NOVEL EBSD-TEM LIKE TECHNIQUE: TEXTURE ANALYSIS, ORIENTATION AND PHASE MAPS ON NANO-STRUCTURED MATERIALS

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ABSTRACT

Spatial resolution limitation of orientation imaging via conventional electron backscattered diffraction (EBSD) analysis in SEM microscopes hinders the investigation of microstructural features whose dimensions are in the range 1 - 5 nm. The use of the recently developed transmission electron microscope (TEM) based technique coupled with electron beam precession, known as ASTAR, offers the possibility to acquire reliable orientation/phase maps with a spatial resolution down to 1 nm. The technique, which can be used with nearly all TEM, consists in scanning the electron beam, in nano-probe mode, over the specimen area while precession electron diffraction (PED) spot patterns are collected and indexed automatically through template matching. Several examples of applications of this tool in investigating microstructure / micro-texture of nano-crystalline materials (metals, ceramics, minerals) are presented.

INTRODUCTION

EBSD attachments for SEM have gained popularity over the last decades as they offer an effective way to characterize bulk crystalline materials through crystal phase and orientation mapping with spatial resolutions of typically 50 nm (FEG-SEM). In order to address higher resolution, transmission electron microscopes have to be considered. Consequently, a novel technique has been developed, thanks to a close collaboration between the Grenoble Institute of Technology (France) and NanoMEGAS SPRL, which enables automated phase and orientation mapping for nano-scaled structures.

Precession microscopy: pattern acquisition and identification

For this tool, sample preparation is not different from standard TEM observations with the same unique effective limitation related to electron beam transparency. During data
acquisition, electron diffraction spot patterns are collected sequentially with a dedicated external CCD camera while the sample area (typically from a fraction to tens of square micrometres) is scanned by the incident quasi-parallel nanobeam (< 2 mrad). The latter is simultaneously precessed around the optical axis of the microscope (Fig. 1) to reduce strong dynamical effects.

**Figure 1.** Schematic illustration of the tool (a) the beam is precessed at a high rate and (b) scanned over the area of interest. The diffraction patterns (c), improved by precession (d) are compared to simulated diffraction patterns to recognize phase and orientation. (f) Overview of the ASTAR hardware components.

Precession is also known to permit the collection of higher order Laue reflections [1] and leads to important improvement in the quality of spot patterns that, in turns, reduces misindexing (Fig. 2). In PED the incident rotating beam describes a cone at a frequency of several hundreds of hertz, with a pivot point focused on the sample while the resulting diffraction pattern is counter-deflected. Consequently, the diffracting spot intensities are integrated over the entire illumination conditions for each successive position of the beam. Beam scanning (translation) and precession (rotation) are generated by a dedicated external hardware unit which also allows the control of the beam pivot point. This device being connected to the TEM beam and image deflector coils control boards, there is no need for the microscope to be equipped with the optional STEM facility.

This automated TEM phase and orientation mapping tool, named "ASTAR", includes a precession unit ("DigiSTAR") and the scan generator (Fig. 1f). An external dedicated fast acquisition optical CCD camera (frame rate ~ 200 frames/sec) is mounted in front of the TEM window and focussed on the usual phosphorus screen [2].
Figure 2. [111] diffraction pattern of mayenite mineral (cubic, $a = 12.5$ Å) at different precession angles from $0$ mrad for conventional ED pattern (dynamical) to $40$ mrad precession angle providing a quasi-kinematical electron diffraction pattern.

While scanning and precessing the incident electron beam, thousands of PED spot patterns are recorded and stored in a computer memory. Phase and orientation identification are performed for each experimental PED spot pattern, by comparing them to the so-called templates that are theoretical kinematical electron diffraction patterns calculated for each crystallographic phase expected to be present in the sample (Fig. 1).

For orientation indexing the cross-correlation matching techniques is performed using templates generated every degree so that the typical orientation resolution is of this order of magnitude. For a typical $500 \times 500$ pixels map, beam scanning (and precessing) over the sample area will take around $20$ minutes ($200$ points per seconds). Comparison with simulated templates can be done off-line and may take about the same time for highly symmetric cubic materials but easily $3 - 6$ times longer for unit cells with lower symmetry as more templates must be generated.

