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Method of measurement and analysis of texture in thin films

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A method of measurement and analysis of texture in thin films is proposed. In this method, the incidence angle of the X-ray beam is low and is kept constant during the measurements. This requirement allows information to be obtained from a thin surface layer of the specimen. However, it limits the area on the pole figure from which data can be measured. Quantitative analysis of various factors and parameters which affect the X-ray penetration depth and the measured area of the pole figure is proposed. The proposed method was implemented and tested and the results obtained were used to calculate the crystal orientation distribution function.

1. Introduction

Texture is one of the most important parameters characterizing the structure of polycrystalline materials. It is normally measured by X-ray [1] or neutron diffraction [2], where the measurements characterizing texture are obtained from layers of 0.01–10 mm thick. Such information is usually considered representative of the texture in bulk metals, polymers or rocks.

There are, however, important fields of materials research where information about textures in layers of thickness of the order of 10–100 nm are necessary. For instance, textures in such thin layers may influence the critical current in thin films of high T_c superconductors, the recording characteristics of magnetic films or the properties of surfaces and coatings.

Many other physical characteristics and properties of materials could be studied and improved if textures of thin films can be measured.

Such measurements cannot be carried out using a normal texture diffractometer, because diffraction and inelastic scattering from the substrate or subsurface layer dominates the diffraction from the surface. For this reason it is necessary to propose a method of measurement which allows registration of the intensity diffracted from the surface layer of the specimen only.

2. Principles of surface texture measurements

A common representation of the texture in materials is the crystal orientation distribution function (ODF). The ODF is routinely calculated from X-ray or neutron diffraction pole figures which represent the two-dimensional distribution of the orientation of crystallographic planes in the reference frame of the specimen. The techniques used for pole figures measurements are described in various textbooks (i.e. [1]) and are usually based on a texture diffractometer, built to allow for the specimen rotation around two or three axes. During these rotations, differently oriented crystallographic planes are rotated to a position where they are perpendicular to the scattering vector and the diffraction from them can be registered.

The Schultz reflection method [1] is commonly used in texture measurements: in this method, the specimen is rotated around the normal to its surface as well as around the axis which lies in the specimen surface and is parallel to the diffraction plane. The peripheral area of the pole figure cannot be measured using this technique.

In suggesting a method for the examination of surface textures, we must limit the depths of penetration of the radiation inside the specimen and also ensure that only intensity diffracted from the surface layers will be detected.

There are several factors which affect the penetration: the linear absorption coefficient, μ, of the material analysed, the angle of incidence, i, and the Bragg angle for the reflection analysed, θ. As we can see from Fig. 1, an elementary volume element, dV, of thickness, dx, at a distance x below the surface will contribute to the diffracted intensity by

$$dI = I \exp(-\mu l) \tag{1}$$

where l, the path length of the beam inside the material, is given by

$$l = x\left(\frac{1}{\sin i} + \frac{1}{\sin r}\right) \tag{2}$$

The total diffracted intensity from the specimen having thickness t_0 is then

$$\begin{aligned} I &= I_0 \int_0^{t_0} e^{-\mu x}\left(\frac{1}{\sin i} + \frac{1}{\sin r}\right) dx \\ &= I_0 \left\{\left[1 - e^{-\mu t_0}\left(\frac{1}{\sin i} + \frac{1}{\sin r}\right)\right]\Big/ \mu\left(\frac{1}{\sin i} + \frac{1}{\sin r}\right)\right\} \end{aligned} \tag{3}$$

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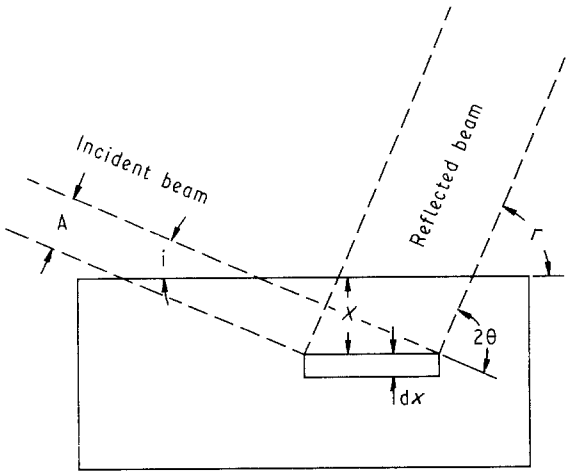


Figure 1 Absorption of the X-ray beam from the specimen in reflection.

We define now, the depth of penetration, t, as the distance measured perpendicular to the specimen surface, for which the diffraction from the inner layer is one-thousandth of that from the surface layer.

From this assumption, the formula for t follows

$$t = \ln 6.9 \Big/ \mu \left(\frac{1}{\sin i} + \frac{1}{\sin r} \right) \tag{4}$$

The penetration depth is influenced here by three parameters. The first parameter, the linear absorption coefficient, obviously affects the depth of penetration; the more a material absorbs the less X-rays penetrate. The other parameters are the incident and reflected angles. A low value of both reduce the effective depth of penetration; however, it is preferable to illuminate selectively the surface layer of the specimen by reducing the angle of incidence. This corresponds to a generation of the diffraction only in the surface layers. Using a low reflecting angle might not be a sufficient solution for eliminating the diffraction from the bulk of the specimen. As an example, results obtained for steel having a linear absorption coefficient $\mu = 24.2 \times 10^4 \, m^{-1}$ are given in Fig. 2, showing the variation of the penetration depth as function of the reflection angle, r, for the different angles of incidence, i.

The following observations can be made: for small i, the penetration depth is independent of the angle of reflection, and to analyse a thickness of 10 nm we have to use an angle of incidence of about 1°. For small angles of i, Equation 4 for the penetration depth, can be simplified to

$$t(\text{deg}) = \frac{0.12\, i}{\mu} \tag{5}$$

It should be mentioned that the existing relationship between the incident and reflection angles, i.e. $i + r = 2\theta$ may introduce other limitations, because the 2θ values are determined by the characteristic radiation of the X-ray tube. After demonstrating the necessity of keeping the value of the incidence angle low, we must now determine how to keep this angle constant during all specimen rotations required for the surface texture measurements.

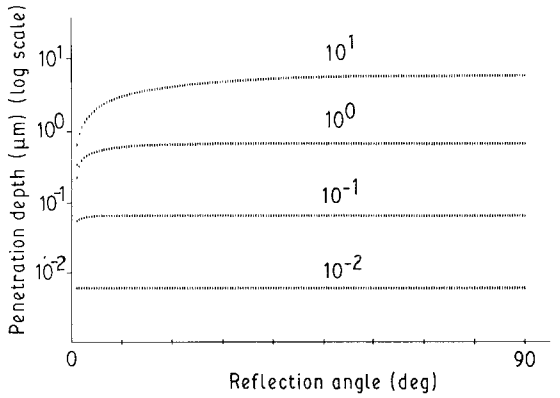


Figure 2 Penetration depth as a function of the reflection angle for steel specimens for the different incident angles.

