

**Plenary Lectures****I - O1****APPLICATIONS OF HIGH-RESOLUTION POWDER DIFFRACTION****A. N. Fitch***ESRF, BP220, F-38043 Grenoble Cedex, France.*

Since May 1996 a dedicated high-resolution powder diffraction beam line has been in user service at the European Synchrotron Radiation Facility in Grenoble. The advantages for powder diffraction of this 6-GeV third-generation synchrotron-radiation source are the very high X-ray intensity, high angular and energy resolution, and access to a wide range of X-ray wavelengths, originally from 0.31 Å to 2.48 Å on the bending-magnet beam line BM16 [1,2], and more recently down to 0.21 Å with the beam line that has replaced BM16. This is built on insertion device ID31, and has been operational since June 2002. The new beam line is powered by three minigap undulators with a minimum magnetic gap of 11 mm which give a much enhanced X-ray flux as compared to the bending magnet.

The increase in X-ray intensity means that diffraction patterns can be measured more quickly and has opened up more opportunities for high-resolution powder diffraction measurements at ESRF, including the application of anisotropic thermal expansion to reduce the effects of peak overlap in diffraction profiles [3], thus allowing larger, more-complex crystal structures to be investigated, and also to follow the structural development of samples as a function of temperature or time, undergoing phase transitions or solid-state chemical reactions, or the evolution of

microstructure. For materials-science applications, the availability of harder X-rays means that much thicker components can be investigated, such as measuring in residual strain, penetrating through 15 mm of Al or 5 mm of Ti (or their alloys).

The talk will give a brief overview of the high-resolution powder diffraction facilities available on ID31 at ESRF, and will illustrate their use with recent examples showing the solving of small-molecule crystal structures, the investigation of phase transitions, high-temperature annealing of ceramics, and the investigation of protein structures, a field pioneered by Von Dreele [4] and being taken up with enthusiasm at ESRF [5].

1. A. N. Fitch, *J. Res. Natl. Inst. Stand. Technol.*, 109 (2004) 133–142.
2. J. L. Hodeau, P. Bordet, M. Anne, A. Prat, A. N. Fitch, E. Dooryhee, G. Vaughan and A. Freund, *SPIE Proceedings*, 3448 (1998) 353–361.
3. K. Shankland, W. I. F. David and D. Sivia, *J. Mater. Chem.*, 7 (1997) 569–572.
4. R. B. Von Dreele, *J. Appl. Cryst.* 32 (1999) 1084–1089.
5. I. Margiolaki and J. P. Wright, to be published.

**I - O2****DIFFRACTION STRESS ANALYSIS OF GRAIN INTERACTION IN POLYCRYSTALLINE MATERIALS****U. Welzel and E. J. Mittemeijer***Max Planck Institute for Metals Research – Heisenbergstraße 3 – 70569 Stuttgart, Germany*

The elastic behaviour of polycrystals depends upon the single-crystal elastic constants of its constituents (grains), the crystallographic texture and the microstructure. However, a straightforward calculation of the mechanical elastic constants (relating mechanical (macroscopic) strains to mechanical (macroscopic) stresses) and the diffraction elastic constants (diffraction stress factors for elastically anisotropic samples), relating (diffraction) lattice strains to mechanical stresses from single-crystal elastic compliances (or stiffnesses) of the crystallites composing the specimen is generally not possible without more ado. A so-called grain-interaction model can be adopted, describing the distribution of stresses and strains over the crystallographically differently oriented grains in the specimen.

Extreme cases for grain interaction are given by the Voigt [1] and Reuss [2] proposals (either the strain or stress tensors of all crystallites are taken equal to the mechanical

strain and stress tensors, respectively), which are generally incompatible with physical reality but set bounds for the mechanical elastic constants [3]. It is common to all traditional grain-interaction models (like the extreme Voigt and Reuss models and the intermediate models as the Neerfeld-Hill [3,4] and the Eshelby-Kröner [5-7] models) that they involve that a polycrystal is mechanically elastically isotropic in the absence of crystallographic texture, as the same grain-interaction assumptions are adopted along all directions in the specimen. They can therefore be called isotropic grain-interaction models [8]. However, even in the absence of crystallographic texture, polycrystals cannot generally be considered as being mechanically elastically isotropic. It can be anticipated that deviations from an isotropic 'microstructure' may have an impact on the elastic properties of polycrystals.



Two microstructural features involving the occurrence of macroscopic elastic anisotropy (even in the absence of crystallographic texture) have been recently considered by the development of appropriate grain-interaction models: the presence of a free surface in thin films, 'surface anisotropy', and morphological (grain-shape) texture, which is also frequently encountered in thin films. The mechanical and diffraction elastic constants can be calculated employing recently developed grain-interaction models. As in such models different grain-interaction assumptions are adopted along different directions in the specimen, these models can therefore be called direction-dependent grain-interaction models.

