

A STUDY OF PREFERRED ORIENTATION BY ENERGY- DISPERSIVE X-RAY DIFFRACTION

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Abstract: The influence of preferred orientation on integrated x-ray intensities in powder specimen using energy-dispersive diffraction method is investigated. The theory used is based upon examination of the polar axis density distribution. The measurements were carried out using the Schulz technique added with defocusing correction. Experimental results are given for three aluminium powder specimens.

1. INTRODUCTION

The aim of the present work is to study the orientation distribution of crystallites in powder specimens using the energy-dispersive x-ray diffraction method. It will be shown that this method can be used for correction in integrated x-ray intensities for preferred orientation.

There are only a few texture studies performed by the energy-dispersive method. Laine and Lähteenmäki¹ applied the energy-dispersive method to the examination of the preferred orientation in the splat-cooled cadmium foils. Szpunar, Ojanen and Laine² showed the applicability of the method to the direct recording of information necessary for inverse pole figure determination. Further, different aspects of technical practice and specific experimental features were considered. Gerward, Lehn and Christiansen³ applied the energy-dispersive method to the quantitative determination of rolling texture.

Järvinen, Merisalo, Pesonen and Inkinen⁴ presented the general theoretical principles of correction method of integrated x-ray intensities for preferred orientation. This method, which is based upon examination of the polar axis density distribution and upon the use of a cubic harmonic expansion in its representation, was applied in the present work.

2. THEORY

For determination of the orientation distribution of crystallites the Schulz reflexion technique⁵ can be applied. The orientation distribution of the crystallites can be described by the polar axis density,

$$W(\nu, \phi) = \frac{4\pi}{V_0} \frac{dV}{d\Omega}, \quad (1)$$

where V_0 is the total volume of crystallites in the specimen and dV is the volume occupied by those crystallites with such an orientation that the surface normal of the specimen falls within a solid angle element $d\Omega$ in the direction ν, ϕ with respect to the internal coordinate system of crystallite.

Järvinen et al.⁴ presented that the values of the integrated intensities corrected for texture are obtained from Equation

$$I_{\text{ran}}^{\text{hkl}} = I_{\text{obsd}}^{\text{hkl}} / W(\nu_{\text{hkl}}, \phi_{\text{hkl}}), \quad (2)$$

where $I_{\text{obsd}}^{\text{hkl}}$ is the observed intensity of reflexion hkl . For specimen without texture (random orientation) the polar axis density, $W(\nu_{\text{hkl}}, \phi_{\text{hkl}}) = 1$ and hence $I_{\text{ran}}^{\text{hkl}} = I_{\text{obsd}}^{\text{hkl}}$.

The polar axis density will possess the symmetry of the crystal structure. Thus it can be given by

$$W(\nu, \phi) = \sum_{ij} C_{ij} K_{ij}(\nu, \phi) \quad (3)$$

in terms of a complete orthogonal set of harmonics $K_{ij}(\nu, \phi)$ of the same symmetry. In this equation, there are two indices: i denotes the order of the harmonics and j labels the linearly independent harmonics in each order. Because $W(\nu, \phi)$ by its physical nature is an even function the index i runs through even values only. Järvinen et al.⁴ showed also that integration of Equation (3) yields

$$I^{\text{hkl}}(\alpha) = T^{\text{hkl}} \sum_{ij} C_{ij} K_{ij}(\nu_{\text{hkl}}, \phi_{\text{hkl}}) P_i(\cos \alpha), \quad (4)$$

where $P_i(\cos \alpha)$ is the Legendre polynomial of the order i , α is the polar angle and T^{hkl} is a proportional coefficient

$$T^{\text{hkl}} = I_{\text{ran}}^{\text{hkl}}. \quad (5)$$

Thus by measuring the integrated intensities of the texture specimen $I^{\text{hkl}}(\alpha)$ for different reflections as a function of polar angle the unknown coefficients, C_{ij} , of the series (3) can be solved with Equation (4). The polar-axis density can be obtained so from Equation (3) and the texture correction for integrated intensities can be made according to Equation (2)

Järvinen et al.⁴ showed also that if the texture is not very strong, it is sufficient to determine the terms of series (3), in which $i \leq 10$ and to measure the intensity values at the tilt angles in steps of 10° . When the discussion is confined to the case of the cubic symmetry the harmonic functions, K_{ij} , are the cubic harmonics. This set does not contain second-order function ($i = 2$). Before it was found that the order i will take only even values. In the orders $i = 0, 4, 6, 8, 10$ in each only one function appears.