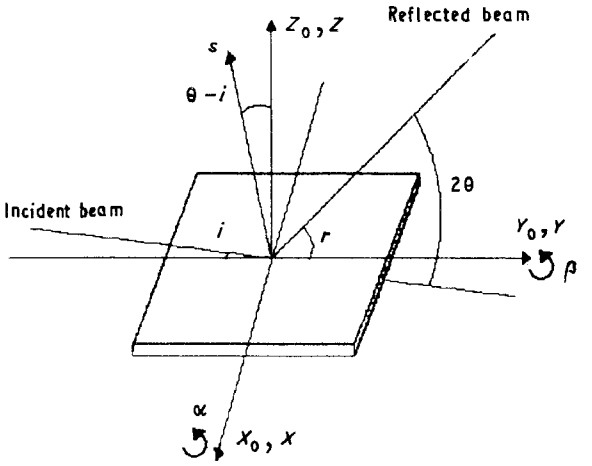


Figure 3 The definition of the reference frames used to determine the specimen rotations for surface texture measurements.

The Schultz method often used in texture studies can no longer be applied, because the rotations involved in the pole figure measurements do not satisfy the condition of the constant angle of incidence.

A new measurement geometry is schematically presented in Fig. 3. The incident beam creates an angle i with respect to the specimen surface while the reflected beam creates an angle of $2\theta - i$. Two coordinate systems are introduced to describe the necessary rotation of the specimen. One system $H(X_0, Y_0, Z_0)$ is related to the texture specimen holder and its axis X_0 is a rotation axis parallel to the diffractometer plane, another axis Y_0 is a diffractometer axis perpendicular to the diffractometer plane, the axis Z_0 is perpendicular to the $X_0 Y_0$ plane. The second reference frame $S(X, Y, Z)$ is the specimen reference frame and its axis is related to characteristic directions on the specimen. Such directions can be, for instance for the rolled sheet, the rolling direction RD, the transverse direction TD and the direction normal to the specimen surface, ND.

When measurements starts, the two reference frames H and S coincide and $X = X_0$, $Y = Y_0$ and $Z = Z_0$. Two consecutive rotations of the specimen will be made: the rotation around the X_0 axis by an angle α and the rotation around the $Y_{0\alpha}$ axis by an

angle β. The matrix representation of these two rotations is

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} \cos\beta & 0 & \sin\beta \\ 0 & 1 & 0 \\ -\sin\beta & 0 & \cos\beta \end{bmatrix}$$

$$\times \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\alpha & \sin\alpha \\ 0 & -\sin\alpha & \cos\alpha \end{bmatrix} \begin{bmatrix} X_0 \\ Y_0 \\ Z_0 \end{bmatrix} \quad (6)$$

Multiplication gives the transformation matrix in the form

$$\begin{bmatrix} \cos\beta & \sin\beta\sin\alpha & \cos\alpha\sin\beta \\ 0 & \cos\alpha & \sin\alpha \\ -\sin\beta & -\sin\alpha\cos\beta & \cos\alpha\cos\beta \end{bmatrix} \quad (7)$$

For a described geometry of diffraction, the scattering vector has the following coordinates in the specimen holder reference frame, H

$$\begin{bmatrix} V_{X_0} \\ V_{y_0} \\ V_{Z_0} \end{bmatrix} = \begin{bmatrix} 0 \\ -\sin(\theta - i) \\ \cos(\theta - i) \end{bmatrix} \quad (8)$$

Using the transformation matrix 7, the coordinates of the scattering vector in the specimen reference frame S are

$$\begin{bmatrix} V_X \\ V_Y \\ V_Z \end{bmatrix} = \begin{bmatrix} \sin\beta\cos(\alpha - \theta + i) \\ \sin(\alpha - \theta + i) \\ \cos\beta\cos(\alpha - \theta + i) \end{bmatrix} \quad (9)$$

The direction of the scattering vector can then be represented by polar coordinates χ and ϕ in S

$$\chi = a\cos[\cos\beta(\alpha - \theta + i)]$$
$$\phi = a\tan[\sin\beta\, c\tan(\alpha - \theta + i)] \quad (10)$$

where χ is the polar angle and ϕ is an azimuthal angle describing the orientation of the scattering vector for a given type of crystallographic plane in the reference frame of the specimen. Both angular coordinates are expressed using two rotation angles, the value of the incidence angle, i, and the diffraction angle, θ. The pole figure for a given crystallographic plane is measured by rotating the specimen around the Z axis, which is always perpendicular to the specimen surface. The azimuthal angle, ϕ, on the pole figure is therefore expressed as the sum of two components, one of which is given by Equation 10 and is dependent on the angles α, β, and i, and another represents the rotation of the specimen around axis Z.

Having established the relationship between the angular coordinates of crystallographic plane and four other angles which characterize the diffraction geometry, we would like to discuss now the conditions which must be imposed on the rotations of the specimen to satisfy the requirement that the angle of incidence i is kept constant during the measurement of the pole figure.

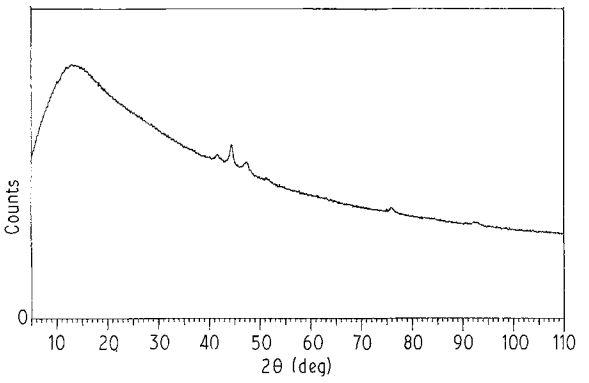


Figure 4 A diffraction pattern obtained using standard powder diffractometry from a 1 μm thick Co–Ni film.

