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SEAMLESS 4D-STEM WORKFLOWS FOR THE CHARACTERISATION OF MATERIALS AND NANOSCALE DEVICES

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1. ABSTRACT

A novel approach to analytical scanning transmission electron microscopy (STEM) measurements, as introduced with the new TESCAN TENSOR electron microscope, is changing the way how materials can be characterised at the nanoscale by enabling precise analyses of morphological, chemical, and structural properties of various samples at ease to a wide range of users, including material scientists, semiconductor technicians as well as transmission electron microscopy (TEM) / STEM method developers. The unique new design has enabled advanced on-the-fly automation of system alignments and adjustments of STEM imaging, STEM analysis and 4D-STEM nanobeam settings without user intervention. Full integration of all microscope modules and synchronisation of beam scanning with beam blanking, beam precession and simultaneous readout of all detectors then facilitated simplification of sample analysis workflows. Consequently, TENSOR offers intuitive user experience, enabling straightforward operations without the need for specialized TEM/STEM operation knowledge. Users can focus on and spend their precious instrument time on the interaction with the studied specimen, whilst spending little to no time on the electron column adjustments and alignments. The unique capabilities of the system are demonstrated here in several examples including fast characterisation of deformation properties of Ni-based superalloy, assessment of structural properties of a battery electrode and by multimodal phase analysis of challenging polycrystalline samples with very similar lattice parameters.

2. INTRODUCTION

The demand for high performing materials and semiconductor devices increasingly necessitates optimisation of structures at the nanoscale. This trend underscores the importance of advanced, accessible, and routine nanoscale analysis to drive progress in material science and technology. The method of choice for these measurements has been established by multimodal scanning transmission electron microscopy (STEM). The conventional TEM/STEM techniques, such as bright-field and dark-field imaging (BF/DF STEM) and energy-dispersive X-ray spectrometry (EDS) compositional analysis are, however, not always sufficient to fully characterise the underlying structural features that determine the mechanical and thermoelectrical properties of the studied materials, alloys, functional materials, composites, nanoparticles, and nanodevices.

Structural information about sample composition can be obtained by electron diffraction down to the atomic level. The development of fast and sensitive pixelated electron diffraction detectors has enabled efficient collection of diffraction patterns in scanning transmission electron microscopes [1]. Collected datasets of two-dimensional diffraction patterns then provide structural information from each individual pixel of the two-dimensional scanned region of interest and are generally referred to as 4D-STEM datasets.

Development of direct electron detectors optimized for electron diffraction, such as the DECTRIS QUADRO detector with hybrid-pixel technology [2], provides high signal to noise ratio in the collected 4D-STEM datasets without risks of detector damage by high currents of the non-diffracted beam. The high dynamic range (~10^7) simultaneously facilities electron counting data collection from single electron events to high intensity diffraction peaks.

The quality of collected diffraction patterns can be substantially improved by using electron beam precession [3]. In this case, the electron beam is precessed during collection of a diffraction pattern from a single pixel in the scanned region of interest. As the beam is precessed the signal given by dynamical scattering, such as Kikuchi lines, is changing during data acquisition, whereas the diffraction spots from kinematical scattering remain unchanged. Consequently, the signal from dynamical scattering is (partly) averaged out in the collected diffraction patterns, whereas the signal to noise ratio of the diffraction spots is increased. Moreover, higher order diffraction spots are excited and present in the diffraction patterns and their intensity is more homogeneous due to signal integration within the precession angle and averaging out the signal from dynamical scattering.

The current implementations of beam precession using the Nanomegas module on conventional TEM/STEM instruments is however limited by non-existent hardware and software integration of beam precession and direct electron detector readout that must be synchronised and aligned independently by using different control units. Here, we present an innovative design of a new analytical STEM instrument that has been optimised for multimodal, precession-assisted electron diffraction measurements and demonstrate its capabilities on several selected use cases.

3. *NEW DESIGN OF AN ANALYTICAL STEM MICROSCOPE WITH INTEGRATED BEAM PRECESSION*

Performance and usability of analytical 4D-STEM techniques [1] are typically compromised by the design of conventional TEM/STEM platforms that were not intrinsically designed for the integration of components required for high quality, fast 4D-STEM data acquisition, analysis, and processing. These components include a fast direct electron diffraction detector, electron beam precession, synchronised beam blanking, and 4D-STEM analysis and processing software. In the new design of TESCAN TENSOR, we integrated and synchronized state-of-the-art components such as a large direct electron detector with hybrid pixel technology [2], electron beam precession, electrostatic beam blanker, and large dual EDS detectors. Ultra-high vacuum engineering then provides near ultra-high vacuum at the specimen area and negligible hydrocarbon contamination from the column. Full integration of all these components facilitated their precise synchronisation and improvement in their performance and overall throughput of STEM, EDS, and 4D-STEM measurements.

