The future of atom probe tomography

The dream of the microscopy and materials science communities is to see, identify, accurately locate, and determine the fundamental physical properties of every atom in a specimen. With this knowledge together with modern computer models and simulations, a full understanding of the properties of a material can be determined. This fundamental knowledge leads to the design and development of more advanced materials for solving the needs of society. The technique of atom probe tomography is the closest to fulfilling this dream but is still significantly short of the goal. The future of atom probe tomography, and the prospects for achieving this ultimate goal are outlined.

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History has taught us that every time a new form of microscopy or type of microscope is introduced, major advances are made in the understanding of materials. For example, the light or optical microscope introduced the world to microbes and micro-organisms around 1600 AD, and the electron microscope to dislocations in materials over 50 years ago. Today many different forms of microscopy have been developed but the ultimate goal of seeing, accurately locating, and identifying all the atoms in a specimen is still elusive. Atom probe tomography and electron microscopy are the mainstays of atomic resolution microscopy of bulk materials. However, neither technique can accomplish this goal in the bulk of a specimen at the present time.

Atom probe tomography enables us to approach this goal by providing the spatial coordinates of atoms and their identities, but its spatial resolution and detection efficiency fall short of the ultimate target. Modern electron microscopes can routinely see the individual columns of atoms in crystalline materials, aid in the identification of the crystal structures from diffraction patterns, and in special cases – with the help of simulations – identify individual atoms, as well as bonding and oxidation states, and chemical, electronic, and magnetic information. Although incremental improvements in the design of current microscopes will surely occur, this level of three-dimensional resolution cannot be achieved for all atoms in a sample of a technologically interesting or important material. The need for such a microscope is
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The roadmap of atom probe developments

The quest along the road to this ambitious goal to detect and identify individual atoms started roughly 60 years ago with the pioneering work of Prof E. W. Müller and the field ion microscope. With this simple glass instrument, Müller and Bahadur were able to produce the first images of individual atoms in 1955-7. Four critical experimental parameters were needed to achieve this milestone. The specimen needed to be in the form of a very sharp needle (end radius typically 50 nm) that was cryogenically cooled to which a positive electric field was applied in the presence of a trace of an image gas (1 x 10^{-3} Pa), such as helium or neon. When the electric field, i.e., the positive voltage, is slowly increased, the helium image gas atoms near the surface are polarized and attracted to the apex of the needle. After becoming thermally accommodated to the cryogenic temperature, an electron can be removed from these atoms by an electron tunneling process, if the electric field is sufficiently high. The resulting ion produced is immediately repelled from the specimen to a phosphor screen located a few centimeters away, where it produces visible light. This process occurs all over the surface of the specimen wherever the atoms protrude slightly from the surface and the resulting map of this intensity of light is the field ion image. If the voltage on the specimen is increased further, the surface atoms of the material can be removed by a process known as field evaporation. This process can be continuously repeated to enable not only the interior of the specimen to be analyzed, but it also allows any irregularities and contamination on the surface to be removed.

Once the individual atoms had been resolved, Müller set about identifying these atoms by exploiting the process of field evaporation. Along with his co-workers Panitz and McLane, Müller built a prototype instrument in 1967 which they called an atom-probe field ion microscope (APFIM). This instrument incorporated a small aperture in the center of the phosphor screen which served as the entrance to a time-of-flight mass spectrometer. In this prototype instrument, the specimen was placed on a sliding glass seal goniometer so that the image of an atom on the surface of the specimen could be aligned with this circular aperture. Then a voltage pulse of amplitude, \( V_p \), was superimposed on the standing voltage, \( V_s \), to remove the atom of interest and simultaneously trigger an oscilloscope scan which was monitoring the output from the single atom sensitive detector at the end of the mass spectrometer. The mass-to-charge state ratio, \( m/n \), and hence the identity of the atom was determined from the flight time, \( t \), and distance, \( d \), and the total applied voltage due to the equivalence of the potential energy of the ion just prior to field evaporation, \( neV = ne(V_s + V_p) \), to its kinetic energy that it acquire after leaving the specimen, \( \frac{1}{2}mv^2 \), where \( e \) is the electronic charge, and \( v \) the speed of the ion. Therefore, the mass-to-charge state ratio, \( m/n = \frac{2e(V_s + V_p)t^2}{d^2} \). The mass resolution of the early instruments was limited by small variations in the energy acquired during the field evaporation event. This limitation was solved by the incorporation of an energy-compensating lens into the mass spectrometer. With this lens and the nature of the time-of-flight mass spectrometer, all elements could be detected with equal sensitivity and the instrument had sufficient mass resolving power to identify their isotopes. When small computers became available, computer-controlled digital timing systems were added to automate the experiment and data collection.

