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Combining structural and chemical information at the nanometer scale by correlative transmission electron microscopy and atom probe tomography

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ABSTRACT

In many cases, the three-dimensional reconstructions from atom probe tomography (APT) are not sufficiently accurate to resolve crystallographic features such as lattice planes, shear bands, stacking faults, dislocations or grain boundaries. Hence, correlative crystallographic characterization is required in addition to APT at the exact same location of the specimen. Also, for the site-specific preparation of APT tips containing regions of interest (e.g. grain boundaries) correlative electron microscopy is often inevitable. Here we present a versatile experimental setup that enables performing correlative focused ion beam milling, transmission electron microscopy (TEM), and APT under optimized characterization conditions. The setup was designed for high throughput, robustness and practicability. We demonstrate that atom probe tips can be characterized by TEM in the same way as a standard TEM sample. In particular, the use of scanning nanobeam diffraction provides valuable complementary crystallographic information when being performed on atom probe tips. This technique enables the measurement of orientation and phase maps as known from electron backscattering diffraction with a spatial resolution down to one nanometer.

1. Introduction

For answering many materials science-related questions, correlative chemical and crystallographic knowledge at the nanometer (nm) scale is required. Examples are numerous and include local phase transformations triggered by segregation [31]; the investigation of precipitation [15] and partitioning phenomena [35]; the characterization of the formation of oxide layers [5] and radiation-induced microstructural changes [26]; the prove that there is no segregation at a lattice defect above the detection limit of APT [25]; the investigation of correlations between segregation and dislocations [6], stacking faults [7], or for understanding the correlation between solute segregation and the character of grain boundaries [14,20,36,4,8]. Atom probe tomography (APT), having the capacity to measure three-dimensional (3D) chemistry with equal detection sensitivity (of a few ppm) for all elements at near atomic spatial resolution [16], can provide answers to some of these questions. In certain cases, the spatial resolution of APT is even high enough to preserve three or more independent lattice planes in the 3D atom maps, enabling unambiguous indexing of grain orientations [1,23,28,39,40]. However, the spatial resolution is material- and measurement condition-dependent. For instance, the spatial resolution usually improves with lower measurement temperature and fewer alloying elements. The ideal material for crystallographic APT analyses has large lattice spacing and shows a regular field evaporation behavior such that the atomic planes are field evaporated in a defined sequence from outside to inside, layer by layer. This behavior is disturbed by lattice defects and by the presence of high concentrations or local enrichments of elements that have a different field evaporation potential than the matrix element. Hence, in most cases, sufficient crystallographic information required for a full-picture description of certain phenomena remains inaccessible by APT alone.

Transmission electron microscopy (TEM), on the other hand, is an excellent tool for structural investigation, even down to sub-Ångstrom scale. However, analytical TEM is often less suited than APT for the quantification of 3D local chemical compositions at the atomic scale. Firstly, TEM suffers from projection effects that make the investigation of non-planar features challenging, and secondly, in the case of chemical analysis by energy-dispersive X-ray spectroscopy and electron energy loss spectroscopy in the TEM, the quantification of absolute concentration values is difficult due to complex spectra that often require deconvolution of integrated signals obtained from illuminated atomic columns, and signals

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that are dependent on many optical parameters [9,17,38]. This holds true especially for low concentrations of light elements embedded in a heavy element matrix. APT has the advantage that the atoms, field-evaporated as ions, are simply identified by their mass-to-charge ratio through time-of-flight spectroscopy, which renders the analysis of absolute concentration values comparatively robust.

The complementary nature of TEM and APT (see also [34]) suggests that both techniques should be subsequently applied to the same sample in order to combine their strengths. This was already realized and subsequently put into practice by Fasth, Loberg and Nordén in the 1960s [10,24], who investigated the sample shape by single-tilt TEM, before and after field-ion microscopy experiments. After the introduction of TEM for the target preparation of grain boundaries in the apex of FIM samples by Papazian [29], Kraukauer and Seidman [18] developed a setup in the 1990s that enabled double-tilt TEM operation followed by one-dimensional atom probe measurements on individual atom probe (AP) tips. More recent and sophisticated approaches have allowed for TEM tomography on individual AP tips prior to APT [13,2], for the purpose of optimization of the reconstruction parameters. In recent years, experimental setups capable of holding several atom probe tips at once have been developed, drastically increasing specimen throughput [11,12]. Following on from these, we present here a versatile experimental setup based on a modified, commercial, high-angle single-tilt TEM retainer, which enables correlative focused ion beam (FIB), scanning electron microscopy (SEM), TEM and APT. Several crucial aspects have been improved compared to former approaches. The exact control of the sample orientation in all instruments makes precise merging of information measured in different devices possible, and enables measurement of atom probe tips in TEM under optimized characterization conditions. The grid containing the atom probe samples can now safely be inserted and extracted from the setup due to an improved grid-holding mechanism and due to a grid design that enhances sample protection. This makes the transfer of the samples to any other standard double-tilt TEM retainer a straightforward procedure, thereby enabling experiments under controlled diffraction conditions and high resolution TEM (HRTEM). Moreover, we introduce the usage of (scanning) nano-beam diffraction (NBD) on AP tips. With this powerful tool, local crystallographic analyses with a spatial resolution of 2 nm or better can be performed on AP tips and even the first 10 nm of AP tips prepared by FIB milling can be investigated.

