X-RAY STUDY OF STRUCTURAL IRREGULARITIES IN DEFORMED METALS*

Recent Trends in Interpretation of Debye-Scherrer Line Shapes and Breadths

T. R. ANANTHARAMAN

Department of Metallurgy, Indian Institute of Science, Bangalore-12

INTRODUCTION

A METAL or alloy is said to be cold-worked or plastically deformed whenever it is strained beyond its elastic limit below its recrystallization temperature. Most metals are plastically deformed by mechanical operations like rolling, drawing, cutting, machining, hammering, filing, etc., at room temperature. The cold-worked metal is characterized by many structural irregularities, but reverts to its normal state on annealing, *i.e.*, heating above its recrystallization temperature, holding there for a sufficient time and cooling slowly to room temperature. Interest in the X-ray study of deformed structures dates back to 1925 when Van Arkel[1] reported that Debye-Scherrer reflections from cold-worked metals are broad and diffuse as compared to the sharp reflections from annealed ones. Until 1950 the observed X-ray diffraction broadening was attributed to two effects of cold work, *viz.*, fragmentation into small coherently diffracting domains and residual internal strain, but the contribution of deformation stacking faults has been increasingly recognised in recent years. Many comprehensive reviews[2-6] have appeared in the last decade focussing attention on the intense research activity in this field and its importance in elucidating the mechanism of plastic deformation in terms of the movement, interaction, multiplication and redistribution of dislocations and other lattice defects in annealed metals.

This review deals with the effects of the structural irregularities introduced by cold work on Debye-Scherrer reflections from the two typical metallic structures, *viz.*, the face-centred cubic (f.c.c.) and the hexagonal close-packed (h.c.p.), and their quantitative evaluation either by simple and quick analytical procedures involving line breadths or by complex and time-consuming Fourier Transform methods utilizing line shapes. A few simplifications and generalizations have proved inevitable in presenting this bird's-eye view of a very wide field of research, but it is hoped that the original papers will be referred to by those interested in further work.

The notation used is explained at the end.

ANALYSIS OF LINE BREADTHS

The convenient starting point for line breadth or Fourier analysis of X-ray diffraction broadening is the accurate photometric or counter-diffractometric record of Debye-Scherrer reflections from the test metal in both the deformed and annealed states. B and b refer to one component of the normal Debye-Scherrer doublet and can be arrived at by graphical resolution[7] or by an analytical procedure.[8] β is then determined with the aid of one of the following equations :

$$\beta = B - b \tag{1}$$

$$\beta = (B^2 - b^2)^{\frac{1}{2}} \tag{2}$$

$$\beta = [(B^2 - b^2)' \cdot (B - b)]^{\frac{1}{2}} \tag{3}$$

$$\beta = B - \frac{b^2}{B}. \tag{4}$$

Equations (1) and (2) are based on the assumption that the profiles leading to B, b and β are *all* expressible as Cauchy functions[9] $(y = 1/1 + m^2x^2)$ and Gaussian functions[10] $(y = e_{td}{}^{2x^2})$ respectively. In actual practice, however, the profile for b rarely follows either function and can be expressed only by functions like : $y = 1/(1 + m^2x^2)^2$. The profile for β is more often a composite of the Cauchy profile for β_D, the Gaussian profile for β_S and the more complex profile for β_F. The third[11] and the fourth[12] equations are based on line profiles intermediate between Cauchy and Gaussian and may be considered the more satisfactory for any preliminary line breadth analysis.

If β is exclusively due to one cause, the following well-established relations will lead to η, ϵ, σ or α values with very small mean deviation from the mean value for a number of hkl- or $HKIL$-reflections :

$$\beta_D = \frac{\lambda}{\eta \cos \theta} \tag{5}$$

$$\beta_S = 4\epsilon \cot \theta \quad \text{(for isotropic strain)} \tag{6}$$

$$\beta_S = \frac{4\sigma}{E_{hkl}} \cdot \cot \theta \ \text{ or } \ \frac{4\sigma}{E_{HKIL}} \cdot \cot \theta \ \bigg\} \tag{7}$$
$$\text{(for isotropic stress)}$$

$$\beta_F = \frac{2\lambda^2 \cdot L}{c^2 \cdot \sin 2\theta} \frac{[1-(1-3a+3a^2)^{\frac{1}{2}}]}{[1+(1-3a+3a^2)^{\frac{1}{2}}]}$$

or

$$\frac{\lambda^2 (h+k+l)}{a^2 \cdot \sin 2\theta} \frac{[1-(1-3a+3a^2)^{\frac{1}{2}}]}{[1+(1-3a+3a^2)^{\frac{1}{2}}]} \qquad (8)$$

