pi h_3^o(1-3^{1/2}V_c)+\pi^{-1/2}(x/4\times 3^{1/2}V_c\beta) \times\sin 2\pi h_3^o(1-3^{1/2}V_c)\},$$

$$\mathrm{FLC}'' = \exp[-\beta(1+3^{1/2}V_c)^2-\gamma(1+3^{1/2}V_c)] \times\{[\mathrm{Re}\, w(z'')\cos 2\pi h_3^o(1+3^{1/2}V_c) - \mathrm{Im}\, w(z'')\sin 2\pi h_3^o(1+3^{1/2}V_c)] \times[(8\times 3^{1/2}V_c\beta)^{-1}(1-2x^2+2y''^2)] + [\mathrm{Re}\, w(z'')\sin 2\pi h_3^o(1+3^{1/2}V_c)+\mathrm{Im}\, w(z'') \times\cos 2\pi h_3^o(1+3^{1/2}V_c)][(2\times 3^{1/2}V_c\beta)^{-1}xy''] - \pi^{-1/2}(y''/4\times 3^{1/2}V_c\beta)\cos 2\pi h_3^o(1+3^{1/2}V_c) - \pi^{-1/2}(x/4\times 3^{1/2}V_c\beta)\sin 2\pi h_3^o(1+3^{1/2}V_c)\}.$$

Similarly, the integrals for model II, with instrumental and strain broadening, become

$$P(h_3^o)/2N_3Y_o = \int_0^{\frac{3}{2}(1-3^{1/2}V_g)} [1-u+\tfrac{4}{27}(1-3V_g^2)^{-1}u^3] \times\exp-(\gamma u+\beta u^2)\cos 2\pi h_3^o u\, du + (3^{1/2}V_g)^{-1}\int_{\frac{3}{2}(1-3^{1/2}V_g)}^{\frac{3}{2}(1+3^{1/2}V_g)} [\tfrac{1}{4}(1+3^{1/2}V_g)^2 - \tfrac{1}{2}(1+3^{1/2}V_g)u+\tfrac{1}{3}u^2-(2/27)(1+3^{1/2}V_g)^{-1}u^3] \times\exp-(\gamma u+\beta u^2)\cos 2\pi h_3^o u\, du, \quad (13)$$

where V_g is the variation coefficient for subgrain diameters. Equation (13) can also be evaluated and the final result is given by

$$P(h_3^o)/2N_3Y_o = (\pi^{1/2}/2\beta^{1/2})\{A_1(\beta,x,y)\,\mathrm{Re}\, w(z) + A_2(\beta,x,y)\,\mathrm{Im}\, w(z) + A_3(\beta,x,y)\pi^{-1/2} - \mathrm{FLC}' - \mathrm{FLC}''\},$$

where

$$x=\pi h_3^o\beta^{-1/2};\qquad y=\gamma/2\beta^{1/2};$$
$$y'=\gamma/2\beta^{1/2}+\tfrac{3}{2}(1-3^{1/2}V_g)\beta^{1/2};$$
$$y''=(\gamma/2\beta^{1/2})+\tfrac{3}{2}(1+3^{1/2}V_g)\beta^{1/2};$$
$$z=x+iy;\qquad z'=x+iy';\qquad z''=x+iy''$$

