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Abstracts of lectures

ANALYSIS OF DIFFRACTION-LINE BROADENING, THE STATE OF ART

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The broadening of X-ray diffraction profiles can be a parasitic effect which is desirable to avoid. This is true especially for XRD structure determination or refinement, for phase analysis and many other cases. On the other hand, it can also be a valuable source of information for the study of real structure of crystals.

The general evaluation procedure consists of several steps. At first, physical line broadening must be extracted from the measured line profile (h) which is a convolution of instrumental (g) and pure physical functions (f). This can be done by some of the deconvolution methods. However, a prospective way may be to include the convolution in a general model function which is subsequently fitted to experimental profiles. This was firstly applied in the Houska analytical method.

The components contributing to the line broadening can be divided into two subgroups: the part independent of the diffraction vector magnitude (crystallite size, subgrain size, stacking faults) - the so-called particle size broadening and the component proportional to the diffraction vector magnitude (dislocation structures, microstresses, stress-active defects) - the so-called strain broadening. There is a number of methods for separation of these components the application of which is more or less justified.

The analysis can be performed in direct or reciprocal space by means of Fourier analysis, moments or line widths. The parameters can be obtained by direct analysis of isolated peaks or by the profile fitting, the method which is necessary for overlapped peaks but can be applied generally. The former method can have main drawbacks in unprecise determination of background and/or profile truncation which can lead to the well-know "hook" effect in Fourier coefficients and also in statistical errors (noice) especially in the region of profile tails. The latter method can distort (pre-determine) real tails and lead to apparent particle-size effect.

In general, more reflection orders are necessary in order to separate the above components. Fourier coefficients give more information than a single parameter (e.g. integral breadth) and "single-line" methods are also available for them. However, their application must be careful since they are based on rather strong approximations. This is usually true also for all integral breadth methods which are the fastest and very useful for the first estimation of the dominating line broadening component and XRD line broadening anisotropy. The anisotropy can be taken as an additional source of information because in some cases it can help to distinguish between different kind of lattice defects.

An important point which must be taken into account is structural inhomogeneity of the scattering object. This includes the distribution of lattice defects in single crystals and also microstructural inhomegeneity of such single crystals in polycrystalline aggregates. In the former case, the most developed theory was elaborated for the distribution of dislocations with weak correlation (Krivoglaz, Wilkens) which was extended for the case of stronger correlation (dipoles) by Groma and Ungar.

Examples are given to show first of all: the use of the so-called Warren-Averbach and Krivoglaz-Wilkens plot for the separation of line broadening components and dislocation density determination, the application of diffraction line broadening anisotropy for estimation of lattice defect types, structural inhomogeneity in textured materials and thin films, and anomalous diffraction profiles for materials with precipitates.

QUANTITATIVE PHASE ANALYSIS OF IRON NITRIDES BY RIETVELD'S METHOD.

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Well known structures of all iron nitrides, oxides and carbides provokes using of Rietveld's method for phase analysis of surface layers of samples prepared by ion--nitridation. One of the best computer programs for quantitative phase analysis by Rietveld method was made by D.B.Wiles (last update May 22, 1981) modified by S.A.Howard (August 22, 1988) for quantitative applications (program name is DBW3.2).

If it is possible to use an internal standard, the program is excellent for quantitative analysis of minerals, ceramics, and so, also if amorphous part is present. For using of metallic specimen there are two principal difficulties: Program is not able to respect elastic anisotropy of (stressed) metallic surface and surface layers of iron nitrides is not homogeneous. Growing content of nitrogen from bulk to surface of specimen means different phase composition inside diffracted layer. Nevertheless is program usefull to use, but the result should be interpreted with care. For example, refined can be only overall isotropic temperature factor and its negative value means, that phase is covered by layer of another phase. Owing to neglecting of elastic anisotropy are positions of α-iron diffractions, especially (200), shifted, but if intensity is correct, the result is fully acceptable.

