RELATIONSHIP BETWEEN CRYSTAL MORPHOLOGY AND PREFERRED ORIENTATION IN POLYCRYSTALLINE SPECIMENS FOR DIFFRACTION EXPERIMENTS

Pavel Fejdi, Attila Holocsy

Department of mineralogy and petrology, Faculty of Natural Sciences, Comenius University,
Bratislava, Mlynská dolina, 842 15 Bratislava, Slovak republic,
E-mail: fejdi@ fns.uniba.sk, holocsy@fns.uniba.sk

Abstract

Preferred orientation in powder diffraction experiments is a frequent problem. Paper deals with use of complementary information obtained from study of crystal morphology, which can be used as input data in correction procedures.

***Keywords*:**
powder diffraction, preferred orientation, and crystal morphology

1. Introduction

Correct preparation of specimens is the crucial problem for any experimental procedure including diffraction experiments. Starting from fundamental principles of diffraction on polycrystalline samples, the **ideal** sample consists of crystals or crystal fragments oriented completely at random. In this case loci of end points of individual reciprocal vectors H_{hkl} are on the surfaces of concentric spheres and orientation of samples is independent on direction of primary beam. In this way the diffraction conditions are always fulfilled without change of sample orientation (only radius of Ewald sphere is the limiting factor). An absolute random orientation of particles can exist only if shape of particles is spherical.

In **real** samples preferred orientation of particles is always present and thus measured intensities of diffractions are incorrect. Treatment of this problem depends on precision of informations required. It can be neglected in routine identification procedure of common phases. In the case of using the data for quantitative phase analyses and for Rietveld refinement procedures, correction of intensities to influence of preferred orientation is necessary.

Preferred orientation can be easy recognised on powder diffraction photographs and on texture goniometer outputs. On standard diffractometer records, information about this phenomenon is completely hidden. To correct intensity data, the most frequent approach is an empirical one, based on trial-and-error method: first we consider that preferred orientation is parallel to (*100*), next to (*010)* and so on... It can be and it is often successful. Unfortunately, if more than one type of preferred orientation is present, this approach is fruitless.

2. Dependence of preferred orientation on specimen type

In general, it is possible to distinguish four types of polycrystalline specimens:

1. Specimens formed by euhedral crystals of appropriate size (within the interval 1 - 10 μm). This type of polycrystalline samples is represented by some thin layers (Fig. 1), clay minerals, natural as well as synthetic zeolites (Fig. 2). Because number of crystal faces in this type of specimens is strongly limited, preferred orientation is always present, and the morphology of crystals is the decisive phenomenon.

2. Specimens with dominant morphological features others than crystal faces. As example can be frequently

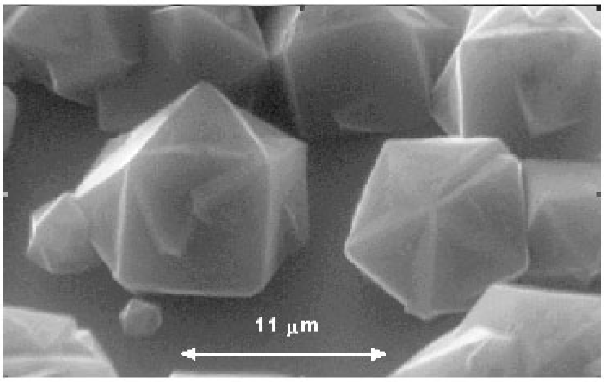

Fig. 1. SEM photograph of diamond thin layer on Si substrate. Cubic system, point-group symmetry $m\bar{3}m$