To enable these advanced diffraction measurements to a wide range of users, the microscope and all integrated components can be controlled from a single user interface that provides seamless workflows and unique user experience. After sample insertion into the microscope and starting a sample analysis session, an overview of the sample is acquired within a few minutes. Users can then explore the sample, zoom-in and identify the region of interest intuitively. Once the region of interest is selected, the user can select from a set of predefined workflows of different analytical measurements. The system will automatically set and refine alignments optimal for each analytical measurement within couple of minutes and the user is left with setting of the key acquisition parameters (such as the pixel size and dwell time of the scan). The key microscope alignments, such as the specimen height, focus, beam precession and beam descan pivot points can be refined manually or by using fully automated functions.

Special dedicated hardware and software has been developed and implemented for beam precession that is routinely used at 72,000 Hz. This fast precession rate enables to run the direct electron diffraction detector at the full speed of 4,500 frames per second (fps), while it still provides 16 precession cycles in each acquired frame. Consequently, precession-assisted 4D-STEM datasets can be acquired within minutes instead of an hour or more.

Importantly, the EXPLORE user interface includes on-the-fly processing and analysis of collected 4D-STEM datasets, while processed and analysed results are already visualized during data collection, which makes sample characterisation an interactive experience instead of batch data acquisition and later post-processing. This new approach results in enhanced system accessibility, utilisation, and productivity for a wide range of users without the need of weeks, if not months, of prior training or experience in using complex high-end TEM/STEM equipment.

The new design of the microscope is also fully open for experienced TEM/STEM operators and method developers. The dedicated user interface, EXPERTPI, provides access to all microscope functions and settings at the Python level. These experienced users can customise all measurement conditions and develop their own data analysis workflows, including the open-source computational packages, such as LIBERTEM, HYPERSPY, or PY4DSTEM [4-6].

4. FAST ANALYSIS OF DEFORMATION PROPERTIES OF Ni-BASED SUPERALLOY

Nickel superalloys are advanced engineering materials for applications in demanding environments, including aerospace and energy generation, where they are subject to oxidising conditions, extreme operating temperatures, and complex mechanical stress states. Understanding of the mechanical properties of these alloys is essential for effective and cost-efficient material selection and preparation procedure optimization.

We employed precession-assisted 4D-STEM automated crystal orientation mapping [3] to analyse crystallographic grain reorientation caused by Vickers indentation induced plastic

deformation at the nanoscale. A focused ion beam (FIB) lamella parallel to the (100) plane was extracted from the plastically deformed region under the indent. The lamella was imaged by BF/DF STEM using a 6.5 mrad convergence semi-angle and 100 pA beam current. For 4D-STEM orientation analysis, a 2 mrad convergence semi-angle and 50 pA beam current were used. The probe dwell time was set to 1 ms (1,000 fps), with a pixel size of 55 nm for the overview map and 6.5 nm for the detail, high-magnification map. A beam precession angle of 14 mrad was employed. Kinematic diffraction templates were generated for the known cubic structure of Ni_3Al.

Initially, a fast overview orientation map acquired from the whole area of the thinned lamella (Fig. 1) was used for checking the diffraction pattern quality, for refining the diffraction template processing parameters, and for localising the region of interest. Within the same microscope session, it was possible to proceed and analyse the selected region with large orientation gradient under the indentation point.

