DEVELOPMENT OF AN X-RAY TECHNIQUE FOR MEASURING GRAIN SIZE AS A FUNCTION OF ORIENTATION IN POLYCRYSTALLINE MATERIALS

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ABSTRACT

A new application of the X-ray technique developed by B.E. Warren [1], is presented here. The method, based on statistical fluctuation of counts recorded by a properly modified X-ray diffractometer, has been used to estimate the average grain diameter of different textural classes in metallic polycrystalline materials; it has been tested to evaluate its reproducibility and precision limits. The method appears to be promising for current applications in industrial research laboratories and for quality control routines since specimen preparation is easy and measurement is automated.

INTRODUCTION

Analysis of the evolution of grain size as a function of orientations resulting from recrystallization or grain growth phenomena is of particular importance in the case of materials whose physical properties are markedly affected by crystal size and orientation.

In order to evaluate the volume fraction that can be assigned to a specific textural component, but without any other information on grain size, the ODF technique, involving measurement of x-rays pole figures, is commonly applied. Other known techniques that, on the other hand, can give dimensional information linked to orientation are the Electron Channelling Pattern (ECP) and Electron Backscattering Pattern (EBSP) performed by scanning electron microscopes [2].

Although the EBSP method is very accurate and can give in principle a complete information about grain orientation and size, it has some disadvantages, such as the need for sufficient statistics (which implies the analysis of many different fields) requiring time-consuming measuring operations. Moreover this technique cannot be completely automated and the presence of a skilful operator is always required.

The method proposed in this paper, based on previous work [1], permits the determination of grain size larger than about 1 μm using a statistical variation analysis of the peak intensity.

THEORY

The main feature of this method is the use of a highly collimated primary beam of small cross-sectional area, falling on a flat-faced sample.

If, as is commonly the case, especially where commercial goniometers are concerned, the ratio between the x-ray spot and the average grain size in the sample is reduced to a value lower than ~ 100, different values will be obtained by repeating the intensity measurement of (hkl) diffracting planes at different positions in the sample. The theory analyses these fluctuations statistically and correlates their amount to a quantity that depends upon the average grain diameter. The approach adopted to the problem in the present paper is more general than in [1] and some limits of the preceding analysis are discussed.

Let us consider a single measurement of scattered intensity from a certain (hkl) plane. During the measurement the sample and the counter rotate respectively through small angles $\Delta\vartheta$ and $2\Delta\vartheta$ determined by the slit width centered on the (hkl) reflection. Angle $\Delta\vartheta$ and length l of the receiving slit determine a small solid angle Ω which contains the normals of all crystals contributing to the measured diffracted energy.

If A_0 is the cross-sectional area of the incident beam and ϑ the Bragg angle for the (hkl) crystal plane, the small irradiated volume element i at depth z has a thickness Δz and a volume $\Delta V_i = (A_0/\sin\vartheta)\Delta z$. The number of crystals of k -th size class in this volume is

$$n_{ik} = \Delta V_{ik}/v_k = F_k \Delta V_i/v_k = (F_k A_0 \Delta z)/(\nu_k \sin\vartheta)$$

in which n_{ik} is the number of crystals, occupying the volume ΔV_{ik} in the i -th layer, belonging to the k -th dimensional class having volume v_k and volume fraction F_k .

The average number of (hkl) crystals of k -th dimensional class in the volume i can be expressed as:

$$\bar{m}_{ik} = n_{ik} j \Omega / 4\pi = (j A_0 \Omega \Delta z) / (4\pi \sin\vartheta) \cdot (F_k / v_k)$$

in which j is the (hkl) multiplicity.

The basic assumption of the method is that in the case $\bar{m}_{ik} < 5$, m_{ik} is a random variable following a Poisson distribution with $\bar{m}_{ik}$ as characteristic parameter. As a consequence the variance will be

$$\langle (m_{ik} - \bar{m}_{ik})^2 \rangle = \bar{m}_{ik} \quad (1)$$

Let y_i be the number of counts recorded from the total distribution of m_{ik} crystals in ΔV_i for one setting of the sample and let $\bar{y}_i$ be the average number of counts from the total distribution of $\bar{m}_{ik}$ average number of crystals in the same volume.