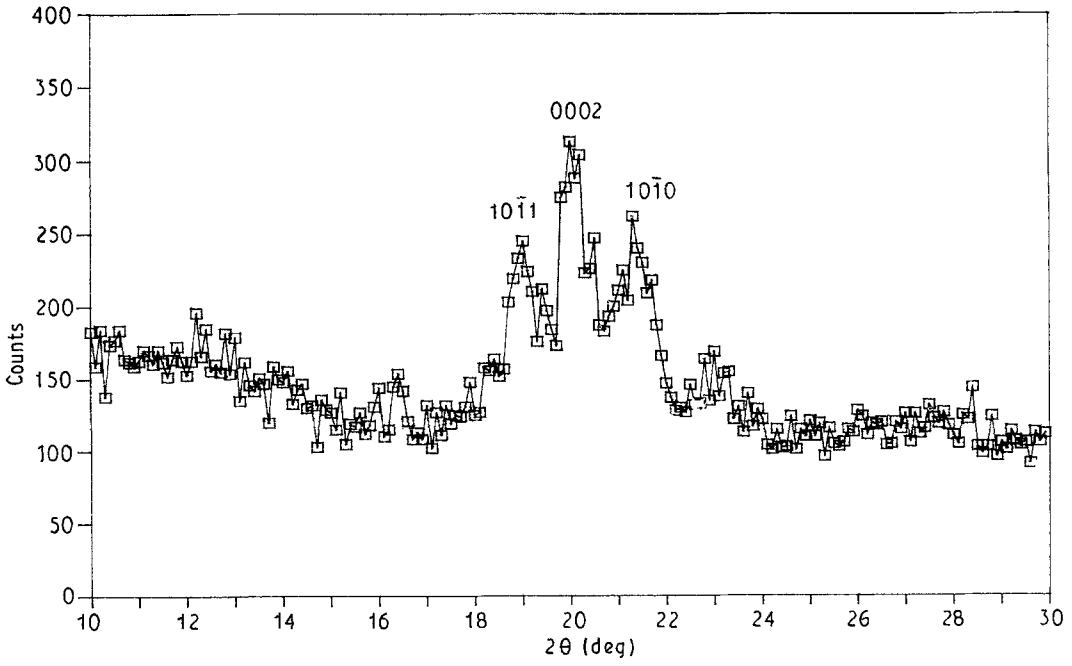


Figure 5 Diffraction pattern obtained using thin film diffractometry for a 1 μm thick Co–Ni film.

The direction of the incident beam has the following coordinates in the H reference frame

$$\begin{bmatrix} I_{X_0} \\ I_{Y_0} \\ I_{Z_0} \end{bmatrix} = \begin{bmatrix} 0 \\ -\cos i \\ \sin i \end{bmatrix} \tag{11}$$

Using the transformation matrix 7, we transform the coordinate of the beam into the specimen reference frame and obtain

$$\begin{bmatrix} I_X \\ I_Y \\ I_Z \end{bmatrix} = \begin{bmatrix} -\sin\beta(\sin\alpha\cos i + \cos\alpha\sin i) \\ -\cos i\cos\alpha + \sin i\sin\alpha \\ \cos\beta(\sin\alpha\cos i + \cos\alpha\sin i) \end{bmatrix} \tag{12}$$

The vector normal to the specimen surface in the specimen reference frame has the following coordinates

$$\begin{bmatrix} N_X \\ N_Y \\ N_Z \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} \tag{13}$$

To keep the incident angle of the beam constant, the following condition must be satisfied

$$\bar{N}\bar{I} = \sin i \tag{14}$$

A multiplication of Matrices 12, 13 show that this condition corresponds to the following relationship between the rotation angles and the value of the incident angle.

$$\sin(\alpha + i) = \sin i/\cos\beta \tag{15}$$

The next question which arises is the limitation of the measured area of the pole figure. Analysis of Fig. 3 tells us that it is not possible to measure the middle zone of the pole figure corresponding angles of χ less than $(\theta - i)$. Also, the peripheral area of the pole figure cannot be measured. This is due to the fact the diffracting beam angle, r, varies with the specimen rotations and there is a position of the specimen where this angle becomes zero and the diffraction cannot be recorded. This limit can be calculated in a similar

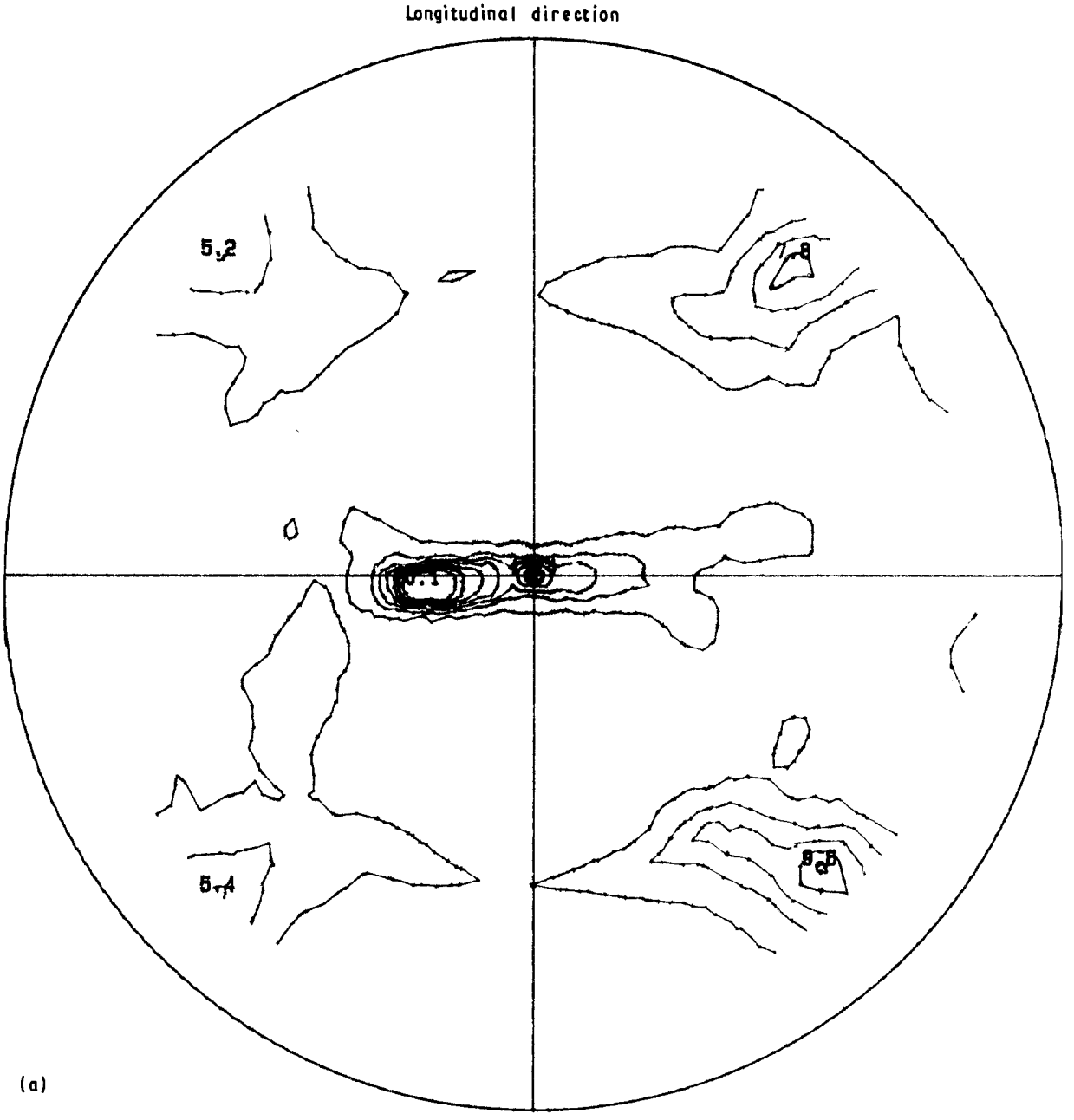


Figure 6 X-ray diffraction pole figures for a thick Fe–Si specimen made using the classical texture measurement method. (a) 2 0 0, (b) 1 1 0, (c) 2 1 1.

