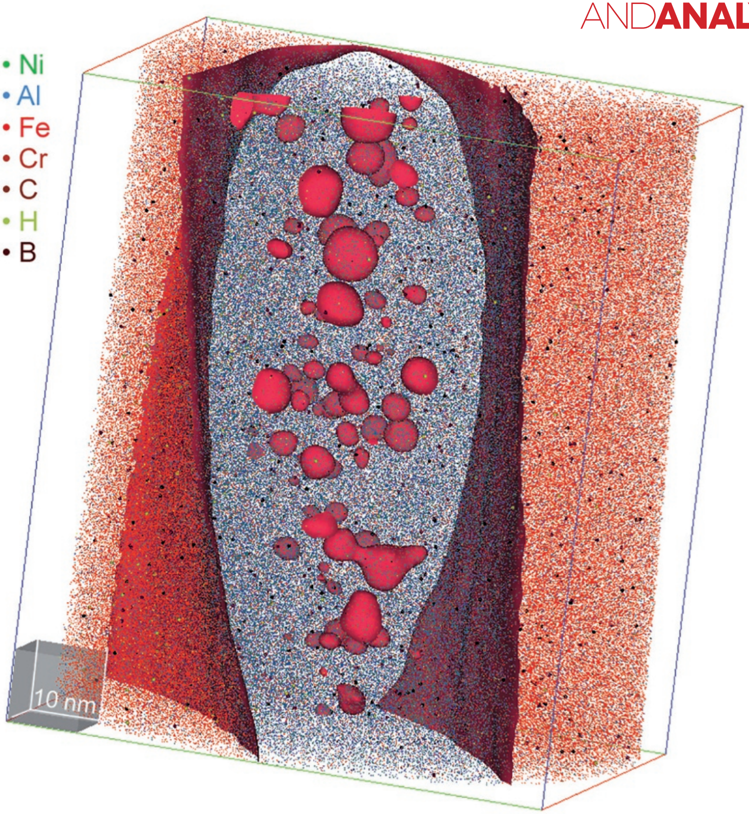
MICROSCOPY
AND ANALYSIS



Atom Probe Tomography

Essential
Knowledge
Briefings

First Edition, 2017

Front cover image: three-dimensional image of a NiFeAlCr-based superalloy showing three phases in the microstructure: a primary Fe-rich phase (alpha-1), a secondary B2 NiAl phase (alpha-2), and a secondary alpha-1 precipitate phase within the alpha-2 phase. The secondary alpha-1 precipitates do not form within ~15nm of large-scale primary regions, *ie* there is a denuded zone or precipitate-free zone near the primary alpha-1 phase. Detailed knowledge of how these complex microstructures vary with composition and processing allows better understanding of precipitation processes and leads to improvements in the engineering of such materials. The Local Electrode Atom Probe (LEAP®) data was acquired at 50 K in voltage pulsed mode. Only a fraction of the ions are displayed for clarity.

Chichester, West Sussex PO19 8SQ, UK
Microscopy EKB Series Editor: Dr Julian Heath
Spectroscopy and Separations EKB Series Editor: Nick Taylor

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Essential Knowledge Briefings, published by John Wiley & Sons, comprise a series of short guides to the latest techniques, applications and equipment used in analytical science. Revised and updated annually, EKBs are an essential resource for scientists working in both academia and industry looking to update their understanding of key developments within each specialty. Free to download in a range of electronic formats, the EKB range is available at www.essentialknowledgebriefings.com

INTRODUCTION

Atom probe tomography (APT) has always offered the enticing prospect of being able to determine the identity and position of nearly every atom in a material, providing the ultimate in elemental analysis. Actually realizing that prospect has taken much time and effort. But with the latest APT systems able to generate three-dimensional (3D) information at near atomic resolution and possessing a chemical sensitivity that can reach parts per million, the technique is now being used to analyze everything from the oldest minerals known to man to the latest nanomaterials.

APT involves applying either ultra-fast voltage pulses or laser pulses to a needle-shaped specimen, stripping away atoms located at the tip of the needle and converting them into charged ions in a process known as field evaporation. These ions are then accelerated by an electric field towards a position-sensitive detector that registers the time it takes each ion to travel from the sample to the detection system, as well as its impact position.

Because the energy applied to the atoms at the surface is known, each ion's mass-to-charge ratio can be calculated from its travel time, and this mass-to-charge ratio is usually sufficient to determine the identity of the original atom. APT is a destructive technique that removes successive layers of atoms from a sample. The impact position and order of detection can reveal the original location of each atom in the sample. Combining these sources of information produces a 3D image showing the atomic structure and chemical composition of the sample, making APT particularly effective at analyzing buried features and interfaces between different regions.