Most deformed f.c.c. and h.c.p. structures display X-ray line broadening that can be explained only as due to more than one cause, if not all three causes. In such cases, the problem can be simplified to one of separating β_D and β_S. Stacking faults in h.c.p. metals broaden only some Debye-Scherrer reflections,[13] *viz.*, those with $H - K \neq 3N$ and $L \neq 0$, and hence some β values can be used to determine a according to equation (8) and the others to separate β_D and β_S. In f.c.c. metals, all X-ray reflections are broadened by stacking faults, but β_F can be calculated for each of them from a arrived at from observed peak shifts.[14] A fault-corrected standard breadth can then be evaluated by compounding b and β_F according to equation (4) for further analysis.[15]

The following relations have been derived for separation of β_D and β_S:

$$\beta = \beta_D + \beta_S \qquad (9)$$

$$\beta = \beta_D \cdot \left(\frac{1-\beta_S}{B}\right)^{\frac{1}{2}} + \beta_S \qquad (10)$$

$$B^2 = \beta_D^2 + \beta_S^2 + b^2 + 2b\beta_D. \qquad (11)$$

Equation (9) has no justification except its simplicity[16] and equation (10) is based on the assumption that equation (4) is generally the best for compounding any two X-ray line profiles.[17] Equation (11) is perhaps the best of all, as it utilizes Cauchy and Gaussian profiles for β_D and β_S respectively and involves the least assumptions.[18] In any case, the values of η and ϵ or σ arrived at from a pair of X-ray reflections should lead to β or B values for other reflections deviating the least from the originally determined β or observed B values respectively.

FOURIER ANALYSIS OF LINE SHAPES

The intensity distribution in the graphically resolved components of any Debye-Scherrer doublet is generally symmetrical about the peak and can be expressed as a cosine Fourier series in terms of a reflection of indices (ool'). The following Fourier series[19] for the profile giving β can be arrived at from the two Fourier series corresponding to the profiles for B and b:

$$P_{2\theta} = M\sum_n A_n \cdot \cos 2\pi nx. \qquad (12)$$

The Fourier Coefficients A_n are arrived at by dividing the coefficients of the profile for B with the corresponding coefficients of the profile for

b, the whole process involving time-consuming and dreary summations in the absence of computers. Every A_n value is then a product of three coefficients,[20] each characteristic of one structural irregularity:

$$A_n = A_n^D \cdot A_n^S \cdot A_n^F \qquad (13)$$

where

$$A_n^D = \frac{1}{n} \sum_{i=n} (i-n) P_i \qquad (14)$$

$$A_n^S = \langle \cos 2\pi n l'\epsilon \rangle \qquad (15)$$

$$A_n^F = [(1-3a+3a^2)^{\frac{1}{2}}]^n. \qquad (16)$$

It is possible in principle to separate the three coefficients by an extrapolation method,[21] but in practice it is simpler to calculate A_n^F from a computed from peak shifts[22] or to consider only reflections unaffected by stacking faults.[18] The problem simplifies therefore to one of separating A_n^D and A_n^S.

When measurements for several orders of (ool') are available, it follows from equations (14) and (15) that A_n^D is independent of the order, but A_n^S is a function of l' and equals unity for $l' = 0$. As A_n is now a product of only A_n^D and A_n^S,

$$\ln A_n (l') = \ln A_n^D + \ln A_n^S (l') \qquad (17)$$

and if $\ln A_n (l')$ is plotted against some function of l' for a fixed value of n, the intercept at $l' = 0$ gives $\ln A_n^D$ directly.[23] The extrapolation to $l' = 0$ is most reliable when $A_n (l')$ is plotted against l'^2.

When data for only one reflection are available, it can be shown on the basis of dimensional disregard of the domains that[24]

$$\frac{dA_n}{dn}\bigg|_{n=0} = \frac{dA_n^D}{dn}\bigg|_{n=0} = \frac{dA_n^D}{dn} = -\frac{1}{\eta}. \qquad (18)$$

η is then evaluated by measuring the initial slope of the A_n vs. n curve.

A third way of separating the effects of η and ϵ is to get back the profile of pure diffraction broadening due to them and analyse it as a Voigt profile made up of one Cauchy and one Gaussian profile.[25] Although the work involved is heavy, a complete separation of the profiles due to η and ϵ is achieved here without any assumption.[17]

CONCLUSION

Although the above methods of analysing X-ray diffraction broadening due to cold work have been applied in recent years to many

metals and alloys, our present understanding of the mechanism of plastic deformation in metallic structures is far from satisfactory. Values of a and ϵ going up to as high as 0·15 and 0·008 respectively and of η going down to as low as 150 Å have been reported, but the nature of the strain, the significance of the domain size and the mode of distribution of stacking faults are yet to be clearly understood for most metals. Filings seem to represent a specially drastic state of cold work and display far more structural irregularities than plastically strained massive polycrystalline specimens. Further accurate and systematic experimental work on a large scale seems to be absolutely necessary before any clear general picture of the cold-worked state can possibly emerge to cover all metals and alloys.