manner. The coordinates of the reflected beam in the specimen holder reference frame H, are

$$\begin{bmatrix} R_{X_0} \\ R_{Y_0} \\ R_{Z_0} \end{bmatrix} = \begin{bmatrix} 0 \\ -\sin(2\theta - i) \\ \cos(2\theta - i) \end{bmatrix} \quad (16)$$

The transformation matrix 7 is used to obtain the coordinates of this beam in the specimen reference frame

$$\begin{bmatrix} R_X \\ R_Y \\ R_Z \end{bmatrix} = \begin{bmatrix} \sin\beta\cos(\alpha - 2\theta + i) \\ \sin(\alpha - 2\theta + i) \\ \cos\beta\sin(\alpha - 2\theta + i) \end{bmatrix} \quad (17)$$

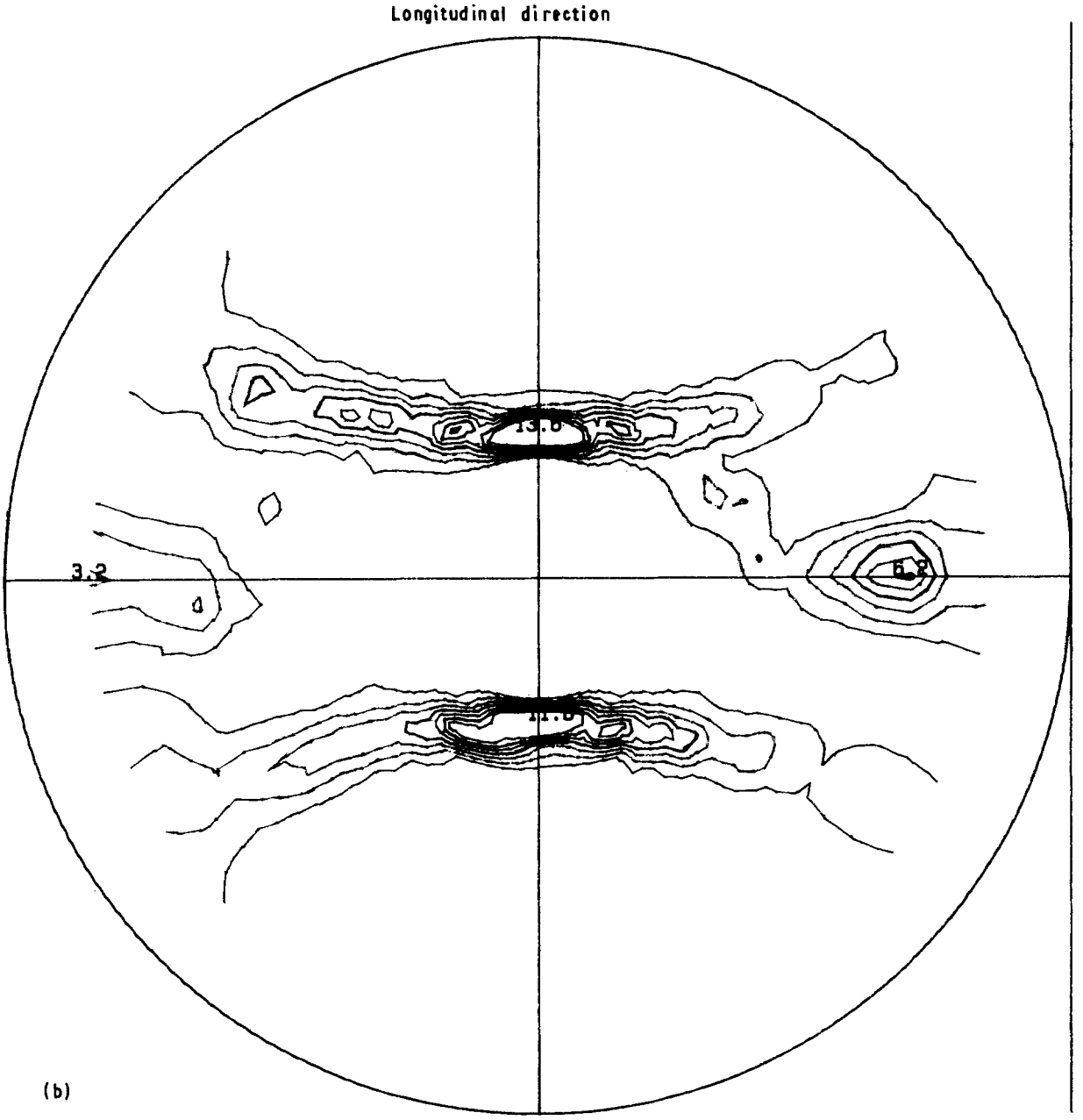
Diffraction can be detected only if the scalar product of the vector which is normal to the specimen and the vector of the reflected beam is less than zero; i.e. if the angle between these two vectors is less than 90°. This geometrical limitation of the texture measurements gives us the following maximum values for α and β.

$$\alpha = 2\theta - i \quad (18)$$

$$\beta = \arccos(\sin i/\sin 2\theta)$$

3. Experimental verification of the method

The methods outlined in the previous section have been implemented using a Siemens D-500 diffractometer system equipped with texture diffractometer, soller slits, and a detector system consisting of a set of a monochromating crystal and a scintillation counter. An advantage of using this system can be illustrated by comparing the two diffraction patterns Fig. 4 and 5. Both are obtained from the same point on the pole figure, for a 1 μm thick Co–Ni film deposited on a glass substrate. Fig. 6 shows the pole figures obtained using the texture system for thin film measure-