When APT was originally developed, its applications were limited, as it was relatively slow and could only analyze good electrical conductors like metals. Much has changed over the past 10–15 years; APT can now rapidly generate useful information on many different types of samples, including semiconductors, ceramics, and even complex structures such as geological and biomineral materials.

This Essential Knowledge Briefing (EKB) will introduce APT and highlight its impressive abilities. It begins with a brief history of the technique, including the most important developments that transformed the 1D atom probe into a high-resolution and highly sensitive 3D instrument. This is followed by a detailed explanation of the steps involved in conducting an analysis with modern-day atom probes, from sample preparation to 3D reconstructions.

The EKB also considers practical issues and potential problems that may occur during an analysis and offers possible solutions. In addition, it details several examples of how this technique is currently being used by scientists in their research, and concludes by looking forward to potential future developments, from automated sample preparation to improved detector performance.

HISTORY AND BACKGROUND

The history of the atom probe technique can be traced back to the early 1950s when German physicist Erwin Wilhelm Müller developed a new type of microscope, known as the field ion microscope (FIM). Utilizing the same basic approach as modern APT, this instrument applied a positive voltage to a needle-shaped specimen to evaporate desorbed gas ions from the surface, producing a field ion image visualized directly on a phosphor screen. With this microscope, Müller and his PhD student Kanwar Bahadur became the first scientists to observe individual atoms directly.

One of the main limitations of FIM, however, was that although it could produce an image of the individual atoms in a sample, it couldn't determine their chemical identity. To introduce this ability, Müller, Panitz and colleagues added a time-of-flight (TOF) mass spectrometer to their microscope in 1969. A TOF mass spectrometer can determine the mass-to-charge ratio of ions with a known energy based on the time it takes for them to travel the fixed distance between the sample and the detector (TOF), with heavier ions taking longer to travel than lighter ions. The identity of the original atom can then be calculated from the ion's mass-to-charge-state ratio; for example, a mass-to-charge ratio of 54 Da (dalton, or equivalently AMU) corresponds to a specific isotope of iron (^{54}Fe), while 206 Da corresponds to a lead isotope (^{206}Pb).

For this technique to work, Müller and his colleagues now needed to apply the voltage as a rapid series of pulses, so that each voltage pulse could mark the start of a TOF measurement for the evaporated ions. This reliance on voltage pulses meant that APT was initially restricted to analyzing good electrical conductors, particularly metallic alloys: refractory metals, steels, aluminium alloys, nickel super alloys, metallic glasses, etc.

In 1980, Tien Tsong and Gary Kellogg from Sandia National Laboratories in the USA found a way to conduct field evaporation with laser pulses, opening up APT to non-conducting materials such as semiconductors, oxides, ceramics, polymers, and geological and biological materials. The first commercial APT systems, which were voltage-pulsed, started to appear in the mid-1980s.

The next breakthrough came in the late 1980s with the development of a position-sensitive detector by Alfred Cerezo, Terence Godfrey and George Smith at Oxford University in the UK, which transformed Müller's 1D atom probe into a rich and detailed 3D atom probe. The position-sensitive detector was simultaneously able to measure the TOF of ions and their point of impact, which was directly related to the original location of the atom in the sample. Now researchers could analyze not only a sample's chemical composition, but also its morphology and the spatial distribution of its elements.

This novel version of APT was extremely successful, but still had limitations: it could take days to collect data and had a limited field of view (around 25 nm). These limitations were overcome in the early 2000s with the introduction of a local counter electrode. By reducing the distance between the counter electrode and the specimen to as low as 50 µm, higher electric fields could be produced with lower voltages, allowing an increase in the voltage pulse rate and expanding the field of view. Known as Local Electrode Atom Probe (LEAP®), this approach is now employed by nearly all modern commercial systems (Figure 1).

