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The Separation of Particle Size and Strain by the Method of the Variance

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The broadening of the powder pattern peaks from cold-worked and annealed SAP-aluminum filings is measured by three techniques, namely Fourier analysis, integral breadth and variance. It is demonstrated that when the proper angular range of integration is chosen, the variance, Fourier analysis and the integral breadth will yield values of particle size and strain that are of the same order of magnitude.

Introduction

Though the variance or mean square breadth is a frequent measure of mathematical distributions, its use has been limited in the field of X-ray diffraction. The applicability of the variance to the analysis of the line broadening of Debye–Scherrer powder pattern peaks has been clearly demonstrated by Wilson (1962*a*, *b*, *c*; 1963*a*, *b*). Wilson (1963*b*) has shown that if the line broadening is due both to small spherically shaped crystallites and to strains within these crystallites, then the variance in 2θ coordinates is given by

$$W(2\theta)=\frac{K\lambda\Delta(2\theta)}{2\pi^2 p\cos\theta}+4\tan^2\theta\langle\varepsilon^2\rangle \qquad (1)$$

where p is the cube root of the particle volume, K is a shape factor, λ is the wavelength used, $\Delta 2\theta$ is the angular range over which the intensity is measured, θ is the Bragg angle, and $\langle\varepsilon^2\rangle$ is the mean-square strain. The effective particle size, D_e, is defined by the ratio p/K. The particle size and strain contributions to the variance can be separated by using multiple orders of reflexions as has been done previously for integral breadth measurements by Williamson & Hall (1953) and for the Fourier analysis method by Warren & Averbach (1950). In a study of the line broadening from deformed tungsten filings, Halder & Mitra (1963) found that the particle size and strain determined by the variance technique were equal to those observed earlier by McKeehan & Warren (1953) using the Fourier analysis method. However, another study by Mitra (1964) on cold-drawn and annealed aluminum contained considerable inconsistencies between the particle sizes and strains as determined separately by both the variance and the Fourier analysis methods. Although Mitra (1964) was apparently aware that the variance is 'extremely dependent upon the choice of the range over which the variance has been determined' no details are given of the experimental procedures or of the precautions taken in selecting the proper value of the range. Mitra (1964) shows further that the particle size and strain computed from the variance are closely approximated by those obtained from the linear method of integral breadths due to Williamson & Hall (1953). In this linear method, the true breadth is the simple sum of the strain breadth and the particle size breadth. The method assumes a Cauchy strain distribution, which, as Warren (1959) has demonstrated, is a physically non-realistic one. Another integral breadth relationship that has been shown to satisfy the requirements of physical reality in both theory (Warren, 1959) and practice (Wagner & Aqua, 1964) is a quadratic one. In the quadratic method, where the strain distribution is Gaussian, the true breadth squared is the sum of the strain breadth squared and the particle size breadth squared.

The purpose of this paper is to demonstrate that the particle size and strain computed from the variance analysis are consistent with the respective values calculated by the Fourier analysis method as well as by the quadratic integral breadth technique. In an earlier study by Wagner & Aqua (1964), it was demonstrated that the particle sizes and strains measured by the Fourier analysis were consistent with those computed from the integral breadth measurements. From the agreement of the results obtained by these two methods, it was concluded that the angular range over which the peak shape had been determined was properly chosen. Therefore, this range should also be the correct one for use in the variance analysis.

Experimental

For this investigation the 111, 200, 220, 311, 222, 400, 331, and 420 reflexions from cold-worked and annealed SAP-aluminum filings were recorded with a GE XRD-5 focusing diffractometer using Cu $K\alpha$ radiation (nickel filtered). All of the diffraction peaks were corrected by the method of Rachinger (1948) to resolve the peak profile of the $K\alpha_1$ peak. This procedure assumes that the $K\alpha_2$ peak is the same shape as the $K\alpha_1$. Experimentally, one finds that the $K\alpha_2$ component is somewhat broader than the $K\alpha_1$ and that both profiles are asymmetrical with respect to the peak maximum, having longer tails on the low-angle side (Wilson, 1964). In