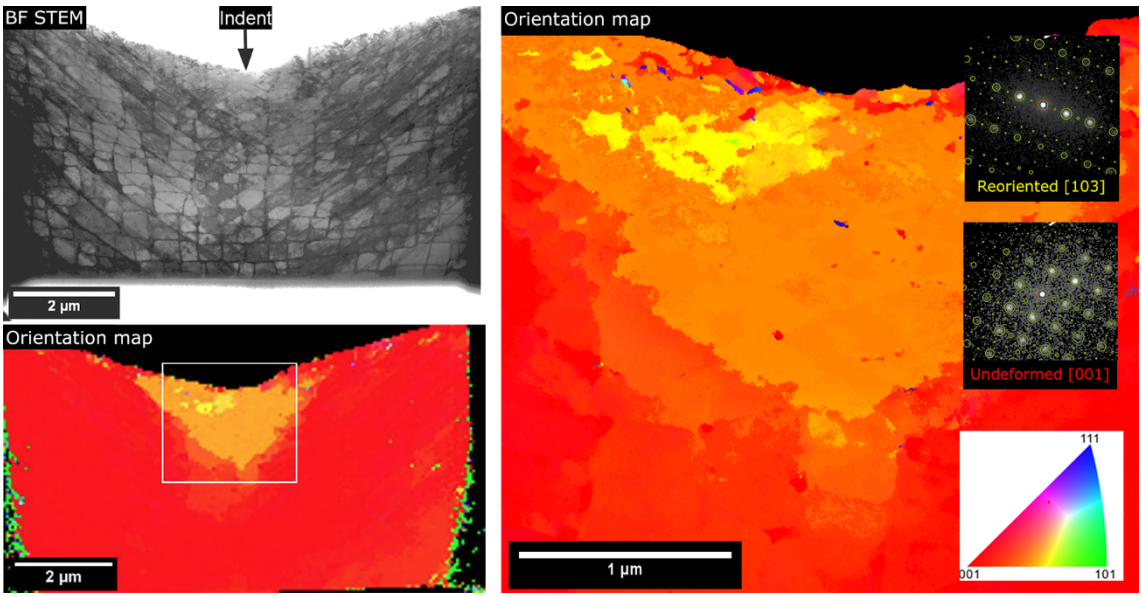

Figure 1. Overview of a prepared FIB lamella of a Ni-based superalloy extracted from bellow of an indent, shown in the bright field STEM image (top left). A quick orientation map of the entire lamella (bottom left) was acquired to check and optimise diffraction data acquisition settings and to identify the region of interest. A detailed orientation map of the region of interest (right) exhibits significant reorientation from the original [001] orientation (red) to the new [103] orientation (yellow) under the indent due to strong plastic deformation.

The higher resolution orientation map (Fig. 1) showed that the areas of heavy slip plane density were correlated with areas showing change in orientation. The change in orientation in the orange region from [001] to [103] showed high indexing quality due to the good diffraction template matching, however the sub-region shown in yellow exhibited larger orientation change and smaller indexing quality, likely because it underwent the largest plastic deformation.

5. *STRUCTURAL CHARACTERISATION OF BATTERY ELECTRODES*

There is significant interest in research into how microstructural engineering improves cycling behaviour, and to what extent synthesis conditions can be tuned to produce desired morphologies. For example, in the case of $LiTi_2(PO_4)_3$, it has been shown that particles with spindle-like morphology synthesized by solvothermal reactions are formed from small sub-particles and contribute to enhanced battery cycling performance compared to sol-gel synthesized material [7]. Previous microstructural analysis of such $LiTi_2(PO_4)_3$ spindle-like particles revealed the presence of two minor secondary phases, identified as TiO_2 nanoparticles and a $LiTiOPO_4$-phase. The majority of the TiO_2 nanoparticles form a three-dimensional network and it has been elusive whether these networks exhibit any form of crystallographic ordering [8].

We employed precession-assisted 4D-STEM to map the different phases and reveal individual grains based on their orientation at the nanoscale, which has been elusive for the conventional techniques, such as phase analysis with TEM selected area diffraction, high-resolution imaging or EDS mapping analysis. A FIB lamella was prepared from synthesized particles and the 4D-STEM dataset for phase and orientation analysis [9] was acquired using a 2 mrad probe convergence semi-angle with 50 pA probe current, 14 mrad precession angle, and a pixel size of 4.5 nm/pix with the dwell time of 1.5 ms (i.e., the acquisition speed of 667 frames per second). The kinematic diffraction templates were generated for the known structures of the TiO_2, $LiTi_2(PO_4)_3$- and $LiTiOPO_4$-phases.

The 4D-STEM data provides more conclusive phase analysis when compared to elemental maps, in which the different phases could not reliably distinguished because of similar elemental composition. The combination of both orientation and phase maps (Fig. 2) revealed that the TiO_2 particles were located at the $LiTi_2(PO_4)_3$ sub-particle boundaries. The $LiTiOPO_4$-phase was detected only in two small discrete regions as a minority phase. The understanding of the grain boundary behaviour and properties of these phases is of significant interest for future research, as the internal sub-particle boundaries can enhance lithium ionic conductivity and improve battery performance.

6. *MULTIMODAL PHASE ANALYSIS OF CHALLENGING SAMPLES*

Although 4D-STEM crystal orientation and phase mapping is a powerful technique for the nanoscale structural characterisation of materials, it is challenging to accurately distinguish and separate phases with similar lattice parameters and symmetries when the difference of lattice parameter difference is below ~5 %. Combination with complementary information, such as EDS signal, can then be efficiently used to guide proper separation of phases with different chemical composition. In such multimodal approach, precise synchronisation between electron beam scanning, electron beam precession and acquisition of both EDS signals and diffraction patterns must be achieved.