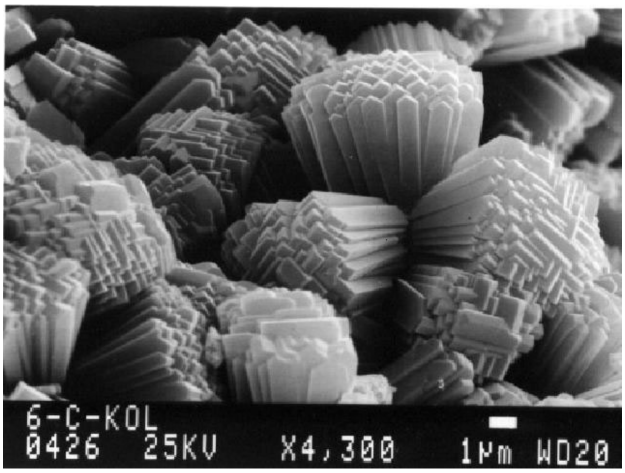

Fig. 2. SEM photograph of synthetic phillipsite $(K,Na,Ca_{0.5},Ba_{0.5})_x[Al_xSi_{16-x}O_{32}]$. 12 H_2O. Monoclinic system, point group-symmetry $2/m$

used quantitative phase analyses of amphibole and chryzotile asbestos mixtures in building materials.

3. Specimens, where suitable size of crystal fragments is obtained by grinding of coarse crystals in agate mortar. This kind of powdered samples consists of crystal fragments which shape is primary influenced by cleavage. If cleavage is perfect (galena PbS, fluorite CaF_2; cubic system, point-group symmetry $m\bar{3}m$, excellent cleavage parallel to (*100*), calcite $CaCO_3$; trigonal system, point-group symmetry $\bar{3}2/m$ preferred orientation parallel to (*10-11*)), crystal fragments are always of the same shape (in examples mentioned here are cubes and rombohedrons, respectively). For these reasons, preferred orientation drastically influences intensities of individual diffractions, like in preceded type. On the other hand, minimum degree of preferred orientation can be obtained from materials having no cleavage and thus crystal fragments have irregular shape (garnets, datolite $CaB(SiO_4)(OH)$, etc.).

4. In fine-grained metallic samples formed by anhedral crystals, textures are the function of preparation and further processing of material (sheet textures of rolled materials, fibre textures of wires).

3. Use of morphological information in correction procedures

Crystal morphology causes preferred orientation of particles in polycrystalline specimens. On the other hand, informations about morphological characteristics of sample can be readily used for correction procedures. Various correction functions are summarised in [1]. In all of them, one of necessary parameters is acute angle between incident X-ray beam and direction of preferred crystallites orientation. To define this parameter, Miller indices in the case of sheet textures and/or indices of lattice lines in the case of fibre textures are very useful tool.

For indexing of crystal faces is useful empirical approach known as **Bravais rule**. According to this rule the relative importance of several forms (that is their area and frequency of occurrence) for a particular crystal species tends to be in the same order as their interplanar spacing and consequently to reticular density of crystal faces (definition taken from [3]). Starting from this rule, indexing of crystal faces or forms can be a simple procedure. For example, crystals having *fcc* structure are usually formed by three most frequent crystal forms: cube (*100*), octahedron (*111*) and rhombododecahedron (*110*), Fig. 4. If other faces are present, their indexing can be based on **complication rule**: Miller indices of those faces are simply sum of indices of neighbouring faces. This approach can be so simply used for hexagonal, trigonal and tetragonal crystals, but only for crystal faces that belong to the [*001*] zone. SEM photographs can be used to determine these morphological features (crystal faces and/or directions) to which orientations of crystal particles are parallel.

Analysing Fig.1 (diamond, space group F*d*-3*m*), one can easily distinguish three systems of preferred orientation: parallel to (*100*), (*111*) and spinel-law penetration twins wit twin and composition plane (*111*). On the Fig. 2, parallel overgrowth of phillipsite crystals according to (*001*) is seen.

