T2 - Real Structure - Line Profile Analysis

T2 - P21

CONVOLUTIONAL WHOLE PROFILE FITTING OF DIFFRACTION PATTERNS USING MODEL BASED PHYSICAL FUNCTIONS

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X-ray peak profile analysis is a powerful method for determining the microstructural properties of dislocated powders and polycrystalline materials. The Convolutional Multiple Whole Profile (CMWP) fitting method has been developed recently for the extraction of physical parameters for crystallite size distribution and dislocation structure from diffraction patterns of cubic, hexagonal or orthorombic materials. In this procedure the whole measured powder diffraction pattern is fitted by the sum of a background function and profile functions. The background is approximated by a spline function or a sum of Legendre polinomials. The profile functions are calculated as the convolution of the theoretical functions for physical broadening and the measured instrumental profiles. The physical profiles are calculated on the basis of the microstructure assuming that the crystallites have lognormal size distribution and the strain is caused by dislocations. The strain profile is based on the Wilkens dislocation theory. Strain and size anisotropy is taken into account by the dislocation contrast factors and the ellipticity of crystallites, respectively. The fitting procedure is based on a nonlinear least squares method and provides the median and the variance of the size distribution, the ellipticity of crystallites and the density and arrangement of dislocations. Since the CMWP method is a microstructural method, the peak positions and peak intensities are not physically interpreted, they are treated as free parameters. However, in order to get the best results, these peak parameters can be refined and are determined along with the microstructural parameters. The procedure will be illustrated by different specific case studies.

T2 - P22

BURGERS VECTOR POPULATIONS IN HOT ROLLED TITANIUM DETERMINED BY X-RAY PEAK PROFILE ANALYSIS

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Commercially pure alpha-titanium was deformed by hot rolling at 268° C for the following reduction rates: 30%, 60% and 80%. The dislocations densities and their distribution at different deformation rates were established using X-ray Peak Profile Analysis. The dislocation model of anisotropic broadening of peak profiles was used to determination the Burgers vector distribution, their evolution as the deformation proceeds to higher degrees and the dislocation densities in alpha-titanium samples studied here. It was found that the <a> dislocation type predominate at all deformation levels investigated in this study. The population of the <c+a> dislocation type is significant after 30% reduction and it becomes marginal for higher reduction rates. The presence of <c> type of dislocation is marginal at all deformation levels. Figure 1. shows the Burgers vector population as a function of reduction rate. It was also estab-

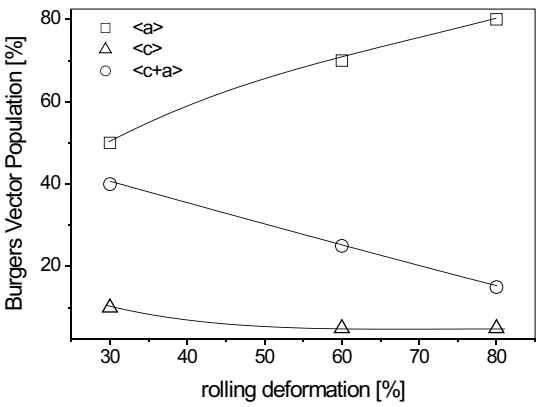

Figure 1. The populations of the three Burgers vector types, <**a**>, <**c**> and <**c+a**>, as a function of the nominal reduction.

lished that the dislocation density is slightly increasing as the reduction degree increases.

1. Dragomir IC, Ungár T. J. Appl. Cryst 2002; 35:556.
2. Jones IP, Hutchinson WB. Acta Metall 1981; 29:951.
3. Kuzel Jr. R, Klimanek P. J. Appl. Cryst 1989; 22:299.
4. Ungár T, Gubicza J, Ribárik G, Borbély A. J. Appl. Cryst. 2001; 34:298.
5. Wilkens M. Fundamental Aspects of Dislocation Theory, In: Simmons JA, Bullough R de it, editors. Nat. Bur. Stand. (US) Spec. Publ. No. 317, vol. II., Washington DC, USA, 1970, p.1195.

T2 - P23

MICROSTRUCTURE OF POST DEFORMED ECAP-Ti INVESTIGATED BY MULTIPLE X-RAY LINE PROFILE ANALYSIS

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The processing of ultrafine-grained or even nano-crystalline materials by severe plastic deformation (SPD) modes (ECAP, HPT) [1] are well established methods to improve material properties, especially ductility, strength and elastic moduli. Thus one of the challenges in modern material science is to adjust these parameters in order to satisfy additional demands like low weight, thermal stability and good bio-compatibility, creating technologically applicable high performance materials.

The characterization of the microstructure of these materials in the as-produced (SPD) state as well as after additional conventional deformation (SPD-postdeformed) is of high interest for the explaination of their mechanical properties. Knowledge of the parameters describing the microstructure is also necessary to perform model simulations which in turn are substantial for the technological improvement of the materials.

Using the MXPA (Multi reflection X-ray Bragg Peak Analysis) the structural size and its distribution in ultra-fine grained materials as well as other microstructural parameters like dislocation density, their arrangement and long range internal stresses can be determined [2, 3].

In the present case 99.5% pure -Ti was deformed by equal channel angular pressing (ECAP) at 450°C for 8 passes in route B. Compression samples were manufactured out of the bulk and deformed by compression up to 80% true strain.

Using four linear position sensitive detectors (PSD) diffraction patterns of up to 11 reflection were recorded and then analysed by Multiple Whole Profile Fitting (MWP) [4].

In the case of a hexagonal crystal system this procedure requires the determination of the dislocation slip systems activated in the sample [5]. The eleven dislocation slip systems in the hexagonal Ti can be classified into three groups according to their Burgers vectors. [6]. In the investigated samples it turned out that only two of these three groups were active during deformation.

The area weighted mean coherently scattering domain size after the ECAP deformation has a relatively small value of about 40nm. It stays more or less constant, whereas the size distribution function shows a slight tendency to broaden during the additional compression. The dislocation density after the ECAP process is already considerably high but still increases significantly with growing post-deformation.

[1] R.Z. Valiev, R.K. Islamgaliev, I.V. Alexandrov, *Progr. Mater. Sci.*, **45**, (2000) 103.

[2] T. Ungár, J. Gubicza, G. Ribárik, A. Borbély, *J. Appl. Cryst.* **34** (2001) 298.

[3] E. Schafler, M. Zehetbauer, T. Ungar, *Mater.Sci.Eng. A*, **319-321**, (2001) 220.

[4] G. Ribárik, T. Ungár and J. Gubicza, *J. Appl. Cryst.* **34** (2001) 669.

[5] I.C. Dragomir, T. Ungár, *J. Appl. Cryst.* **35** (2002) 556.

[6] R. Kuzel jr., P. Klimanek, *J. Appl. Cryst.* **22** (1989) 299.

T2 - P24

THE DISLOCATION STRUCTURE IN POLYCRYSTALLINE Cu DETERMINED IN-SITU AT AN ELETTRA SYNCHROTRON SOURCE

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Coarse grained texture free polycrystalline copper specimens were deformed in compression in a dedicated compact materials testing mashine. The testing mashine was placed in the eucentric centre of a robust and open three axis goniometer. The position of the X-ray beam impinging on the specimen was monitored by a long focus and large aperture microscope with short depth of sharpness. This enabled to keep always the same specimen position in the X-ray beam. The beam size on the specimen was about 500 m in diameter. Individual grains were selected for the measurement of the profiles of 400 Bragg reflections. The deformation was carried up to = 0.6. The diffraction profiles were recorded at intervals of about = 0.01 steps. The profiles were evaluated for the average and the local dislocation densities in the whole graine and the dislocation cell interior- and cell wall materials, respectively. From the asymmetries of the peak profiles the long-range internal stresses prevailing between cell wall and cell interior regions were also detemined. Unlike in 100 orientation single crystals oriented for ideal multiple slip, the dislocation densities and the dislocation arrangement parameters are increasing monotonously with deformation. The long-range internal stresses are increasing up to about =0.4. Above this deformation value these stresse seem to disappear. The results are discussed in terms of the differences in the deformation mechanisms in 100 oriented single crystals and polycrystalline materials.

T2 - P25

THERMAL STABILITY OF THE MICROSTRUCTURE OF SEVERELY DEFORMED COPPER

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Severe plastic deformation (SPD) is an effective tool for producing bulk nanostructured metals. One of the most common SPD methods is equal channel angular pressing (ECAP) – a technique that results in a homogeneous sub-micron grain structure (down to the 100 nm range) of the material [1,2]. Copper specimens were deformed by ECAP using 1, 2, 4 and 8 pass schedules. The microstructure produced was studied by high resolution X-ray diffractometry using the Multiple Whole Profile (MWP) fitting method [3,4]. The formation of the submicron grain structure was studied as a function of the number of ECAP passes, along with the crystallite size distribution and the density of dislocations.

