A further reason why such a series may be more useful for fixed-angle diffractometry than for conventional diffractometry arises simply from the fact that the angle is fixed; the numerical values of the moments of each aberration need to be known only for that angle, and not as functions of the Bragg angle over practically the full range 0 to $\frac{1}{2}\pi$.

References


Determination of Particle Size and Strain in Hexagonal (β-Phase) Silver–Antimony Alloys by the Method of Variance

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The method of variance has been applied to some cold-worked hexagonal (β-phase) silver–antimony alloys to determine the particle size and strain values, and the values thus obtained have been compared with those from Fourier analysis of line shapes. Assuming small anisotropy, the agreement in the particle size and strain values has been found to be quite satisfactory. The low values of the effective particle sizes obtained from variance analysis along the faulted planes 101, 102 and 103 clearly indicate the influence of stacking faults which has been found to decrease with increasing solute content.

The applicability of the method of variance to the analysis of the line broadening of powder pattern peaks has been clearly demonstrated in a series of papers by Wilson (1962a, b, c; 1963a, b) and Langford (1968a, b) but its use has so far been restricted to some pure metals (Langford & Wilson, 1963; Halder & Mitra, 1963; Mitra, 1964; Aqua, 1966; Halder & Wagner, 1966; Misra & Mitra, 1967). The difficulty lies in the choice of the range of integration of the broad and overlapping X-ray line profiles on which the variances are extremely dependent. However, the method provides specific advantages such as the additivity of the variances for the different causes of broadening and the absence of any assumptions regarding the mathematical description of the line profiles. So, if a reasonable estimate of the range of the line profiles and of background level is possible the method can successfully be adopted in line-profile analysis. There has been considerable interest recently in the application of this method. Particle size and strain measurements have been made in cold-worked f.c.c. alloys of Ag–Zn, Ag–Pd and Cu–Sb (De & Sen Gupta, 1970), in f.c.c. Cu–Si–Mn alloy (Vasudevan, 1970) and in evaporated thin films of aluminum (Grimes, Pearson, Fane & Neal, 1970). Edwards & Toman (1970a, b; 1971a) have critically examined the variance method for the satellite group, non-additivity and curvature corrections and an application of these considerations has been made in their recent studies with powder samples of iron and high-speed steel (Edwards & Toman, 1971b).

In the present investigation an attempt has been made to apply for the first time the method of variance to the line-profile analysis of hexagonal close-packed alloys of Ag–Sb and to compare the results with those obtained previously by the method of Fourier analysis (De & Sen, 1968).

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Considering reflexions of the type hkl, 2h2k2l, etc. as 00l0, 002l0, etc. by a proper choice of axes and attributing the broadening to particle size, faulting and lattice strain, the variance $W(2\theta)$ of a line profile in

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where \( \lambda \) is the wavelength used, \( \sigma \) is the angular range (in \( 2\theta \)) over which the intensity is measured, \( \theta \) is the Bragg angle, \( D^2 \) is the effective or apparent particle size in a direction normal to the reflecting plane and \( \langle \varepsilon^2 \rangle \) is the mean-square strain. In this equation (1), the taper parameter \( L=0 \) and the Scherrer constant \( K=1 \) for particles having the shape of a cube. The assumption is quite valid, irrespective of the actual shape of the particle, since the 'apparent' particle size yields the thickness of the particle normal to the reflecting planes.

Re-arranging equation (1), one gets (De & Sen Gupta, 1970):

\[
W(2\theta) \cos \theta/\lambda \sigma = 1/2\pi^2 D^2 + 4\langle \varepsilon^2 \rangle \sin \theta \tan \theta/\lambda \sigma . \quad (2)
\]

If multiple orders of reflexions are available equation (2) can safely be applied to separate the particle-size and strain contributions to the variance of the line profiles with proper choice of \( W, \sigma \) values. This has been done earlier in some f.c.c. alloy systems (De & Sen Gupta, 1970; Vasudevan, 1970). Alternatively, in the absence of higher-order reflexions one can express the variance–range function in the form of a polynomial, the coefficients of which lead to an estimate of particle size and strain (Edwards & Toman, 1971).

