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Microbeam analysis — Analytical electron microscopy — Method of determination for apparent growth direction of wirelike crystals by transmission electron microscopy

Analyse par microfaisceaux — Microscopie électronique analytique — Méthode de détermination de la direction apparente de croissance des cristaux filiformes par microscopie électronique en transmission

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Foreword

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This document was prepared by Technical Committee ISO/TC 202, *Microbeam analysis*, Subcommittee SC 3, A*nalytical electron microscopy*.

Introduction

Wirelike crystals (including beltlike crystals) are a main component in some advanced materials, especially nanomaterials, and also appear in traditional materials, such as needle-shaped precipitates in steels and alloys. Controlling the microstructure of these materials during fabrication is very important for quality control considerations. To control the microstructure and thereby improve the service properties of the relevant materials, the apparent growth direction or the longest axis of the wires is one of the essential parameters. This direction is generally determined for wirelike crystals whose diameter or thickness and width is ranged from tens to hundreds of nanometres by transmission electron microscopy (TEM).

Microbeam analysis — Analytical electron microscopy — Method of determination for apparent growth direction of wirelike crystals by transmission electron microscopy

1 Scope

This document prescribes a method for the determination of apparent growth direction by transmission electron microscopy. It is applicable to all kinds of wirelike crystalline materials fabricated by various methods. This document can also guide in ascertaining an axis direction of the second-phase particles with a rod-like or polygonal shape in steels, alloys or other materials. The applicable diameter or width of the crystals to be tested is in the range of tens to hundreds of nanometres, depending on the accelerating voltage of the TEM and the material itself.

NOTE In the present document, wirelike crystals, beltlike crystals, needle-shaped second-phase particles, etc. are all subsumed by the broad category of wirelike crystals.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 24173, *Microbeam analysis — Guidelines for orientation measurement using electron backscatter diffraction*

ISO 25498:2010, *Microbeam analysis — Analytical electron microscopy — Selected-area electron diffraction analysis using a transmission electron microscope*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 24173 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at http://www.electropedia.org/

— ISO Online browsing platform: available at http://www.iso.org/obp

3.1
wirelike crystal
crystal resembling a thread with a diameter or width measuring in nanometres

3.2
apparent growth direction
crystalline direction which is parallel to the longest dimension of a single crystal

Note 1 to entry: Apparent growth direction does not involve mechanisms of the phase interface migration.

3.3
Miller notation
indexing system for diffraction patterns, which describes a crystal lattice by three axes coordinate

3.4
Miller-Bravais notation
indexing system for diffraction patterns of hexagonal crystal, which describes the lattice by four axes coordinate

4 Specimens

4.1 The sample crystals shall be clean, without contamination or oxidation. They are stable under electron beam irradiation during TEM analysis.

4.2 Powder or extracted powder specimens of the crystals may be analyzed. The sample powder shall be well dispersed by a suitable technique so that individual crystals can be observed under the TEM.

NOTE One of the techniques in common use is ultrasonic dispersion. In this method, the sample powder is immersed in ethanol or pure water and dispersed by ultrasonication for about 0,5 h to 1 h, then dropped onto the supporting film surface of a microgrid. Afterward, the microgrids are dried at room temperature. The wirelike crystals are usually parallel to the supporting film plane. Other techniques to prepare individual crystal specimens can also be adopted, depending upon the physical characteristics of the sample[2].

4.3 The precipitates or second-phase particles in steels, alloys and the like may be extracted, then treated as powder specimens; see 4.2.

4.4 Thin-foil specimens of various solid substances prepared by suitable methods are applicable. The specimen shall be thin enough to transmit the electron beam[3].

5 Analysis procedure

5.1 Setting the TEM operating condition

5.1.1 Preparation of the TEM

The TEM working condition shall comply with ISO 25498:2010, 8.1.

5.1.2 Accelerating voltage

The applicable accelerating voltage of the TEM for the analysis mainly depends upon the thickness of the specimen to be studied. Stability of the crystals under electron beam irradiation is also important for the accelerating voltage setting. As long as the structure and/or morphology of the specimen are not altered during the analysis, clear images and sharp diffraction patterns can be obtained on the TEM. The corresponding accelerating voltage or higher may be suitable for the work.

5.1.3 Setting the specimen

Place the specimen to be tested firmly in the double-tilting or tilting-rotation specimen holder, then insert the holder into the specimen chamber. It is recommended to use the cold finger of TEM before conditioning.

5.1.4 Calibration of the rotation angle

As specified in ISO 25498:2010, 8.1.6, to be able to successfully correlate the axis of interest in an image with the corresponding diffraction pattern, the rotation angle between the micrograph and its corresponding diffraction pattern may need to be calibrated. A molybdenum trioxide crystal specimen

may be used as a reference for the rotation angle calibration. The analyst may refer to textbooks such as References [4] and [5] for the experimental procedure for this calibration.