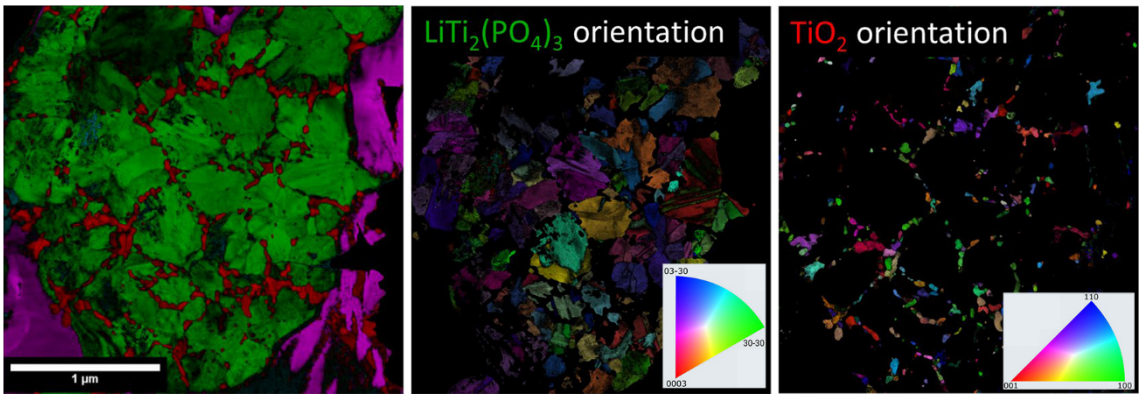

Figure 2. Precession assisted 4D-STEM phase map (left) of the $LiTi_2(PO_4)_3$ (green) and TiO_2 (red) phases with their respective orientation maps and legends (middle and right). The minority phase of $LiTiOPO_4$ is shown in cyan in the phase map (left).

The TENSOR has been designed to provide exactly such synchronisation. To test the performance of the system, we used a sample of a polycrystalline aluminium foil with added gold nanoparticles. The aluminium and gold exhibit similar lattice constants of 4.049 Å and 4.078 Å respectively (i.e., < 1 % difference in the lattice parameters). Collection of the precession-assisted 4D-STEM dataset for phase and orientation analysis [9] was acquired using a 2 mrad probe convergence semi-angle, 50 pA probe current, and 7 mrad precession angle. In Fig. 3, grains in polycrystalline aluminium and gold nanoparticles are well characterised. However, phase mapping using the standard algorithm [9] for phase determination by 4D-STEM fails, as can be seen in comparison with the acquired EDS map. To properly differentiate between the phases of aluminium and gold, the chemical information obtained from EDS signal at each pixel was utilised to assign weights to the diffraction templates of each phase used in template matching. As a result, the quality and reliability of 4D-STEM phase mapping was substantially improved, and the phase map then accurately corresponds to the observed EDS map.

To demonstrate the improved performance of 4D-STEM phase mapping with EDS signals, we tested this approach on a challenging semiconductor device. The EDS map in Fig. 4 reveals multiple metallic layers in the device. However, the standard 4D-STEM phase mapping algorithm fails to distinguish the TiN- and Ti_3AlN-phases. Including EDS signals in the algorithm then results in more accurate separation of these phases and characterisation of the grain size and orientation distribution in each respective layer.