It was found that the crystallite size is reduced to a few tens of nanometers already after the first ECAP pass and was not further refined with subsequent ECAP passes. At the same time, the dislocation density increases gradually up to 4 ECAP passes. The strength was found to be controlled by the density of dislocations rather than by the crystallite size. The thermal stability of the microstructure was also examined by differential scanning calorimetry (DSC). Differences in the kinetics of grain growth and recovery during heat-treatment of specimens with different ECAP histories were revealed.

[1] S. C. Baik, Y. Estrin, H. S. Kim, H. T. Jeong and R. J. Hellmig, *Mater. Sci. Forum* **408** (2002) 697-702.

[2] V. V. Stolyarov, Y. T. Zhu, I. V. Alexandrov, T. C. Lowe and R. Z. Valiev, *Materials Science and Engineering A* **343** (2003) 43-50.

[3] T. Ungár, J. Gubicza, G. Ribárik, A. Borbély, *J. Appl. Cryst.* **34**, (2001) 298-310.

[4] G. Ribárik, T.Ungár, J. Gubicza, *J. Appl. Cryst.* **34** (2001) 669-676.

T2 - P26

SPATIAL FLUCTUATIONS OF THE MICROSTRUCTURE DURING DEFORMATION IN Cu SINGLE CRYSTALS

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X-ray line profile analysis has been developed into a powerful tool which can be used to characterize the microstructure of deformed materials of deformation degrees up to several hundred percents [1]. In previous work this method has been applied very extensively to samples *after* deformation, using samples prepared separately for each investigated deformation degree [2]. Using the very high intensity of Synchrotron radiation together with X-ray Bragg Peak profile analysis (XPA), it was possible to study the evolution of several microstructural quantities, such as the density of dislocations , their arrangement M, and the internal stresses | w − c| related to dislocations, with high resolution either in time or lateral, *during* deformation.

Observing copper single crystals during compression repeatedly showed an increase in dislocation density of a wavy character. A similar behaviour of the dislocation density was also observed in *spatial* scans, also done during the deformation of the sample. This can be interpreted as a consequence of the propagation of deformation fronts in contrast to the homogeneous deformation observed in polycrystals. This effect has been recently documented by strain measurements of metal single crystals which exhibit a distinctive single slip behaviour in the initial stages of deformation [4].The results are discussed in terms of the formation of a network of deformation cells [5], continuously interacting with newly produced mobile dislocations.

1. T. Ungár, *Mat. Sci. Eng. A* **309-310** (2001) 14.
2. M. Zehetbauer, T. Ungar, R. Kral, A. Borbely, E. Schafler, B. Ortner, H. Amenitsch, S. Bernstorff, *Acta mater.* **47**, No.3, 1053 (1999).
3. E. Schafler, M. Zehetbauer, I. Kopacz, T. Ungar, P. Hanak, H. Amenitsch, S. Bernstorff, *phys.stat.sol. a*, **175**, No.2, 501-511, (1999).
4. L. B. Zuev, V. I. Danilov, *Phil.Mag. A* **79**, 43 (1999).
5. T. Ungar, M. Zehetbauer, *Scripta metall.mater.* **35**, 1467 (1996).

T2 - P27

THE DISLOCATION STRUCTURE AND CRYSTALLITE SIZE DETERMINED BY X-RAY LINE PROFILE ANALYSIS IN FORSTERITE DEFORMED AT 11 GPa AT 1400 ^{O}C

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Synthetic forsterite has been deformed at 11 GPa, 1400 °C in a multianvil high pressure apparatus at the Bayerisches Geoinstitut (Universität Bayreuth, Germany). The X-ray diffraction patterns were measured by a special high resolution double crystal diffractometer with negligible instrumental effects. The monochromatised parallel $K_{\alpha 1}$ X-ray beam has a footprint on the specimen of about 0.1 1 mm^2. This fine beam condition provides good diffraction patterns of the small specimens of the size of about 0.2 2 mm^2. High resolution enables to carry out line profile analysis on the reflections which are well separated from the reflections of platinum and corrundum which are unavoidable due to the small and compact specimen structure. The dislocation densities were found to decrease with the holding time at 1400 °C from about between 16x10^{14} m^{-2} to 0.04 10^{14} m^{-2}. Good correspondence of the dislocation structure determined by X-ray line profile analysis and TEM observations have been established.

T2 - P28

DIFFRACTION ANALYSIS OF THE DISLOCATION CONTENT OF POLYCRYSTALLINE TUNGSTEN AND INCONEL 718 DEFORMED IN COMPRESSION IN A WIDE RANGE OF STRAIN RATES AND TEMPERATURES

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The influence of the strain rate and the temperature on the dislocation structure of b.c.c. Tungsten and f.c.c. alloy Inconel 718 was studied in uniaxial compression tests in the range 10^{-4} s^{-1} < 2 10^{3} s^{-1} and 20 °C T 1000 °C. The quasi–static deformation (< 10 s^{-1}) was performed with a servohydraulic testing system MTS 810, and for the dynamic tests (10^{2} s^{-1}) a ballistic plastometer [1] was available.

The microstructure of the deformed materials was investigated by X-Ray diffractometry (analysis of peak broadening according to [2,3]) and Electron Backscattering Diffraction (estimation of subgrain size and misorientation [4,5]). In order to control the influence of texture and substructure inhomogeneity on the X-ray data of the bulk samples, the methodology of the X - ray analysis was checked by means of filings. Using optimised fractions of screw and edge dislocations (80:20 in W, 50:50 in Inconel 718) and taking into account the elastic behaviour of the sample materials, in both cases complete agreement with the predictions of the theory of diffraction – peak broadening in polycrystals with random orientation was found.

In the deformed bulk specimens the strain - broadening of the reflections depends, in most cases, significantly on the orientation of the scattering crystallites and indicates structural inhomogeneity due to different dislocation content or different deformation behaviour of the texture components of the samples. The EBSD data show that, in both materials dislocation walls are formed and at larger strains activation of rotational deformation modes (formation of partial disclinations) take place. This is in agreement with TEM imaging of the sub-structure. According to the lattice type and the melting temperature of the sample materials, the influence of the deformation temperature on the substructure evolution of tungsten is small, while in Inconel 718 the influence of dynamic recovery increases and, finally, dynamic recrystallisation take place.

[1] Ostwaldt, D., Pantleon, W., Klimanek, P.: *Materialwiss. und Werkstofftechnik* **27** (1996), pp. 417 - 425.

[2] Krivoglaz, M. A.: Theory of X – ray diffraction by nonideal crystals. Springer, Berlin 1996.

[3] Breuer, D., Klimanek, P., Pantleon, W.: *J. Appl. Cryst.* **33** (2000) pp. 1284-1294.

[4] Randle, V.: Microtexture Determination and its applications, The Institute of Materials, London 1992.

[5] Masimov, M., Klimanek, P. Motylenko, M.: Submitted to Scripta Mater.

T2 - P29

SYNCHROTRON X-RAY STUDIES OF DISLOCATION POLYGONISATION IN THE $LaNi_{5-X}Sn_XH_Y$ SYSTEM

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The hydriding of many intermetallic alloys can lead to the formation of an extended dislocation network, creating microstructural features that can determine vital functions such as the loss of recoverable hydrogen capacity (RHC) with cycling. Traditional AB_5 hydrides such as $LaNi_5$ or $CaNi_5$ suffer a loss of RHC with cycling [1] that renders them ineffective for example as battery or fuel cell materials. The parent $LaNi_5H_x$ system displays very strong anisotropic line broadening [2] as a result of the creation of a super polygonised a/3= E2 wall network [3] with a density in the order of 10^{12} /cm^2 [4,5], that persists in part above 500 °C [6]. It is now recognised that the production of intermediate AB_5H_x (typically 0.9<x<4.9) phases plays an important role in the production of free metallic *fcc* Ni and the loss of RHC. In-situ *intrinsic* neutron diffraction ageing experiments [7] reveal that the intermediate phase

