



## B5 - Materials Science

### B5 - O1

# GRAIN-BY GRAIN MAPPING THE REAL STRUCTURE OF POLYCRYSTALLINE MATERIALS

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X-ray diffraction analysis of polycrystalline materials is usually performed using the Bragg-Brentano parafocusing diffractometer [1]. Millions or even billions of crystals are irradiated and diffract in such an arrangement. The collected diffraction pattern represents a superposition of the more or less overlapped diffractions of all these crystals. Therefore, it is a function of the large number of parameters describing the distribution of the size, shape, orientation and position of crystallites in the irradiated region of the analyzed sample. The number of these parameters by far exceeds the information content of such a diffraction pattern, i.e. the amount of information that can be acquired by its evaluation. And this is the main cause of all problems and the reason of the low efficiency of the x-ray diffraction analysis of the real structure („mesostructure“) of the polycrystalline materials as (when) executed in the usual way [2].

Much greater efficiency may be achieved by a topographic technique analysing resolved diffractions of individual crystals of the polycrystalline aggregate (grain-by-grain method). A narrow primary beam is used for this goal in order that the number of irradiated crystals is small [3,4]. And, the intensity of diffracted radiation is measured not only along a single curve of the reciprocal space, which is enough in case of the Bragg-Brentano parafocusing arrangement. The topographic technique requires mapping of two-dimensional areas of the reciprocal space. These are the tracts in which the plane surface of the area position sensitive detector applied intersects the conical surfaces of diffracted beams. And, it is through out these tracts, where the azimuthal distribution of the diffraction spots is determined [5,6].

The examination of the azimuthal diffraction line profile, i.e. the size, number and shape of individual diffraction spots that discontinuous diffraction line consists of, reveals useful information on the materials' structure which cannot be obtained by other techniques. Such an information can be to advantage used in the development and optimization of technological processes [7] as well as, in the monitoring of processes which degrade the materials structure in course of their service [8].

So we used the x-ray diffraction topography (grain-by-grain mapping) to the monitoring of changes in the internal structure of high-pressure turbine casings in the course of their long-term service. The casings serve for admission, line and outlet of expanding steam, being reckoned among the most exposed components of the stator part of turbines. Therefore, their microstructure changes throughout the continuance of service which results in the degradation of their mechanical properties. We have found that the azi-

muthal profile of the diffraction lines of casings, becomes really too much different during their many years' work. From these changes of the diffraction pattern we deduced e.g. that the crystallites of the iron matrix of a high-pressure turbine casing have grown in size from some 0.1  $\mu\text{m}$  to more than 10  $\mu\text{m}$  in the course of about 100 000 hours service. This huge structural change (by two degrees of order) was in no way perceptible under a light microscope. The grains which are seen by using the microscope are composed of crystals (mosaic blocks) which cannot be perceived through the microscope. But x-rays diffracted by these blocks (crystallites) are incoherent and that is why we can recognize the mosaic blocks, into which some grains are broken up, on diffraction patterns. This demonstrates the usefulness of the topographic technique of x-ray diffraction (grain-by-grain mapping) in monitoring structural degradation of steels which occurs in the course of service of steam turbines made of these steels and in their residual-life prediction. That is to say, that mosaic blocks considerably influence the movement of dislocations and in this way also the strength characteristics of materials.

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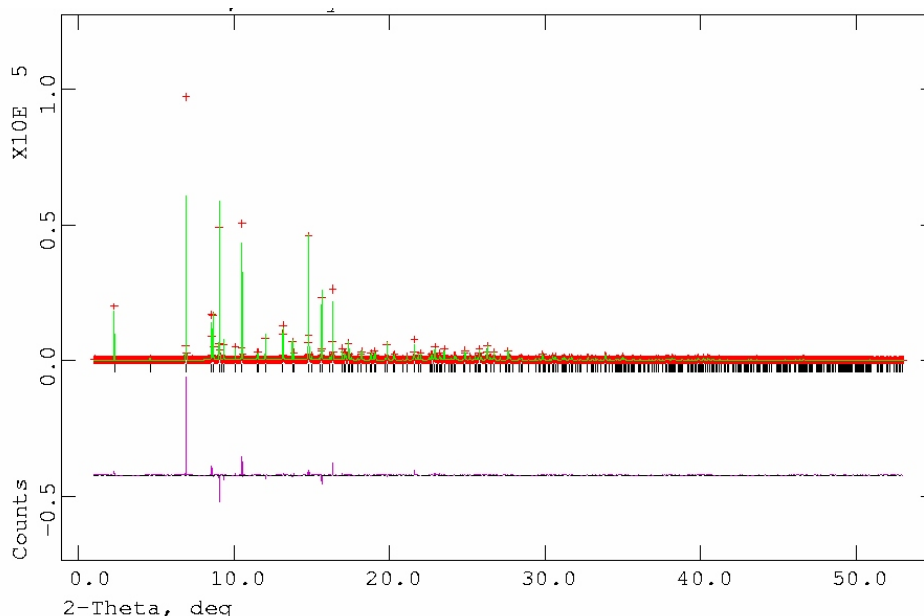
## B5 - O2

