Viewpoint article

Spatially correlated electron microscopy and atom probe tomography: Current possibilities and future perspectives

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ABSTRACT

Performing electron microscopy and atom probe tomography at the same location on the same specimen combines the strengths of electron microscopy, which is primarily the analysis of defects and crystal structures, with the strengths of atom probe tomography, which is primarily the robust, accurate and sensitive three dimensional compositional analysis. This viewpoint article provides a summary of the broad range of electron microscopy techniques that have been performed on atom probe specimens to date. It describes what technique is best suited to address a specific materials science question and finishes with an outlook on possible future developments in the field.

1. Introduction

The strengths of atom probe tomography (APT) and electron microscopy (EM)[1] are remarkably complementary and many materials science questions require their joint application on the same location in order to be answered. The major strength of APT is the three dimensional (3D) local, quantitative elemental analysis at the near-atomic scale. APT is inherently a three-dimensional technique, and it combines high mass resolution with high elemental sensitivity in the range of 10 parts-per-million, irrespective of the element [1]. This even enables the quantification of trace amounts of light elements in the bulk of a matrix composed of heavy elements. In an APT mass spectrum, ionic species can, in most cases, simply be identified according to their mass-to-charge ratio, which makes interpretation and quantification of absolute concentrations rather robust. In electron microscopes, the main techniques to quantify local chemical compositions are energy-dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS). The elemental sensitivity of EDX depends on the atomic number of the element; the lighter the element, the higher the associated measurement error [2]. Therefore, the concentration of light elements is usually determined through other means, e.g. in transmission electron microscopes (TEM) EELS is typically used because it does not suffer from this shortcoming (although it often has difficulties in detecting heavy elements). The element-specific edges in EELS spectra are superimposed on a strong background caused by the tails of plasmons, single electron

excitations or by other element-specific edges, making the quantification of absolute concentrations challenging. For these reasons, quantitative chemical analysis at the near-atomic scale can be conducted in many cases more easily, and more accurately, by APT rather than by EM.

However, electron microscopes are excellent for crystallographic/structural analysis since electron diffraction and imaging can be performed at the (sub-)nanometer scale. Grain orientations can be measured, the structure of complex phases can be identified based on diffraction patterns, defects such as interfaces, dislocations, slip bands, or stacking faults can be imaged, even the structure of defects or strain gradients can be investigated with spatial resolutions capable of resolving individual atomic columns. Although crystallographic analysis is also possible by APT, this is mainly restricted to the analysis of grain orientations [3–7]. One of the factors that determine the spatial resolution of APT datasets is the regularity of the field-evaporation sequence. In the ideal case, the specimen maintains the shape of a half-sphere on top of a truncated cone throughout the experiment. This ideal behavior is disturbed by local compositional changes or at lattice defects due to the dependence of field-evaporation on grain orientations and on the local bonding state [8]. These effects lead to a reduction of the spatial resolution in the reconstructed 3D atom maps; particularly at locations where the highest spatial resolution is desired — at the defects. Therefore, EM is in most cases better suited for crystallographic analysis of defects than APT.

EM and APT are thus complementary techniques, enabling the synergistic characterization of materials at the atomic level. For the investigation of materials science phenomena that involve both compositional and crystallographic changes at near atomic scale, such as the segregation to defects, the onset of nucleation of a new phase or

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[1] Here: both, scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

mechanically-induced mixing, conducting only EM or APT alone is often not sufficient. Getting a full picture understanding of these phenomena often requires combining both techniques on the same location of the same specimen, i.e. performing spatially correlated microscopy. This manuscript focuses on work that has been performed with an experimental setup described in ref. [9], it details for which materials scientific question which EM technique is best suited and comments on potential future developments in this field.

2. Experimental setup

Fundamental to the experimental setup is a modified commercial high-angle single-tilt TEM retainer of the type JEOL EM-21311HTR that carries up to four APT specimens on a TEM grid cut in half [9]. This setup is a further development of existing ones [10–13]; it combines high specimen throughput and exact control of the specimen orientation with a flexible and robust experimental procedure [14]. APT specimens are positioned onto the grid using standard focused ion beam (FIB) lift-out techniques [11,15]. Half of the grid-containing section of the retainer, hereafter referred to as the "grid holder", was removed to give access to the specimens in the dual-beam scanning electron microscope (SEM)/FIB instrument and in the atom probe (here: FEI Helios Nanolab 600i and Cameca LEAP 3000HR, respectively). Compatibility between the grid holder, the dual-beam instrument and the atom probe was established by customized adapters that enable precise control about the specimen orientation [9]. Single-tilt TEM experiments were done directly using the grid holder in a JEOL JEM-2200FS microscope. For double-tilt TEM experiments in this microscope, or for the measurement in a Philips CM20 and a FEI Titan Themis, the grid containing the specimens was transferred into the respective double-tilt TEM retainers using a vacuum pick-up tool. The SEM techniques of electron channeling contrast imaging (ECCI) and transmission Kikuchi diffraction (TKD) discussed in this manuscript were conducted using the above described experimental setup with corresponding adapters for the grid holder. This approach is not confined to the microscopes described here. With the help of customized adapters it can be conducted on other dual beam SEM/FIBs, atom probes and TEMs as well.