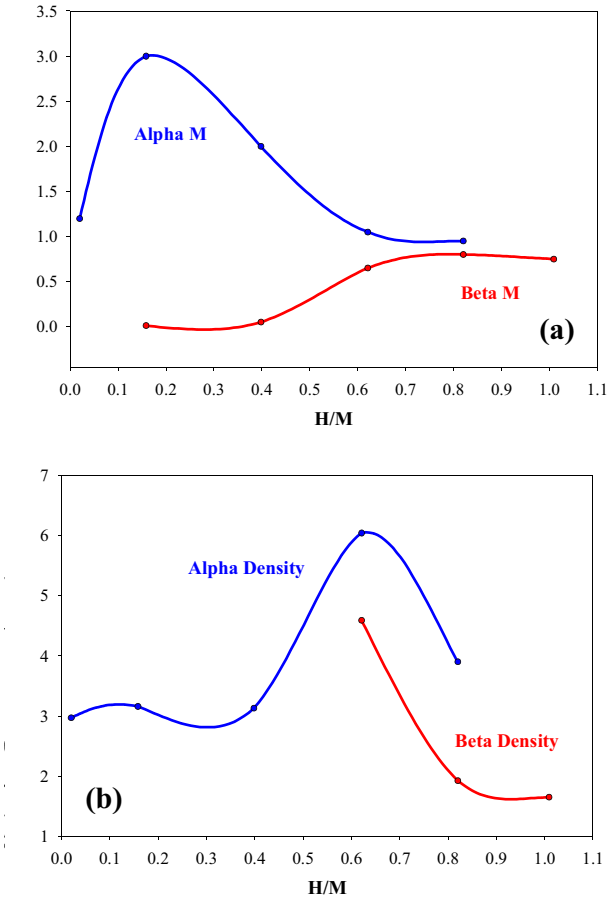

Fig. 1. Variation of *M* parameter (a) and dislocation density (b) in the and phase along the absorption isotherm of the $LaNi_{4.8}Sn_{0.2}$ system, at 40şC during cycle 5.

in the $LaNi_5$ system displays a dislocation free morphology that plasticises upon desorption with rapid attendant E2 dislocation formation. Indeed, this intrinsic behaviour emulates *extrinsic* cycling behavior observed in substituted AB_5 systems. With substitution, such alloys can initially display a reversal in dislocation content, with large a/3= E1 basal core densities, in preference to E2 types. However, with cycling, high E1 alloys eventually display a strong change in line broadening, from isotropic to anisotropic, demonstrating E2 production with cycling [8].

Substitution of Sn for Ni in the $LaNi_{5-x}Sn_xH_y$ system strongly reduces the anisotropic line broadening [9], demonstrating the removal of prismatic E2 cores. The avoidance of E2 dislocation formation corresponds to a greatly extended cycle life, and apparently also inhibits the formation of any intermediate phases [9], making $LaNi_{5-x}Sn_xH_y$ (in contrast to $LaNi_5H_x$) powders viable candidates for cryo-cooler space applications [10].

To understand the process of removal of the strongly plasticised super E2 network, Sn = 0.0, 0.1 and 0.2 samples have been studied in-situ using the high resolution powder diffractometer at the Swiss-Norwegian Beam Line (SNBL) at the ESRF. Twelve different de-hydrided samples have also been studied to evaluate the optimal preparation technique of the alloy.

To analyse the dislocation content, a variation of the Krivoglaz [11]/Wilkens [12] models has been implemented in the Australian diffraction code Rietica [13]. Line broadening analysis of all Sn=0.0, 0.1, 0.2 contents reveals an interesting feature. Fig. 1 (a) shows that the characteristic *M* dislocation distribution parameter [12, 13] for E2 cores can reduce to near zero magnitudes, corresponding to the disappearance of any gaussian broadening component. With the analysis technique of fitting a Voigt function, such low *M* values render the calculation of a dislocation density intractable (see the cut off in estimated density in Fig. 1 (b)) with the current restrictedly random model of Wilkens for individual edge and screw dislocations.

In physical terms, the gaussian component going to zero indicates a different dislocation morphology, with the cases of dipoles [14] or walls [15] both displaying a lorentzian-only type of broadening. Efforts are currently under way to implement both wall and dipole models in Rietica, to allow the modelling of mixtures of such cases, and to further investigate the correlative limits of mixed modelling within the Voigtian lineshape.

[1] P. D. Goodell, *J. Less-Common Met.*, 99 (1984) 1.

[2] A. Percheron-Guégan, C. Lartigue, J.C. Achard, P. Germi and F. Tasset, *J. Less-Common Met.,* 74 (1980) 1.3] G. Kim, C. Chun, S. Lee and J. Lee, *Acta Metall. Mater.*, 42(9) (1994) 3157.

[4] E. Wu, E.H. Kisi and E.MacA. Gray, *J. Appl. Cryst.*, 31 (1998) 363.

[5] R. Cerny, J.-M. Joubert, M. Latroche, A. Percheron-Guégan and K. Yvon, *J. Appl. Cryst.*, 33 (2000) 997.

[6] E.H. Kisi, E. Wu and M. Kemali, *J. Alloys Comp.*, 330-332 (2002) 202.

[7] M.P. Pitt, PhD thesis, Griffith University, 2003.

[8] Y. Nakamura, K. Sato, S. Fujitani, K. Nishio, K. Oguro and I. Uehara, *J. Alloys Comp.*, 267 (1998) 205.

[9] S. Luo, J.D. Clewley, T.B. Flanagan, R.C. Bowman Jr. and J.S. Cantrell, *J. Alloys Comp.*, 253-254 (1997) 226.

[10] B.D. Freeman, E.L. Ryba, R.C. Bowman Jr and J.R. Phillips, *Int. J. Hyd. Energy*, 22(12) (1997) 1125.

[11] M.A. Krivoglaz and K.P. Ryaboshapka, *Fiz. Metal. Metalloved.*, 15(1) (1963) 18.

[12] M. Wilkens, *Acta Metall.*, 17 (1969) 1155.

[13] E. Wu, E.MacA. Gray and E.H. Kisi, *J. Appl. Cryst.*, 31 (1998) 356.

[14] V.V. Pototskaya and K.P. Ryaboshapka, *Metallofizika.*, 24 (1968) 97.

[15] M.A. Krivoglaz, K.P. Ryaboshapka and R.I. Barabash, *Fiz. Metal. Metalloved.*, 30(6) (1970) 1134.

T2 - P30

AN X-RAY DIFFRACTION STUDY ON DISLOCATION MICROSTRUCTURE OF AS-PREPARED Al-Al_2O_3 COMPOSITES

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Particle reinforced metal-matrix composites of Al - -Al_2O_3 were prepared in the powder metallurgy route with 20, 50 and 75wt% of aluminium powder. The differences in thermal expansion coefficients and elastic constants of the two phases lead to volume misfit, residual stress & elastic distortion and for too large misfits, lead to plastic deformation. Wide-angle X-ray powder diffraction is a powerful non-destructive method for determining simultaneously the long-range residual stress and dislocation density. Here diffraction profile at any diffraction angle can be described as:

$$Y_c(2\ ) \quad [B\ \ (I_s\ \ I_A)](2\ ) \quad Bgk \ (1)$$

Following the present-day-state-of-art, the line profile analysis of the composites was done in the Whole-Pattern Fitting procedure based on the Rietveld structure refinement codes. It also incorporates the microstructure refinement codes based on either phenomenological parameters (viz. coherent domain size, microstrain) [1] or physically based model parameters (viz. dislocation density, dislocation arrangement parameters, crystal/grain size and related parameters) [2]. Here the microstructures of -Al_2O_3 containing Al-based composites were studied in terms of ab-initio quasi-composite model of dislocation cell structure [3] and ellipsoidal log-normal distribution of crystallite size. It was observed that the postproduction plastic deformation of the Al grains and hence stress relaxation of the composites have taken place during cooling from the sintering temperature (500 ^oC). It was also noticed that in the composites with lower concentration of Al, each reflection of Al could be fitted with two peaks having different widths indicating dissimilar fragments with different dislocation density and arrangements. -Al_2O_3, present in the composites, affects dislocation motion during stress relaxation at room temperature and may produce such a dislocation sub-structure. The region of high (~ 8 x 10^9 cm^{-2}) [Al(2)] and low (~ 2 x 10^9 cm^{-2}) [Al(1)] dislocation density (Table 1) has been characterized as cell walls and cell interiors respectively with compressive and tensile stresses respectively in accordance with the quasi-composite model. However, for Al_2O_3-75 wt% Al, the two –peak structure of Al reflection could not be well established. The results are in gross agreement with TEM studies [4].

[1] L. Lutterotti, P. Scardi, P. Maistrelli, *J. Appl. Cryst.* 25 (1992) 4597.

[2] R. Ribarik, T. Ungar, J. Gubicza, *J. Appl. Cryst.* 34 (2001) 669.

[3] H. Mughrabi, *Acta metall.* 31 (1983) 1367.