2. Materials and methods

The method development was performed on two iron-based material systems: a binary Fe–9Mn (wt%) martensitic alloy, annealed for two days at 450 °C to create small austenitic, Mn-enriched precipitates; and a hypereutectoid pearlitic steel with composition Fe–0.98C–0.31Mn–0.20Si–0.20Cr (wt%), cold-drawn by $\varepsilon = 6.02$ true strain and annealed for 2 min at 400 °C to create a microstructure composed of columnar grains with an average diameter of about 30 nm and some intergranular cementite particles [22].

The samples were extracted from the surface of the bulk material by standard FIB lift-out procedures, deposited on a bisected, electropolished TEM grid, and subsequently measured by TEM and then APT as described by Felfer et al. [11]. The approach described here pays special attention to gain exact control of the sample orientation in all instruments in order to optimize characterization conditions in each instrument, to create damage tolerance during sample manipulation, allow transfer of samples into other standard TEM holders, and to simplify electropolishing. The detailed experimental setup and procedure is given below.

A commercial molybdenum TEM grid (1GM 100, Pyser-SGI) was fixed between two glass slides and cut using a razor blade, two grid rows above the center (Fig. 1a). This procedure effectively avoids bending of the grid which is a prerequisite to guarantee that all samples are within the range of the eucentric height in TEM. It is also important for protection of the electropolished tips and the samples during grid manipulation. Only if the tips are located right on the center plane of an undistorted grid point, can it be guaranteed that the grid can be laid with both sides onto a flat substrate without damage to the tips. The larger half of the bisected grid was then mounted at its outermost end into a v-shaped holder specifically designed for electropolishing (Fig. 1b). Using a v-shaped adapter for electropolishing (Fig. 1b) has the

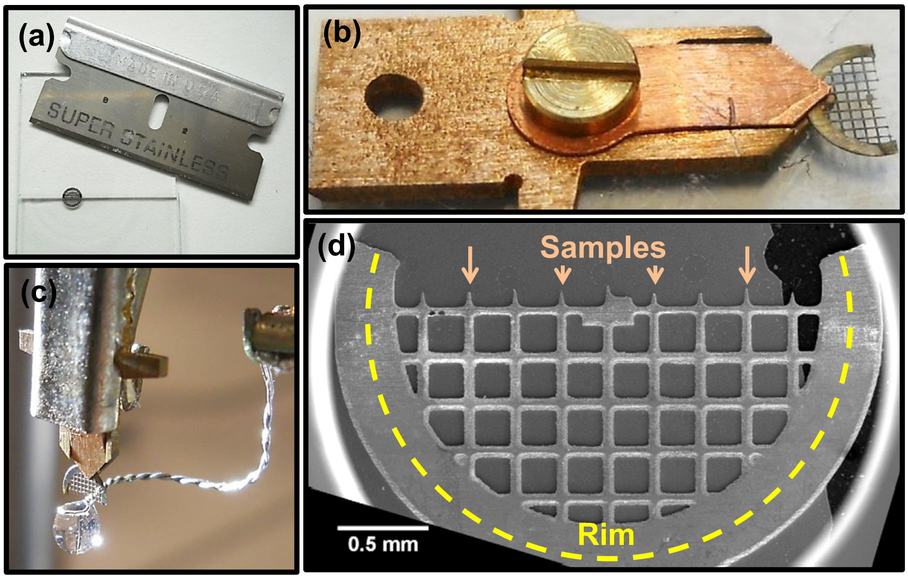

Fig. 1. Preparation of a commercial TEM grid for sample deposition by a FIB lift-out procedure. (a) Sectioning of grid fixed between two glass slides using a razor blade. (b) Mounting of grid into special holder for electropolishing. (c) Setup during electropolishing. (d) SEM micrograph of electropolished grid. Only the posts of the grid are shortened and tapered during electropolishing, ready for FIB lift-out sample deposition. The rim of the grid is not removed and serves as protection for the samples against mechanical damage.