The first commercial atom probe field ion microscope, the VG FIM100, was introduced in 1985. The potential for this instrument for near atomic scale materials characterizations was immediately recognized by materials scientists.

During this period, Kellogg and Tsong implemented an alternative method to remove atoms from the specimen by applying a laser pulse to momentarily increase the temperature of the apex of the specimen so that the field due to the standing voltage was sufficient to promote field evaporation. This method did not introduce the energy variations of the voltage pulsed method so high mass resolutions were possible with long flight distances. More importantly, it has also enabled semiconducting and poor-electrically-conducting materials to be examined. The pulsed laser mode of operation opened up the application of the technique to all areas of materials science rather than just metallurgical studies.

The development of the 10 cm atom probe by Panitz inspired the next generation of wide field-of-view three-dimensional atom probes. The primary goal of atom probe tomography (APT) was to increase the field of view from the narrow 1 – 2 nm diameter cylinder of analysis produced in the APFIM to larger dimensions without sacrificing the spatial or mass resolutions. Several approaches were pursued successfully that used different types of position-sensitive detectors, including high speed video cameras, wedge-and-strip anodes, multi-anode variants, and combinations thereof. Due to the simple projection of the image, the lateral coordinates of the impact position on the detector are directly related to the coordinates of the atom on the surface of the specimen. The third coordinate is derived from the order in which the atoms are detected. In the some variants, an energy-compensating reflectron lens was incorporated into the mass spectrometer to improve the mass resolution.

The next generation of three-dimensional atom probes was stimulated by the scanning atom probe introduced by Nishikawa et al. in which an electrode with a small aperture was moved across a two-dimensional rough surface. This configuration did not permit reliable materials analysis due to trajectory aberrations caused by the rough nature of the surface. However, in the local electrode atom probe (LEAP), a funnel-shaped aperture is positioned close to the apex of the standard needle-shaped specimen, as shown in Fig. 1. As a result, a significant improvement in energy resolution was achieved.

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close proximity (20 – 50 μm separation) counter electrode with a small aperture (20 – 50 μm in diameter) reduced the voltage required for field evaporation, the use of lower voltage pulses was practical. This enabled a new generation of solid state high voltage pulse generators with an order of magnitude higher pulse repetition rates (up to 200 kHz) and high speed position-sensitive detectors to be used which significantly reduced the data acquisition time. Both non-energy-compensated and energy-compensated versions of the LEAP® are in commercial production. This local electrode design also permitted the use of multi-tip arrays of specimens that are fabricated by ion milling methods in a dual-beam focused-ion-beam (FIB)/scanning electron microscope. The three-axis nanopositioning stage permits the individual tips on the array to be aligned with the aperture so that each one can be characterized in turn.

The FIB-based milling technique also enables site-specific specimens to be fabricated from regions of interest so that features, such as grain boundaries and other interfaces, phases, multilayers, or structures that are present in low volume fractions or number densities, embedded or implanted regions, etc. can be analyzed. The method also permits the volume and hence activity of irradiated materials to be minimized and enables potential new high stability materials for advanced energy systems, such as future generations of fission and future fusion reactors, to be investigated.

Atom probe tomography is a destructive technique, as it consumes the specimen during the experiment. Fortunately, this nature is mitigated because the analysis and interrogation of the data are performed after the experiment is completed. This post processing procedure allows many different types of analyses to be performed on the same data. Some different types of data visualizations and types of analyses that are possible with atom probe tomography are shown in Figs. 2 to 5.

The solute distributions across a 32 nm technology nFET transistor extracted by a focused ion beam-based technique from a commercial Intel® i5-650 microprocessor is shown in an atom map in Fig. 2. The solute distributions for the gate oxide (80 at. % Hf+O 20 at. % Si), source and drain regions (25 at. % Ge maximum), and channel region of a 32 nm technology nFET transistor extracted by a focused ion beam-based technique from a commercial Intel® i5-650 microprocessor. The distributions of the B and As are clearly shown. Courtesy Dr. D. J. Larson.
drain regions either side of the channel region contained a maximum of 25 at. % Ge. The distributions of the B and As atoms are clearly shown in relationship to the source and drain regions. In the mechanically alloyed 14YWT nanostructured ferritic steel, Ti-, Y-, Cr- and O-enriched nanoclusters are present, as shown in Fig. 3. The solute distribution within these 1 to 2 nm diameter nanoclusters is clearly non-uniform with a Y-enriched core region, possibly indicating the initial nucleus. The grain boundaries are also decorated with nanoclusters and other precipitates as well as chromium and tungsten segregation, as shown in Fig. 4. The nanoclusters, precipitates, and solute segregation pin the grain boundaries and thereby minimize creep at elevated temperatures. Ultrafine 2 nm diameter copper-enriched precipitates and phosphorus