These quantities will be given by relationships as:

$$y_i = \alpha_z \sum_k m_{ik} ; \bar{y}_i = \alpha_z \sum_k \bar{m}_{ik} \quad (2)$$

with $\alpha_z = K \exp [-(2\mu z)/\sin\vartheta]$ where μ is the linear absorption coefficient. From eqs. (1) and (2) the fluctuation can be written as

$$\langle (y_i - \bar{y}_i)^2 \rangle = \alpha_z^2 \sum_k v_k \bar{m}_{ik}$$

If $Y = \sum y_i$ is the whole number of counts recorded by the sample for one specific setting and $\bar{Y} = \sum \bar{y}_i$ the average number of counts from the sample, assuming that the distributions in the different layers i are independent, the fluctuation of the counts can be written as

$$\langle (Y - \bar{Y})^2 \rangle = \sum_i [\alpha_z^2 (\sum_k v_k \bar{m}_{ik})] \quad (3)$$

Writing now α_z and $\bar{m}_{ik}$ in explicit form and replacing the sum by an integral in the range $(0, \infty)$ we obtain from eq. (3)

$$\langle (Y - \bar{Y})^2 \rangle = (K^2 j A_0 \Omega) / (16\pi \mu \sin\vartheta) \cdot \sum_k F_k v_k \quad (4)$$

In the same way the quantity $\bar{Y}$ becomes

$$\bar{Y} = [\sum_i \alpha_z (\sum_k v_k \bar{m}_{ik})] = (K j A_0 \Omega) / (8\pi \mu \sin\vartheta) \quad (5)$$

Finally, from the ratio between eqs. (4) and (5) we have

$$\frac{4\pi\mu}{j A_0\Omega} = \frac{\langle(Y-\bar{Y})^2\rangle}{\bar{Y}^2} \sum_k F_k v_k = \sum_k \left[\frac{f_k v_k}{\sum_k f_k v_k} \cdot v_k \right] = \frac{\sum_k f_k v_k^2}{\sum_k f_k v_k} = V^* \quad (6)$$

in which f_k are the numeric frequencies satisfying the condition $\sum f_k = 1$. The quantity V^* can be further expressed from eq. (7) as

$$V^* = \bar{V}^2/\bar{V} = \bar{V} + \sigma_V^2/\bar{V}$$

If the grains are considered to have a spherical shape then

$$V^* = (\pi/6) D^{*3}$$

where D^* is an equivalent diameter. It should be noted that since $V^* > \bar{V}$ then is always $D^* > \bar{D}$. Solving eq. (6) for D^{*3} we obtain the relationship:

$$D^{*3} = (3 j A_0\Omega\gamma)/(2 \pi^2 \mu) \cdot \langle(Y-\bar{Y})^2\rangle/\bar{Y}^2 \quad (7)$$

where D^{*3} is the average cube diameter and the factor γ is included for the case of a textured sample and represents the ratio between the integrated intensity of the (hkl) peak and that measured on a random sample.

EXPERIMENTAL

The statistical factor $\langle(Y-\bar{Y})^2\rangle/\bar{Y}^2$ appearing in the final relationship (7) is deduced from the count fluctuation between the measurements performed on different points of the sample for the (hkl) plane: the greater the fluctuation, the greater the resulting average cube diameter.

Details on the conditions for estimating the angle Ω in eq. (7) and the background corrections of the counts are given in [1].

A Siemens D500 texture goniometer has been used for practical realization of the measurements. This instrument permits automatic data acquisition and the change of the sample position both using a slightly eccentric collimator (to perform measurements around circles - ϕ rotation) and the sample translation facility of the sample holder.

By putting a small aperture close to the X-ray tube and another one of the same diameter as close as possible to the sample surface, the beam divergence effects are strongly reduced.

If the method is applied to a powder sample it is possible to choose any intense reflection to measure the average particle diameter. In the work reported here a different aspect of this technique was used for the first time: in a polycrystalline massive sample, in which some texture certainly exists, evaluation of the average grain diameter for various (hkl) planes allows an estimate to be made whether some dimensional differences exist between the analyzed textural classes.