and

$$A_1(\beta,x,y)=1+y\beta^{-1/2} -\tfrac{4}{27}(1-3V_g^2)^{-1}y\beta^{-3/2}(\tfrac{3}{2}+y^2-3x^2)$$
$$A_2(\beta,x,y)=x\beta^{-1/2}-\tfrac{4}{27}(1-3V_g^2)^{-1}x\beta^{-3/2} \times(\tfrac{3}{2}-x^2+3y^2)$$
$$A_3(\beta,x,y)=-\beta^{-1/2}+\tfrac{4}{27}(1-3V_g^2)^{-1}\beta^{-3/2}(1-x^2+y^2)$$
$$B_1(\beta,x,y')=-\tfrac{2}{27}(3^{1/2}V_g)^{-1}(1-3^{1/2}V_g)^{-1}y' \times\beta^{3/2}(\tfrac{3}{2}+y'^2-3x^2)$$
$$B_2(\beta,x,y')=-\tfrac{2}{27}(3^{1/2}V_g)^{-1}(1-3^{1/2}V_g)^{-1} \times x\beta^{-3/2}(\tfrac{3}{2}-x^2+3y'^2)$$
$$B_3(\beta,x,y')=\tfrac{2}{27}(3^{1/2}V_g)^{-1}(1-3^{1/2}V_g)^{-1} \times\beta^{-3/2}(1-x^2+y'^2)$$
$$B_4(\beta,x,y')=\tfrac{4}{27}(3^{1/2}V_g)^{-1}(1-3^{1/2}V_g)^{-1}\beta^{-3/2}xy'$$
$$C_1(\beta,x,y'')=\tfrac{2}{27}(3^{1/2}V_g)^{-1}(1+3^{1/2}V_g)^{-1} \times y''\beta^{-3/2}(\tfrac{3}{2}+y''^2-3x^2)$$
$$C_2(\beta,x,y'')=\tfrac{2}{27}(3^{1/2}V_g)^{-1}(1+3^{1/2}V_g)^{-1} \times x\beta^{-3/2}(\tfrac{3}{2}-x^2+3y''^2)$$
$$C_3(\beta,x,y'')=-\tfrac{2}{27}(3^{1/2}V_g)^{-1}(1+3^{1/2}V_g)^{-1} \times\beta^{-3/2}(1-x^2+y''^2)$$

$$
\begin{aligned}
C_4(\beta, x, y'') &= -\tfrac{4}{27}(3^{1/2}V_g)^{-1}(1+3^{1/2}V_g)^{-1}\beta^{-3/2}xy'' \\
\mathrm{FLC}' &= \exp -[\tfrac{9}{4}\beta(1-3^{1/2}V_g)^2-\tfrac{3}{2}\gamma(1-3^{1/2}V_g)] \\
&\quad \times\{[\mathrm{Re}\, w(z')\cos 3\pi h_3^o(1-3^{1/2}V_g) \\
&\quad -\mathrm{Im}\, w(z')\sin 3\pi h_3^o(1-3^{1/2}V_g)]B_1(\beta, x, y') \\
&\quad +[\mathrm{Re}\, w(z')\sin 3\pi h_3^o(1-3^{1/2}V_g) \\
&\quad +\mathrm{Im}\, w(z')\cos 3\pi h_3^o(1-3^{1/2}V_g)]B_2(\beta, x, y') \\
&\quad +\pi^{-1/2}\cos 3\pi h_3^o(1-3^{1/2}V_g)B_3(\beta, x, y') \\
&\quad +\pi^{-1/2}\sin 3\pi h_3^o(1-3^{1/2}V_g)B_4(\beta, x, y')\} \\
\mathrm{FLC}'' &= \exp -[\tfrac{9}{4}\beta(1+3^{1/2}V_g)^2-\tfrac{3}{2}\gamma(1+3^{1/2}V_g)] \\
&\quad \times\{[\mathrm{Re}\, w(z'')\cos 3\pi h_3^o(1+3^{1/2}V_g) \\
&\quad -\mathrm{Im}\, w(z'')\sin 3\pi h_3^o(1+3^{1/2}V_g)]C_1(\beta, x, y'') \\
&\quad +[\mathrm{Re}\, w(z'')\sin 3\pi h_3^o(1+3^{1/2}V_g) \\
&\quad +\mathrm{Im}\, w(z'')\cos 3\pi h_3^o(1+3^{1/2}V_g)]C_2(\beta, x, y'') \\
&\quad +\pi^{-1/2}\cos 3\pi h_3^o(1+3^{1/2}V_g)C_3(\beta, x, y'') \\
&\quad +\pi^{-1/2}\sin 3\pi h_3^o(1+3^{1/2}V_g)C_4(\beta, x, y'')\}.
\end{aligned} \tag{14}
$$