Fig. 3 A set of atom maps of a 2 nm diameter Ti-, Y-, Cr, and O-enriched nanocluster selected from an atom probe tomography dataset of a 14YWT nanostructured ferritic steel. Each sphere represents the position of a single atom. W does not partition to the nanocluster. The extents of the Ti and O are larger than that of Y.
The future of atom probe tomography

A tantalizing peek at the prospective future of atomic-scale microscopy is shown in Fig. 6 in which a high resolution transmission electron microscopy (HRTEM) image is juxtaposed to atom probe tomography data from the same Al-Cu-Mg alloy. The HRTEM image provides a 3D projection image with lattice resolution along the <110> zone axis, although convolutions in the scattering processes from the different elements make unequivocal, quantitative distinctions between the various atomic species impossible. This is because this alloy, and many such engineering materials of technological importance are multi-component solid solutions with a non-periodic solute architecture. The atom probe tomography data shown in Fig. 6 is a 3D tomographic image that has been oriented in a similar ‘side-on’ orientation to facilitate the comparison. The 3D perspective of a subset of the APT data shows the tomographic nature of the data better. The enormous possibilities for data-mining are showcased by a series of species-specific radial distribution functions, Fig. 6, whereby the relative frequency of incidence...
of particular solutes, both individual and combined, are plotted as a function of distance from the reference atom. The spatial resolution of the APT data can be improved because of the recent development of the so-called lattice rectification (LR) technique. The potential for the atom probe to record both crystallographic and chemical information is clear, and the opportunities to hybridize APT and TEM data are the very frontier of atomic scale microscopy. Whilst we anticipate further refinements to the LR technique, there are other exciting frontier areas of atom probe besides what can be done to improve the tomographic reconstruction, most particularly in the hardware, and data analysis methods.

The most obvious hardware improvement is to increase the detection efficiency of the single atom detector to a point where every atom is detected. Current single atom detectors use a pair of microchannel plates to provide the ion-to-electron conversion and the subsequent electron multiplication process, and a crossed delay line detector (with 2 or 3 serpentine anodes) to provide the position information. The mechanical strength of current glass-based microchannel plates dictates that they have a significant area in between the channels in which the electron multiplication process occurs. The area does not contribute to the electron multiplication process so the detection efficiency is primarily defined by the open channel area which is approximately 60 %. In addition, the field-defining mesh on the entrance/exit to the energy-compensating reflectron lens further reduces the detection of the ions. Therefore, nearest neighbors in the data are not necessarily nearest neighbor atoms in the sample. This uncertainty prohibits or limits the effectiveness of certain types of analyses, such as element-specific radial distribution functions, and methods to investigate short and medium range order. The importance of detection efficiency for analyzing short range order is shown for simulated data in Fig. 7. Larger signal-to-noise ratios would also improve the minimum detection level which is particularly important for small features. New types of microchannel plates are under development that use a stronger and thinner support structure on which a secondary electron emitting (SEE) layer of Al$_2$O$_3$, SiO$_2$, ZrO$_2$ or MgO are atom layer deposited.

The mass resolution and high signal-to-noise ratio of modern instruments is currently sufficient to resolve all the isotopes of every element. However, several elements have isotopes with the same isobar, e.g., $^{54}$Fe and $^{54}$Cr. In order to distinguish these cases, almost two orders of magnitude increase in the mass resolution would be required. It is currently not possible to achieve this increase without sacrificing detection efficiency and, in most cases, these overlaps can be deconvoluted for compositional analyses by taking into account the isotopic abundances of the other isotopes of the overlapping elements. However, it is not possible to uniquely identify the atom for these cases. As the instrument estimates the mass-to-charge state ratio, overlaps between elements in different charge states are also common and more problematical, e.g., $^{48}$Ti$^{3+}$ and $^{16}$O$^+$. Some of these cases can be distinguished from the other isotopes but in a few cases, such as $^{28}$Si$^{++}$ and $^{14}$N$^+$, neither element has other isotopes in sufficient

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**Fig. 6** Towards new frontiers in atomic resolution microscopy. High resolution transmission electron microscope (HRTEM) image and corresponding lattice-rectified atom probe tomography from an Al-Cu-Mg alloy. The precise solute architecture is available both for visualization and mathematical analysis by, for example, radial distribution functions for the individual species. The APT data and analyses are courtesy of Drs Michael Moody and Leigh Stephenson of The University of Sydney.