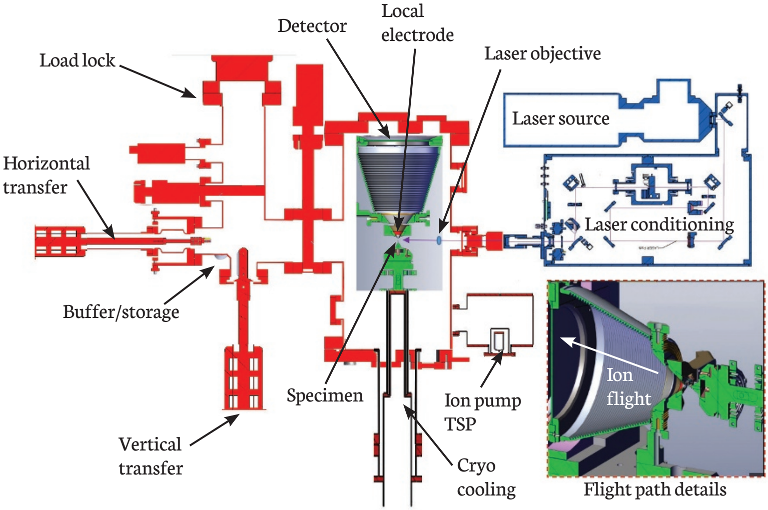


Figure 1. Schematic of a modern atom probe

Such modern systems also benefit from further advances in the detection instrumentation. Once an ion evaporates from a sample, it now first hits a transducer amplifier known as a microchannel plate (MCP), which converts the single ion into a flow of electrons. By amplifying the signal in this way, the MCP is able to detect single ions in both time and location with high precision and high speed.

The structure of the microchannel plate is relatively simple, consisting of a thin metallized glass disc penetrated by micro-channels with a high secondary electron coefficient, which can amplify the signal by a factor of about 1000. To further increase this amplification, some systems possess two of these plates, producing an assembly that can achieve an amplification of between 100000 and 1000000 electrons.

The resulting cloud of electrons then travels through a delay line detector, creating electromagnetic (voltage) pulses that can be processed by standard electronics. Modern APT detectors contain

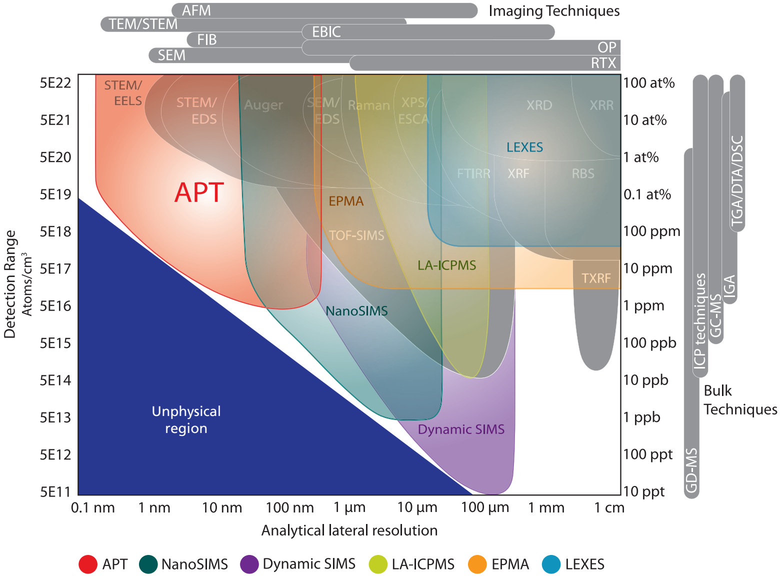
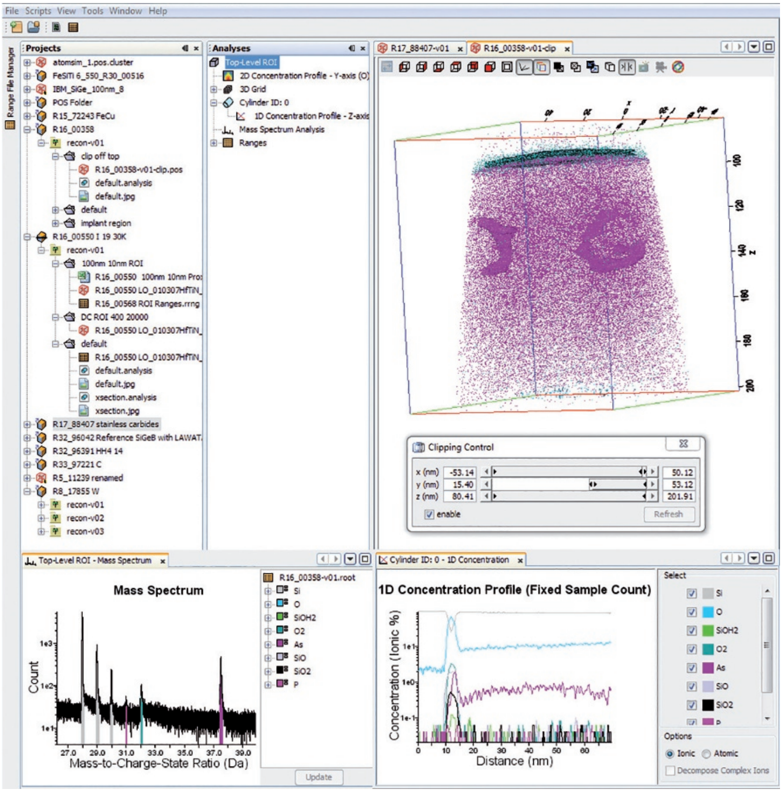