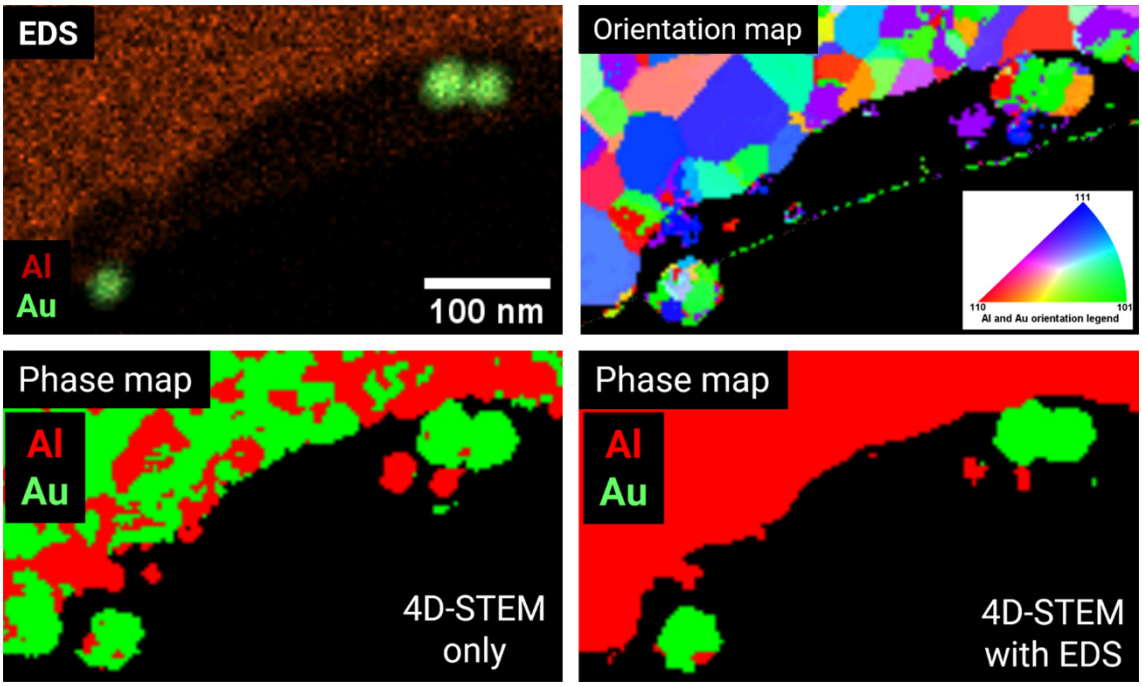

Figure 3. EDS map shows the regions of aluminium foil (red) and gold nanoparticles (green) in the sample field of view (top left). The orientation map (top right) reveals individual grains in the aluminium foil and gold nanoparticles, respectively. The phase map determined by using only the 4D-STEM dataset (bottom left) fails to correctly distinguish and separate the aluminium and gold phases. When the 4D-STEM data are complemented with simultaneously acquired EDS signal, the phases are correctly separated (bottom right).

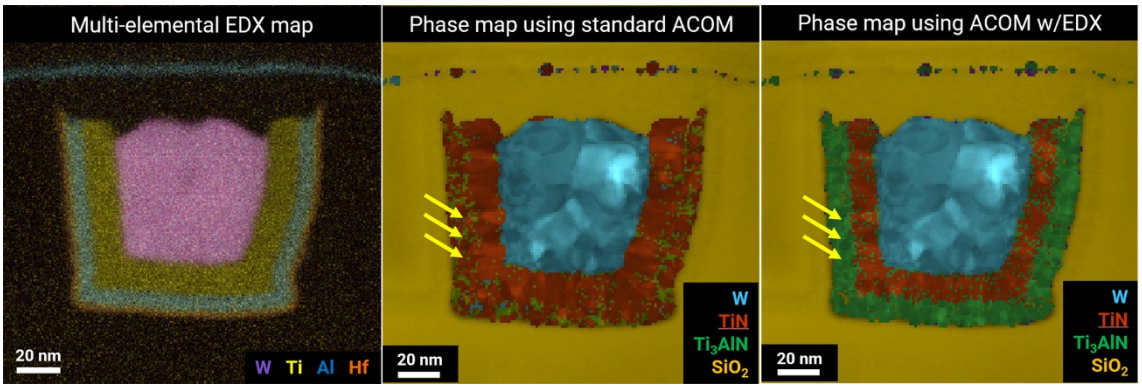

Figure 4. EDS map of a semiconductor device (left) reveals several metallic layers in the device architecture. However, 4D-STEM phase mapping fails to distinguish and separate the TiN- and Ti_3AlN-phases (middle). Once EDX signal is included in the 4D-STEM phase mapping algorithm, the TiN and Ti_3AlN layers are more correctly separated (yellow arrows).

7. CONCLUSIONS

The new design of the analytical scanning electron transmission microscope optimised for precession-assisted diffraction measurements with fully integrated hardware and software has

enabled fast and intuitive sample analysis using seamless 4D-STEM workflows. Novel insights into the deformation behaviours of Ni-based superalloys and the distribution of lithium and titanium phases in spindle-like battery anode nanoparticles were gained by using precession assisted 4D-STEM phase and orientation techniques. Such results could not be obtained by using the conventional techniques, including EDS compositional analysis, selected aperture electron diffraction and/or high-resolution imaging. Additionally, it has been shown how true multimodal data acquisition provided by complete synchronisation of beam scanning with beam precession and readout of all analytical detectors can be used to enhance accuracy of 4D-STEM phase analysis by using simultaneously acquired EDS signals and correctly separate phases in multi-phase materials and semiconductor devices despite very similar lattice parameters of the different phases.

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