3. EXPERIMENTAL

The aluminium powder used was Koch-Light Laboratories Ltd 8912 W. The powder having the particle size from 8 to 15 μm was pressed into disks whose diameter was 13.0 mm and thickness about 3 mm. For decreasing the porosity the pressure chamber was evacuated. Three pressures were used in the sample preparation:

sample 1, 40 MPa
 sample 2, 300 MPa
 sample 3, 450 MPa

It was intended that sample 1 was to be prepared as an ideal powder sample as possible. Inkinen, Pesonen and Paakkari⁶ showed experimentally that if the moulding pressure was less than 50 MPa no significant effects of preferred orientation were discernible. Furthermore, by the suitable compression of the powder, the effects of porosity and surface roughness on the integrated intensities can be minimized. The preliminary measurements revealed that applying pressures of 300 MPa (sample 2) and 450 MPa (sample 3) obvious preferred orientation effects can be found.

When the preferred orientation is investigated by the x-ray reflexion method the specimen must have a certain minimum thickness, t , which can be calculated from Equation

$$t = \frac{3.46}{\mu} \sin \theta, \quad (6)$$

where μ is the linear absorption coefficient and θ the Bragg angle. When $2\theta \leq 32^\circ$, the energies corresponding to the first three diffraction reflections of aluminium are below 20 keV, and the ratio of the density of the sample to that of the bulk is above 0.6, we have the value $t = 1.70$ mm for the minimum thickness.

The schematic illustration of the energy-dispersive diffraction system used in this work is shown in Figure 1. A flat-faced specimen was placed in the sample holder of Siemens texture goniometer and the specimen was in "white," polychromatic radiation of an x-ray tube (copper target, 40 kV and 18 mA). The spectrum of the scattered x-rays was measured by an Ortec Series 7000 lithium-drifted silicon detector whose energy resolution was 175 eV FWHM at 5.9 keV. Signals from the preamplifier were fed to a pulse-shaping amplifier and then to the multichannel pulse-height analyser (Northern

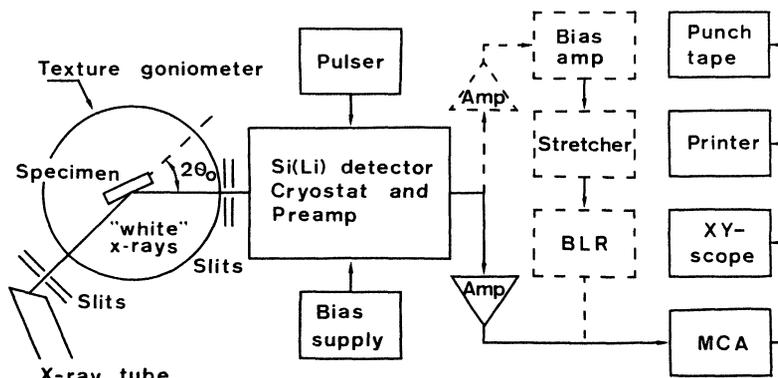


Figure 1. Block diagram of the energy-dispersive x-ray diffraction system used in this work.