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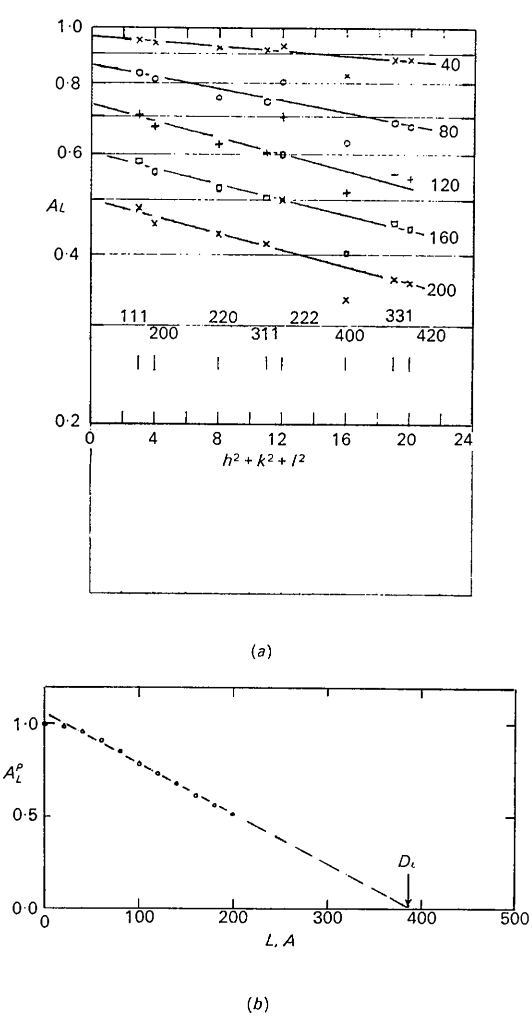
practice, these discrepancies are small and will be masked by the contributions of the geometrical aberrations to the instrumental broadening (Keating, 1959). The powder pattern peaks from the annealed filings were used for the instrumental broadening correction by each method, *i.e.* by the Stokes (1948) method for the Fourier analysis, by the parabolic-approximation method (Wagner & Aqua, 1964; Rao & Anantharaman, 1963) for the integral-breadth method, and by the additivity property of the variance (Wilson, 1963*b*). The Fourier coefficients, integral breadth and variance calculations for each powder pattern peak were made with the aid of an IBM 709 computer (Aqua, 1964).

In the Fourier-analysis method, the particle size and strain are separated by the Warren & Averbach (1950) method, using multiple orders of the *hkl* reflexion according to the following relationship:

$$\ln A_L = \ln A_L^P - 2\pi^2 L^2 \langle \varepsilon_L^2 \rangle (h^2+k^2+l^2)/a^2 \qquad (2)$$



(*a*)

(*b*)

Fig. 1. (*a*) Stokes corrected, Fourier coefficients A_L as a function of the order of reflexion $h_0{}^2 = h^2+k^2+l^2$ for selected values of the distance L. (*b*) Strain-free particle size coefficients $A_L{}^P$ as a function of the distance L.

where A_L are the Fourier coefficients corrected for instrumental broadening by the Stokes (1948) method, A_L^P are the strain-free particle size coefficients, a is the lattice parameter, $\langle \varepsilon_L^2 \rangle$ is the mean-square strain component in the direction normal to the reflecting planes, and L is a distance normal to the reflecting planes. Shown in Fig. 1(*a*) are the A_L for deformed aluminum filings plotted as a function of the order of reflexion, $h^2+k^2+l^2$. The effective particle size $D_e(hkl)$ is defined in terms of the Fourier coefficients as

$$-\left.\frac{dA_L^P}{dL}\right|_{L=0} = \frac{1}{D_e(hkl)} \qquad (3)$$

or as the intercept on the L axis of the initial slope of the $A_L^P(L)$ curve, as shown in Fig. 1(*b*).

It was observed that both the strain and the particle size are independent of crystallographic orientation, *i.e.* that they are both isotropic. The isotropic particle size and a representative value of the root-mean-square strain are listed in Table 1.

Table 1. *Particle size and strain as computed by the variance analysis, Fourier analysis and integral-breadth technique*

Quantity	Variance	Fourier analysis	Integral-breadth
Particle size, A	500 ± 50	400 ± 40	650 ± 65
Strain	0·0022	0·0007	0·0010

When one uses the integral breadth as a measure of the peak profile, the particle size and strain contributions to the true integral breadth (corrected for instrumental broadening) can be separated by using the following equation

$$(b\cos\theta/\lambda)^2 = 1/D_I^2 + 16\,\varepsilon^2(\sin\theta/\lambda)^2 \qquad (4)$$

where b is the true integral breadth; D_I is the integral-breadth particle size; and ε is the integral-breadth strain. The graph of equation (4) is shown in Fig. 2. The particle size and strain computed from the integral breadth measurements are listed in Table 1. The measurement of the particle size and strains in deformed aluminum filings by the Fourier analysis and integral breadth techniques has been previously reported by Wagner & Aqua (1964).