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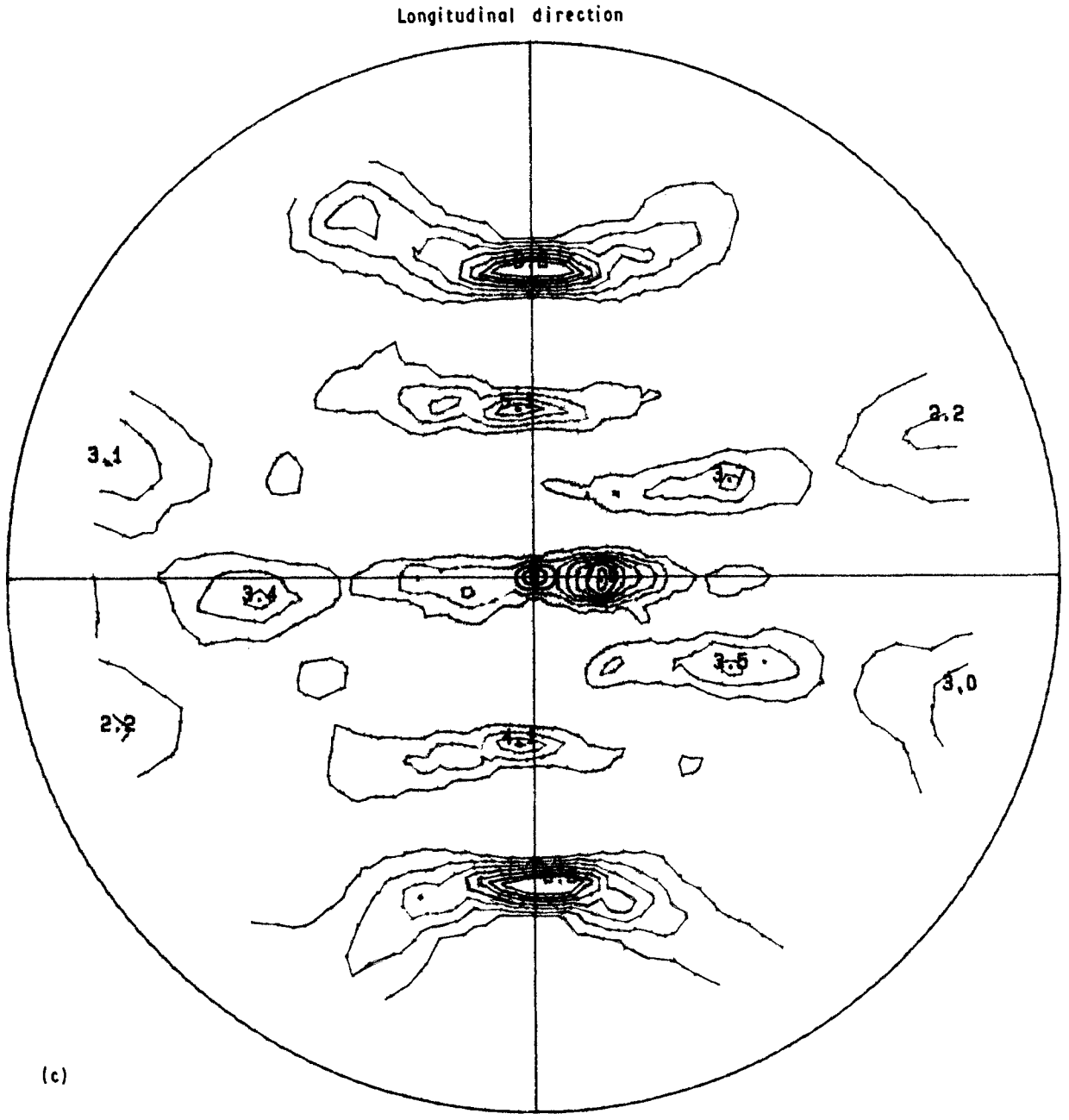

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ments (MoK_α radiation). One can see from this figure that the peak to background ratio has improved significantly and texture can be measured.

In order to verify the method, texture measurements were carried out using a specimen which is known to exhibit inhomogeneity through the specimen thickness; however, at the depth which was investigated, the type of texture is the same as in the bulk of the specimen. A hot-rolled Fe–Si 3% steel specimen was selected for these measurements. The specimen was polished so that the subsurface layer at depth of 25 μm was exposed to the X-ray beam.

Measurements of the (1 1 0), (2 0 0) and (2 1 1) pole figures were made using the Schultz reflection method and the results are presented in Fig. 6.

Measurements of the surface texture could be done only in the angular interval specified by Equation 18. For a steel specimen measured with MoK_α X-ray radiation, the relative radius of a circle within which the pole figure cannot be measured is presented in Fig. 7 as a function of 2θ value for different values of the incident angle i. For a low value of the incident

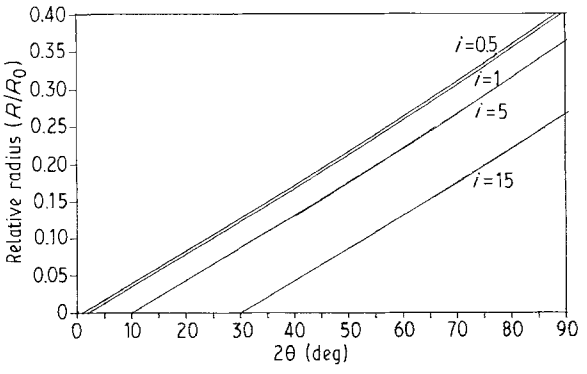


Figure 7 The relative radius of a circle on the pole figure within which the surface pole figure cannot be measured. Calculations for different incident angle i are presented.

angle and a small 2θ value, the area of the pole figure which cannot be measured is quite small.

The radius of the other limiting circle, outside of which the pole figure cannot be measured, is presented in Fig. 8 as a function of 2θ for various incident angles. For an angle of incidence of $i = 0.5°$, the relative radius of the circle is between 0.9 and 1.0. This means, that only a small peripheral area on the pole figure cannot be measured.

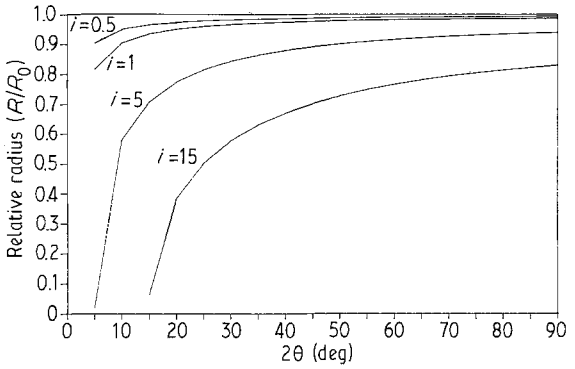


Figure 8 The radius of the circle on the pole figure outside which the texture cannot be measured. Calculations were made for different values of the incident angle, *i*.

As an example, the (1 1 0), (2 0 0) and (2 1 1) pole figures measured at an incident angle of $i = 1°$, using K_α radiation of the molybdenum tube are presented in Fig. 9. The points at which the intensity was measured are marked and we clearly see the area which has not been measured due to the limitations imposed by the geometry of measurements. The diffracted intensity in each pole figure is marked by a sign which corresponds to one of six intervals of intensity. The intensity displayed on the pole figures has already been corrected for background and defocusing. The background was measured only as a function of χ angle and subtracted from the total measured intensity. The defocusing corrections were estimated by measuring the intensity changes in a non-textured standard powder specimen. The corrections used for the given three pole figures are presented in Fig. 10. We can see that for our geometry of measurements, significant corrections are only necessary for angles of χ which are greater than 70°.