**Fig. 7** The cluster-size frequency distribution within simulated APT data were calculated from model data wherein the solute exhibits a short-range order parameter of $\alpha = 0.10$. Cluster ‘size’ is measured in number of atoms. Thus, the effects of detector efficiency, $\varepsilon$, on cluster analysis is modeled. It is seen that decreasing detector efficiency reduces both the distribution and measured size of observed clusters. Using expectation-maximisation methods to fit a mixture of binomial distributions, an estimation of the original distribution can be deconvoluted from APT measurements and the success of this approach in the simulated data is demonstrated by the convergence between the ‘estimated’ and ‘original’ distributions. Courtesy Dr Leigh Stephenson, University of Sydney.
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abundances for this deconvolution procedure to be fully quantifiable. This problem is further complicated by the occurrence of MX\(^{n+}\) ions, where M is a metal atom and X is a C, N, or O atom. As these ions have different charge states, they also have different kinetic energies. Therefore, as suggested by Kelly\(^53\), new types of single-atom sensitive detectors that can also measure the kinetic energy would be able to distinguish these cases. If kinetic energy resolution is available, ions that evaporate on the pulse could be distinguished from those ions that evaporate on the standing voltage and appear as noise. Filtering may be able to eliminate the need for background noise subtraction and thereby improve the signal-to-noise ratio and hence the quality of the composition determinations. In addition, the background noise atoms from random field ionization and evaporation of residual gas atoms in the vacuum system could be used to produce digital field ion images which could provide information on the shape of the surface of the specimen at the time of the evaporation of each ion. This information would enable more accurate reconstructions of the atom positions and improve the spatial resolution.

One of the most serious deficiencies of the technique that limits the spatial resolution is the quality of the reconstruction algorithm for the atom positions combined with the exact nature of the field evaporation process and the resulting trajectories of the ions as they leave the surface. The current reconstruction method is based on an algorithm developed by Blavette et al.\(^54\) and Bas et al.\(^25\) that assumes the specimen has a hemispherical end cap. However, some additional refinements for the wider field-of-view have been incorporated and proposed\(^54-60\). A recent analysis of the origins of resolution in atom probe tomography demonstrate that the resolution is anisotropic, as may be expected in a truly 3D technique: it is routinely below 0.15 nm in the lateral x-y direction and routinely below 40 pm in the depth direction for some materials\(^59\). However, the spatial resolution is not quite to the level where the crystal structure can be determined. The well-known issues of the different evaporation fields of second phases and the resulting local magnification effects\(^61\) together with their different atomic densities and crystal structures, and trajectory aberrations at the atomic terraces of crystallographic poles and zone lines have not been successfully solved.

A bold concept has been suggested to improve the spatial resolution by combining a local electrode atom probe (LEAP\(^®\)) into the objective lens of a scanning transmission electron microscope (STEM)\(^62\), as shown in Fig. 8 and to improve the detection efficiency through the use of new types of single atom position-sensitive detectors. The resulting instrument, called the atomscope, would take advantage of the two data streams to reproduce a volume that is close to achieving the ultimate goal of detecting, identifying and correctly positioning all the atoms in the sample as well as determining the bonding and oxidation states, and obtaining chemical, electronic, and magnetic information. It is envisaged that the atomscope could be used in at least four unique modes of operation in addition to conventional stand-alone operation as a STEM and a LEAP. In all modes, an initial STEM characterization is performed to evaluate the features of interest in the microstructure and the suitability of the specimen for further analysis. Mode I: an asynchronous experiment would involve performing the TEM characterization followed by the destructive APT experiment. In this mode, there are no limitations on the type of STEM experiments that may be performed prior to the APT characterization, and these experiments might include electron tomography, phase identification, or characterization of the general microstructural, grain boundaries, dislocations, etc. Mode II: a user-driven asynchronous experiment would consist of repetitions of short sections of electron tomography combined with other types of characterizations as appropriate (electron energy loss spectroscopy (EELS), energy dispersive spectroscopy (EDS), high resolution electron microscopy (HREM), diffraction, high angle angular dark field (HAADF), etc.) followed by short sections of APT. This mode should result in sub-nanometer resolution three-

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Fig. 8 Conceptual drawing of the components of a local electrode atom probe installed within the polepiece of an ultra-high vacuum scanning transmission electron microscope. The needle-shaped specimen is mounted on the central connection to the stage and protrudes through the local electrode. Field evaporation is performed either by laser pulsing (not shown) the cryogenically-cooled atom probe specimen or voltage pulsing the local electrode.
dimensional datasets. Mode III: a more time-intensive experiment that would involve sequential collection of both streams of data under full computer control. In this sub-Ångtrom resolution mode, a time-sliced method would be applied to perform short sequences of electron tomography, including HREM and/or surface profiling, followed by short APT sections. Mode IV: a synchronous experiment would involve the simultaneous and continuous EDS/EELS or spectrum imaging of the near-surface regions of the sample while analyzing the sample by APT. However, at this point, the influences of the positive voltage on the needle-shaped specimen during electron microscopy and of the up to 200 keV electron beam on the APT experiment are largely unknown. We anticipate that this new concept instrument has the potential to herald a new era in microscopy, as the dream of every atom in three dimensions starts to be realized, enabling a merger between microscopy and computational modeling approaches.

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