In order to separate the contributions to the true variance (corrected for instrumental broadening) from the lattice strains and small particle size, one uses a more appropriate rearrangement of the terms in equation (1), namely

$$\frac{W(2\theta)}{\Delta(2\theta)}\,\frac{\cos\theta}{\lambda} = \frac{1}{2\pi^2 D_e} + \frac{4\sin\theta\tan\theta}{\lambda\Delta(2\theta)}\langle\varepsilon^2\rangle. \qquad (5)$$

The plot of equation (5) is shown in Fig. 3. Listed in Table 2 are the values of the variance for the deformed and annealed filings and the angular range over which they are determined. The particle size and strain computed from the variance analysis are listed in Table 1.

Table 2. *Variance analysis data*

hkl	2θ	Variance (°2θ)^2 Annealed	Deformed	Range (°2θ)
111	38·36	0·0046	0·0188	1·28
200	44·63	0·00537	0·0250	1·44
220	65·03	0·00513	0·0355	1·76
311	78·16	0·00575	0·0429	1·76
222	82·38	0·01295	0·0466	2·00
400	99·00	0·00920	0·1409	3·00
311	111·95	0·00992	0·1193	3·00
420	116·51	0·01322	0·1385	3·24

Discussion

From an examination of Table 1, it is apparent that the particle sizes and strains computed by the three methods of line broadening analysis, namely the variance analysis, Fourier analysis and the integral-breadth method, are of the same order of magnitude. The limits of accuracy indicated for the particle sizes represent the reproducibility of the peak profile determination. The particle sizes obtained by the Fourier analysis and variance analysis are smaller than that determined by the integral-breadth method. This result is in agreement with the different definitions of the 'apparent particle size' in each case. In the integral-breadth method, the apparent particle size is directly proportional to the cube root of the particle volume; the proportionality factor describes the shape of the particle. In the Fourier analysis and variance methods, the apparent or effective particle size is the thickness of the particle in the direction normal to the (*hkl*) reflecting plane. Since

$$\langle D^3\rangle^{1/3} \geq D \qquad (6)$$

the integral breadth particle size will be greater than or equal to the particle size as determined by the Fourier analysis or variance. When the particle size values are only slightly different, one can conclude that the distribution of particle sizes about the mean value D is rather sharp.

The lattice strains obtained by each of the three methods differ in a manner consistent with their re-

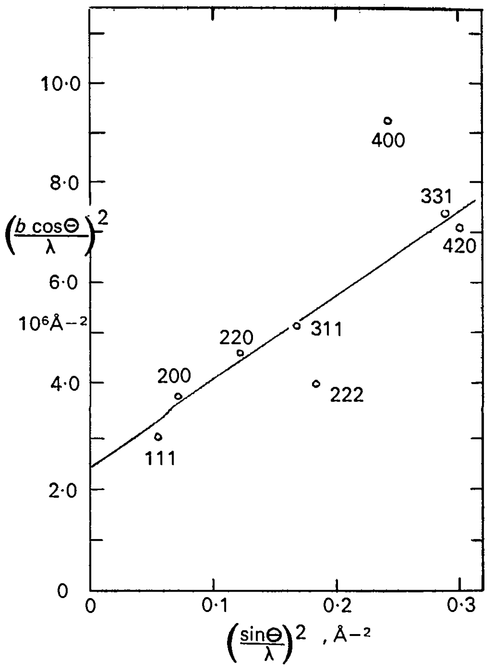


Fig. 2. True integral breadth as a function of $(\sin\theta/\lambda)^2$ for eight reflexions, 111–420.

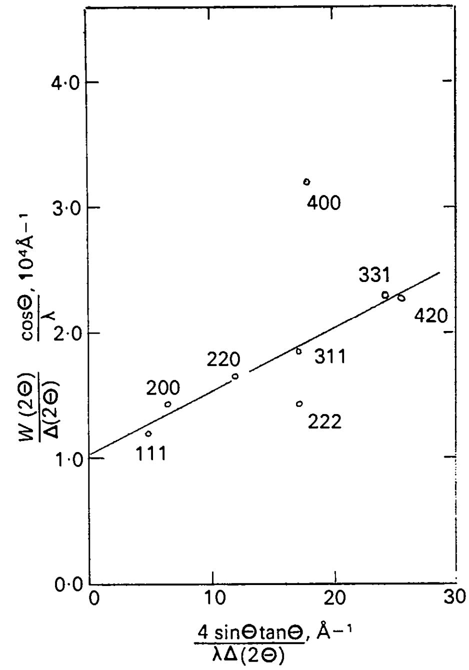


Fig. 3. True variance as a function of $4\sin\theta\tan\theta/[\lambda\Delta(2\theta)]$ for eight reflexions, 111–420.