The limit of (14) as $V_g \to 0$ gives essentially the profile shape from a statistically spherical subgrain with non-uniform microstrains and is given by (9). Similarly, the limit of (12) as $V_c \to 0$ gives the profile shape from a uniform column of height N_3, with microstrains, *i.e.*

$$
\begin{aligned}
P(h_3^o)/2N_3Y_o &= \pi^{1/2}/2\beta^{1/2}(\mathrm{Re}\, w(z)(1+y\beta^{-1/2}) \\
&\quad + x\beta^{-1/2}\,\mathrm{Im}\, w(z) - \pi^{-1/2}\beta^{-1/2} \\
&\quad -\exp(-\beta-\gamma)\{[\mathrm{Re}\, w(z')\cos 2\pi h_3^o \\
&\quad -\mathrm{Im}\, w(z')\sin 2\pi h_3^o]y'\beta^{-1/2} \\
&\quad +[\mathrm{Im}\, w(z')\cos 2\pi h_3^o \\
&\quad +\mathrm{Re}\, w(z')\sin 2\pi h_3^o]x\beta^{-1/2} \\
&\quad -\pi^{-1/2}\beta^{-1/2}\cos 2\pi h_3^o\}),
\end{aligned} \tag{15}
$$

where

$$
x = \pi h_3^o\beta^{-1/2}; \qquad y = \gamma/2\beta^{1/2};
$$
$$
y' = \gamma/2\beta^{1/2}+\beta^{1/2};
$$
$$
z = x+iy, \qquad z' = x+iy'.
$$

For $V_c > 0{\cdot}707$, even more complicated models must be used.

In the development of (9), (12) and (14), bending strains have been neglected. Mathematically, it is very difficult to introduce the bending strain along with a distribution of column heights. But for a uniform column of height N_3, the profile shape with bending strain has already been obtained (Rao & Houska, 1986).

Results and discussion

Equation (9), which is based upon the column distribution from a sphere of constant diameter, gives essentially the same profiles as an earlier treatment by Houska & Smith (1981). The main difference is that the earlier treatment made use of a numerical convolution based upon a nine-point Gauss-× Legendre quadrature. Similarly, Houska & Smith (1981) used a 19-point Gauss-Legendre quadrature to obtain the instrumental broadening function instead of (10). The difference in accuracy between these two approaches is very small (<3%), and well within present day experimental errors with both requiring about the same computer time. We believe that the present approach using the computer routine *MERRCZ* is more precise and that this accounts for the small differences. Both approaches are capable of providing well defined confidence levels for particle size and strain determinations when combined with an appropriate statistical fitting routine. And both make use of the line profile rather than merely the half width and (or) integral breadth. With the availability of computer-controlled diffractometers and high-speed computers for data storage and data reduction it has become much more preferable to make full use of the available diffraction line profiles. Two orders, *i.e.* *hkl* and *nh,nk,nl* must be used if both particle size and strain broadening are present.

The development of models I and II represents a refinement of the single-size-sphere model. When the