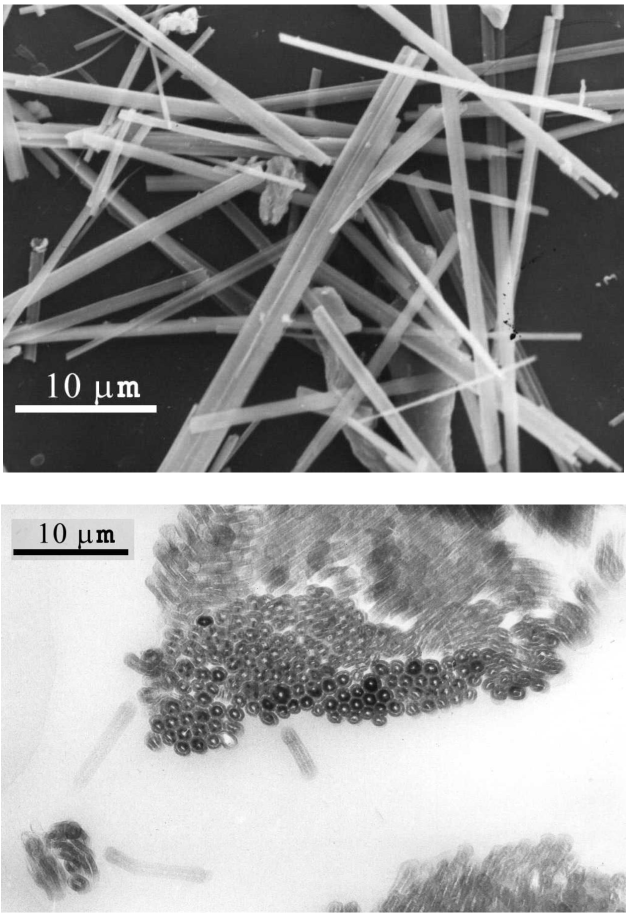

Fig. 3. a) TEM photograph of amphibole asbestos fibres parallel to [*001*], b) TEM photograph of chryzotile asbestos tubes (“bishop’s stick”sections), parallel to [*100*]

Fig. 3a illustrates preferred orientation of amphibole asbestos fibres (parallel to [*001*]). Chryzotile asbestos tubes (Fig. 3b) are parallel to [*100*] - this direction of preferred orientation of this material is frequently misinterpreted to be the same as in the case of amphibole asbestos (for example [2]).

Further informations can be obtained using polarising microscope. In transmitted light, it can be readily distinguish - for example - in the case of monoclinic transparent crystals faces lying in the zone [*010*] (parallel) from others (oblique extinction).

In metallic fine-grained samples an additive information can be obtained by inspection of etch figures. Distribution on surface as well as symmetry of etch figures must correspond to plane point group symmetry of crystal face. On Fig. 4, hypothetical cubic crystal with point-group symmetry $m\bar{3}m$ is shown. On the drawig, the plane point-group symmetry of most common faces on cubic crystal and corresponding etch figures with the same symmetry are indicated. On Fig. 5, practical determination of grain orientation on the basis of shape of etch figures on electrochemical etched platinum wire is illustrated.

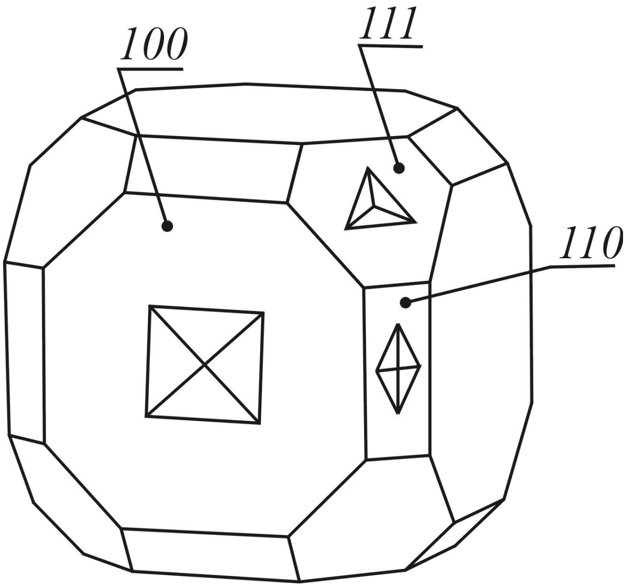

Fig. 4. Schematic drawing of a cubic crystal with point-group symmetry $m\bar{3}m$. Etch figures correspond to the plane point-group symmetry: on (*100*) face 4*mm*, on (*111*) 3*m* and on (*110*) 2*mm*