[4] C. Y. Barlow, N. Hansen, Y. L.Lin, *Acta Mater.* 50 (2002) 171.

Table 1

	Al_2O_3 - 20 wt % Al		Al_2O_3 - 50 wt % Al		Al_2O_3 - 75 wt % Al
	Al(1)	Al(2)	Al(1)	Al(2)	
m(Å)	1584	783	2805	618*	2847
	0.007	0.47	0.05	0.65	0.018
	0.88	0.41	0.45	----	0.507
d(Å)	1188	1284	2113	2005	2138
L_0(Å)	1056	913	1875	1173	1900
(10^9cm^{-2})	1.80	7.60	2.30	8.60	7.70
M	0.78	>>1	>>1	>>1	1.80

* Spherical Crystal Model

m = Median of distribution, **s** = Variance of distribution, **e** = Ellipticity, **D** = Volume-weighted column length; **L0** =Area-weighted column length (at L= 0), **r** = Dislocation density, **M** = Arrangement parameter

T2 - P31

CRYSTALLINE MICROSTRUCTURE OF SEPIOLITE INFLUENCED BY GRINDING

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A reference sample of sepiolite and products of its comminution by dry grinding were studied through X-ray diffraction pattern analysis and complementary field emission electron microscope images and surface area measurements. The specimen of the Two Crows sepiolite, which is a rather pure sepiolite mineral [1] considered as a useful standard in comparing sepiolites from different sources [2], were obtained from the Source Clay Minerals Collection of the Clay Minerals Society. An experiment of mechanical comminution was performed by using a laboratory vibrating cup mill with the agate grinding set (disk and ring) working at 1500 rotations per minute. Small granules (of size less than 2mm) of the reference sample were obtained by knife cutting and then the 15g samples were treated by dry grinding during 3, 6, 12, 24, 36, 48 and 60 seconds. The powder was pressed into tablets which were investigated in an X-ray diffractometer with a copper anode, a graphite monochromator and the sample holder spinning. The X-ray diffraction patterns were recorded by step scanning with the 0.02ş diffraction angle step. The model of the crystalline structure of sepiolite proposed in [3], confirmed by the electron diffraction structure study [4] and by the results of [5], was applied in the microstructure study. The chemical formula of half-unit cell (without substitutions) is $Si_{12}Mg_8(OH)_4O_{30}(H_2O)_4.8H_2O$ and the space group is orthorhombic *Pncn* (52) with the unit cell parameters a =13.46 Å, b = 26.88 Å, c = 5.281 Å (according to the 26-1226 file of the ICDD PDF2 database). The model of polycrystal, developed recently in [6,7,8], was applied for determining the crystalline microstructure through interpreting the X-ray diffraction data. Due to strong overlapping of most peaks only four of them (110, 060, 131, 260), which could be uniquely indexed, were selected to perform the study. The polycrystalline powder was interpreted as a system of crystallites of the same shape and characterised by the volume-weighted crystallite size distribution and the second-order crystalline lattice strain distribution together with the shape parameters. Since in polycrystalline materials the internal stresses are concentrated at the high-angle boundaries of crystalline grains and at the low-angle boundaries of crystallites, the crystallites can be treated as homogeneously strained with respect to a perfect lattice of average unit cell parameters. Hence the crystallites are considered as being crystalline domains of perfect lattice of the unit cell parameters slightly different to each other (i.e. the domains scattering X-rays coherently). The second-order strain is interpreted as the dispersion of the crystallite lattice parameters with respect to the average magnitudes. Another defects of crystalline lattice are neglected. In the computations the crystallites were modelled as spheres, cylinders or rectangular prisms. The characteristics of the crystalline microstructure were computed to achieve the best possible approximation of X-ray diffraction patterns, simulated for model polycrystal, to the measured ones. A parallelepiped of edges parallel to principal crystalline axes (of different edge length ratios for different samples) was found as the most probable model of crystallites in all samples. The volume-weighted crystallite size distributions, determined after the X-ray diffraction data (without any assumption about their shapes), occurred very close to the logarithmic-normal distributions of the same ratio of the standard deviation to the mean value. The second-order strain distributions, determined after the data, occurred very close to the functions $f(x) = \max\{0,[1-(x/a)^2]^m\}$ of different parameters. In each case one could with good accuracy represent all distributions by one function, by introducing a dimensionless variable (actual-to-mean-size ratio for sizes and actual-to-mean-absolute-strain ratio for strains). The average microstructure characteristics, calculated after the size distributions and the strain distributions, for all samples studied are shown in the table. The volume-weighted mean crystallite is a parallelepiped of edges *A*, *B*, *C* parallel to principal axes [100], [010], [001], of aspect ratios $F = C/A$, $G = C/B$ and of standardised size $H =$

T [s]	A [Å]	B [Å]	C [Å]	F	G	H [Å]	S	E	Z
3	94	228	1332	2.4	14.0	306	0.50	0.0035	0.66
6	107	200	225	1.9	2.1	169	0.51	0.0034	0.67
12	112	192	215	1.7	1.9	167	0.52	0.0037	0.69
24	117	172	205	1.5	1.8	161	0.50	0.0039	0.72
36	95	157	174	1.7	1.8	137	0.54	0.0043	0.68
48	80	142	143	1.8	1.8	117	0.54	0.0048	0.68
60	64	119	153	1.9	2.4	105	0.52	0.0062	0.65

$(ABC)^{1/3}$; S is the ratio of the standard deviation to the mean size for a volume-weighted crystallite size distribution; E is the mean-absolute second-order strain; Z is the ratio of the standard deviation to the mean-absolute strain for a second-order crystalline lattice strain distribution; T is the grinding time.

The mean crystallite sizes determined via the X- ray diffraction are in agreement with those estimated on the scanning electron microscope images. The sepiolite aggregates consist of lath-shaped agglutinations of prisms and pinacoids elongated along 001 , each lath including several crystallites in that direction. The surface area magnitudes measured by BET method are in good agreement with those calculated after the results of X-ray diffraction study by taking into account both the crystallite shape and the size distribution and are in the range of previous experimental measurements of other sepiolites. The evolution of crystalline microstructure with the grinding time is evident: the longer the time the smaller the crystallites and the larger the strains. Moreover the crystallites, in the reference material elongated in direction [001], crack into short pieces in a consequence of grinding.

[1] J.L. Post, (1978): Sepiolite deposits of the Las Vegas, Nevada area. Clays Clay Min., 26, 1, 58-64.

[2] J.L. Post , N.C. Janke (1984): Ballarat sepiolite, Inyo County, California; in A. Singer and E. Galán, (Editors). Palygorskite- Sepiolite. Occurrences, Genesis and Uses. Developments in Sedimentology, Nr. 37, 159-169. Elsevier, Amsterdam, 352 pp.

[3] K. Brauner, A. Preisinger (1956): Struktur und Entstehung des sepioliths; Tsch. Mineral. Petrogr. Mitt. 6, 120-140.

[4] M. Rautureau (1974): Analyse structuralle de la sepiolite par microdiffraction electronique. These. Université d´Orleans, 89 pp.

[5] E. Galán, I. Carretero (1999): A new approach to compositional limits for sepiolite and palygorskite; Clays Clay Miner., 47, 4, 399-409.

[6] M. A. Kojdecki, W. Mielcarek (2000): Dependence of sizes and shapes of crystallites in zinc oxide powder on annealing temperature; Materials Science Forum, 321-324, 1040-1045.

[7] M.A. Kojdecki, J. Bastida, F. J. Serrano, J.V. Clausell (2001): Sizes and shapes of crystallites in mullites produced by thermal treatment of kaolin-alumina mixture; Materials Science Forum, 378-381, 747-752.

[8] M.A. Kojdecki (2004): Approximate estimation of contributions to pure X-ray diffraction line profiles from crystallite shapes, sizes and strains by analysing peak widths; Materials Science Forum, 443-444, 107-110.