Tracor 750). As the recording system an x-y scope, a printer and a tape punch were used. The Bragg equation can be written, in the case of the cubic system, by the expression

$$E = \frac{6.199(h^2 + k^2 + l^2)^{\frac{1}{2}}}{a \sin \theta} \quad (7)$$

where E is the energy of the hkl reflexion. Using Equation (7) the suitable 2θ angle was predetermined. This result is shown in Figure 2, in which the energies of the fluorescence peaks can also be seen. The fixed scattering angle must be

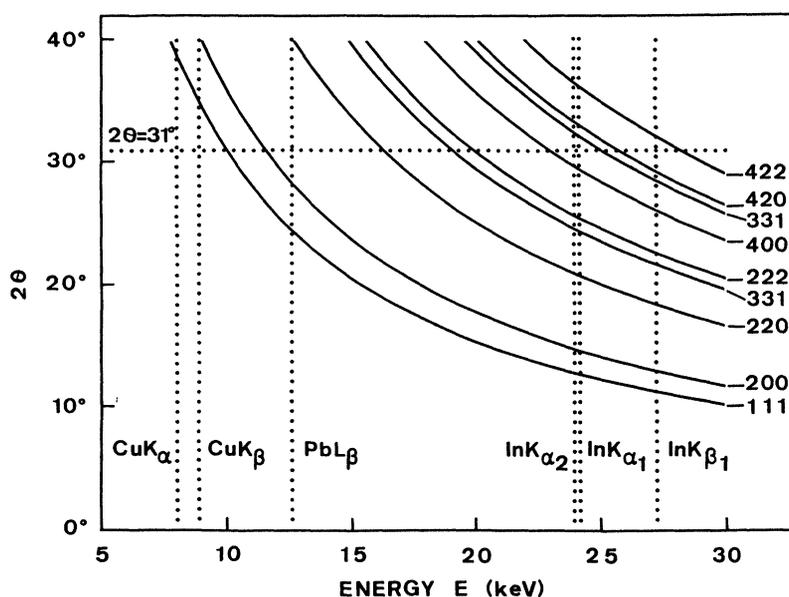


Figure 2. 2θ as a function of photon energy for different hkl values of aluminium. CuK_α , CuK_β , PbL_β , $\text{InK}_{\alpha_{2,1}}$ and InK_β , are the harmful fluorescence peaks appearing in the energy-dispersive spectrum.

selected so that the diffraction peaks do not overlap with the fluorescence peaks. On the basis of Figure 2 the optimum value of 31° for the fixed $2\theta_0$ angle was obtained. The energy scale of multichannel analyser was calibrated with a standard source of ^{57}Co , the spectrum of which contains three accurately known energy peaks: 6.40 keV (FeK_α), 7.06 keV (FeK_β) and 14.40 keV (γ -peak). The system was adjusted to record the energy region from 0.04 keV to 20.44 keV, which was divided into 512 channels. The measurements were carried out by the method originally proposed by Schulz.⁵ In this method the specimen rotates about its own normal and it is also inclined with respect to the vertical plane. The measuring time for one diffraction spectrum was 1000 s. The integrated intensities were calculated by using the computer program which sets a third-degree spline-function through the points observed and makes the background correction.

Chernock and Beck⁷ showed that effects of defocusing of the diffracted x-ray beam caused by the geometrical configuration of the instrument can be minimized by very accurate specimen alignment, by decreasing the width of the main slit, and by increasing the length of the receiving slit. In general, these procedures are not enough, but it is in need of correction factor for the loss of intensity as a function of the tilt angle α . Some equations^{8,9} have been derived for correction of defocusing, but it can be performed also by means of a good sample without texture. The measured intensity ratios of sample 1 $I_{pw}^{hkl}(\alpha)/I_{pw}^{hkl}(0)$ for the first three reflections as a function of the tilt angle are shown in Figure 3. The values of the measured intensities are the

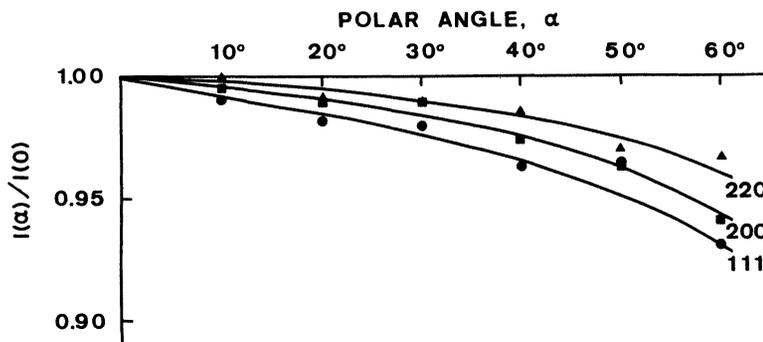


Figure 3. Effect of defocusing for integrated intensities in three reflexion of 111, 200 and 220 obtained from sample 1.

mean values of five measurements, and furthermore, these are symmetrized. The correction of defocusing was performed by means of these curves. The corrected integrated intensities are obtained by multiplying the observed intensity by the correction coefficients A^{hkl} given in Table I.