There is a broad range of EM techniques available to be correlated with APT. The choice of the EM technique depends on the materials science question being answered and on the required spatial resolution. Not all questions have to be addressed by TEM. In many cases the spatial resolution of an SEM is sufficient, which is in general less time consuming than TEM experiments. The following section lists a selection of materials science questions that were answered by correlative EM/APT. The ensuing section details the specific advantages of the various EM techniques when being conducted on APT specimens.

3. Application examples

3.1. Grain boundary segregation

One of the core applications of correlative EM/APT is the investigation of grain boundary segregation. For the complete crystallographic description of a grain boundary five parameters must be known — three that specify the misorientation between the adjacent grains and two that specify the orientation of the grain boundary plane [16]. Each of the five parameters has a strong influence on solute segregation, and thus none of them can be neglected for the investigation of this phenomenon. Segregation often involves light elements that may be only slightly enriched/depleted within a distance that is typically below 2 nm from the interface. EM is ideally suited to characterize the crystallography of grain boundaries and APT for characterizing the solutes segregated to them. In the case of coarse grained materials, four crystallographic grain boundary parameters can be detected on a metallographically prepared specimen by electron backscatter diffraction (EBSD). After site-specific preparation of the interface of interest in the dual beam SEM/FIB, the missing fifth grain boundary parameter (the inclination angle of the interface in the depth of the bulk specimen) can be determined on the lift-out piece using the SEM [9]. When working with grain sizes of less than 50 μm, conducting site-specific lift-outs becomes challenging. In such cases four crystallographic grain boundary parameters can be characterized by conducting non-site-specific lift-outs and then either performing EBSD directly on the lift-out [17,18] or TKD directly on the APT specimens [19,20].

In the case of very fine grain sizes, all five crystallographic parameters have to be determined by TEM. The combination of scanning nanobeam diffraction (NBD) to determine grain misorientations, and scanning transmission electron microscopy (STEM) imaging to determine the grain boundary plane orientation was shown to be an efficient and accurate approach to solving this challenging task. This is illustrated in Figs. 1 and 2 on the example of a cold-drawn pearlitic wire. NBD and STEM were performed in a JEOL JEM-2200FS TEM operated at 200 kV. The spot size, step size and exposure time used for NBD were 0.5 nm, 1.5 nm and 40 ms, respectively. APT was conducted in a Cameca LEAP 3000HR, operated in voltage mode at a set-point temperature of 70 K, 15% pulse fraction and 0.5% target evaporation rate. Using scanning NBD it is possible to investigate nanocrystalline materials with columnar grains with 30 nm diameter. With this grain size, each APT measurement usually contains more than 10 grain boundaries. Using this approach it is thus possible to accurately and efficiently quantify the solute excess and the five crystallographic parameters for a large number of interfaces [16].

However, the possibilities of this approach go beyond of what was demonstrated in [16]. One further complex materials science topic that can be investigated with this combination of techniques is heterogeneous nucleation. Understanding this phenomenon is required to further develop the concept of segregation engineering [21,22]. The local crystal structure and chemical composition of the nucleation site as well as the orientation relationship between precipitate and matrix and corresponding chemical gradients must be known to get the full picture. All this information is contained in the combined STEM image/scanning NBD/APT datasets as demonstrated for the case of position "X" in Fig. 2. The NBD pattern reveals that a cementite precipitate has formed at this grain boundary. From this diffraction pattern, and the ones of the adjacent ferrite grains, the orientation relationship between both grains and the precipitate can be extracted. Moreover, the NBD inverse pole figure map allows for extracting orientation gradients. This makes it possible to estimate the density of geometrically necessary dislocations in proximity to the interfaces. The grain boundary plane can be clearly seen in the STEM image (Fig. 2(b)) but not the cementite precipitate at the position "X" or its interfaces. However, APT gives access to this information. Using this technique, it is not only possible to quantify what kind of elements segregate at the ferrite-ferrite grain boundary, but also what is the position, size, morphology and composition of the precipitate, if there is a concentration gradient inside of the precipitate or what kind of solutes are enriched at its phase boundaries. The APT dataset further tells if there is a pile-up of elements or a depletion zone at the precipitate/ferrite interfaces and what is the composition of the surrounding ferrite matrix.

3.2. Phase identification

Displacive phase transformations such as the transformation of austenite into martensite go along with a change in structure but not in composition. This can make it difficult for APT to distinguish a phase that has formed by a displacive mechanism from its parent phase. Besides TKD, scanning NBD can be used to create phase maps of APT specimens [23]. Apart from being able to characterize grain orientations, this TEM technique can deliver the complementary crystallographic information needed to distinguish different phases with a lateral spatial resolution of 1–2 nm [9,24].