Figure 2. Analytical resolution versus detection limit for APT and various other analytical techniques

three serpentine wires arranged in different directions, allowing them to pinpoint, with great accuracy, the original position of each ion in the sample. The latest APT systems have a lateral resolution of 0.3–0.5 nm and a depth resolution of 0.1–0.3 nm; this compares favourably to other analytical techniques (Figure 2).

Alongside these advances in instrumentation have come associated improvements in analyzing, interpreting and reconstructing the resultant data. Generating meaningful information from the raw APT data offers a number of challenges. For instance, different ions can have similar or identical mass-to-charge ratios, making identification difficult, while variations in the field required to evaporate different atoms can interfere with accurately determining their relative positions in a sample.



x (nm) -53.14 50.12
y (nm) 15.40 53.12
z (nm) 80.41 201.91
☑ enable

Options: ● Ionic ○ Atomic
☐ Decompose Complex Ions

Figure 3. A single windows-based program calibrates, reconstructs and analyses the raw APT data

Nevertheless, the latest APT software can generally deal with these and other challenges, and present the resultant analytical information in a range of different formats (Figure 3). These include raw mass spectra in which ions with distinct mass-to-charge ratios appear as individual peaks, 3D images of the sample showing overall elemental composition, individual slices through those 3D images, the distribution of specific elements in the sample, and the chemical composition of distinct volumes.

All of these advances have led to APT becoming a viable analytical technique in many different fields, including nanosciences and microelectronics, and being applied to the study of samples that would once have been impossible. For example, in geology APT is now being used to study rocks and fossils. In medicine and dentistry, it is being used to analyze the junction between prosthetic and biological tissue, to determine how kidney stones are formed, and to assess the development of cavities in teeth.

IN PRACTICE

Before the advent of modern commercial instruments, data collection was the main bottleneck in atom probe analyses, taking days to obtain sufficient data. However, with all the improvements to APT introduced over the past few years, this step can now take less than an hour. One part of the process that remains less automated, and therefore needs more operator input, is sample preparation, which can be a delicate and time-consuming operation.

To ensure effective field evaporation, the targeted region of interest (usually around 100 x 100 x 100 nm^3 in volume) needs to be needle shaped. One commonly used method for producing this shape is known as electropolishing, which can be applied to metals and metal alloys. An example electropolishing method uses a sample with a thin, wire-like geometry that is dipped into a thin layer of electrolyte floating on top of a dense inert liquid, such that only the mid-section of the sample is immersed in the electrolyte. Applying an electrical current then causes material to be removed, or polished, from this immersed mid-section. A number of other geometries and chemistries can also be used for electropolishing depending upon the material being analyzed.

As more and more material is removed from the mid-section (necking), the sample eventually breaks to leave one end with the required needle shape and sharpness (Figure 4f). By using gradually less concentrated solutions of the electrolyte to ensure a controlled break, this method can also produce a needle shape at both ends. Although the electropolishing process is often monitored using an optical microscope, the sample can also be checked with a transmission electron microscope (TEM) or a scanning electron microscope (SEM).

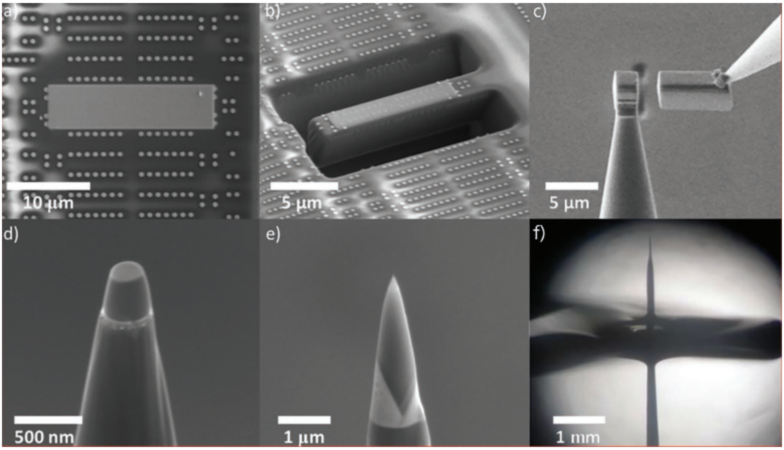


Figure 4. Specimen preparation: (a–c) standard FIB lift-out and mounting of a specimen; (d–e) sharpening the sample with the region of interest left at the very apex; (f) electropolishing of a wire geometry sample