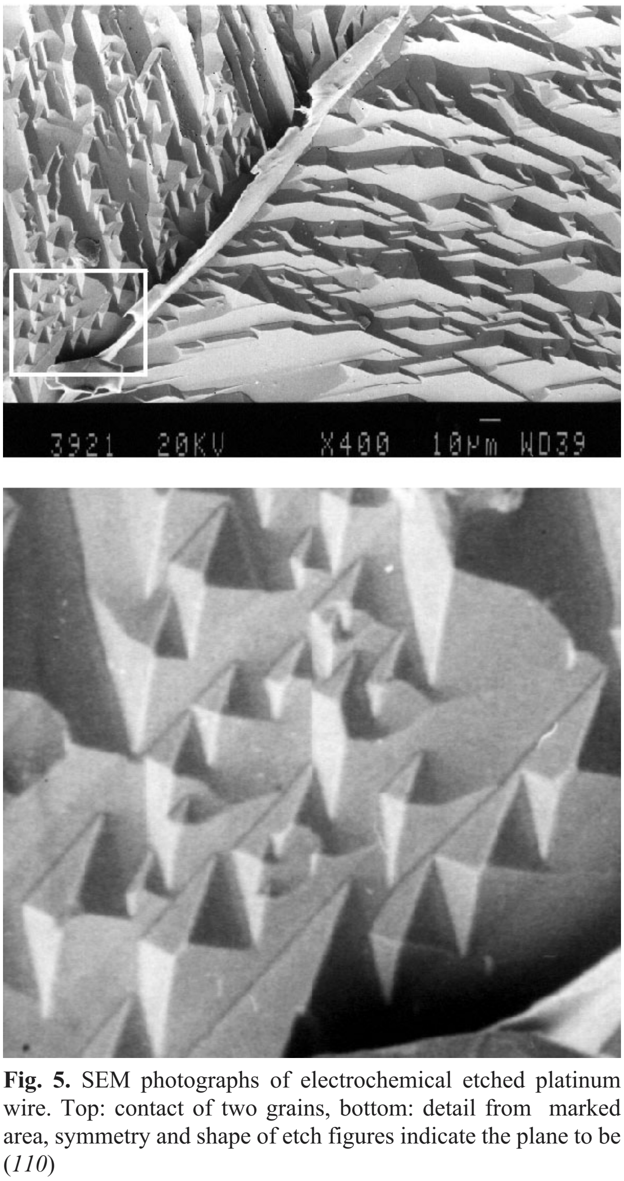

Fig. 5. SEM photographs of electrochemical etched platinum wire. Top: contact of two grains, bottom: detail from marked area, symmetry and shape of etch figures indicate the plane to be (*110*)

4. Conclusions

As follows from previous chapters, morphology of particles in polycrystalline samples affects their preferred orientation. On the other hand, knowledge of this phenomenon could be successfully used in correction procedures.

If the material is stable in vacuum and beneath of electron beam, SEM and TEM experiments (apparatuses are frequently available) can give additional information about the manner of preferred orientation. Indexing of crystal faces and/or lattice directions from SEM and TEM micrographs can be simple, as mentioned above.

To correct influence of preferred orientation in examples given, following procedure is recommended:

Empirical trial-and-error approach can be used without any problems for example 2 (phillipsite overgrowths).

Diamond thin layer (example 1) must be formally treated as mixture of three sets of crystals with identical chemical composition.

Asbestos mixtures (example 3) are real mixtures. To estimate quantitative proportions of both phases, TEM experiments are indispensable and corrections for preferred orientation of fibres must be applied ([*001*] direction for amphibole and [*100*] for chryzotile asbestos respectively).

Acknowledgements:

SEM photographs were kindly supposed by doc. Dúbravcová (Dept. of Microelectronics, Faculty of Electrotechnics and Informatics, Technical University, Bratislava, Fig. 1), Dr. Šamajová (Geological Institute, Faculty of Natural Sciences, Bratislava, Fig. 2) and Ing.Čaplovičová (CLEOM, Faculty of Natural Sciences, Bratislava, Figs. 3, 5).

References

[1] Dollase, W. A. (1986), *J. Appl. Cryst*. **19**, 267.

[2] Havlíček, D. (1999), *Materials Structure* **6**, 45.

[3] Buerger, M. J. (1956), *Elementary crystallography*, John Willey & Sons, Inc. New York, 528 pp.