In fact, for each ϕ_{hkl} Bragg angle only the grains whose (hkl) planes are parallel to the sample surface contribute to the diffracted intensity but this is irrespective of how the crystallographic directions lying on such a crystal plane are oriented in the sample reference system. Although incomplete, this information can be very useful for evaluating selective grain growth during primary recrystallization or extended grain growth especially if the measurements are integrated with ODF calculations in order to assign the exact evolving texture component to the (hkl) fibre of which the average grain diameter is measured.

Experiments on compressed iron powder, used also as random texture sample, are discussed first. On this sample the average grain diameter was evaluated by SEM, the value being $3.5 \pm 0.7 \mu\text{m}$.

An example of four sets of 120 measurements for each (hkl) plane is reported in Table 1 [3]. The average result of the statistical fluctuation method (SFM) is $3.4 \pm 0.2 \mu\text{m}$, which is in quite good agreement with the previous value.

Table 1 - Average grain diameters (μm) estimate for different crystal planes of a random Fe powder (Mo- α radiation used).

(110)	2.5	2.7	2.7	3.0
(200)	2.4	2.6	2.5	2.5
(211)	3.6	3.3	3.3	3.7
(310)	3.2	3.1	3.2	3.4
(222)	5.0	4.8	4.9	4.8
Average	3.3	3.3	3.3	3.5

Use was also made of another set of samples, on which various measurements were performed by a combined etch-pitting and automatic image analysis technique (EP-AIA). These materials are grain oriented Fe-3%Si sheets in a stage following the primary recrystallization process. Three samples were further annealed at different temperatures, namely 830, 850 and 890°C, for a soaking time of 1 hour to permit grain growth.

Table 2 reports the results of the 3 samples together with the comparative values from the EP-AIA technique. The average values reported in the last row are computed, for SFM, by averaging the grain diameters using the textural factors as weights. This experiment shows that the global average values provided by the two different methods are in good agreement: acceptable agreement exists with the determination of single crystal planes too. Generally the SFM values increase with temperature, following the expected trend of growth phenomenon but with some small local faults probably due to sample inhomogeneities. When comparing the results it must be remembered that the intrinsic uncertainty of the EP-AIA method is essentially due to the not very high orientation selectivity. On the other hand the error associated with the SFM measurement must be analysed in more detail.

Table 2 - Comparison of average grain diameters (μm) in Fe-3%Si samples annealed at different temperatures measured by the Statistical Fluctuation Method (120 measured points) and EP-AIA technique.

Plane	830°C		850°C		890°C	
	$\bar{D}_{\text{SFM}}$	$\bar{D}_{\text{EP-AIA}}$	$\bar{D}_{\text{SFM}}$	$\bar{D}_{\text{EP-AIA}}$	$\bar{D}_{\text{SFM}}$	$\bar{D}_{\text{EP-AIA}}$
(110)	12.6	13.7	15.1	14.5	14.9	16.0
(200)	11.1	13.1	13.5	14.4	16.2	15.2
(211)	11.6	-	17.0	-	18.2	-
(310)	14.1	-	16.2	-	21.2	-
(222)	14.0	13.5	13.7	13.6	14.3	15.2
Average	13.1	13.5	13.9	14.1	15.0	15.4

Firstly the number of measurements that can be considered statistically sufficient for one diameter determination ranges from 90 to about 120, there being substantial convergence of final values (Table 3). Secondly the instrumental error, due to the intrinsic reproducibility of the measuring apparatus, can be limited to very low values. Table 4 gives the results of repeated measurement on the same 120 points for three planes of an 890°C sample. The average diameters for the same plane differ by not more than $0.3 \mu\text{m}$ in all cases. The problem of sample inhomogeneity is different because of the greater amount of variation in grain diameter.

Table 3 - Significance of the number of measured points.

Measured points	90	180	270	360	450	540	630	720	810	900
$\bar{D}_{(200)}(\mu\text{m})$ 830°C	12.1	12.0	12.2	12.4	12.4	12.3	12.2	12.4	12.4	12.3
$\bar{D}_{(110)}(\mu\text{m})$ 890°C	14.9	13.5	14.4	14.5	14.0	14.2	14.2	14.2	14.3	14.4

Table 5 reports the results of 10 average grain size determinations, each obtained by a 90 measurement set, for crystal planes (200) and (110) for the Fe-3%Si samples respectively 830°C and 890°C of Table 2. Each group is measured by rotating only the ϕ angle maintaining the rotation centre on the same sample position. Sample translation was performed between the different values, changing the rotation centre position on the sample. Each group of 90 measurements has been processed separately, the overall value being reported in the last row of Table 5. The determination error can be evaluated considering the standard deviation of the 10 partial measurements for both planes; the results are ± 0.6 and $\pm 1.4 \mu\text{m}$.