The corrected (1 1 0), (2 0 0) and (2 1 1) pole figures were then used to calculate the orientation distribu-

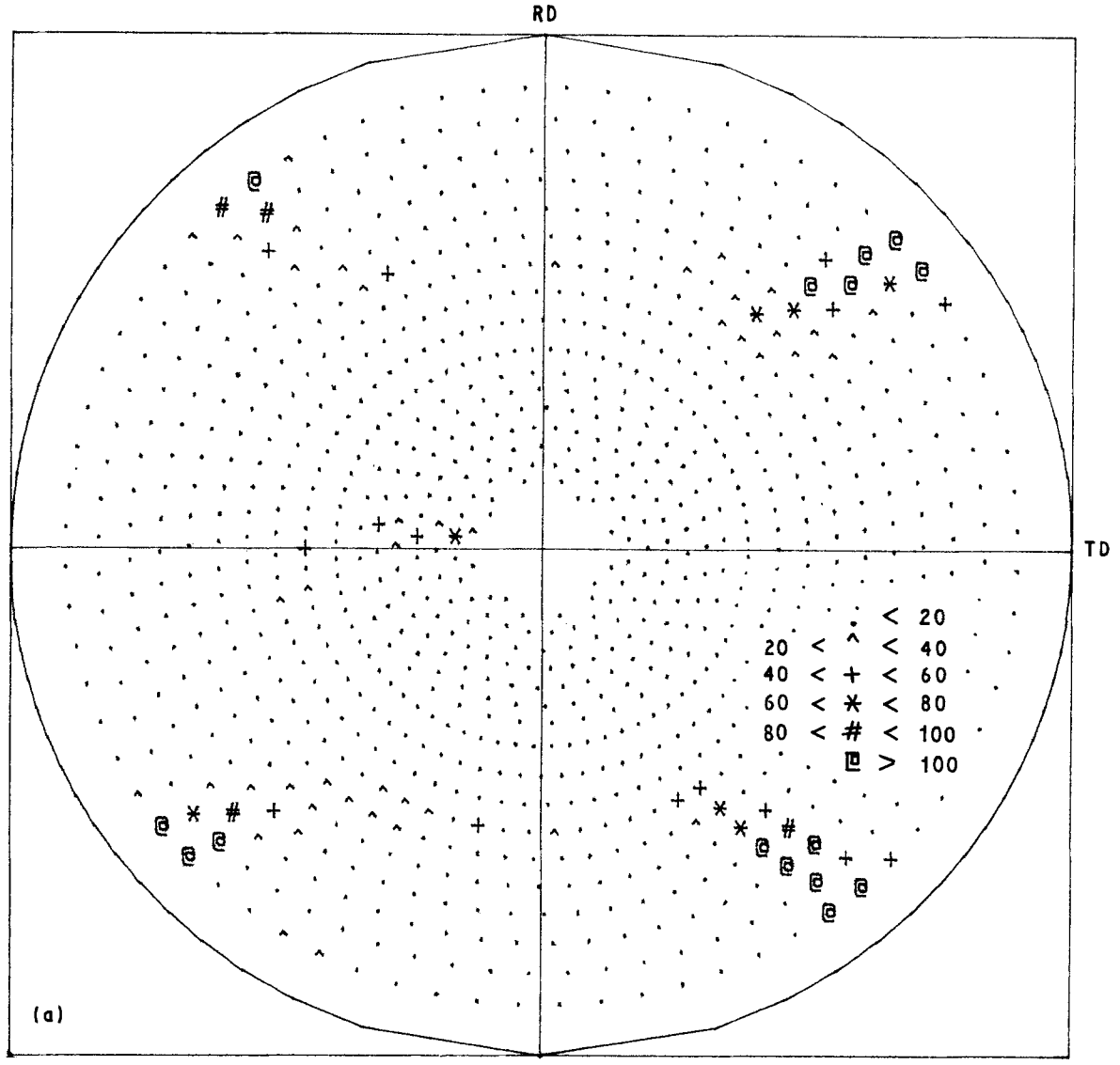


Figure 9 X-ray diffraction pole figures at the surface measured using thin-film technique. (a) 1 1 0, (b) 2 0 0, (c) 2 1 1.

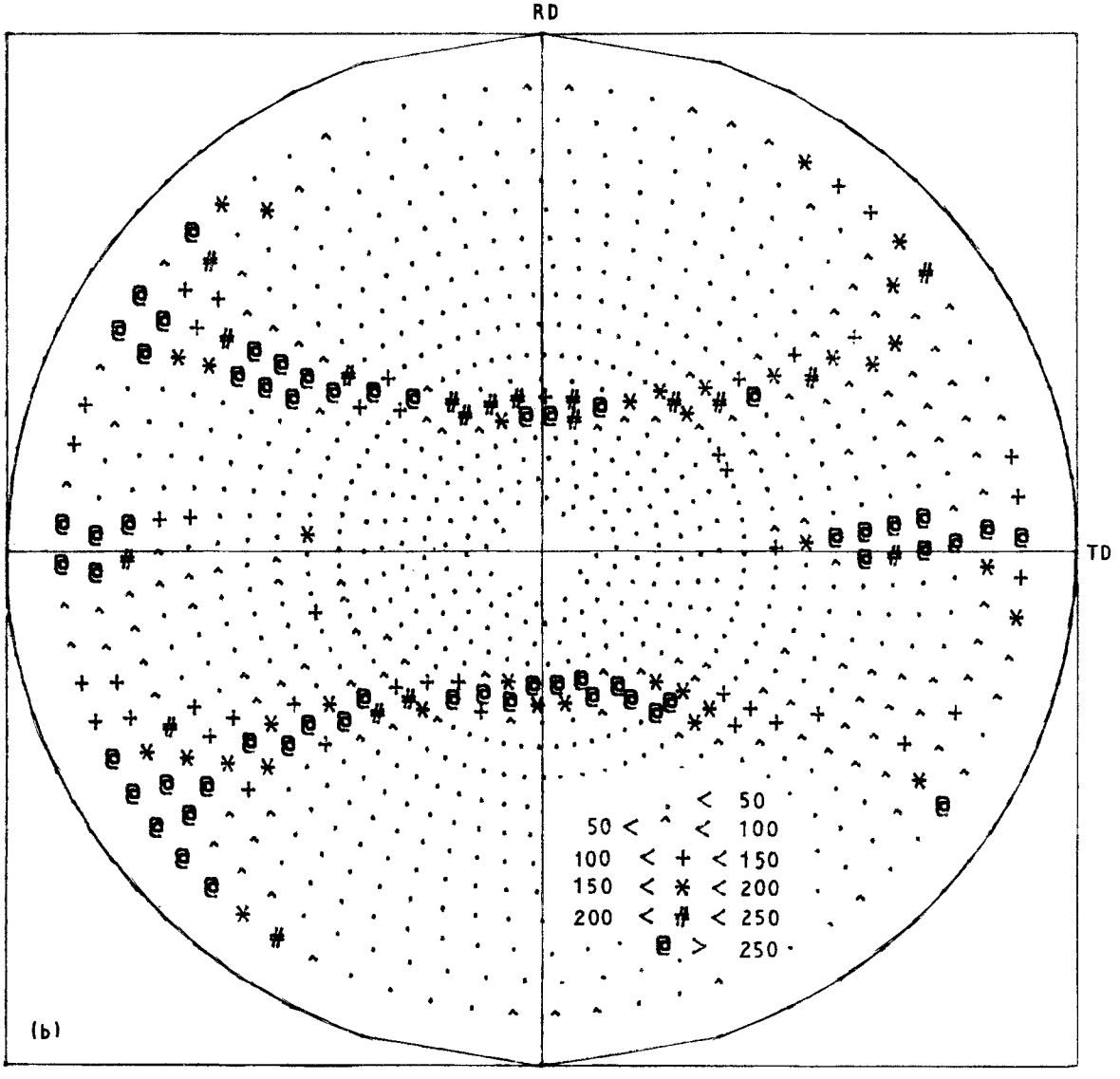
tion function. Because the pole figures are incomplete due to the internal and peripheral parts being missing, the normal techniques of ODF calculation by solving a system of linear equations relating the expansion coefficients of the pole figures and the coefficients of the ODF, cannot be applied. Therefore a different technique which was applied earlier for ODF calculations [3] was used. In this technique, a least-squares fit is made between the ODF and the isolated experimental points. The calculated ODF is presented in Fig. 11.