Template generation is done on the basis of inputs of the crystal structure parameters of the known phases (for which the spatial distribution is to be mapped) to the software. Typical mapped areas are of the order of $5 \times 5$ μm; the spatial resolution is about half the primary electron beam size, i.e., $10$ nm to $20$ nm spot size for TEM-LaB$_6$ and as small as $0.5$ nm for FEG equipped TEMs. It is of interest to mention that ASTAR can be adapted to most of the existing TEMs (Fig. 3). Moreover, the flexibility of the equipment is such that a given unit may be adapted to several TEMs in the same laboratory and easily displaced from one microscope to the other.

The software, developed specifically for the technique, produces crystal orientation maps, STEM type bright field maps (called virtual bright field image), correlation index maps (i.e., matching intensity) and reliability index maps (i.e., matching quality).

In particular, the virtual bright field image (VBF) is of interest: it is obtained by plotting the intensity fluctuations of the transmitted beam at every location of the scanned area. Such maps are quite helpful to locate and recognize the area by comparing them to real bright-field TEM images. Also, due to recession, VBF is less suffering from diffraction contrast and
Figure 3. ASTAR phase/orientation mapping unit interfaced to various TEMs: (left to right) Jeol ARM 200 FE Cs probe corrected (Jeol Factory Tokyo, Japan), FEI Tecnai 30 FEG (University of Kiel Germany), and Libra 120 (Zeiss) microscope (IIT, Pisa, Italy).

Curvature contrast than real bright field images. Correlation index maps are giving interesting images that emphasize structural details such as grains, precipitates, holes, etc. Besides, the reliability index, analogous to the SEM-EBSD confidence index, is defined as:

\[ R = 100 \left(1 - \frac{Q2}{Q1}\right) \]

where Q1, Q2 are the correlation indices for the selected (best) solution and the second best matching template. Reliability index is decreasing when more than one solution is possible for the diffraction pattern so that Reliability maps clearly reveal grain and phase boundaries.

APPLICATIONS

The tool, that was been initially developed (2008) to deal with metallurgical samples subjected to plastic deformation, it has been currently applied to a broad range of research subjects as illustrated below.

Grain orientation determination in deformed metals

While EBSD-SEM tools are undoubtedly very efficient to derive orientation maps with impressive spatial resolution when they are coupled to a SEM-FEG, they still experience difficulties when the level of plastic strain in metals is increased. This results from the poor quality of the Kikuchi patterns when the crystals contain a high density of dislocations that leads to local misorientations. The same is observed for TEM Kikuchi patterns. Indeed, the Kikuchi lines being very sensitive to the crystal orientation, they rapidly fade away if the diffracting volume suffers distortions. By contrast, these distortions will have a limited effect on the spot patterns because small misorientations will affect the intensities of the diffracting beams, not their position. This is illustrated in Fig. 4 that concerns an Al thin film analyzed.
before and after tensile deformation. Essentially, it is noted that strains have not affected the capability of the tool to provide reliable information, i.e., orientation maps, grain size, crystallographic texture [3].

![TEM image, Orientation map, Grains close to <001>, Grain size distribution, Pole Figures](image)

(a) Aluminium before deformation

![TEM image, Orientation map, Grains close to <001>, Grain size distribution, Pole Figures](image)

(b) Aluminium after deformation

**Figure 4.** Al thin film before (a) and after (b) 22% tensile straining. From left to right TEM image, orientation map, a structural view highlighting grains close to <001> orientation, grain size distribution and pole figures.

Nano-crystalline metals and alloys exhibit outstanding mechanical properties, in particular superior hardness, strength and fatigue properties, compared to their coarse grained counterparts. For these ultra-fine grained (UFG) metals, modified or even new deformation mechanisms are expected to dominate the mechanical properties. Consequently, it appears of interest to characterize quantitatively and for different strain states features like the grain size distribution, the so-called local texture or twin density for metallic samples exhibiting grain sizes below 30 - 50 nm. Such works are made possible with the present tool. For example Weis et al. [4] studied the deformation mechanisms in nano-crystalline palladium and palladium alloys by using mechanical testing in combination with ex-situ and in-situ TEM analysis. Besides, Descartes et al. [5] obtained grain refinement by applying high-pressure torsion to pure iron and used the tool capability to characterize the resulting fine grained structure after severe plastic deformation (Fig. 5).
Figure 5. Grain refinement analysis in severely deformed pure iron. Orientation map with the colour related to: a) x axis; b) z axis with grain boundaries highlighted; c) grain size distribution; and d) \{111\} pole figure. The colour code for the orientation maps is shown on the right.