T2 - P32

MICROSTRUCTURE OF CRYSTALLINE PHASES IN ELECTROTECHNICAL PORCELAINS

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Two types of porcelain insulators are mostly used, the silica and alumina porcelains [1,2]. In the silica porcelain high temperatures or long firing time leads to a reduction of the solid quartz content in the ceramic body because of the melting of quartz grains. This reduction causes the decrease of the mechanical strength of the porcelain because the differences between thermal expansion corresponding to quartz grains and the surrounding liquid phase result in a mechanical stress, which can produce microcracks in the porcelain. Intense changes of piece temperature can lead to increasing the already existing microcracks, causing reduction of mechanical strength under load. In the alumina porcelains the major portion of quartz is replaced by aluminium oxide. This leads to the increase of the mechanical strength (related to smaller number of microcracks). During the sintering process mullite and corundum are formed and the porcelain is obtained with high content of the glass phase that leads to non-porosity without the melting of the aluminium oxide grains (thus, high temperature or long time of firing do not affect the mechanical strength). The alumina porcelains are insensitive to temperature changes and their mechanical strength is mainly controlled by the quantity of corundum (and not by the amount of mullite as in silica porcelains) [1,2]. In the previous work [3] a comparative study of the silica and alumina porcelain insulators was performed. The samples of commercial porcelains were analysed by the X-ray powder diffraction methods to find their mineralogical and chemical compositions which were related with their thermomechanical properties. The aim of the present work is to complete that study by analysing the crystalline microstructure by the X-ray powder diffraction to reveal relation between the microstructure and the macroscopic properties of porcelains. The analysis was performed on commercial samples (of different formulae of raw materials) of the silica and alumina porcelain insulators obtained at 1300 C, with the same time of firing. The study was carried out on mullite, corundum and quartz. The porcelain

		Corundum			Quartz			Mullite		
Sample	S(MPa)	*C*(%)	*Z*(Å)	*E*	*C*(%)	Z(Å)	*E*	*C*(%)	Z(Å)	*E*
S1	125	33.2	945	0.00039	12.1	1502	0.00074	3.3	587	0.00058
S2	131	34.2	1065	0.00041	10.8	907	0.00042	4.0	682	0.00073
S3	144	35.3	1161	0.00036	8.5	648	0.00043	5.0	584	0.00068
S4	147	34.9	917	0.00040	8.4	1345	0.00067	5.8	666	0.00060
S5	103	8.8	881	0.00039	23.0	689	0.00060	5.4	656	0.00063
S6	98	8.9	1132	0.00044	23.8	779	0.00049	5.9	611	0.00052
S7	99	8.5	1221	0.00036	22.6	712	0.00059	5.1	938	0.00081

samples finely crushed were split using a rotatory splitter and grounded in an agate mortar and pestle. The samples of dried material were pressed into standard tablets. The powder diffraction patterns were recorded at room temperature (22 ± 2 C) with a diffractometer in step-scanning mode, using CuK radiation obtained with a secondary graphite monochromator. The diffraction patterns of the samples were recorded over the range 5 - 90) with the scanning step of 0.02 (2). The standard line profiles for correcting the instrumental line broadening were obtained from the diffraction pattern of the standard reference material LaB_6 (SRM 660a), and registered between 20 and 131 (2) using variable steps. The pure line profiles were computed through regularised deconvolution from pairs of groups of overlapped experimental line profiles and corresponding standard line profiles; being symmetric and overlapped much less than the experimental peaks they were separated by modelling them as Pearson VII type curves. The strongest pure line profile from each principal crystalline phase were selected for further analysis. The model of polycrystal, developed recently in [6], was applied for determining the crystalline microstructure through interpreting the X-ray diffraction data. The polycrystalline powder was interpreted as a system of crystallites of the same shape and characterised by the volume-weighted crystallite size distribution and the second-order crystalline lattice strain distribution together with the shape parameters. Since in polycrystalline materials the internal stresses are concentrated at the high-angle boundaries of crystalline grains and on the low-angle boundaries of crystallites, the crystallites can be treated as homogeneously strained with respect to a perfect lattice of average unit cell parameters. Hence the crystallites are considered as being crystalline domains of perfect lattice of the unit cell parameters slightly different to each other (i.e. the domains scattering X-rays coherently). The second-order strain is interpreted as the dispersion of the crystallite lattice parameters with respect to the average magnitudes. Another defects of crystalline lattice are neglected. In the computations the crystallites were modelled as spheres, cylinders or rectangular prisms (in orthorhombic mullite) and hexagonal prisms (in hexagonal corundum and quartz). The characteristics of the crystalline microstructure were computed to achieve the best possible approximation of X-ray diffraction patterns, simulated for model polycrystal, to the measured ones. As the most probable model of crystallites there were found in all samples parallelepiped in mullite, hexagonal prism in quartz and sphere in corundum. The volume-weighted crystallite size distributions, determined after the X-ray diffraction data (without any assumption about their shapes), occurred very close to the logarithmic-normal distributions in quartz and to the bimodal logarithmic-normal ones (i.e. the sums of two logarithmic-normal) in mullite and corundum. This bimodality of size distribution can be interpreted as the result of formation of secondary mullite at the high temperature of firing. The average microstructure characteristics, calculated for the three principal phases after the size distributions and the strain distributions, are shown in the table. The volume-weighted mean crystallite is characterised by standardised size *Z* equal to cubic root of its volume; *E* is the mean-absolute second-order strain; *S* is the flexural strength and *C* is the weight content of each mineral phase in a sample; some correlations between *C* and *S*, *Z*, *E* can be noted.

[1] Liebermann J., The standard and trend for alumina porcelain insulators, Cfi-Ceramic Forum International, 2000, 77(6), 17-23.

[2] Liebermann J., Reliability of materials for high voltage insulators, American Ceramic Society Bulletin, 2000, 79(5), 55-58.

[3] Amigó J.M., Clausell J.V., Esteve V., Delgado J.M., Reventós M.M., Ochando L.E., Debaerdemaeker T., Martí F., X-ray powder diffraction phase analysis and thermomechanical properties of silica and alumina porcelains, Journal of the European Ceramic Society, 2004, 24, 75-81.

[4] M. A. Kojdecki, W. Mielcarek (2000): Dependence of sizes and shapes of crystallites in zinc oxide powder on annealing temperature; Materials Science Forum, 321-324, 1040-1045.

[5] M.A. Kojdecki, J. Bastida, F. J. Serrano, J.V. Clausell (2001): Sizes and shapes of crystallites in mullites produced by thermal treatment of kaolin-alumina mixture; Materials Science Forum, 378-381, 747-752.

[6] M.A. Kojdecki (2004): Approximate estimation of contributions to pure X-ray diffraction line profiles from crystallite shapes, sizes and strains by analysing peak widths; Materials Science Forum, 443-444, 107-110.

T2 - P33

ANALYSIS OF POLYDISPERSE BALL-MILLED FLUORITE POWDERS USING A FULL PATTERN TECHNIQUE

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X-ray powder diffraction is particularly suited to the analysis of nanocrystalline materials. Both structural and microstructural information can nowadays be obtained simultaneously by full pattern processing techniques.

Among those, Whole Powder Pattern Modelling (WPPM) outperform most traditional Line Profile Analysis (LPA) techniques by giving a direct interpretation of the diffraction pattern in terms of physical microstructural models. In the present work we illustrate a recent evolution of the WPPM approach, allowing the refinement of a general domain-size distribution, not related to any a priori fixed analytical profile or size distribution shape. Besides the description of the new algorithm we show the results of the analysis of ball milled synthetic fluorite powders. The new WPPM procedure provides a detailed information on the evolution of the grinding process with time: the decrease and change of shape of the grain size distribution with the milling time is accompanied by a steady increase in defect content. The increased defectivity is shown to be a main responsible for the higher reactivity and therefore for the high dissolution rates shown by ball-milled fluorite powders.

Acknowledgement
This work was supported by the basic research funds of the Italian Ministry of University and Research, PRIN 2003-2004 project "Mechanisms of surface interactions in mineral phases: kinetics of dissolution, of crystal growth and their modeling"

T2 - P34

CRYSTALLITE SIZE ANALYSIS IN THE RANGE OF 10-100 M FOR ORGANICS BY X-RAY DIFFRACTION

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Particle sizing problem arises in many fields of science, technology and material production. Methods based on X-ray diffraction lines broadening cover size interval of 10-1000 nm and are well documented. Larger crystallites demonstrate no line broadening and require alternative methods for size determination. Several techniques based on different physical principles are available for particle size analysis in microns range, for example, laser low angle light scattering, microscopy, electrozone sensing and others, all having their own advantages and limitations.

Since most of organic substances are obtained as polycrystalline powders X-ray diffraction method would be the ideal tool for size analysis. When crystallites are relatively large and a small volume of the sample is irradiated the diffraction pattern exhibits discrete spots instead of continuous diffraction lines. We base our approach on the linear correlation between average crystallite's size and diffraction spots dimensions which is valid for crystallite size above 5 m.

T2 - P35

INCREASING THE INFORMATION CONTENT OF DIFFRACTION PATTERN AS A RESULT OF INDIVIDUAL PROFILE ANALYSIS

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Many key materials in modern technology possess the complex diffraction pattern due to overlapped diffraction peaks, which may arise due to various reasons. The most commonly encountered sources are low symmetry of the studied phases. A further source of overlapped lines is various physico-chemical processes proceeding at thermal or mechanical processing of materials. The most complex case when handling diffraction pattern is the so-called phase separation that originates from changed environmental conditions.