4. Discussion and conclusions

The method of measuring the surface texture proposed in this paper allows for the measurement of the texture in thin films and coatings. The results obtained can be used directly to calculate the ODF and thus obtain a fully quantitative texture description.

As described earlier, the typical experimentation necessary for these texture measurements has its limitations. The strictly geometrical limitations have been already discussed. However, one must add that there are other factors, both of physical and experimental nature, which influence the experiments. The angle of incidence used in our experiment, is 1°, although an angle of 0.1° is used by Siemens to measure powder diffraction pattern from the surface. This minimum incident angle of $i = 0.1°$ seems to be a practical limitation to the surface texture measurement. Another limitation is due to total reflection of the X-ray beam due to refraction. For a steel specimen and CuK_α radiation, the refraction index is about 10^{-6}, and consequently the incident angle corresponding to the total reflection of the beam is about 5′. This angle should be considered as a physical limitation.

In addition to a low angle of incidence, another parameter which can be used to obtain surface texture information is the wavelength of radiation. Low-energy characteristic X-rays are, in principle, preferable for surface measurement, although, for a given structure, this entails that the number of observable diffraction maxima is decreased and, consequently, a lower number of pole figures can be measured. Furthermore, higher θ values (see Fig. 7), mean that there is less textural information in the middle part of the pole figure and more in the peripheral area. Obviously the



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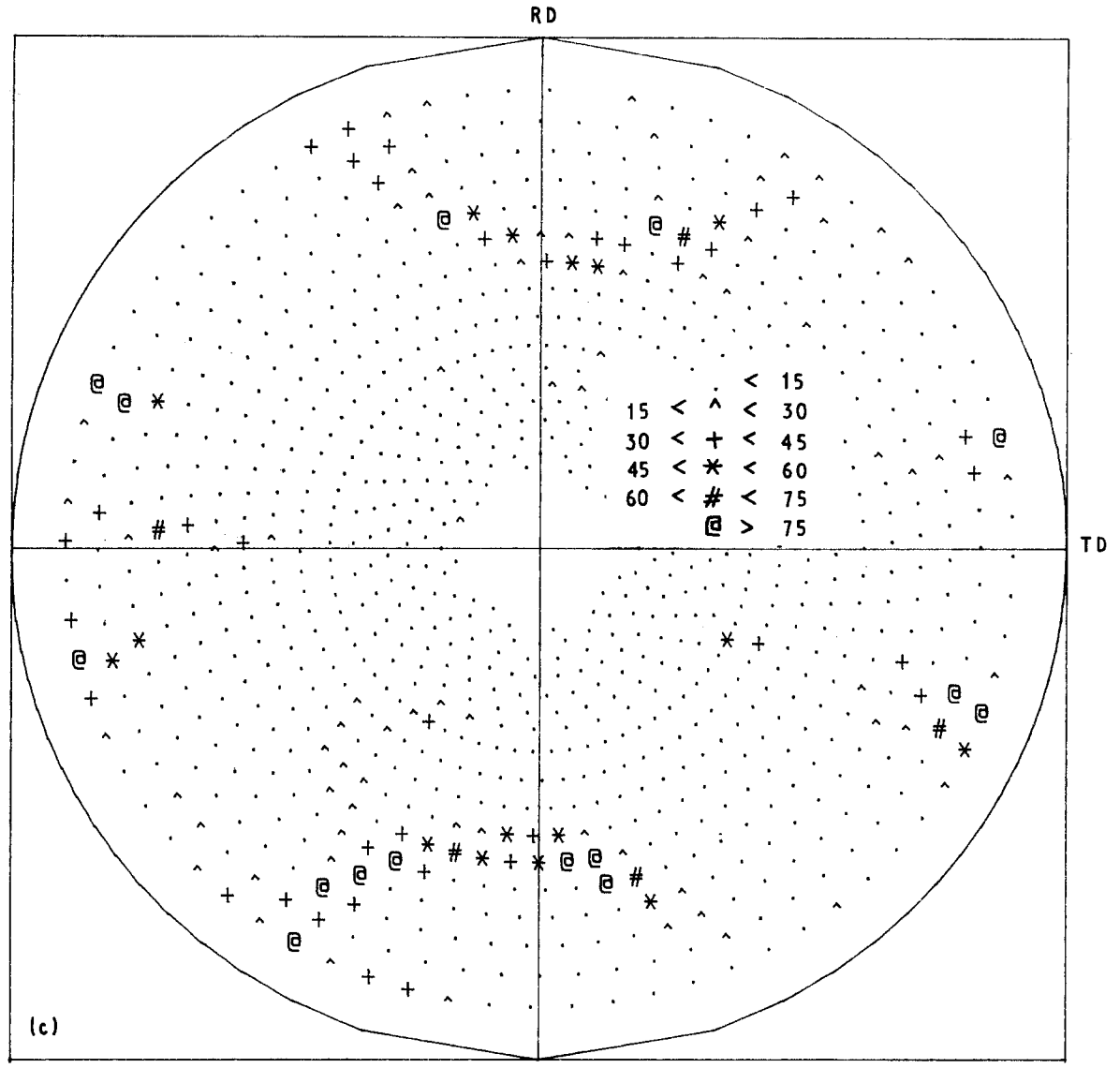