The line profiles used in this analysis are those of hexagonal (\( \beta \)-phase) Ag–Sb alloys, namely, Ag–12-24 Sb, Ag–14-45 Sb and Ag–16-08 Sb (De & Sen, 1968). The alloy composition Ag–11-23 Sb has not been considered here owing to the uncertainty involved in obtaining proper variance values for this highly deformed case. The deformation has been brought about by hand-filing at room temperature (30±1°C) and copper \( K\alpha \) radiation has been used to record the reflexions 100, 002, 110, 110, 102, 103 and 004 in each of the three alloy compositions. Amongst these, 100, 002, 110 and 004 are stacking-fault-unaffected reflexions and the reflexions 101, 102 and 103 are fault-affected, as revealed by Fourier analysis (Warren, 1959). The variances of these reflexions for both deformed and annealed samples have been evaluated for different values of range \( \sigma \), using a computer program written for the IBM 1130, and plotted as a function of range \( \sigma \). The true values of the variances \( W(2\theta) \) and ranges \( \sigma \) for the line profiles have been determined from the linear portion of the variance–range curve as adopted previously (De & Sen Gupta, 1970). The ranges so determined have been found to correspond to the Fourier-truncation ranges and when expressed on a wave-length scale lie within the factor of 1.5. The variances of the annealed profiles have been used to correct for the instrumental effects arising from spectral distribution and instrumental aberrations. The satellite-group correction, being less important for Cu \( K\alpha \) radiation (Edwards & Toman, 1970) has not been made. Considering the fault-unaffected reflexions 100, 002, 110 and 004, plots of \( W \cos \theta/\lambda \sigma \) vs. \( 4 \sin \theta \tan \theta/\lambda \sigma \) have been made for the alloy compositions (Fig. 1) to evaluate the mean particle size \( D^2 \) and the mean strain \( \langle \varepsilon^2 \rangle \) from the relation (2) assuming small anisotropy in the particle-size and strain values along these directions. This assumption is similar to that made in Fourier analysis (De & Sen, 1968) in the absence of suitable higher-order reflexions and more or less justified from the proximity of the points in the graphical plot (Fig. 1). However, as appears from Fig. 1, the anisotropy for the \( h00 \) reflexion is more pronounced in the present variance analysis, specially magnified in the first composition and, as such, 110 reflexions could not be considered along with others. The mean strain values obtained from the slopes of the plot for the fault-unaffected reflexions and the corrected variance values of the fault-affected 101, 102, 103 reflexions were then utilized to obtain the effective particle sizes \( D^2 \) from equation (2) for the reflexions concerned in the three alloy compositions with the earlier assumption that the strain broadening remains the same for the fault-affected reflexions too (De & Sen, 1968). The mean particle-size and strain values and the effective particle size values from variance and also from Fourier analysis (De & Sen, 1968) are shown in Table 1.

A close examination of the data presented in Table 1 brings out the following features. The mean particle-size values obtained from variance analysis in the present measurement are nearly 1.6 times as high as those from Fourier analysis. This may be due to several
Table 1. Particle-size and strain values in β-Ag–Sb alloys from Fourier and variance analyses

<table>
<thead>
<tr>
<th>Composition</th>
<th>Particle size $D^*$ (Å) from fault-free reflexions</th>
<th>Mean strain ($\times 10^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fourier</td>
<td>Variance</td>
</tr>
<tr>
<td>Ag-12.24 Sb</td>
<td>128</td>
<td>211</td>
</tr>
<tr>
<td>Ag-14.45 Sb</td>
<td>131</td>
<td>230</td>
</tr>
<tr>
<td>Ag-16.08 Sb</td>
<td>155</td>
<td>253</td>
</tr>
</tbody>
</table>

Effective particle size $D^*_e$ (Å) for fault-affected reflexions

<table>
<thead>
<tr>
<th>Composition</th>
<th>(101) (102) (103)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fourier Variance</td>
</tr>
<tr>
<td>Ag-12.24 Sb</td>
<td>67 70</td>
</tr>
<tr>
<td>Ag-14.45 Sb</td>
<td>95 112</td>
</tr>
<tr>
<td>Ag-16.08 Sb</td>
<td>150 133</td>
</tr>
</tbody>
</table>

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