The further development of the analytical method (the new iterative procedure for refinement of diffraction profile parameters [1]) has been carried out for extracting diffraction image on the individual components of the profiles.

Handling the silicides measuring data is performed in several steps using the CSD complex. The diffraction profile was described by pseudo-Voigt functions and the modeling of each individual peak was carried out. The examples of handling the diffraction pattern in the cases of the samples with cubic symmetry of the basic phase (when a set of phases with similar values of parameter of crystal lattice arises) are presented.

This study support partly within ISTC-Project.

[1] B.N. Kodess, I.P. Jouravlev, The 51st Annual Denver X-ray Conference, 29 July - 2 August 2002, D-031, p. 50.

T2 - P36

INVESTIGATION OF DECOMPOSITION OF THE PdB_y SOLID SOLUTION BY TIME-RESOLVED X-RAY POWDER DIFFRACTION

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The palladium-rich terminal solid solution PdB_y (*fcc* arrangement of Pd, B randomly occupies interstitial octahedral sites) shows an interstitial solubility of B up to approximately $PdB_{\sim 0.20}$ above about 450°C and two-phase areas as well as several low temperature phases at lower temperatures. A remarkable feature of the PdB_y solid solution is a miscibility gap with a critical temperature of T_{crit} = 410 °C (Figure 1) [1, 2] which covers at the monotectic temperature of T_{mono} = 312 °C a composition range of about $0.03 < y < 0.10$.

This work presents the results of X-ray powder diffraction investigations (CuK $_1$ radiation in Bragg-Brentano geometry and synchrotron radiation with = 1.1315 Å on the B2, HASYLAB, Hamburg) performed on initially homogeneous PdB_y alloys (y = 0.050, 0.065) which were first quenched from 800 °C (i.e. 'within' the single phase solid solution field) and then annealed at 340 °C and 355 °C, (i.e. 'within' the miscibility gap) for various periods of time. The decomposition of the solid solution into a boron-rich solid solution phase and a boron-poor solid solution phase is clearly visible due to the corresponding splitting of the Bragg reflections. However, even after the longest applied heat-treatment times (8 weeks at 340 °C and 2 weeks at 355 °C), still considerable diffraction-line broadening remains.

The diffraction-line profiles were fitted, applied to several reflections simultaneously, in a Rietveld like fashion [3], considering a convolution of several line-broadening contributions:

1. The instrumental line-broadening

2. A quasi-continuous composition distribution density function $p(y)$, which was approximated by a step-function between $y = 0$ and $y = 0.12$ with equal concentration intervals of y in the range of 0.0005 - 0.002 (value chosen depending on the resolution of the diffraction data), and adopting a Vegard's law behaviour for the lattice parameter of PdB_y [4]:

$a = 3.8920$ Å $+ 0.6882$ Å y

3. Anisotropic microstrain-broadening due to internal stresses according to Refs. [5, 6]

The use of small step sizes for $p(y)$ leads to strong correlations between the $p(y)$ values of adjoining compositions y‘ y, y‘, y‘+ y. This problem can be overcome by incorporating 'penalty functions' in the overall fitting procedure which add to the ^{2} value due to the deviation of the fitted from the observed profile. This penalty function in-

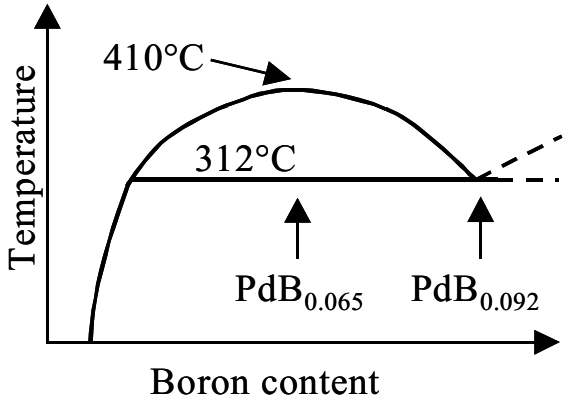

Figure 1: Section of the Pd-B phase diagram with the miscibility gap [8].

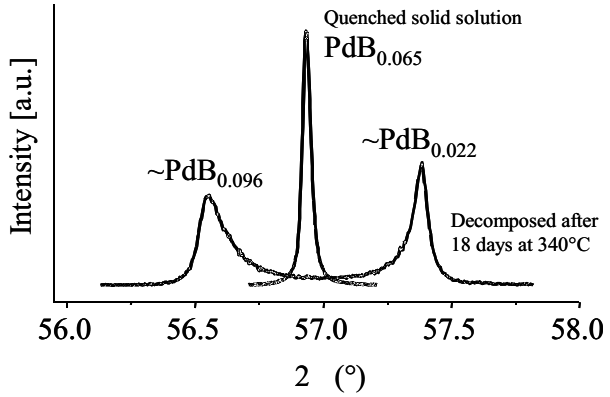

Figure 2: 311-Diffraction peak group (Pattern taken using synchrotron radiation with = 1.1315 Å).

creases with the square of the second derivative of $p(y)$ for each value of y; the second derivative is especially large if 'unnatural' fluctuations of $p(y)$ occur.

The diffraction-line broadening due to variation in composition as expressed by $p(y)$ also masks line broadening due to microstresses (e.g. due to dislocations). However, the latter contribution is clearly detectable due to its usually significant anisotropy (which derives from the Pd crystals intrinsic mechanical anisotropy) [5], whereas broadening due to composition variations is isotropic for cubic crystals [7].

The time-dependent changes of $p(y)$ can be summarised as follows:

i. For short annealing times a distinct boron-rich phase (relative to the initial solid solution's composition) and a distinct boron-poor phase appear, whereas the solid solution of the original composition is still present. The compositions of the product phases are closer to the initial composition than predicted by the phase diagram.

ii. The fraction of the original phase decreases (and finally disappears) and the two product phases increase with annealing time. Simultaneously, the compositions of the product phases 'move' towards the respective equilibrium values.

iii. Upon increasing annealing times an apparently stable composition distribution $p(y)$ is reached, which however, does not correspond to the sum of two delta functions located at the two boundary compositions of the miscibility gap at the annealing temperature. Instead, an apparent probability for intermediate concentrations occurs in the form of 'tails' connected with the two maxima of $p(y)$ towards intermediate y (see Fig 2).

1. R. A. Alqasmi, H. Brodowsky, H.-J. Schaller, *Z. Metallkd.* 73 (1982) 331.
2. M. Beck, E. J. Mittemeijer, *Z. Metallkd.* 92 (2001) 1271.
3. TOPAS, General Profile and Structure Analysis Software for Powder Diffraction Data, V2.0, Bruker AXS GmbH, Karlsruhe, Germany.
4. M. Beck, M. Ellner, E. J. Mittemeijer, *Acta Mater.* 49 (2001) 985.
5. A. R. Stokes, A. J. C. Wilson, *Proc. Phys. Soc.* 56 (1944) 174.
6. P. W. Stephens, *J. Appl. Crystallogr.* 32 (1999) 281.
7. A. Leineweber, E. J. Mittemeijer, *J. Appl. Crystallogr.* 37 (2004) 123.
8. P. K. Liao, K. E. Spear, M. E. Schlesinger, *J. Phase Equilib*. 17, (1996) 340.

T2 - P37

'-Fe_4N FORMATION UPON ANNEALING -Fe_3N: A POWDER DIFFRACTION STUDY USING SYNCHROTRON RADIATION

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The investigation of iron nitrides is largely motivated due to their role in metallurgy and also their possible potential as magnetic recording materials. The most important iron nitride phases are -FeN_y (y = 0.22-0.49) and '-Fe_4N. The crystal structure of -FeN_y is based on a hcp arrangement of Fe whereas in '-Fe_4N the arrangement of Fe is fcc. In both cases N occupies octahedral interstitial sites. Most studies on iron nitrides were performed on compound layers generated on the surfaces of iron or steel. The iron nitrides in such layers contain strong nitrogen concentration gradients caused by the inward diffusion of nitrogen during nitriding.