The integrated intensities of the reflexions 111, 200 and 220 for samples 2 and 3 were measured by tilting the

Table I. The correction coefficients, A^{hkl} , of integrated intensities for defocusing effects for different reflexions of aluminium.

| α | A^{111} | A^{200} | A^{220} |
|----------|-----------|-----------|-----------|
| 0° | 1.000 | 1.000 | 1.000 |
| 10° | 1.008 | 1.004 | 1.002 |
| 20° | 1.015 | 1.009 | 1.005 |
| 30° | 1.024 | 1.016 | 1.010 |
| 40° | 1.034 | 1.024 | 1.016 |
| 50° | 1.049 | 1.037 | 1.025 |

sample up to $\alpha = \pm 50^\circ$ at intervals of 10° . The integrated intensities obtained, $I^{hkl}(\alpha)$, were corrected for defocusing and symmetry. The corrected integrated intensities were substituted directly to Equation (4) for determination of the coefficients C_i and T^{hkl} ($i \leq 10$) to every reflexion hkl separately. The equation group was solved by the computer program. The values of the coefficients C_i obtained are presented in Table II.

Table II. The values of the coefficients C_i to the reflections 111, 200 and 220 of the texture samples.

| hkl | C_0 | C_4 | C_6 | C_8 | C_{10} |
|--------------------|--------|--------|---------|---------|----------|
| a) <u>Sample 2</u> | | | | | |
| 111 | 1.0000 | 0.0285 | -0.0856 | 0.0687 | 0.0117 |
| 200 | 1.0000 | 0.0619 | -0.0486 | 0.0151 | 0.0086 |
| 220 | 1.0000 | 0.0571 | -0.0384 | 0.0149 | -0.4829 |
| b) <u>Sample 3</u> | | | | | |
| 111 | 1.0000 | 0.1061 | -0.0726 | 0.0011 | -0.0096 |
| 200 | 1.0000 | 0.0489 | -0.0122 | 0.0022 | 0.0015 |
| 220 | 1.0000 | 0.1401 | -0.0722 | -0.0006 | 0.3937 |

When the coefficients, C_i , are known, the polar axis densities can be determined from Equation (3).

4. RESULTS AND DISCUSSION

No significant effects of texture were discernible in sample 1 prepared by applying the pressure of 40 MPa. On the other hand, the compression decreases noticeably the influence of the other sample effects to the integrated intensity. Thus sample 1 can be considered a quite good powder sample and it was used also for correction of defocusing effect. It was found in samples 2 and 3 that the compression produced the preferred orientation, where the cube face (100) tends to lie parallel to the surface of the sample. This can be seen from the highest polar axis density of the reflexion 200. Comparing with samples 2 and 3, it is found that the stronger compression causes also the higher texture. The influence of the preferred orientation to the integrated intensities of Al-powder samples investigated is presented in Table III. The measured intensities have been normalized by using $I_{pw}^{200} = 100$. In Table III, the relative difference of the polar axis densities is also given,

$$\Delta = [I_{obsd}^{hkl}(0)/W^{hkl} - T^{hkl}]/T^{hkl} \quad (8)$$

Table III. The polar axis densities and their relative differences obtained from samples 2 and 3.