Texture determination in rapidly solidified alloys

Kulovits et al. [6] have carried out studies using high time resolution TEM, to observe rapid solidification dynamics in 80 nm thick Al thin films after pulsed laser melting. The nanometre spatial and 15 nanosecond temporal resolutions of the dynamic transmission electron microscope (DTEM) allowed them to study the morphology and dynamics of the transformation front moving at speed of 0.1 - 10 m/s during rapid solidification. They have used ASTAR for the post-mortem analysis of grain orientations of the solidified microstructure near the position of the solid liquid interface at the start of solidification.

Besides, Lagrange et al. [7] used automated orientation indexing technique to study an exotic Cu microstructure developed by pulsed, high-power sputter deposition. The growth mode under pulsed deposition develops columnar grains with large aspect ratio, that contain a high density of fine twins oriented parallel to the substrate in the plan of the film. ASTAR was used to map changes in grain orientation and grain boundary area fraction. Maps of above $10^6$ pixels were used for this purpose.
Phase and orientation distribution in metals and alloys

Wang et al. [8] have studied forced chemical mixing in nanostructured Ag60Cu40 eutectic alloys during severe plastic deformation by high pressure torsion (HPT) that enables quantitative measurement of the processing variables. ASTAR was used to evaluate structural evolution of phases, compositions and grain shape, size and orientation. Rauch et al. [9] have used the EBSD-TEM like technique to analyze texture and phase distribution of ferritic/austenitic (containing also Zn hexagonal phase) industrial steel and obtained an accurate phase/orientation analysis for a ferrite/austenite steel containing ε martensite. Similar analysis have been carried out [10] in transformation induced plasticity (TRIP) ferritic steel containing a small volume fraction of austenite. In that work, ASTAR PED based crystal phase maps show, as expected, retained austenite only at the grain boundaries while observation based on data collected without precession gave misindexed austenite ‘inclusions’ within ferritic grains. This result is to be related to the dramatic improvement in the diffraction pattern quality with precession mentioned above.

Cizek et al. [11] applied TEM automated orientation indexing facility to analyze microscale and mesoscale crystallographic textures in electrodeposits nano-crystalline Ni, Ni-20%Fe, and Ni-50%Fe. In these samples, nano-sized grains are arranged in coarse mesoscale colonies (Fig. 6). In the as-deposited state, the bulk texture of the Ni-20%Fe alloy displays a dominant <001> fibre parallel to the macroscopic deposition direction (DD). The grains are elongated along the <001> crystal lattice direction, which is mostly parallel to the local DD, producing a well-defined <001>//DD fibre micro-texture on a local scale.

Figure 6. Orientation map showing an area containing a boundary (dotted line) between two neighbouring mesoscale colonies (upper and lower parts) in the Ni-20%Fe specimen with corresponding pole figures.
Phase and orientation distribution in nanoparticles and nanowires

As spatial resolution of a few nanometres can be obtained on a TEM-FEG microscope, the technique is ideal for mapping orientation/phase maps in nanoparticles as is shown in Fig. 7 on a Ni-Fe alloy sample (grain size 10 - 100 nm). Rouvimov et al. [12] have successfully used ASTAR to distinguish phases out of a mixture of iron oxide nano-crystals (magnetite and maghemite), which have essentially similar cubic cell parameters but different space group symmetries. Gemmi [13] used a 120 kV Libra 120 TEM to obtain 5 nm resolution orientation maps in Au nanoparticles (Fig. 8) and analyze Fe3O4 nano-particles used as drug delivery compound. Besides, Estrade et al. [14] have used the same technique to determine crystal orientation changes in 50 nm thick P:Co semiconductor nanowires and in heavily bent Ge nano-wires only 10 nm thick.

![Figure 7. Orientation maps for Ni-Fe polycrystalline alloy. Above: from left to right: colours refer to inverse pole figure for respectively axis z, y and x and {111} pole figure (step size 4 nm, Jeol 2200 FS 200 KV, Humboldt University Berlin). Below: disorientation and grain size distributions.](image)