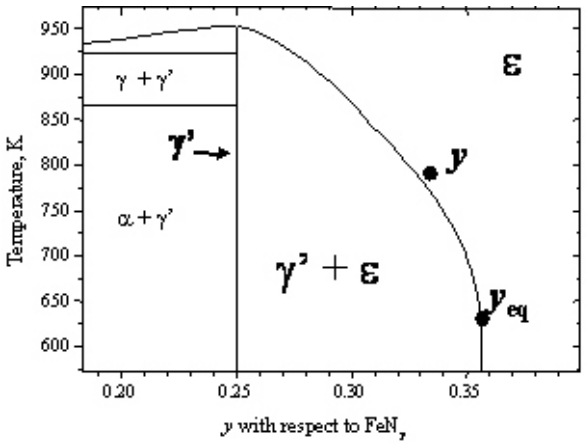

Figure 1. Simplified section of the Fe-N phase diagram. y is the concentration of the initial phase after nitriding, and y_{eq} is the concentration of the phase in equilibrium with the precipitated ' at the applied annealing temperature.

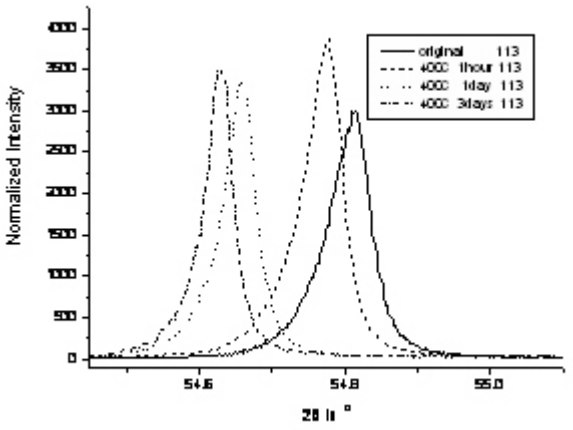

Figure 2. 113 reflection of -FeN_y as obtained by powder diffraction using synchrotron radiation: original sample (after nitriding) and sample annealed at 673 K for 1 hour, 1 and 3 days, respectively. The shifts of the reflections are mainly caused by an increase in nitrogen content.

Homogeneous iron nitrides can be prepared e.g. by nitriding of thin iron foils or powders for moderate times. Such iron nitride powders are well suited for structural analysis by powder diffraction methods. X-ray powder diffraction is able to determine quantitatively very small changes in composition [1] and the presence of compositional inhomogeneities [2].

Previous experiments on the behaviour of -iron nitride powders upon annealing showed [3] that at 350°C -$FeN_{0.33}$ forms precipitates of '-Fe_4N, which leads to an enrichment of the remaining -phase with nitrogen (final composition $FeN_{0.36}$), in accordance with the phase diagram (Figure 1) and as also observed for bulk specimens [4]. However, details of the transformation mechanism are unknown at present.

In this paper high resolution powder diffraction data obtained using synchrotron radiation (B2 at HASYLAB, Hamburg, = 1.13985 Å) on original and heat treated (up to 3 d at 360°C and 400°C, respectively) $FeN_{0.33}$ powder (particle size 2-5 m) are presented. The data reveal with increasing annealing time the formation of '-Fe_4N and a gradual increase of the N content in -FeN_y, as evidenced by the emergence of reflections of '-Fe_4N and shifts of the reflections of the present -FeN_y (Figure 2). Furthermore, anisotropic and asymmetric diffraction-line broadening of the reflections was observed.

The narrowest reflections are observed for the sample annealed for 3 d at 400°C, in which apparently equilibrium between and ' has been reached already.

An analysis of the dependence on the directions of the diffraction vector of the broadening and the asymmetry of the reflections of the different samples shows an important contribution due to inhomogeneities (local variations in the N content [4]). These inhomogeneities can be reduced by further annealing leading to their virtual disappearance after 3 d at 400°C.

Transmission electron microscopy performed on the powder particles (Figure 3) reveals that '-Fe_4N grains are formed only in relatively few powder particles. These observations together with the finding the narrow reflections in the powder diffraction patterns taken after long-term annealing exclude the presence of large local composition variations (e.g. from particle to particle), it can be concluded that the nitrogen atoms can move from powder particle to powder particle. This can only occur via direct contact of the mainly spherical particles, since N transport via the gas phase can be excluded: loss of N_2 to the atmosphere is well known to be fully irreversible [5].

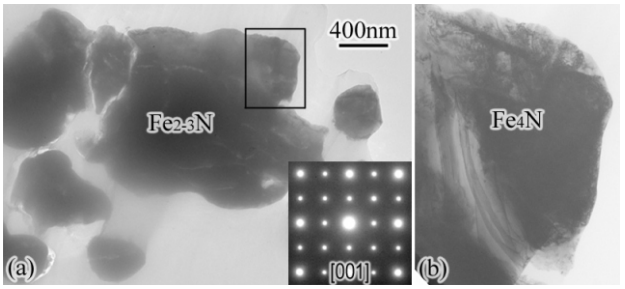

Figure 3. (a) Bright field image of some particles in an -FeN_y + '-Fe_4N sample. Inset is an '-Fe_4N diffraction pattern ([001] zone) of the top right area of the central $Fe_{2-3}N$ (FeN_y) particle. (b) The Fe_4N grain outlined in (a).

1. T. Liapina, A. Leineweber, E. J. Mittemeijer, W. Kockelmann, *Acta Mater.* 52 (2004) 173-180.
2. A. Leineweber, E.J. Mittemeijer, *J. Appl. Crystallogr.* 37 (2004) 123-135.
3. A. Leineweber, PhD thesis, University of Dortmund (1999).
4. T. Liapina, A. Leineweber, E.J. Mittemeijer, *Scr. Mater.* 48 (2003) 1643-1648.
5. E. Lehrer, *Z. Elektrochem.* 36 (1930) 383-392.

T2 - P38

WHOLE DIFFRACTION PATTERN-FITTING OF POLYCRYSTALLINE HEXAGONAL MgB_2 SUPERCONDUCTOR

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The recent discovery of the 39K superconductivity in MgB_2 by Akimitsu and co-workers has attracted the attention of numerous researchers. We have prepared polycrystalline MgB_2 superconductor from low-pressure synthesis route [1]. As the microstructure and crystalline defects highly influences the superconductivity property it is interesting to study the detail microstructure of the prepared sample.

X-ray diffraction line profile from a polycrystalline sample gets broaden due the instrumental broadening, lattice defects (especially line or plane defects) and finite size of coherent diffraction domains. Therefore, the characteristic broadening of the diffraction profile from a polycrystalline sample contains a lot of information about the microstructure of the sample. We have analyzed the X-ray diffraction profile of the prepared polycrystalline MgB_2 superconductor to extract the microstructural information of the sample. The complete diffraction profile of the sample is modelled with pseudo-voigt function using the program MarqX [2]. The program permits simultaneous refinement of the lattice parameters as well as several parameters related to microstructure and lattice defects responsible for line broadening effects. The contribution of the instrumental broadening effect is also incorporated in the program. The refined parameters and quality of the fitting (R values) are shown in table 1. The volume weighted domain size and microstrain are obtained from the Williamson-Hall (WH) plot. The WH plot and the corresponding results are shown in Figure 1. We have also carried out Warren-Averbach (WA) analysis on the diffraction profile. The size coefficient obtained from the WA analysis is plotted against the Fourier length L and the surface weighted domain size is found out from the initial slope of the curve. The value of the dislocation density is found to be 5.9 10^{14}.Thus it is found that the low-pressure synthesis route for preparing MgB_2 generated dislocations, which entangled among themselves to create domains or grains.

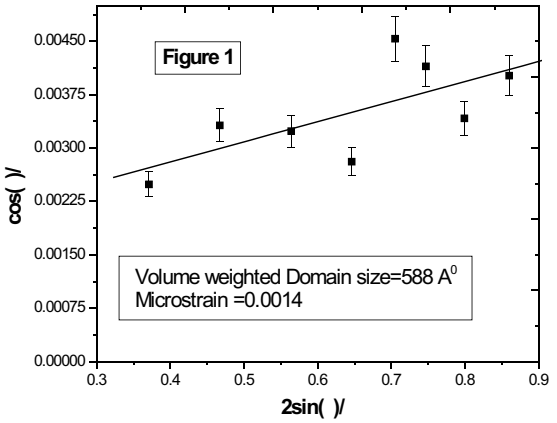

Table 1

	Refined values	Standard uncertainity
Lattice parameters		
a,b (Å)	3.0566	0.0003
c (Å)	3.5004	0.0005
, ( )	90.001	0.004
( )	119.921	0.005
Modelling indices		
R_{wp}	26.29%	
R_{exp}	19.59%	
GoF	1.34	

The lattice strain with in the domains is found to be very small.