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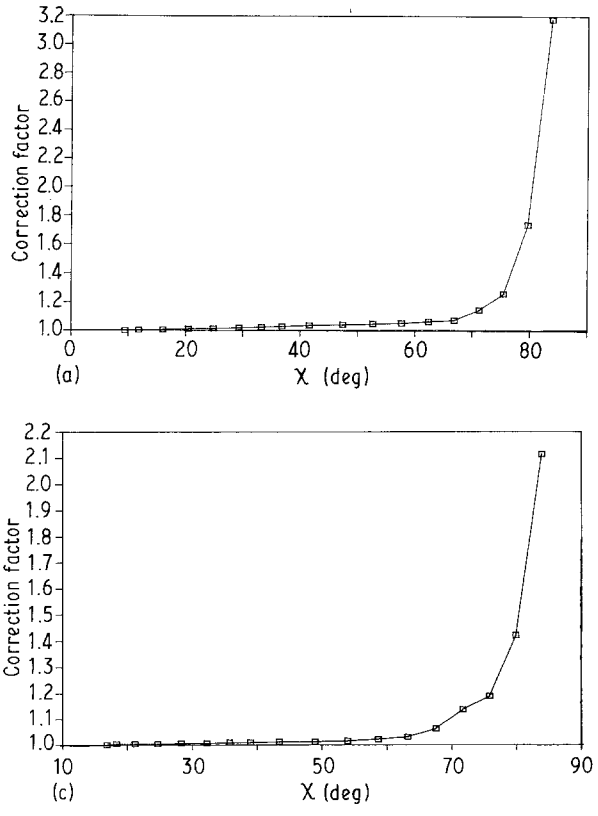

Figure 10 Values used to correct the pole figures measured at the surface. (a) 1 1 0, (b) 2 0 0, (c) 2 1 1.

experimental conditions for measurements can be optimized taking into account the crystallographic structure of the material being investigated.

The problem of the pole figure defocusing correction has been solved by using a bulk powder specimen of the same material. Significant corrections are only necessary for χ angles higher than 70°. Corrections obtained in this fashion account for a number of rather complicated phenomenon of parafocusing

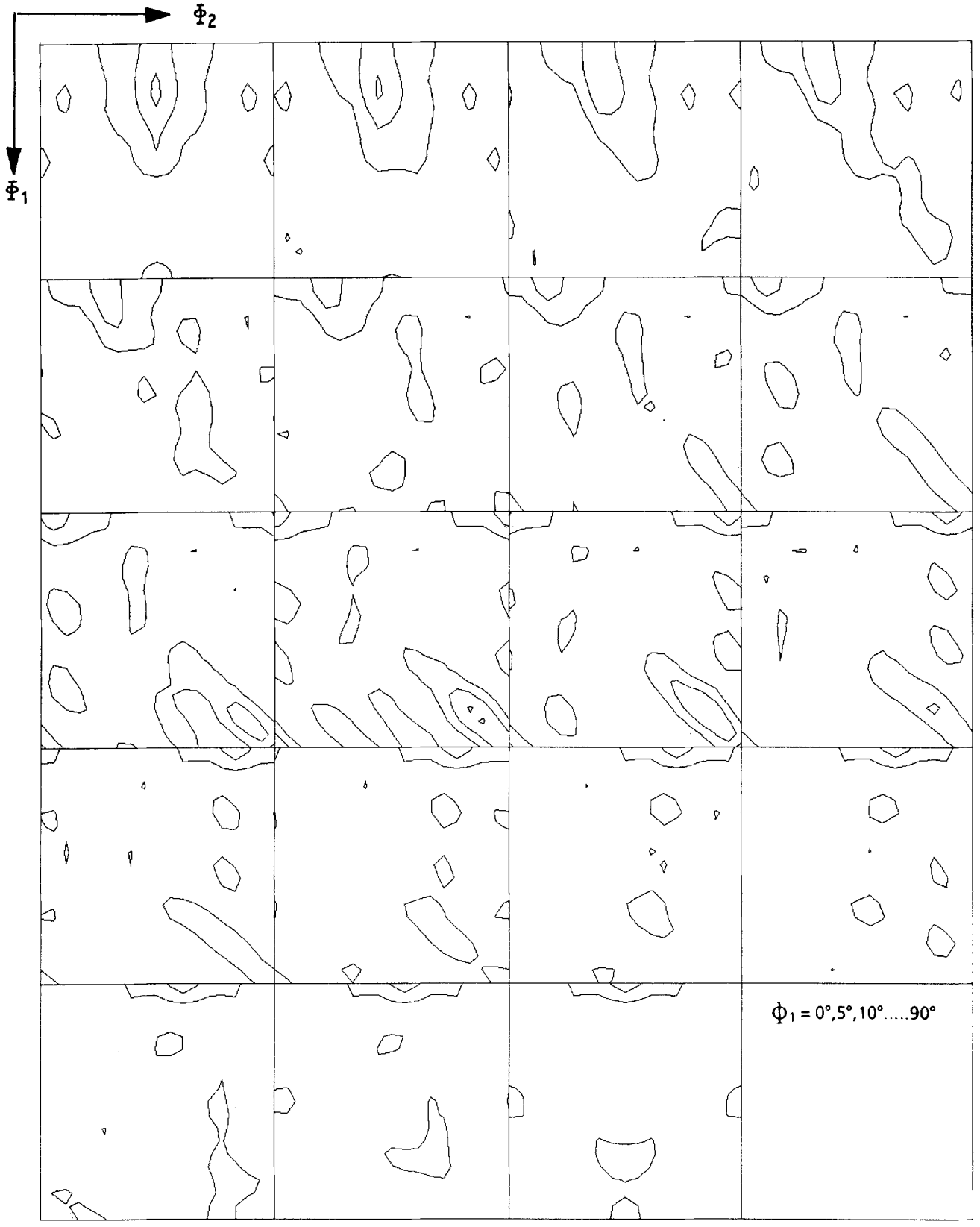

Figure 11 ODF calculated from the surface pole figure data, maximum orientation density is about 25.

which affects the divergence of the beam, both in the plane defined by the incident and reflected beams, i.e. longitudinal parafocusing, and in the plane orthogonal to it, i.e. lateral parafocusing. The longitudinal parafocusing is controlled by a Soller slit. The focusing corrections also depend on the collimation used and the value of i and θ. A more detailed discussion of the experimental diffraction geometry will be presented in a following paper.

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References

1. H. J. BUNGE (ed.), "Experimental Techniques of Textures Analysis" (DGM Informationsgesellschaft, 1986).
2. J. A. SZPUNAR, *Atom. Energy Rev.* **14** (1976) 198.
3. J. A. SZPUNAR and D. C. HINZ, *J. Mater. Sci.* **23** (1990) 2846.

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