The present paper presents an overview of recent work on the development of direction-dependent elastic grain-interaction models and the diffraction analysis of elastic grain interaction in polycrystalline material [8-12]. The extension of the applicability of the newly developed grain-interaction models to the plastic deformation regime will also be discussed on the basis of selected examples.

1. Voigt, W., 1910, *Lehrbuch der Kristallphysik* (Leipzig-Berlin: Teubner).

2. Reuss, A., 1929, *Zeitschrift für angewandte Mathematik und Mechanik* **9**, 49.
3. Hill, R., 1952, *Proc. Phys. Soc. London* **65**, 349.
4. Neerfeld, H., 1942, *Mitt. K.-Wilh.-Inst. Eisenfor.* **24**, 61.
5. Eshelby, J. D., 1957, *Proc. Roy. Soc. A* **241**, 376.
6. Kröner, E., 1958, *Z. Physik* **151**, 504.
7. Kneer, G., 1965, *Phys. Stat. Sol.* **9**, 825.
8. Welzel, U. & Mittemeijer, E. J., 2003, *J. Appl. Phys.* **93**, 9001.
9. van Leeuwen, M., Kamminga, J.-D. & Mittemeijer, E. J., 1999, *J. Appl. Phys.* **86**, 1904.
10. Leoni, M., Welzel, U., Lamparter, P., Mittemeijer, E. J. & Kamminga, J.-D., 2001, *Philos. Mag. A* **81**, 597.
11. Welzel, U., Leoni, M. & Mittemeijer, E. J., 2003, *Philos. Mag.* **83**, 603.
12. Koch, N., Welzel, U., Wern, H. & Mittemeijer, E.J., 2004, submitted for publication.

I - O3

## EXPLOITING PREFERRED ORIENTATION TO RESOLVE OVERLAPPING REFLECTIONS

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If it weren't for the fact that reflections with similar scattering angles ( $2\theta$ ) overlap in a powder diffraction pattern, structure solution for polycrystalline materials would be as straightforward as it is for single crystals. It is the ambiguity in the relative intensities of these overlapping reflections that hinders the determination of the structures of many industrially important materials. In recent years, a number of clever methods have been developed to circumvent this problem, both by adapting existing methods to cope with the intensity ambiguity and by introducing chemical information into the structure determination process [1], but if the ambiguity could be resolved in some way, the powerful techniques that have been developed over the years for single-crystal data could be applied directly.

One way of addressing this problem is to adopt a more elaborate data collection strategy in which several different, but related, data sets are collected on the same polycrystalline sample. For example, a sample with a preferred orientation of the crystallites will yield diffraction patterns whose intensities are dependent upon the orientation of the sample in the X-ray beam. By collecting data with the sample in several different orientations, more information about the relative intensities of reflections that overlap in  $2\theta$ , but not in orientation space, can be gleaned.

The concept, which involves a full texture analysis followed by a deconvolution procedure, was described by Hedel et al. in 1997 [2], and its practical viability was demonstrated by Wessels et al. in 1999 with the determination

of the structure of the high-silica zeolite UTD-1F with 117 non-H atoms in the asymmetric unit [3, 4]. However, the reflection mode geometry used for that structure determination required a relatively large, uniformly textured sample and three days of synchrotron beamtime. In an attempt to reduce the amount of beamtime required and to eliminate the need for a large homogeneous sample, the method has since been adapted to work with data collected in transmission mode using a small sample and a 2-dimensional detector.

The transmission geometry, with an area detector, requires much less synchrotron beamtime, is insensitive to sample inhomogeneities, and yields a dataset that is more complete. However, the reflection geometry, with a pre-detector analyzer crystal, produces data with a much higher resolution in  $2\theta$  and no limitation (beyond the wavelength) on  $d_{min}$ . Examples of the application of both methods and a discussion of their advantages and disadvantages and of possible improvements will be presented.

1. David, W.I.F.; Shankland, K.; McCusker, L.B.; Baerlocher, Ch. (Eds): *Structure Determination from Powder Diffraction Data*, Oxford University Press, 2002.
2. Hedel, R.; Bunge, H.J.; Reck, G.: *Textures Microstruct.* **29** (1997) 103-126.
3. Wessels, T.; Baerlocher, Ch.; McCusker, L.B.: *Science* **284** (1999) 477-479.
4. Wessels, T.; Baerlocher, Ch.; McCusker, L.B.; Creyghton, E.J.: *J. Am. Chem. Soc.* **121** (1999) 6242-6247.