Electropolishing may be relatively easy and cheap to perform, but it is not suitable for every material, particularly non-conducting materials or where the region of interest is very site specific. This is why a second method known as focused ion beam (FIB) milling, which involves essentially carving samples into the desired shape using a beam of ions, is often used. Almost any material can be shaped this way, including semiconductor devices, carbon filaments, ceramics, insulators, and even biological and geological samples. FIB milling can also produce the needle shape in specific areas of a sample, allowing APT to target grain boundaries, interfaces or even single transistors. FIB is often combined with SEM in commercial systems, allowing the milling process to be monitored in real time. Because such FIB-SEM systems can also perform other types of analysis, such as energy dispersive X-ray spectroscopy (EDX), a whole range of information can be gathered during sample preparation.

With FIB milling, APT samples are typically prepared using the lift-out method. This involves using an ion beam to carve out a small wedge of material, which is extracted, mounted on the end of a sample carrier and then milled into the required needle shape. The ion beam typically employs currents of between 50 pA and 10 nA; higher currents produce faster milling, while lower currents achieve a higher resolution.

In a process that is very similar to the FIB preparation of samples for TEM analysis, the region of interest is first covered with a protective layer to avoid accidental damage. The ion beam is then used to cut angled trenches on either side of this wedge-shaped region of interest, followed by a cut at the base of the wall formed by the initial trenches. This cantilevered section is then removed with a micromanipulator and attached to a carrier tip with FIB-deposited material (*eg* tungsten, platinum). The same steps can be repeated to produce multiple samples from the same wedge of material.

At this stage, the sample still needs to be milled into a needle shape. This is typically done using a multi-step process: first, an annular milling pattern produces a cylinder around 1–2 µm in diameter; next, patterns with sequentially lower diameters and lower beam energies are applied to obtain a conical shape with a radius of curvature of less than 100 nm at the apex (see Figure 4).

Once the sample is ready for analysis, it is placed in the specimen mount, which is then inserted into the ultra-high vacuum (UHV) system and cooled to cryogenic temperatures of 20–100 K. The analysis starts when a standing positive voltage is applied to the sample, together with either nanosecond or shorter laser pulses or nanosecond voltage pulses. Older instruments were only able to collect thousands to tens-of-thousands of ions for each analysis, but today's systems can achieve a significantly higher rate of detection, collecting hundreds of millions of ions.

As APT is a destructive technique, the sample will inevitably change shape during analysis. In fact, as soon as the first few layers are field-evaporated, the radius of the tip tends to increase and the sample becomes blunter. For this reason, the standing voltage needs to be increased gradually to maintain a constant electric field and to avoid fluctuations in the evaporation rate. In modern APT systems, this gradual increase in voltage is controlled automatically.

The raw data from an analysis includes: an x,y value for the position of each impact; the voltage applied at the moment of evaporation; and the TOF. This raw data is typically analyzed with the commercial Integrated Visualization and Analysis Software (IVAS^{TM}) from CAMECA®, but other software tools, such as GPM3D-soft created by researchers at the University of Rouen in France, are being developed as well. Figure 5 shows examples of the type of data that can be produced by an APT analysis.

Most of the time, the process of determining chemical composition from the spectral data is relatively straightforward. Exceptions occur when two or more ions impact the detector in close proximity in space and time, or when the spectral peaks of two ions directly overlap. Situations where this may occur and possible ways to solve it are discussed in the ***Problems and Solutions*** chapter.

Optimizing an APT analysis for a specific material can be time consuming, as it involves optimizing a whole range of sample preparation and analysis conditions, including specimen size and shape, acquisition pulse rate, base temperature and detection rate.