One-dimensional diffraction on very small crystallites with layered structure

JEDNOROZMĚRNÁ DIFRAKCE NA VELMI MALÝCH KRYSTALITECH S VRSTEVNOU STRUKTUROU

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Při analýze některých látek s vrstevnou strukturou konvenčními práškovými rtg. difrakčními technikami (uspořádání na odraz) máme velmi často k dispozici jen tzv. bazální difrakce typu 00*l*. Tato okolnost je zapříčiněna především vysokým stupněm přednostní orientace částic v preparátu a podpořena častou neuspořádaností kladu vrstev ve struktuře těchto látek, která způsobuje difuzitu nebazálních difrakcí. Mezi takové látky patří například uhlíkaté materiály a jílové minerály. Profily bazálních difrakcí těchto látek bývají také deformovány (rozšíření, asymetrie) a to především díky velmi malým velikostem krystalitů (koherentně difraktujících domén). K rozptylu záření zde nedochází jen v Braggových difrakčních úhlech a jeho intenzitu lze vyjádřit intenzitní funkcí

$$I(\Theta) \sim \Phi(\Theta) \,.\, G^2(\Theta) \,.\, Lp(\Theta)$$

kde $G(\Theta)$ je úhlově závislý strukturní faktor vrstvy, $Lp(\Theta)$ je Lorentz-polarizační faktor a $\Phi(\Theta)$ je interferenční funkce. Na rozdíl od strukturního faktoru $F(00l)$, který je definován v 00*l* pro krystal nekonečné velikosti, jsou do výpočtu $G^2(\Theta)$ zahrnuty jen atomy jedné vrstvy, jako nejmenší stavební jednotky struktury (BSU) s konečnou velikostí. Tvar funkce $G^2(\Theta)$ závisí na typu atomů v BSU, na jejich vzdálenosti z_j od zvoleného počátku, ale obecně také na volbě počátku v BSU:

$$G(\Theta) = \Sigma f_j(s) \cos(4\pi \; z_j s) + i \, \Sigma f_j(s) \sin(4\pi \; z_j s)$$

kde $s = \sin\Theta / \lambda$. Tvar interferenční funkce

$$\Phi(\Theta) = [\sin^2(2\pi \; N d s)]/[\sin^2(2\pi \; d s)]$$

je ovlivněn veličinou $D = Nd$, reprezentující lineární velikost krystalitů, a čím je tato veličina menší, tím jsou profily širší. N je počet BSU v krystalitu a $d = d(001)$. Tvar výsledných profilů intenzitní funkce $I(\Theta)$ je však závislý nejen na veličině N, ale na také na průběhu strukturního faktoru vrstvy. Zahrnutí tohoto faktoru do výpočtu $I(\Theta)$ může způsobovat nejen asymetrii profilů, ale také posun maxima profilu. Tato skutečnost je zvýrazněna zejména u difrakcí v nízkoúhlové oblasti. Není zvláštností, když se u některých typů jílových minerálů s velmi malými krystality ($D \sim 50$ Å) jedná o posuny dosahující hodnoty $\Delta d = 0{,}5$ Å. Chceme-li tedy z experimentálního difrakčního záznamu popisovaného typu látky stanovit skutečné hodnoty d(00l), které by měly odpovídat polohám maxim profilů interferenční funkce, musíme provést nejen korekci na Lp faktor, ale také korekci na strukturní faktor vrstvy $G(\Theta)$.

TWINNING IN OD STRUCTURES

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Cronstedtite, $(Fe^{2+},Fe^{3+})_3[(Si,Fe^{3+})_2O_5](OH)_4$, is a member of the serpentine-kaolin group. Due to the almost ideal OD character of its structure, this mineral yields a wealth of more or less disordered polytypes. The crystals of the polytype, 1*T* (space group *P*31*m*, $a_1 = 5.512$, $a_2 = 5.512$, $c = 7.106$ Å) contain *within coherently scattering blocks* variable concentrations of stacking faults such that domains of the basic structure can be translationally shifted by $1/3(\mathbf{a}_2\text{-}\mathbf{a}_1)$ or $1/3(\mathbf{a}_1\text{-}\mathbf{a}_2)$ - the socalled *OD twinning*. This manifests itself in the diffraction pattern so that the diffractions with $h\text{-}k \equiv 0 \pmod 3$ - the *family diffractions* - are always sharp, whereas the remaining diffractions - the *characteristic polytype diffractions* are more or less smeared out along diffuse streaks parallel to **c***. The intensities of the latter are thus underestimated during diffractometer measurements and, for a refinement of the structure, they have to be assigned a separate scale factor.

An analysis of this kind of multiple OD twinning revealed that the square *q* of the scale factor of the characteristic polytype diffractions can be expressed by the equation

$$q = 3(x^2\text{-}x+1)\, p^2\text{-}3p+1$$

where $p_{\in}$ (0,1) is the proportion of the structure transferred from the basic position into the two twin positions and $x_{\in}(0,1)$ is the ratio how this proportion is distributed between them.

From the equation (1) whose validity is not restricted to hexagonal/trigonal structures it follows that the solution and/or refinement of the structure may not be unambiguous. At the same time, this equation has a surprising impact on the Laue symmetry in the reciprocal space.