I - O4

## NANOCRYSTALLINE MATERIALS STUDIED BY POWDER DIFFRACTION

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Crystalline materials can be defined, in a broader sense, as nanocrystalline if the average grain size is smaller than a micron. It can be either in the form of loose powder or in the form of polycrystalline bulk materials. Since *nanocrystalline materials* is one of the major buzz-words in the present decade, the procedures to produce them vary from single atom or cluster condensation [1], through different chemical reactions [2] down to crystallisation from the bulk amorphous phase [3] or fragmentation by ball milling and different techniques of severe plastic deformation [4]. Latter are, in particular, the methods of equal channel angular pressing (ECAP) [5], high pressure torsion (HPT) [6] or corrugated cold rolling (CCR) [7]. Depending on the way the material was produced the grain size and size distribution and the strain or stress state, frozen into the crystallites, are varying over wide scales. The average crystallite size in inert-gas condensed metals like copper or palladium can vary between 5 to 20 nm together with dislocation densities at the order of magnitude of several times  $10^{15} \text{ m}^{-2}$  [8,9]. Nanocrystalline foils produced by electrodeposition can contain extremely high densities of stacking faults [10]. Stacking faults can become one of the major type of lattice defects in materials with very high stacking fault energy, e.g. in aluminium [11,12], in which under conventional circumstances stacking faults can not be observed. Powder specimens produced by the chemical precursor method can be as small as 5 to 10 nm without even a single dislocation [13]. Hexagonal materials like titanium can be produced by the ECAP method to have an average grain size of about 50 nm and dislocation densities as high as  $10^{16} \text{ m}^{-2}$  [14]. The strength of this material can exceed the strength of its conventional grain size counterpart by one order of magnitude [14].

Depending on the purpose for what the material has been prepared and the procedure by which it has been produced the microstructure can be very different. Due to constantly improving diffractometers [15] and sometimes sophisticated X-ray optical devices in the home laboratories [16] and high intensities and high angular resolution at powder diffraction beam lines at synchrotrons [17], powder diffraction has become one of the most powerful tools to determine the microstructure of nanocrystalline materials.

According to the kinematical theory of powder diffraction if the crystallites are free from lattice defects and the average crystallite size is larger than a few microns, however, not much larger than about 10 microns, the *physical* line profiles of the diffraction peaks are delta functions [18]. In the measured powder patterns these delta functions are convoluted with the instrumental functions of the diffractometer. To the best knowledge of the present EPDIC community such a powder pattern is realised by the measurement of a good LaB<sub>6</sub> standard specimen, e.g. the

LaB<sub>6</sub> standard specimen provided by one of the laboratories of NIST. If the crystallites become smaller than about a micron or the lattice becomes distorted by any kind of lattice defects the *physical* line profiles will no longer remain delta functions. The deviations from the ideal delta function type can be very different. The diffraction peaks can be: (i) shifted, (ii) can broaden, (iii) can become asymmetric, (iv) the broadening can be anisotropic with *hkl* and (v) any combination of the former cases can occur. In recent years it has been shown that the physical origin of strain anisotropy is the extremely anisotropic strain field of dislocations [19-22]. The effect of dislocation on the broadening of different *hkl* reflections, especially in polycrystalline materials, can be summarized in a fairly simple form of average dislocation contrast factors [23]. The fundamental parameters in determining the contrast factors can be determined by whole profile fitting numerical procedures. The physical interpretation of these parameters can reveal several details about the dislocation structure in nanocrystalline materials. The same whole profile fitting procedures provide size distribution density functions of the coherently diffracting domains [24,25]. The interpretation of the this size distribution either in terms of crystallite size distribution or in terms of other physical units in the material is the virtue of the experimenter.