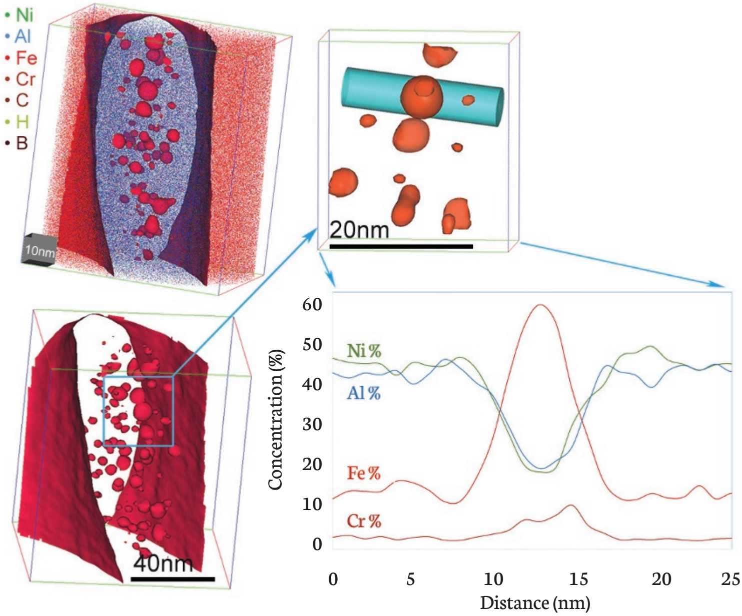


Figure 5. Example APT data showing the ability to observe microscale and nanoscale features with the same resolution and compositional accuracy

Optimum conditions tend to differ for different materials, and determining them is mainly a matter of trial and error (see Table 1 in *Problems and Solutions* for a list of analysis conditions). Once these conditions have been defined for a material, however, the same methodology can be adopted for every analysis. One reason for this simplicity is that, generally speaking, APT does not require any chemical standards, as the delay line detector detects all ions with equal probability. This means there is no need to include sensitivity factors in the analysis.

Reconstructing data for a 3D analysis can be more complex. There are several methods for doing this, but the most commonly used method assumes the needle-shaped sample has a hemispherical end, on which the position of the detected ions is back-projected. This assumption is not consistent with complex samples containing different layers or specific features with wildly variable evaporation efficiencies; however, these oversimplified assumptions often still yield reasonable reconstructions in most cases. There are occasions where the variety of features in the sample is too extreme to get minimally accurate reconstructions with the standard method, so more complex mathematical models are required.

CASE STUDY 1. Combining APT and EDX

Researchers are becoming increasingly aware that the key to improving efficiency in electronic devices is to be found at the nanoscale. However, current methods for analyzing materials at the nanoscale, such as X-ray diffraction and TEM, cannot guarantee accurate readings in terms of composition and structure. So, when Bastien Bonef and his team at the Université Grenoble Alpes in France wanted to analyze nitride-based alloys at this scale, they decided to adopt a new approach, combining APT with EDX.[1]

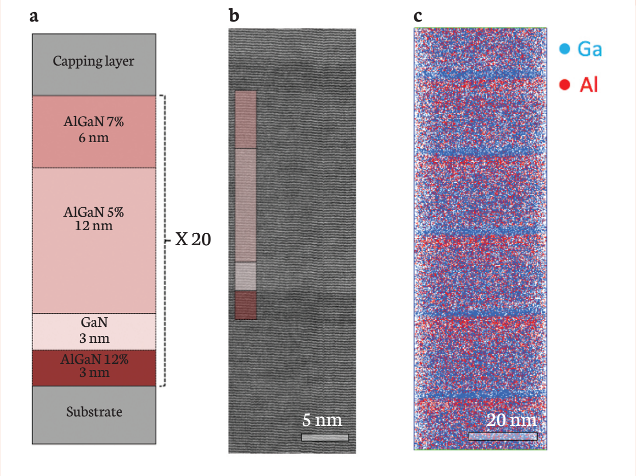
In theory, APT seems to be the ideal technique for determining chemical composition and 3D structure at the nanoscale, but current limitations in data reconstruction for layered samples (see Problems and Solutions*) meant that it might not prove that reliable for nitride-based alloys such as AlGaN.*

'In the case of APT on nitrides, the problem is can we trust the quantification?' explains Bonef. 'In most cases, APT will give you the correct quantification, but it's not always the case.' This is why EDX is seen as a welcome addition to the system. 'Combining EDX with APT just makes the analysis much more reliable and using EDX on the structure gives us a reference to perform the 3D reconstruction of the APT volume.'

Preliminary results seem promising. While APT could clearly identify two separate layers in the alloys, the results improved when the analysis conditions for APT were fine-tuned using information provided by EDX. This included defining the most efficient laser energy to use during data collection, as well as a way to calibrate the subsequent 3D reconstruction.

'People were originally skeptical about APT because of the time required to prepare the sample, perform the analysis and the data treatment,' says Bonef. 'In the case of nitrides, the time required to get to the final data is not that long and indeed is much faster than getting this information from TEM.'