**STRUCTURE OF THE QUATERNARY ALLOY  $Zn_{0.6}Mn_{0.4}In_2S_4$  BY SYNCHROTRON POWDER DIFFRACTION AND ELECTRON TRANSMISSION MICROSCOPY****Rosario Ávila-Godoy<sup>1</sup>, Asiloé J. Mora<sup>2</sup>, Dwight Acosta-Najarro<sup>3</sup>, Andrew N. Fitch<sup>4</sup>, Gerzon E. Delgado<sup>2</sup>, Andrés E. Mora<sup>1,5</sup>, John Steeds<sup>5</sup>**<sup>1</sup>*Departamento de Física, Universidad de Los Andes, Mérida-Venezuela*<sup>2</sup>*Departamento de Química, Universidad de Los Andes, Mérida-Venezuela*<sup>3</sup>*Instituto de Física, Universidad Nacional Autónoma de México, DF, México*<sup>4</sup>*European Synchrotron Radiation Facility, Grenoble Cedex, France*<sup>5</sup>*University of Bristol, UK*

When the solid solution of  $Zn_{0.6}Mn_{0.4}In_2S_4$  is formed, the material departs from the stoichiometry of the parent compound  $ZnIn_2S_4$  [1], a defect-type layered semiconductor that has octahedral and tetrahedral sites in which the cations can be accommodated. Therefore, it is possible that some cationic positions lose their point symmetry, because it becomes necessary to accommodate different proportions of the Zn, In and Mn cations in these sites. Hence, a change of crystalline symmetry from  $Rm$  to  $R3m$  is possible. Also, taking into account the ionic size, oxidation state and coordination number of  $Mn^{2+}$ , it is probable that the magnetic ions occupy either octahedral or tetrahedral positions. Optical and magnetic measurements are contradictory in this matter [2]. The objective of the present work was to determine the structure of the quaternary alloy  $Zn_{0.6}Mn_{0.4}In_2S_4$ , and to locate in a precise way the positions of the  $Mn^{2+}$  ion in the crystalline cell. This was accomplished by means of two complementary techniques: X-ray

powder diffraction using synchrotron radiation and Electron Transmission Microscopy techniques, such as High Resolution Microscopy (HRM) and Convergent Beam Electron Diffraction (CBED).

In spite of collecting the diffraction data in a spinning borosilicate capillary with the powder diffractometer of beamline ID31, ESRF, preferred orientation along the [001] direction due to the crystal morphology was present. However, the presence of reflection 006 at  $14.3^\circ 2\theta$ , implied that the structure could be non-centrosymmetric  $R3m$ , and Rietveld refinements using different cationic arrangements were performed. A model in which the tetrahedral sites were occupied by a random distribution of Zn, Mn and In atoms, but with local  $3m$  symmetry, gave the best results. The Rietveld refinement of this model led to figures of merit:  $R_{wp} = 9.9\%$ ,  $R_p = 9.2\%$ ,  $\chi^2 = 11.21$  and  $R(F^2) = 0.1146$ . The final Rietveld plot showing the observed, calculated and difference patterns of the  $Zn_{0.6}Mn_{0.4}In_2S_4$  is



**Fig. 1.** Final Rietveld plot showing the observed, calculated and difference patterns of the  $Zn_{0.6}Mn_{0.4}In_2S_4$



shown in Figure 1. Selected Area Electron Diffraction (SAED) patterns and High Resolution Micrography along [001] showed the rhombohedral configuration (Figure 2a). From CBED patterns perpendicular to [001] the  $6mm$  symmetry breaking to the  $3m$  symmetry associated to the  $R3m$  space group can be observed in Figure 2b.