PRECIPITATION AND DISSOLUTION OF SOLID PHASES IN REACTION ZONE BETWEEN ACID INDUSTRIAL WASTE AND NEUTRALISATION SOLUTIONS

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Interaction between acid industrial waste and neutralisation solutions has been studied under light microscope as a result of chemical staining techniques. Acid industrial waste may be defined as the thermodynamic system $Al_2(SO_4)_3$ -H_2SO_4-H_2O and neutralisation solution by system Na_2CO_3 — H_2O. Chemical process from $pH < 1$, in acid industrial waste to $pH > 7$,. In neutralisation solution, and some local changes in chemical composition of liquid phase are stained by Bromocresol Blue as pH indicator. A variety of precipitated and coprecipitated solid phases dependent on pH of liquid phase as $Al(OH)_3$, $Al_2(SO_4)_3.17H_2O$ and $NaAl(SO_4)_2.12H_2O$ were identified by XRD, FTIR, light microscopy, electron microscopy, and electron microanalysis. Crystal structure parameters of selected well-crystallised phases are refined by Rietveld method. It is shown that the relative distribution of Al between its various complexes dictates dissolution and precipitation of components from reaction zone. In system solid phase-amorphous phase-liquid phase. Time- dependent chemical processes are documented as colour changes of Bromocresol Blue on colour photos.

SHOCK LOADED DOLOMITE – AN X-RAY POWDER DIFFRACTION STUDY

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Introduction: Dolomite ($CaMg(CO_3)_2$) represents large volume of impact-comminuted materials in many impact structures on the Earth. In addition, the KT event assigns an important environmental role to dolomite, because of the potential liberation of carbon dioxide during shock-induced compression and subsequent pressure release. The present study focuses on the behavior of dolomite and its crystal structure using samples subjected to experimental shock pressures of known amplitude.

Experimental: Sample disks (8 mm diameter and 0.6 mm thickness) were manufactured from a non-porous, massive, polycrystalline dolomite-rock. Experimental shock loading, employing a powder gun and flat metal flyer plates, and recovery of the specimen, were conducted at NASA JSC, following the methods of [1]. The peak shock pressures were (in GPa): 4.6, 8.2, 16.9, 17.0, 17.6, 19.2, 20.0, 24.1, 26.0, 29.8, 41.0, 55.2, 65.2, and 68.0. Pressures above 70 GPa led to disintegration of sample containers, apparently due to excessive vapor production.

Electron probe analyses confirmed that the target material consisted mostly of Ca-rich dolomite and subordinate K-feldspar, quartz and pyrite. EPMA and XRD data revealed stringers of tungsten melt droplets disseminated in highly shocked materials (above 40 GPa). Also, grains of tungsten carbide and scheelite ($CaWO_4$) appeared in these samples due to local melting of containers and reaction with carbonate.

For the individual peak profile fitting (IPPF) of step-scanned powder patterns, the program XFIT [2] was used, which includes classic split Pearson VII profile shape functions (PSF) and fundamental parameters (FP) convolutions for peak modeling [3-5]. Parameters addressed by Pearson VII PSF were peak position, intensity and half-width; while the FP routine refines peak position, intensity, crystallite size and strain. Also, Rietveld crystal structure refinements were carried out using FullProf.98 [7, 8] to address cell size, position of atoms within the crystal structure, and half-widths of reflections.

Results: The X-ray diffraction study confirmed dolomite as the major phase, roughly 85 wt.% of the starting material. The remainder is predominantly quartz and minor orthoclase. The amounts of crystalline quartz and feldspar gradually decrease with increasing peak pressure and the most intense quartz peak degrades into a very weak and broad feature at 29.8 GPa. This identifies quartz as a good, independent indicator of peak stress in these samples, consistent with earlier studies. At pressures > 30 GPa several peaks corresponding to periclase (MgO – a decomposition product of starting dolomite) appeared.

Individual peak profile fitting (IPPF) has revealed that FWHM (full-widths at half-maximum) values correlate tightly with peak pressure in the range between 15-80 2Θ; peaks at higher diffraction angles cannot be easily approximated by PSFs because their intensities are lowered excessively at the higher pressures. FWHM values increase as peak pressure increases. Crystallite size is decreased dramatically at 5 GPa, by approximately a factor of 2, and continues to decrease in more gradual fashion up to 30 GPa, beyond which it remains almost invariant. Strain has just the opposite trend – it increases with increasing pressure until it becomes constant at circa 30 GPa, akin to the evolution of domain size.