1. Bonef B, Lopez-Haro M, Amichi L, *et al.* Composition analysis of III-nitrides at the nanometer scale: comparison of energy dispersive x-ray spectroscopy and atom probe tomography. *Nanoscale Res Lett* 2016;11:461. (http://dx.doi.org/10.1186/s11671-016-1668-2)



(a) Schematic of the AlGaN superlattice showing its chemical composition. (b) Scanning transmission electron microscopy image of one period of the superlattice. (c) APT 3D reconstruction of four periods of the superlattice

CASE STUDY 2. Applying APT to geological samples

When he first encountered a LEAP atom probe almost 10 years ago, geologist Alberto Pérez-Huerta at the University of Alabama in the USA was instantly fascinated by this technology. Up to that point, the university's atom probe had solely been used to study metals and alloys. Very quickly, however, Pérez-Huerta and his colleagues saw the potential for applying APT to geological samples in order to probe the chemistry of minerals at the nanoscale.

'This instrument was designed for metals, but it has improved so much that you can do non-conductive materials, such as minerals and ceramics and insulator materials,' says Pérez-Huerta. 'We believe it gives us the capacity to look at the atomic scale composition of any mineral out there.'

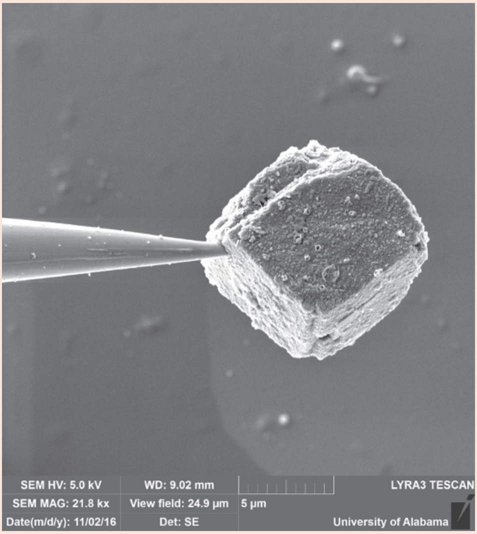
The reason APT is so valuable to geologists is that as well as revealing a mineral's chemical composition, it can also help determine how the mineral formed. For example, explains Pérez-Huerta, 'we can look at volcanic rock and understand things about the eruption, or we can look at the chemistry of coral and understand about climate changes in the past'.

After a few tests to ensure APT could reproduce the composition of standard minerals, like carbonite,[1] *Pérez-Huerta and his colleagues are now set on expanding the type of geological samples analyzed with APT. This list already includes minerals like pyrite, magnetite, quartz and calcite, as well as biominerals like biocalcite and bioaragonite from seashells and fossils like egg shells. They are now even contemplating using APT to analyze bone tissue.*

One practical limitation lies in sample preparation. 'It's very difficult to prepare samples, it takes a long time and we have to be very careful because many of these minerals have cleavage planes and are brittle,' says Pérez-Huerta. 'Minerals start forming these nanocracks and when you put them in the LEAP and start ionizing them, these nanocracks are going to be areas of failure.'

Despite these problems, Pérez-Huerta is determined to get the rest of the geological community to realize the impressive potential of APT. 'It still blows my mind we can see atoms in three dimensions,' he admits.

1. Pérez-Huerta A, Laiginhas F, Reinhard DA, *et al.* Atom probe tomography (APT) of carbonate minerals. *Micron* 2016;80:83–9. (http://dx.doi.org/10.1016/j.micron.2015.10.001)



Example of the FIB lift-out of a single geological crystal for analysis by APT

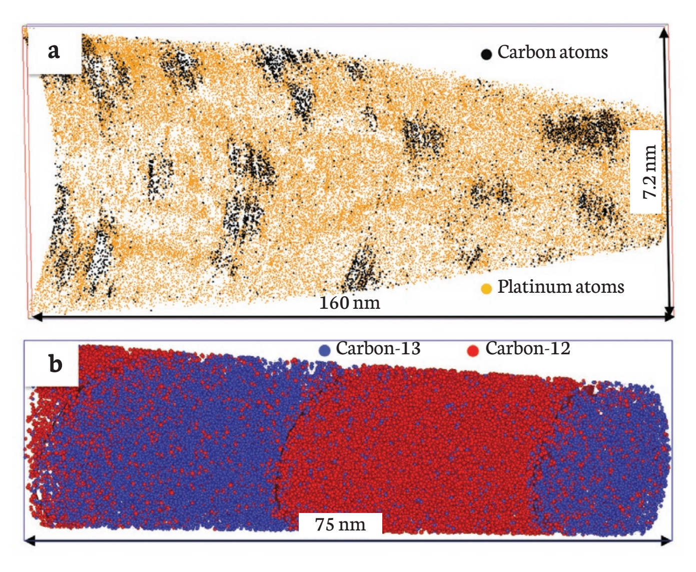
CASE STUDY 3. Admiring diamonds with APT