Notation Used in the Text

λ	..	Wavelength of X-radiation.
θ	..	Bragg angle of Debye-Scherrer reflection.
b	..	Integral breadth (i.e., total integrated intensity divided by peak intensity) of instrumental broadening (i.e., normal X-ray reflection from the annealed metal).
B	..	Integral breadth of X-ray reflection from the deformed metal.
β	..	Integral breadth of pure diffraction broadening.
$\beta_D, \beta_S, \beta_F$	..	Integral breadth of broadening due to domains, strain and stacking faults respectively.
A_n	..	Cosine Fourier Coefficient for pure diffraction broadening.
A_n^D, A_n^S, A_n^F	..	Cosine Fourier Coefficients for broadening due to domains, strain and stacking faults respectively.
η	..	Average size of domains in the deformed metal.
ϵ	..	Average internal strain in the deformed metal, also referred to as $<\epsilon^2>^{1/2}$.
σ	..	Average internal stress in the deformed metal.
a	..	Deformation stacking fault parameter (i.e., area of faulted planes divided by

		total area of close-packed planes).
E_{hkl}, E_{HKIL}	..	Young's modulus in direction perpendicular to f.c.c. planes $\{hkl\}$ and h.c.p. planes $\{HKIL\}$ respectively.
l'	..	Index on conversion of (hkl) or $(HKIL)$ to (ool') on orthorhombic axes.
a, c	..	Only f.c.c. lattice parameter and second h.c.p. lattice parameter respectively.
$P_{2\theta}$	..	Distribution of intensity for pure diffraction broadening.
P_i	..	Fraction of columns of length i cells.
x, y	..	Variables.
M, m	..	Constants.
N, n	..	Integers or Zero.

1. Van Arkel, A. E., *Physica*, 1925, **5**, 208.
2. Barrett C. S., *Structure of Metals* (McGraw-Hill, New York), 1952.
3. Greenough, G. B., *Progress in Metal Physics*, 1952, **3**, 176.
4. Guinier A, *Théorie et Technique de la Radiocristallographie* (Dunod, Paris), 1956
5. Hirsch, P. B., *Progress in Metal Physics*, 1956, **6**, 276.
6. Warren, B. E., *Ibid*. 1959, **8**, 147.
7. Rachinger, W A, *J. Sci. Inst*, 1948 **25**, 353
8. Anantharaman, T R. and Christian, J. W., *Brit J. App. Phys.* 1953, **4**, 155.
9. Scherrer, P. Zsigmondy 'Kolloidchemie', 1920
10. Warren B E and Biscoe, J., *J. Am. Ceram Soc.*, 1938, **21**, 49
11. Taylor. A. *Phil. Mag*, 1941, **31**, 339.
12. Anantharaman T. R. and Christian, J. W., *Acta Cryst*, 1956, **9** 479.
13. Wilson, A J. C., *Proc. Roy Soc.*, 1942, **180** A. 277.
14. Paterson, M S, *J. Appl. Phys.*, 1952, **23**, 805.
15. Anantharaman, T. R, *Golden Jubilee Research Volume* (Indian Institute of Science, Bangalore), 1959.
16. Hall, W. H, *Proc. Phys Soc.*, 1949, **62** A. 741.
17. Rama Rao, P. and Anantharaman, T. R, Unpublished work.
18. — and —, *Curr. Sci.*, 1962, **31**, 144.
19. Stokes, A. R, *Proc Phys. Soc.*, 1948, **61**, 382.
20. Houska, C. R. and Averbach, B. L., *Acta Cryst.*, 1958, **11**, 139.
21. Warren, B. E. and Averbach, B. L., *J. Appl. Phys.*, 1952, **23**, 497.
22. Christian, J W. and Spreadborough, L., *Proc. Phys. Soc.*, 1957 **70 B**, 1151.
23. Warren, B E. and Averbach, B. L., *J. Appl. Phys.*, 1952 **23**, 1059.
24. Pines, B. Ya. *D. K. Akad. Nauk. SSSR*, 1955, **103**, 601.
25. Van de Hist and Keesnack, J. J. M., *H . A.*, 1947, **106**, 12.

4