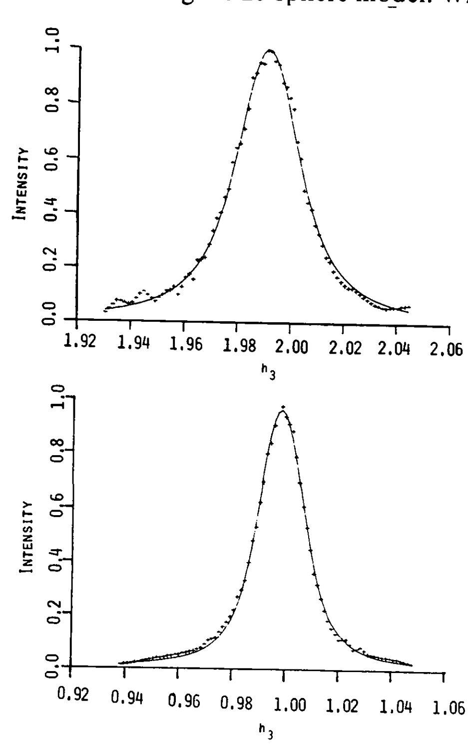

Fig. 1. Least-squares fit of the line profiles from the 200 (top) and 400 reflections of a partially stabilized zirconia sample using (14). Solid line → theoretical fit, + → experimental data.

profile data are sufficiently accurate and complete along the tail regions, this approach is preferred because additional information about the column-height distribution is obtained. This, of course, is made possible by the introduction of the variation coefficient and is illustrated by the following experimental example.

The line profiles from the 200 and 400 reflections were obtained from the wear debris of a partially stabilized zirconia sample. These profiles were used to determine the average column height, variation coefficient of the column-height distribution and the amount of microstrain present in the sample. The instrumental parameters, a_γ and a_β, were determined by least-squares fitting the line shape of the 110 and 211 reflections from an Mo powder standard to the Voigt function. A high-resolution diffractometer with a quartz monochromator was used to obtain the line shape experimentally. This effectively eliminated the $K\alpha_2$ component of the Cu $K\alpha$ doublet. A least-squares fit using (14) for the line broadening of the 200 and 400 reflections indicated that the average column length is 86 Å, the variation coefficient of the column-height distribution is 0·51 and the non-uniform r.m.s. strain component, $\langle\varepsilon_{1D}^2\rangle^{1/2}$, which can be attributed to dislocations, is equal to 0·022 (see Fig. 1). The non-uniform strain component, $\langle\varepsilon_{1U}^2\rangle^{1/2}$, was found to be insignificant or zero. The magnitude of the strain component, $\langle\varepsilon_{1D}^2\rangle^{1/2}$, is surprisingly close to that found in cold-worked metals and metal films, indicating a high density of dislocations in partially stabilized zirconia wear debris. If it is assumed that the geometrical arrangement of dislocations is statistically spherical, a variation coefficient of 0·51 indicates that the dislocations that define the subgrains are not uniform in size. A least-squares fit of the experimental line shape with the single-sphere model (9) showed significant misfit in the first-order reflection, which is most influenced by subgrain size. Therefore, we must conclude that a distribution of spherical subgrains is in best agreement with the data. Also, it must be further concluded that the more complete analysis using (12) and (14) provides a more accurate analysis of subgrain size and strain. It was found that the particle size obtained using the single-sphere model is 12% larger while $\langle\varepsilon_{1D}^2\rangle^{1/2}$ is 5% larger than the results obtained using the more complete analysis that includes the variation coefficient. For some applications these differences may not be important; however, information on subgrain-size distribution is lost.

The funding for the theoretical development of this paper was made available by National Science Foundation Grant No. DMR-8000933. Funding for the data collection of the partially stabilized wear debris as well as the sample preparation was derived from a DOE Energy Conversion and Utilization Technologies (ECUT) Program or subcontract 19B07733C.

The authors would like to thank Mary Colby for collecting the X-ray data.

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Acta Cryst. (1986). A**42**, 19–23

An Analytical Function for Absorption Correction

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(*Received* 1 *April* 1985; *accepted* 15 *May* 1985)

Abstract

A new analytical function is proposed for absorption correction. It is expressed by surface harmonics with polar angles that specify the primary and secondary beam directions. This function has an advantage over Fourier expansion because it is rotationally invariant. Two empirical methods are used to determine the expansion coefficients. One uses the intensity deviations of equivalent reflections, and the other uses the calculated intensities at the stage of structure refinement. The utility of the analytical function is demonstrated with a model and with actual data.

0108-7673/86/010019-05$01.50