Rietveld crystal structure refinements confirmed the dependence of FWHM on shock pressure. Pressures higher than 30 GPa did not result in additional peak broadening, yet this seems consistent with the development of domain size and strain that became invariant at about 30 GPa as mentioned above. The unit cell dimensions also change with peak pressure, contrary to the observation of e.g. [9]. The maximum volume change (V/V_0) of the unit cell is 0.2 %. The trend of V/V_0 is again very similar to other observed parameters: it increases systematically with pressure up to 30 GPa and remains invariant at still higher pressures. The plot of c/a indicates that dolomite deforms preferentially in one crystallographic direction – along a – in response to shock compression. Fractional atomic coordinates allow atomic distances to be calculated. There are three major atomic groups in the crystal structure of dolomite: octahedra around Ca and Mg and triangles around C. There was no systematic change of Mg-O distances at any pressure, but the C-O distances increase modestly at > 30 GPa. The Ca-O distances behave in an opposite way to the C-O distances.

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INFORMACE O PROJEKTU INDUSTRIAL APPLICATIONS OF X-RAY DIFFRACTION

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Úplně na začátku (4.11.1996) byl dopis, z něhož jsme se dověděli, že americké nakladatelství *Marcel Dekker, Inc.* požádalo F.H.Chunga (Marson Corporation, Chelsea, MA) a D.K.Smitha (State College, PA), aby jako editoři připravili příručku *Industrial Applications of X-ray Diffraction*. Zároveň s touto informací nám bylo nabídnuto napsat do knihy kapitolu *Residual stress and stress gradients*. V polovině prosince 1996 přišel od editorů časový harmonogram: do 30. listopadu 1997 musí být kompletní text předán k recenznímu řízení!

Protože autoři i editoři všechno včas stihli, bude příručka k dispozici už letos jak při konferenci v Denveru, tak na Kongresu IUCr v Glasgow. Na sepsání 42 kapitol (1100 stran) se podílelo 59 autorů 44 institucí ze 14 zemí. Bývalé Československo je kromě *napětím* “reprezentováno” také *hydrometalurgií* T. Havlíka a M. Škrobiána z Košic.

OBSAH KNIHY

I. Introduction.
The Principles od Diffraction Analysis, The Practice of Diffraction Analysis, Progress and Potential of X-ray Diffraction

II. Industrial Application
High-Tech
Semiconductors, Superconductors, Aerospace, Automotive, Petroleum Exploration and Production, Petroleum and Petrochemicals, Catalysts in Refineries, Validity of Catalysts Research
Metals
Hydrometallurgy, X-ray Fractography
Minerals and Ceramics
Mining, Cement, Silica, Glass-Ceramics
Polymers and Composites
Polymer Industry, Paint and Pigment Industry, Pharmaceuticals
Chemicals
Energy, Lighting, Photography, Detergents and Cleaners, Museum, Forensic Science, U.S. Customs Laboratories, Commercial Service Laboratories

III. Specialty Techniques
Radiations
Synchrotron Usage by Industry, Electron Microscopy in Industry
Microstructures and Instrumentation
Line Profile and Sample Microstructure, Thin Films and Multilayers, Residual Stress and Stress Gradients, Residual Stress Development and Texture Formation During Rolling Contact Loading, Warren-Averbach Applications, Microbeam Crystallographic and Elemental Analysis, High Temperature and Non-ambient X-ray Diffraction
Diffraction Patterns
NIST Standard Reference Materials for Characterization of Instrument Performance, Grain Orientation and Texture, Structure Analysis from Powder data

Kapitola *Residual Stress and Stress Gradients*, která byla svěřena nám, má 4 hlavní části (Load and Residual Stresses, Macroscopic State of Stress of Crystal Lattice, Stress Measurement by Monochromatic X-rays, Illustrative Examples of Industrial Applications) a čtenáři ji najdou na stánkách 793 až 811.

PRELIMINARY CRYSTALLOGRAPHIC STUDY OF γ-D-CRYSTALLINE OBTAINED FROM PATIENT’S EYE.

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Crystals forming eye cataract were obtained by surgery from patient eye lens (three-year-old boy). Proteins from crystals were characterized by SDS-PAGE and N-terminal sequencing. Homology search proved that crystals contain γ-D-crystalline. Sequence of corresponding patient genome DNA shows mutation in one allele for γ-D-crystalline (36Arg>Ser). Two crystals of γ-D- crystalline were measured to resolution 3.5 Å at 150 K. The structure was solved by molecular replacement.