[1] A. Talapatra, S. K. Bandyopadhyay, Pintu Sen, A. Sarkar, P. Barat, *Communicated to Bulletin of Materials Science.*

[2] Y. H. Dong, P. Scardi, *J. Appl. Cryst.* 33 (2000) 184.

T2 - P39

OBSERVATION OF X-RAY PEAK PROFILES FROM INDIVIDUAL BULK GRAINS

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An x-ray diffraction technique has been developed that enables observation of individual bulk grains with a reciprocal space resolution of the order of the characteristic length of dislocation structures. The technique employs high energy synchrotron radiation, area detectors, and a multi-grain indexing program for identification of individual grains in a polycrystal. It is applied to study the evolving dislocation structure within FCC metals under tensile deformation up to about 5%. Case studies include the measurement of axial strain components of several bulk grains as indication of the importance of grain-grain interactions [1], and reciprocal space maps of an individual aluminium grain. Currently attempts are made to follow a selected reflection during dynamic loading.

The presented technique is an extension of the 3-Dimensional X-ray Ray Diffraction method [2] to high reciprocal space resolution. The potential benefits are revealed by comparison to conventional macroscopic peak profile investigations. Firstly, the measurements are specific to each grain. As such, the amount of averaging over various spatial heterogeneities is substantially reduced. The importance of such variations can be judged by comparing results from different grains. Likewise, the macroscopic results are based on ensembles of grains with parallel reflecting lattice planes, but of different orientations around the lattice plane normals. Secondly, instead of measuring a few one-dimensional profiles, for each grain tens of 3D distributions are available, one for each reflection characterised. Hence, the information content in the data is substantially enhanced. This should allow for more reliable matching procedures to potentially more complex models, as well as for internal consistency checks, by comparing crystallographically equivalent entities.

The experiments were performed at the 1-ID-XOR beamline of the Advanced Photon Source (APS) at the Argonne National Laboratory. A narrow bandwidth beam ($E/E<10^{-4}$) of typically 35 keV was provided by a flat Si double crystal monochromator. An area detector is placed at large distance from the sample providing high reciprocal space resolution. A tension rig holding the sample is mounted on a 3-circle diffractometer. In addition a second large area detector was positioned closer to the sample but only one detector is used at a time. This detector sampled all low-index diffraction spots arising from all illuminated grains as input to the multi-grain indexing program GRAINDEX [3].

In a feasibility test, a fixed set of 20 reflections from a selected grain within an 1 mm thick Al sample were measured at tensile loads of 0.01%, 1%, 2.5%, and 4.5%.

The reciprocal space projection in Fig. 1 appear surprisingly smooth in radial direction, given the assumption that they are caused by a heterogeneous dislocation structure. However, they are integrated over one transversal q-direction, spanning several hundred times the instrumental resolution. For a discussion of the peak profiles see [4].

Acknowledgements
Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Basic Energy Science, Office of Science, under Contract No. W-31-109-Eng-38. BJ, HFP, and WP acknowledge the Danish National Research Foundation for supporting the Center of Fundamental Research: Metal Structures in Four Dimensions, as well as the Danish Research Council SNF for financial support via Dansync.

[1] Lienert, U., Han, T.-S., Almer, J., Dawson, P.R., Leffers, T., Margulies, L., Nielsen, S.F., Poulsen, H.F., and Schmidt, S. (2004) *Acta Mater.* (in press).

[2] Poulsen, H.F.,R Juul Jensen, D., and Vaughan, G.B.M. (2004) *MRS Bull.* **29**, 166-169.

[3] Lauridsen, E.M., Schmidt, S., Suter, R.M., and Poulsen, H.F. (2001) *J. Appl. Cryst.* **34**, 744-750.

[4] Pantleon, W., Lienert, U., Almer, J., and Poulsen, H.F. (2004) *Mater. Sci. Eng. A* (in press).

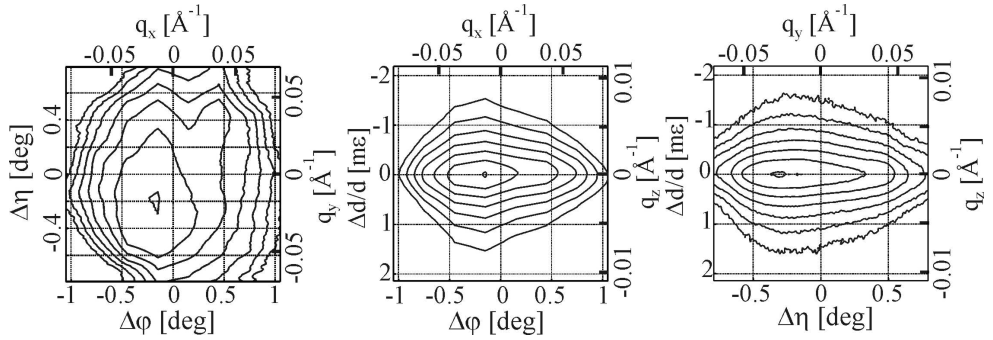

Fig 1. Reciprocal space projections for the -113 reflection of a single embedded Al grain at a strain of 2.5%. Contours are drawn at relative intensities of 0.955, 0.398, 0.158, 0.063, 0.025, 0.010, and 0.004

T2 - P40

MATERIALS PREPARED BY SEVERE PLASTIC DEFORMATION STUDIED BY X-RAY LINE PROFILE ANALYSIS

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Small-crystalline samples (about 100 nm) of simple metals (Cu, Fe, Mg) and semiconductors (Ge) prepared by a severe plastic deformation in UFA (Russia) [1] were studied using a conventional powder x-ray diffraction (XRD). Complex microstructure of such strongly deformed materials shows many interesting features [1] and makes physical interpretation of XRD measurements difficult. Broadening of XRD profiles is in this case caused mainly by microstrains induced by dislocations but also by small size of grains. In this work we focused in analysis of measured XRD data by traditional methods of line profile analysis (Williamson-Hall , Warren-Averbach plot) and progressive methods (such as the whole powder pattern modelling - WPPM [2-5]). Obtained conclusions can be compared with results of other techniques - a TEM and a positron annihilation spectroscopy. Besides, x-ray back scattering photos were acquired to qualitatively inspect homogeneity of grains sizes. Programs employing the WPPM approach developed by teams of P. Scardi (PM2000 [2-3]) and T. Ungar (MWM-fit[4-5]) were used. For calculation of dislocation contrast factors the program ANIZC [6] was used. We were able to separate size and deformation effects of line broadening, but we have problems with proper determination of a dislocation arrangement (connected with the so called cut-off radius parameter). To study thermal stability samples were subjected to an isochronal annealing and temperature dependence of grains size and dislocation density was examined. From x-ray measurements can be deduced, in agreement with other techniques, that during the annealing at higher temperatures an ultra fine microstructure of samples is essentially changing. All measurements were realised on common laboratory diffractometers and hence for some methods (Warren-Averbach analysis, program MWP-fit) diffraction data deconvolution was necessary. We tried many methods [7-9] and mostly we used a method of M. A. Kojdecki [7].

Acknowledgement
We thank our co-workers, mainly J. Cizek, for their investigations by other techniques and a group of R. K. Islamgaliev from Ufa, Russia for providing their samples. We would like to express our thanks to teams of T. Ungar and P. Scardi for providing their computer programs.

The research is supported by the Grant Agency of the Czech Republic (106/02/1521).

[1] R.Z.Valiev. R.K.Islamgaliev, I.V.Alexandrov, *Progress in Materials Science* 45 (2000) 103-189.

[2] P.Scardi, M.Leoni, *Acta Cryst.* A58 (2002) 190-200.

[3] P.Scardi, M.Leoni, Y.H.Dong, *Eur. Phys. J. B* 18 (2000) 23-30.

[4] G.Ribarik, T.Ungar, J.Gubicza, *J. Appl. Cryst.* 34 (2001) 669- 676.

[5] T.Ungar, J.Gubicza, G.Ribarik, A.Borbely, *J. Appl. Crys.* 34 (2001) 298-310.

[6] A.Borbely, J.Dragomir-Cernatescu, G.Ribarik, T.Ungar, *J. Appl. Cryst.* 36 (2003) 160-162.

[7] M.A.Kojdecki, *Mater. Sci. Forum* Vol. 378-381 (2001) 12-17.

[8] M.Cernansky, Restoration and preprocessing of physical profiles... in R.L.Snyder, J.Fiala & H.J.Bunge (eds.) *Defect and Microstructure Analysis by Diffraction*, Oxford 1999.

[9] W.H.Press, S.A.Teukolsky, W.T.Vetterling, B.P.Flannery, *Numerical Recipes in C. 2nd ed.*, Cambridge 1992.