To that respect, Ganesh et al. has [15] obtained local orientation information from grains as small as 3 nm in a completely automated manner. Such information of local texture can be combined with finite elements stress analysis to obtain local stress and stress gradients in narrow CI lines and address reliability issues like stress induced void formation.
Brandstetter et al. [16] have also performed an intensive TEM-ASTAR orientation analysis study of pattern size dependence of grain growth in Cu interconnects. The same group analyzed Cu-Cu interface bonding by interdiffusion of copper (Fig. 9) and took advantage of the mapping tool to emphasize grain growth from one layer to the other. Hausler et al. [17] studied with ASTAR crystallite phase and orientation determinations of (Mn,Ga)As/GaAs-crystals using PED patterns. (Mn,Ga)As crystallites are embedded as precipitates into the GaAs matrix; using PED and template matching the precipitate crystal structure matched best to the monoclinic P21/m phase while hexagonal, orthorhombic and trigonal phases were considered together leading to over 38,000 templates in total. Similarly, orientation of Al(Ga)N layers on patterned sapphire have been studied by Kirmse et al. [18] and phase identification of both AlN and GaN crystals has been possible, revealing the sensitivity of the technique to crystals having the same cell parameters but different chemical content. These authors also studied polycrystalline ZnO and its orientation relationship with the sexiphenyl organic compound 6P, on which it is deposed. Due to completely divergent structural and chemical properties of ZnO and 6P phases are not expected to be epitaxial which was confirmed by automatic orientation analysis in a more effective and less tedious was than through HREM-TEM measurements [19].

Figure 8. Gold nanoparticles scanned on a Libra 120 leading to a 5 nm spatial resolution. Matching index (left) and crystal orientation map (right). Courtesy Dr. M. Gemmi IIT, Pisa, Italy.

Figure 9. Copper direct bonding observed with STEM type image generated by ASTAR (upper picture), the orientation map (middle). Twin boundaries are easily recognized and highlighted (red) on the index map (lower picture). These results freely adapted from Martinez et al. 2012 Thin Film Solid (in press / available on line).
**Phase and orientation mapping in ceramics, thin layer films and minerals**

An illustrative example of automated indexing used in combination with PED concerns energy related materials and has been recently published by Brunetti *et al.* [20]. In this work, ASTAR was used to distinguish between LiFePO$_4$- and FePO$_4$-phases at the nanometre-scale level on a large number of particles whose sizes ranged between 50 and 300 nm in a partially charged battery. Despite the similarity of the two phases (the difference of lattice parameters is $<5\%$), the method gives clear results that have been confirmed using high-resolution transmission electron microscopy (HRTEM) and energy-filtered transmission electron microscopy/electron energy loss spectroscopy (EFTEM/EELS) experiments. The phase maps show that the particles are either fully lithiated or fully delithiated and, therefore, bring a strong support that a domino-cascade process is operative at the nano-scale level.

Rauch *et al.* [21] used the EBSD-TEM like ASTAR technique also to analyze the texture of Pt, Cu, and W thin films prepared by sputter deposition onto oxidized Si substrates. ASTAR has also been further used for mineral orientation and phase identification (Fig 10). Phase recognition is not limited by the number of phases considered but by the capability of the tool to clearly distinguish between the diffraction patterns pertaining to all of them.

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**Figure 10.** Orientation relationship in a mixture of α- FeO(OH) sticks (goethite) and TiO$_2$ particles (brookite) both phases are orthorhombic. Area scanned on a Jeol 3010 TEM-LaB$_6$ with a spot size of 15 nm (courtesy: L. Andre IFP, C. Chaneac LCMCP).
Future trends: phase and orientation mapping in organic crystals and beam sensitive materials

Orientation and phase mapping in organic crystals is one of the most promising areas for future developments of the EBSD-TEM like technique. Organic crystals or beam sensitive materials in general, may still give orientation/phase information providing the specimen area is scanned at a sufficiently high speed to capture ED/PED patterns before irradiation damage may degrade them substantially. Veron et al. [22] used ASTAR to reveal orientation mapping from an organic TRIS crystal (SG Pna21- unit cell 0.7768 x 0.8725 x 0.8855 nm C16H48N4O12), and demonstrated that it is possible to collect orientation information even without using cryo TEM techniques. Other organic structures ([Fe(Htrz)2(trz)]BF4) [23] have revealed orientation information with ASTAR and the topic is clearly promising for future developments.

CONCLUSIONS

EBSD-TEM like technique in combination with PED diffraction allows orientation and phase mapping in materials with spatial resolution down to 1 nm, bringing traditional EBSD-SEM studies into new possibilities with TEM microscope. Samples (from metals and ceramics up to beam sensitive organic crystals) can be studied with any TEM microscope and do not need any special specimen preparation.

REFERENCES


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