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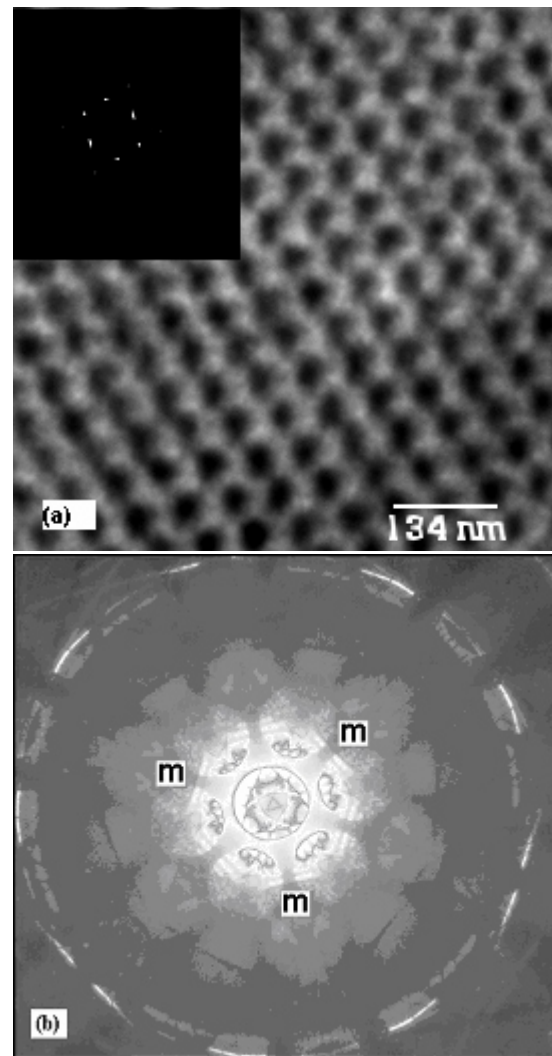


Fig. 2: (a) High-resolution micrograph, (b) CBED pattern of  $Zn_{0.6}Mn_{0.4}In_2S_4$  along [001] showing the  $3m$  symmetry that validate the  $R3m$  space group.

B5 - O3

## COMBINATION OF X - RAY AND ELECTRON DIFFRACTION FOR DETAILED ANALYSIS OF DEFORMATION SUBSTRUCTURES

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A detailed description of complex deformation – induced substructures (Fig. 1) in both single crystals and polycrystalline materials requires the use of different methods of investigation, realizing the microstructure analysis on different length and volume scales, respectively. An important tool for this purpose is the combined use of electron microscopy and X – dif-fraction. The application of the techniques is demonstrated by results obtained with [001] oriented Cu and Ni single crystals and polycrystalline – brass CuZn23 after deformation by uniaxial compression up to strains  $\epsilon=1$ . For the analysis the following methods were applied:

Transmission electron microscopy (TEM, e.g. [1]) for the direct imaging of the substructure and the identification of special lattice defects or defect configurations,

Electron backscattering diffraction (EBSD, e. g. [2,3]) for the estimation of substructure parameters as the size and the misorientation of cell – blocks or subgrains from orientation maps of the sample surface, and

X – ray diffractometry (XRD), which allows the determination of various characteristics of the dislocation structure (e.g. lattice strains and rotations related to the total dislocation content [4,5] and the density of excess dis-

locations stored in dislocation walls [3,6,7]) from the broadening of X – ray reflections.

In the single crystals both the TEM and the REM data describe the dislocation-induced sub-structure. In the polycrystalline material the REM data are influenced by twinning and the grain size, but if their effect is taken into account, very good agreement of the results of TEM and EBSD is obtained. Dislocation – induced lattice misorientations and densities of excess dislocations, respectively, can be determined in single crystals from the broadening of X – ray rocking curves as well as from EBSD orientation maps. In polycrystals only the application of EBSD is possible, because the measurement of rocking curves of individual crystallites by conventional X–diffractometry is usually impossible. It is therefore, important, that EBSD gives useful values of the dislocation – induced misorientations even at larger strains, where rotational deformation modes (Formation of disclinations) are activated.