1. Gleiter, H. (1989) "Nanocrystalline Materials", *Progr. Mater. Sci.*, **33**, 223-315.
2. Guillou, N., Auffrédic, J. P. and Louër, D. (1995). *Powder Diffr.* **10**, 236-240.
3. Révész, Á., Heunen, G., Varga, L.K., Suriñach, S., Baró, M.D. *J. Alloys & Compounds*, **368**, 2004, 164-168
4. R. Z. Valiev, R. K. Ishlamgaliev and I. V. Alexandrov: *Progr. Mater. Sci.* Vol. 45 (2000), p. 103.
5. V.M. Segal, *Mater. Sci. Eng. A* 197 (1995) 157-164.
6. R.Z. Valiev, R.K. Islamgaliev, I.V. Alexandrov, *Progress in Materials Science* 45 (2000) 103-189.
7. M.J. Zehetbauer, H.P. Stüwe, A. Vorhauer, E. Schafner, J. Kohout, *Advanced Engineering Materials* 5 (2003) 330-337
8. J. Y. Huang, Y. T. Zhu, H. Jiang and T. C. Lowe, *Acta mater.* 49 (2001) 1497-1505
9. Ungár, T., Ott, S., Sanders, P., Borbely, A. & Weertman, J. R. (1998). *Acta Mater.* 46, 3693-3699.
10. Krill, C. E. & Birringer, R. (1998). *Philos. Mag. A*, 77, 621- 640.
11. D. Jia, K.T. Ramesh, E. Ma, L.Lu and K. Lu, *Scripta mater.*, 45 (2001) 613.
12. X. Z. Liao, F. Zhou and E. J. Lavernia, S. G. Srinivasan, M. I. Baskes, D. W. He, and Y. T. Zhu, *Appl. Phys. Lett.*, 83, 2003, 632-634.



13. N. Audebrand, N. Guillou, J. P. Auffrédic and D. Louer, *Thermochim. Acta*, 286 (1996) 83-87.
14. Y.T. Zhu and J.Y. Huang, J. Gubicza and T. Ungár, Y.M. Wang and E. Ma, R.Z. Valiev, *J. Mater. Res.*, 18 (2003) 1908.
15. V.V. Stolyarov, Y.T. Zhu, I.V. Alexandrov, T.C. Lowe, and R.Z. Valiev, *Mater. Sci. Eng. A299*, 59 (2000).
16. A.C. Vermeulen and E. Houtman, *Mater. Sci. Forum*, 347-349, 2000, 17-22.
17. A. N. Fitch, *Mater. Sci. Forum* 228-231, 219 (1996).
18. B.E. Warren, *X-ray Diffraction*, Dover Publ., New York, 1969 and 1990.
19. Klimanek, P. and Kuzel Jr., R. *J. Appl. Cryst.* 21, (1988) 59-66.
20. Kuzel Jr., R. & Klimanek, P. *J. Appl. Cryst.* 21, (1988) 363-368.
21. Ungár, T. and Borbély, A. *Appl. Phys. Lett.*, 69, (1996) 3173-3175.
22. Ungár, T., Dragomir, I., Révész, Á., and Borbély, A., *J. Appl. Cryst.* 32, (1999) 992-1002.
23. Ungár, T. and Tichy, Gy. *Phys. Stat. Sol. (a)* 171, (1999) 425-434.
24. J.I. Langford, D. Louër and P. Scardi, *J. Appl. Cryst.* 33 (2000) 964-974.
25. T. Ungár, J. Gubicza, G. Ribárik and A. Borbély, *J. Appl. Cryst.* 34 (2001) 298-310.

I - O5

## MULTICRYSTAL APPROACH TO CRYSTAL STRUCTURE SOLUTION AND REFINEMENT

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We present a method in which the contributions from the individual crystallites in a polycrystalline sample are separated and treated as essentially single crystal data sets. The process involves the simultaneous determination of the orientation matrices of the individual crystallites in the sample, the subsequent integration of the individual peaks, and filtering and summing of the subsequent integrated intensi-

ties, in order to arrive at a single-crystal like data set which may be treated normally. In order to demonstrate the method, we consider as a test case a small molecule structure, cupric acetate monohydrate. We show that it is possible to obtain a single-crystal quality structure solution and refinement, in which accurate anisotropic thermal parameters and hydrogen atom positions are obtained.

I - O6

## IN-SITU CHARACTERIZATION OF MATERIALS BY SYNCHROTRON DIFFRACTION

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Diffraction methods are appropriate techniques for the characterization of polycrystalline materials, providing information about composition and structural details. A specific challenge in materials science is the investigation of structural changes in materials as response to external variable parameters. In-situ studies under real operation conditions are in the centre of interest, because relaxation phenomena or changes of the environment can falsify observations of processes in materials during application. The use of intensive and high-energetic synchrotron radiation enables considerably improved and qualitatively novel methods for the characterization of materials as part of devices in operation, mainly due to the penetration capability at very short photon wavelengths. Such investigations elucidate underlying processes and, hereby, contribute to understand working principles on one hand. On the other hand, materials degradation due to aging or fatigue can be

followed, providing the basis for materials optimization strategies.

Specific set-ups are described as already available or proposed. The actual performances are demonstrated by selected examples. Materials under investigation include cathode materials in rechargeable batteries, PZT as piezoelectric actuators or sensors and solid catalysts. Recent activities in these fields at dedicated facilities are reviewed, added by results from beamline B2 at HASYLAB. Existing capabilities are discussed in the light of future possibilities.

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