NOTE For some transmission electron microscopes, the rotation angle has been compensated by the manufacturer. In this case, step 5.1.4 can be ignored.

5.2 Data acquisition

5.2.1 Select the target crystal

On the viewing screen, TV monitor, or computer screen of the TEM, get an overview image of the specimen in low magnification mode. Select an individual crystal which is clean and free from damage or distortion as the target. Under bright-field imaging mode, adjust the magnification to get a clear magnified image of the target crystal. Adjust the specimen height (Z axis) to the eucentric position. Focus the image.

5.2.2 Obtaining diffraction patterns

5.2.2.1 General

Various electron diffraction techniques may be applicable for determination of the crystal axis direction. The selected area electron diffraction (SAED) and microbeam diffraction techniques are in common use; however, for the present purpose, the spot diffraction patterns or the patterns formed by the incident beam through a small angle aperture are preferred.

5.2.2.2 Procedure

The procedure for taking diffraction patterns and images of the target crystal is as follows.

a) Select a suitable position of the target crystal in the specimen and select a diffraction mode (SAED, microdiffraction, or other suitable mode). Switch to the diffraction mode to get a spot diffraction pattern. Tilt the specimen slightly so that the brightness distribution on the diffraction pattern is symmetrical and a zero-order Laue zone pattern is displayed. Therefore, the zone axis, Z_1 (with index $[u_1v_1w_1]$), of this diffraction pattern is nearly reverse parallel to the incident beam direction, B. Record this diffraction pattern, Z_1, and take note of the reading on the X and Y tilting angle of the double tilting specimen stage as X_1 and Y_1, respectively.

   Refer to the instruction manual provided by the microscope manufacturer for the operation procedure for each diffraction mode.

b) Switch back to the imaging mode without changing the specimen orientation to get a correlative bright field image, M_1, of the target crystal. Check the focus of this image and take a photo or save it in the computer system. This image, M_1, is formed under the incident beam direction, B_1, which is approximately reversely parallel to the zone axis, Z_1.

c) Return to the diffraction mode and tilt the specimen to produce a second diffraction pattern with zone axis Z_2. Record this diffraction pattern, Z_2, and take note of the reading on the X and Y tilt angle of the specimen holder as X_2 and Y_2, respectively.

d) Repeat step b) to form the second bright field image, M_2, of the target crystal. This image, M_2, is formed under the incident beam direction, B_2, which is nearly reversely parallel to the zone axis, Z_2, of the specimen.

e) The angle, ψ, between the two specimen holder positions (that is, the angle ψ^* between the zone axis, Z_1, with index $[u_1v_1w_1]$ and Z_2, with index $[u_2v_2w_2]$) can be obtained from the differences between the readings on the X and Y tilting angles at each position (see ISO 25498:2010, 8.2).

5.2.3 Determining interplanar spacing

To determine the interplanar spacing, d_{hkl}, of the plane (hkl) in crystals, the simplified Bragg law, as shown in Formula (1), shall be followed.

$$R_{hkl} \times d_{hkl} = L\lambda \tag{1}$$

where

L	is the camera length;
λ	is the wavelength of the incident electron beam;
$L\lambda$	is the camera constant;
R_{hkl}	is the distance between the central spot and the diffracted spot of crystalline plane (hkl) in the diffraction pattern.

When the camera constant $L\lambda$ is known, the interplanar spacing d_{hkl} can be found, in principle, using Formula (1) by measuring the distance R_{hkl}. However, in practice, $2R_{hkl}$ (the distance between the spots hkl and $\overline{hkl}$) shall be measured, then divided by two to calculate the distance R_{hkl}.

In most cases, the camera constant, $L\lambda$, shall be calibrated for the present work. The practical procedure for camera constant calibration is specified in ISO 25498:2010, 8.3.

Camera constant, $L\lambda$, calibration is usually performed by using a reference specimen such as polycrystalline pure gold or pure aluminium. At a given accelerating voltage, record the ring diffraction pattern of the reference specimen. Index the diffraction rings and measure the diameters $2R_{hkl}$ of the corresponding ring (hkl), respectively. Find the interplanar spacing d_{hkl} for plane (hkl) of the reference specimen by the crystallographic formulae. The diffraction constant, $L\lambda$, can then be calculated using Formula (1). In practice, either the $L\lambda \sim D/2$ plot or an average value of the camera constant may be used.

When crystalline structure and the confident lattice parameters of the specimen are already known, the diffraction constant, $L\lambda$, may be calculated from its diffraction pattern directly. The approximate value of $L\lambda$ can be found on a console readout display of a modern TEM.

5.2.4 Index diffraction patterns

For specimens comprised of crystals in the nanometer size regime, most of the time, only spot diffraction patterns can be observed. Kikuchi patterns seldom appear owing to their small thickness. Therefore, only the procedure for indexing spot diffraction patterns is specified in this document.