| hkl | $I_{obsd}^{hkl}(0)$ | W^{hkl} | I_{ran}^{hkl} | T^{hkl} | $\Delta \%$ |
|--------------------|---------------------|-----------|-----------------|-----------|-------------|
| a) <u>Sample 2</u> | | | | | |
| 111 | 131.5 | 0.927 | 141.9 | 144.0 | -1.46 |
| 200 | 104.9 | 1.044 | 100.5 | 100.4 | 0.10 |
| 220 | 216.4 | 1.020 | 212.2 | 212.2 | 0.00 |
| b) <u>Sample 3</u> | | | | | |
| 111 | 129.4 | 0.847 | 152.8 | 148.6 | 2.83 |
| 200 | 106.8 | 1.043 | 102.4 | 101.5 | 0.87 |
| 220 | 221.6 | 1.038 | 213.5 | 214.6 | -0.051 |

For defocusing and symmetry corrected intensity ratios, $I^{hkl}(\alpha)/I^{hkl}(0)$, for the reflexions 111, 200 and 220 of both

textured samples 2 and 3 are given in Figure 4 and Figure 5, respectively.

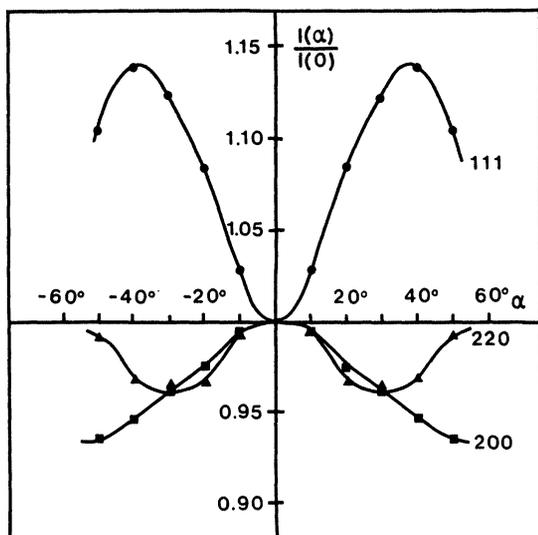


Figure 4. Intensity ratios as a function of polar angle for the first three reflexions obtained from sample 2.

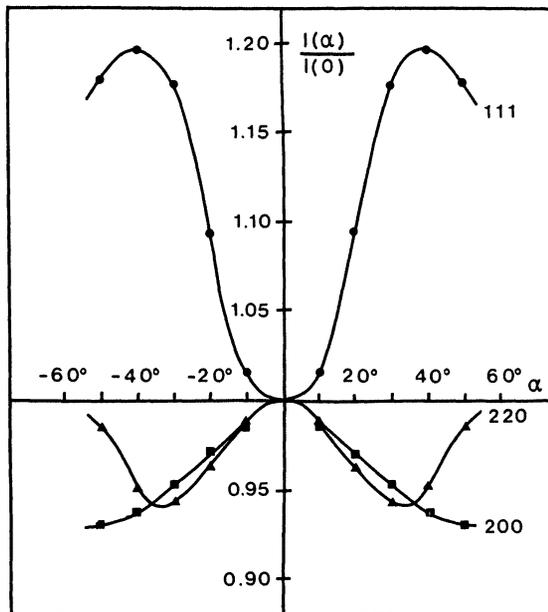


Figure 5. Intensity ratios as a function of polar angle for the first three reflexions obtained from sample 3.

In the calculation of the results it was necessary to know only the intensity ratios, but not the true relative intensities. Thus it was not necessary to correct the integrated

intensities with the quantum counting efficiency factor of the detector, as in general in adaptations of the energy-dispersive method. When calculating, using intensity ratios also, the effects of thermal diffuse scattering (TDS), Compton scattering and surface roughness on the integrated intensities decrease, because 2θ is constant in energy-dispersive method. The careful adjustment of texture goniometer system is absolutely important in texture measurements. This is easier in energy-dispersive method than in angle-dispersive method because the Bragg angle is constant. In practice, it is still necessary to carry out small defocusing and symmetry corrections for the intensities measured.

When the sample is prepared by compression of the powder, many sample effects, excluding the textural one, are minimized, and by determining the effect of texture on integrated intensities, the scattering intensity, independent on sample effects, can be obtained.

The accurate measurements of integrated Bragg intensities make the exact determination of Debye-Waller factor and structure factor, for example, also possible.

The present results show that the energy-dispersive x-ray diffraction method is well suited for accurate texture investigations.

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