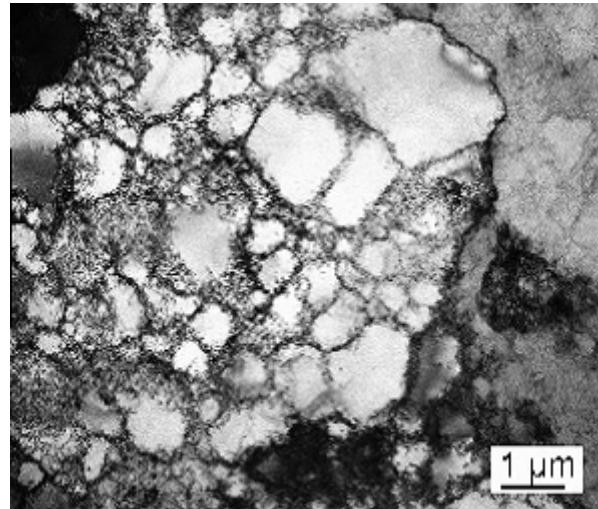


Fig. 1: Dislocation –cell structure in Ni after compression to  $\epsilon=0.3$

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B5 - O4

## IN-SITU SMALL- AND WIDE ANGLE X-RAY SCATTERING AT THE ELETTRA SAXS BEAMLINE ON Al-Zn-Mg ALLOYS

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The high flux focused beam of 16 keV photons at the Small Angle X-Ray Scattering (SAXS) beamline of the ELETTRA synchrotron in Trieste has been used to follow the decomposition of the solid solution state in two different Al base Al-Zn-Mg alloys. The specimens were quenched from 470 or 600 °C into room temperature (RT) water in the experimental hutch and have been transferred directly into the sample holder. The SAXS measurements were started within between 60 and 120 s after quenching. The small- and wide angle range scattering and diffraction have been recorded by two gas filled linear position sensi-

tive detectors. The diffraction patterns have been saved in 60 s frames up to time periods ranging from about 30 to 90 min. The SAXS patterns are evaluated for the average size and the volume fractions of the Guinier-Preston (GP) zones. From the shifts of the peak positions of the 111 and 200 Bragg reflections the change of the Mg and Zn content of the solid solution during zone formation is evaluated. The offcentre of the diffuse halo appearing around the fundamental 111 and 200 Bragg reflections enables to conclude about the elastic strains produced by the GP zones.



B5 - O5

## IN SITU X-RAY DIFFRACTION STUDIES OF DISPLACEMENT REACTIONS IN INTERMETALLIC SYSTEMS

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Several studies have been made on intermetallic structures, which can accommodate lithium with minimal structural changes:  $\text{Cu}_6\text{Sn}_5$  (NiAs-type structure) [1], InSb (Zinc-blende type structure) [2] and  $\text{Cu}_2\text{Sb}$  ( $P_4/nmm$ ) [3]. Several of these, *i. e.*  $\text{Cu}_6\text{Sn}_5$ ,  $\text{Cu}_2\text{Sb}$  and MnSb have proven to form isostructural intermediate ternary phases on lithiation,  $\text{Li}_2\text{CuSn}$ ,  $\text{Li}_2\text{CuSb}$  and  $\text{Li}_2\text{MnSb}$  (Zinc-blende type structure). These reactions involve metal extrusion and structural rearrangements of the parent structures. For  $\text{Cu}_6\text{Sn}_5$ , it involves a displacement of 50% of the Sn atoms within the structure accompanied by extrusion of some Cu. This reaction corresponds to a volume expansion of 59%. For  $\text{Cu}_2\text{Sb}$ , the phase transformation to  $\text{Li}_2\text{CuSb}$  is facilitated by the very strong structural relationship between the two phases. The Sb atoms of  $\text{Cu}_2\text{Sb}$  create a slightly distorted face-centered framework that, on lithiation, undergoes small displacements to create the “CuSb” face-centered array of  $\text{Li}_2\text{CuSb}$ . This reaction corresponds to a volume expansion of 25%. Both the  $\text{Li}_2\text{CuSb}$  and  $\text{Li}_2\text{CuSn}$  phases show a solid-solution behavior of lithium within the structures. Further lithiation of  $\text{Li}_2\text{CuSb}$  results in extrusion of the remaining Cu atoms and the formation of  $\text{Li}_3\text{Sb}$ , a process during which the Sb face-centered array is kept virtually invariant. The cubic-cubic phase transformation from  $\text{Li}_2\text{CuSb}$  to  $\text{Li}_3\text{Sb}$  involves a volume expansion of only 13%. The reactions for the  $\text{Cu}_2\text{Sb}$  system can be summarized as follows:



In this presentation, emphasis is placed on the structural transformations of two intermetallic systems:  $\text{Mn}_2\text{Sb}$  ( $\text{Cu}_2\text{Sb}$ -type structure) and MnSb (NiAs-type structure), shown in Fig. 1. The similarities/discrepancies between these systems and the earlier studied structures are explored in terms of structural transformations and electrochemical performance.

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