The practical procedure for indexing diffraction patterns may refer to ISO 25498:2010, Clause 9. For the convenience of applying this document, the indexing process is briefly summarized as follows[4][5][6][7]:

a) Select two diffracted spots, $h_1k_1l_1$ and $h_2k_2l_2$, from the diffraction pattern such that these spots are nearest and next-nearest to the central spot, 000, respectively. Measure the length of correlative vectors, $g_{h_1k_1l_1}$ and $g_{h_2k_2l_2}$, which are defined as the distances from the origin, 000, to the diffraction spot $h_1k_1l_1$ and the spot $h_2k_2l_2$, respectively. Then calculate the corresponding interplanar spacing, d_{hkl}, and assign tentative index (hkl) values for each spot.

b) Measure the included angle between the vectors $g_{h_1k_1l_1}$ and $g_{h_2k_2l_2}$, as well as the angle between $g_{h_2k_2l_2}$ and $g_{h_2-h_1,k_2-k_1,l_2-l_1}$, respectively, where $g_{h_2-h_1,k_2-k_1,l_2-l_1}$ is defined as the reciprocal vector of the diffraction spot with index $h_2 - h_1$, $k_2 - k_1$, $l_2 - l_1$. Adjust the indices for each spot such that the angle is coincident with the calculated angle by the crystallographic formulation. If the experimental value is consistent with the known value within error, the diffraction spots can be indexed.

c) Calculate the zone axis, Z, of the diffraction pattern [u:v:w] by the zone multiplication law; see Formula (2):

$$u : v : w = (k_1 l_2 - k_2 l_1) : (l_1 h_2 - l_2 h_1) : (h_1 k_2 - h_2 k_1) \quad (2)$$

If the indices u, v and w contain a common integral factor *n*, divide them all by the common factor *n*.

d) Assign consistent indices to the remaining spots on the diffraction pattern by using the vector addition rule.

e) When suitable software is installed with the TEM, measurement of and calculations on the diffraction patterns can be carried out by the computer system.

5.2.5 Non-uniqueness of the indexing result

For a diffraction pattern containing only two-dimensional information (i.e. a planar section of single-crystal diffraction patterns), the indexing of this pattern is not unique. Causes for non-uniqueness of the indexing may be considered from two factors.

Firstly, the indexing non-uniqueness may result from a multiplicity of crystals with high symmetry. Different variants of a diffracting plane may be equally indexed. Accordingly the zone axis of a diffraction pattern may have a different index, i.e. variants of the zone axis, but on the stereogram, the poles of these variants are located at different positions.

Secondly, the 180° rotational symmetry of the indices (hkl), of a plane allow the index to also be described as $\overline{h}\overline{k}\overline{l}$, similarly, indices [uvw] of a direction can also be $\overline{u}\overline{v}\overline{w}$. Therefore, it is necessary to obtain two or more diffraction patterns, Z_1 and Z_2, successively by tilting the specimen. The angle, ψ^*, between the zone axes, Z_1 and Z_2, of the two patterns shall be coincident with the angle between the two specimen holder positions. Also, the indices for all of the patterns shall be consistent with each other.

5.3 Determination of the crystalline direction

5.3.1 General approach

5.3.1.1 Define the projection direction

a) Specify the projection direction, A_1, of the crystal to be determined on its micrograph, M_1. As an example, micrograph M_1 and diffraction pattern Z_1 of a rod-like particle is given in Figure 1 a) and b), respectively. The particle is phosphide M_2P with hexagonal structure[8][9]. Align the diffraction pattern Z_1 with the image M_1 carefully, after compensation of the rotation angle. Draw a line, N_1, perpendicular to the projection direction A_1 of the crystal on the diffraction pattern Z_1. This line, N_1, is the normal of the projection direction, A_1. On diffraction pattern Z_1, identify the diffraction spot with index, $h_1k_1l_1$, which is closest to the line N_1. The vector, $g_{h_1k_1l_1}$, from the central spot, 000, points toward the diffraction spot $h_1k_1l_1$, and is the normal of plane $(h_1k_1l_1)$. Measure the angle, φ_1, between the line N_1 and vector $g_{h_1k_1l_1}$. The projection direction A_1 of the rod-like particle and its normal, N_1, are delineated on the diffraction pattern. The spot indexed as 201 is the closest one to the line N_1. The angle φ_1 between the line N_1 and g_{201} is nearly zero in this case.

NOTE 1 In Figure 1, the specimen is a phosphide (M_2P) precipitate of hexagonal structure with c/a = 0,576, a = 0,609 nm and c = 0,351 nm, in steels.

b) Carry out a similar operation as step a) on the second diffraction pattern, Z_2, and the image M_2. Define the second projection direction, A_2, of the crystal on the diffraction pattern Z_2. Measure the angle, φ_2, between the normal N_2 of projection direction A_2 and the closest direction of vector $g_{h_2k_2l_2}$, namely the normal of plane $(h_2k_2l_2)$ on the diffraction pattern Z_2.