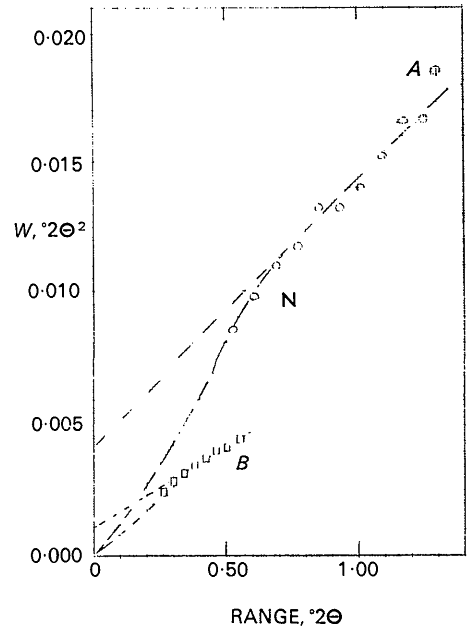


Fig. 4. Variance as a function of range of integration for the 111 reflexion; circles: deformed; squares: annealed.

spective definitions. In the Fourier analysis, the lattice strain is a function of the distance L in the crystal. The Fourier analysis strain listed in Table 1 represents the root-mean-squared strain averaged over the dimension of the effective particle size, a value independent of L. The variance strain, also independent of L, is observed to have the magnitude of the Fourier analysis strain at $L \rightarrow 0$, and would be consistently larger than the average Fourier-analysis strain. The integral-breadth strain has been shown (Wagner & Aqua, 1964) to be approximately 25% larger than the Fourier analysis root-mean-squared strain as averaged over the particle size dimension.

Another measure of the lattice strain may be obtained from the variation of the variance with the range. The value of the range $\Delta 2\theta$ over which the peak profile is defined is critical. As Langford & Wilson (1963) have demonstrated, the variance of the peak is properly chosen when the ratio $W(2\theta)/\Delta(2\theta)$ is a constant. To ascertain whether the range used for the Fourier analysis and integral breadth also satisfied the requirements for the variance analysis, the dependence of the variance as the range was investigated. One example is shown in Fig. 4 for the 111 reflexion. One notes that points A and B, the values used for the particle size and strain determination, are certainly in the region of constant slope. Using the difference in the intercept values of W_0 for deformed and annealed powders, one can compute the root-mean-square strain (see Langford & Wilson, 1963) using the following equation:

$$\bar{\varepsilon} = \tfrac{1}{2}(W_o)^{\frac{1}{2}} \cot \theta \, . \tag{7}$$

For the (111) reflexion the strain $\bar{\varepsilon} = 1{\cdot}4 \times 10^{-3}$, a value that agrees with those computed by the other methods.

In summary, one sees that when the proper angular range is chosen the variance, Fourier analysis and integral breadth will each yield values of particle size and strains that are mutually consistent.

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Structure Cristalline Précise du Sélénite de Magnesium à Six Molécules d'Eau

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The crystal structure of magnesium selenite hexahydrate, $MgSeO_3 \, . \, 6H_2O$, has been determined and refined, with the use of three-dimensional F_o and $(F_o - F_c)$ Fourier and least-squares methods. The space group is $R3$. The dimensions of the hexagonal unit-cell are: $a = b = 8{\cdot}944$ Å, $c = 8{\cdot}936$ Å. The structure is built from octahedral $[Mg(H_2O)_6]^{2+}$ and pyramidal $[SeO_3]^{2-}$ ions; the distance Se–O is 1·69 Å and the interbond angle O–Se–O is 100° 41′.

Introduction

En 1950 est parue une étude cristallographique sur le sélénite de magnésium à six molécules d'eau montrant que ce composé était vraisemblablement isotype du sulfite de nickel à six molécules d'eau (Cavalca & Ferrari, 1950). Afin de compléter ces travaux et d'obtenir des données précises sur l'ion sélénite, la détermination de la structure cristalline de $MgSeO_3 \, . \, 6H_2O$ a été entreprise.