Table 4 - Test of instrumental reproducibility of SFA method. Average diameters (μm) for sample 890°C (120 meas. for each determination).

Plane	(110)	(200)	(310)
	14.9	16.2	21.2
	14.0	16.3	20.9
	15.0	15.9	21.0

Table 5 - Test of sample inhomogeneity effect on SFA method (10 groups of 90 measurements, each group is related to different zones of the sample).

	$\bar{D}_{\text{total}}$
$\bar{D}_{200}(\mu\text{m})$ (sample 830°C) 12.1,12.0,11.8,12.5,12.2,12.2,11.1,13.2,11.6,10.9	12.3
$\bar{D}_{110}(\mu\text{m})$ (sample 890°C) 14.9,11.7,16.0,14.6,11.8,14.9,14.4,14.1,14.6,16.0	14.4

Table 6 shows two sets of measurements, carried out on two samples (A and B) of non-oriented silicon iron (3.2%Si) heat treated after cold rolling for 5 minutes at 850 and 950°C respectively. Though the total average values weighted by the texture factors are in quite good agreement with the measurements performed using the linear intercept method, nothing can be said about the size differences between corresponding (hkl) planes, since no independent measurements are available for them at the moment.

Table 6 - Grain size measurements in samples with relatively large grains.

	(110)	(200)	(211)	(310)	(222)	Average	Average by linear intercept
A (850°)	18.2	14.0	24.0	25.3	33.6	28.0	26.0 $\pm$ 3
B (950°)	23.4	29.1	28.8	28.9	34.9	32.2	34.0 $\pm$ 4

It should be pointed out that this method can indicate the right order of magnitude of grain size in a range where the average diameters are increased by a factor of 10 (see Tables 1,2 and 6).

Moreover under normal conditions the measurements can detect the differences in grain diameter up to $2\mu\text{m}$.

However in general it has been noted that for large grains ($> 30\mu\text{m}$ in iron) under various experimental conditions, a certain saturation effect in the measured average grain size becomes evident and appears much more significant at low ϑ angle (see for example (110) and (200) planes in Table 6). This saturation effect causes an underestimate of the measurement and also an increasing grain size as 2ϑ increases (see Table 6).

This can probably be ascribed to the limited X-ray penetration which, in coarse-grained samples, is of the same order of magnitude as the grain size or less. If this aspect is taken into account, the original theory can be modified, giving rise to a different expression for eq. (7) in which appears a correction factor, depending upon the diffraction angle.

For sake of space this and other improvements of the theory will be discussed elsewhere [4].

Furthermore some general developments of this method can be briefly described: firstly it is possible to apply this technique using other radiations than X-rays in order to take advantage of their specific interaction with the matter (e.g. neutrons); secondly the use of a texture goniometer allows a reduction of the crystal direction indetermination that is now present in the measurements if, after a previous screening of the direct pole figures, one performs measurements on a specific pole whose χ and φ angles are fixed.

CONCLUSIONS AND FURTHER WORK

The method presented here can be considered a powerful and relatively simple tool for rapid average grain diameter determination when this information must be correlated with texture evolution.

Application of this method to different iron samples indicates good agreement of the results with the average grain size independently measured and, where the comparison was possible, also with the size of the individual texture components. Reproducibility of the size measurements appears quite good and in normal conditions only a relatively small number of measured points is necessary to ensure a quite low relative error in the global measurement. Full automation of the goniometer and the measuring procedure makes the system quite efficient. However a specifically designed goniometer would enhance the intensity of the X-ray spot and specimen movements, thus further improving system efficiency.

Finally more accurate size-orientation measurements (ECP and similar) should be used to carefully verify the general applicability of the method, the measurements also being extended to non ferrous materials.

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