Dieter Isheim at Northwestern University in Evanston, USA, first became curious about diamonds a few years ago. Debating whether the nanoscale diamonds found in some meteorites predated the formation of the sun, he and his team decided to measure the ratios of two different isotopes of carbon (carbon-12 and carbon-13). Presolar material is known to be characterized by isotopic abundances markedly different to those found in substances formed after the sun formed. As one of the only analytical techniques capable of distinguishing isotopes in individual nanoscale objects, APT was an obvious choice for this work.

During their analysis, however, the researchers noticed a unique behavior when the nanodiamonds were placed under a high electric field. 'With metals, [APT] is easy because metals have such a high concentration of free charge carriers that the electric field is always concentrated at the surface', says Isheim. 'The problem with diamonds is that they're dielectric. This means the electric field penetrates into it and it's not concentrated at the surface, and the residual field at the surface is not strong enough to cause field evaporation.'

The solution that he and his team came up with involved applying a pulse energy significantly higher than normal, in order to promote impact ionization. This way, explains Isheim, 'you can create charge carriers which can push the electric field to the surface, so that field evaporation can happen'.

Using this novel APT method, Isheim and his team discovered that the vast majority of these meteoritic nanodiamonds didn't form before the sun after all,[1] *and have since gone on to use the same*



(a) Individual nanometer-sized meteoritic nanodiamonds (carbon atoms: black dots), atomically resolved in an APT reconstruction.[1] For preparation purposes, the nanodiamonds were dispersed in a platinum matrix (orange dots). (b) Atomically and isotopically resolved APT reconstruction of a nano-layered diamond material with alternating layers of carbon-13 (blue) and carbon-12 (red) atoms[2]

method to test diamonds in other applications. For example, specially designed diamonds with alternating layers of carbon-12 and carbon-13 are being investigated as novel materials for microelectronics. While diamond may not have been a popular material in this field so far, its thermal, mechanical and electrical properties make it an ideal choice for increasing computer reliability and allowing the use of high-power systems.

'It turns out the layers are not perfectly isotopically pure and with APT we can measure not only the layer composition but also the transition at the interface,' says Isheim. In this case, APT can

accurately determine the concentration and distribution of each isotope, which is essential for understanding how these specially designed diamonds perform under different conditions.[2]

1. Heck PR, Stadermann FJ, Isheim D, *et al.* Atom-probe analyses of nanodiamonds from Allende. *Meteorit Planet Sci* 2014;49:453-67. (http://dx.doi.org/10.1111/maps.12265)
2. Mukherjee S, Watanabe H, Isheim D, *et al.* Laser-assisted field evaporation and three-dimensional atom-by-atom mapping of diamond isotopic homojunctions. *Nano Lett* 2016;16:1335-44. (http://dx.doi.org/10.1021/acs.nanolett.5b04728)

PROBLEMS AND SOLUTIONS

APT may be a particularly sensitive analytical technique at the nanoscale level, but it still has some important limitations. For a start, researchers still don't completely understand the process of field evaporation and how it works with different elements. This can have a major impact, especially for samples made up of different layers or containing a particular feature with a different chemical composition, as the data analysis can become complicated at the interface between these different regions.

A poor understanding of factors affecting field evaporation also means that detection efficiency may be lower than expected. To detect an atom that has been removed from the surface of the needle tip, field evaporation needs to be synchronized with a laser pulse and the atom needs to be evaporated as a charged ion. This is not always the case. Researchers suspect some atoms evaporate as neutral molecules, which can't be detected, or evaporate between distinct voltage or laser pulses, preventing an accurate measurement of TOF. For example, nitrogen (N) can evaporate as N_2; while gallium can evaporate at energies below those provided by a voltage or laser pulse.

In addition, unlike with other analytical techniques, it can be difficult to know accurately the magnification for each sample. Although APT can determine chemical composition and 3D structure very effectively, it can struggle to determine the size of a specific feature accurately or precisely. One possible solution is to synergistically combine APT with other analytical techniques, such as TEM. In other cases, it may be possible to calculate the size of a particular feature, such as a precipitate or a cluster, by knowing the number of atoms collected and the shape of the feature.

In practical terms, one of the most common problems with APT analyses is sample fracture. This can occur because the sample is under high mechanical stress during analysis, and any weak point, such as a crack or a surface notch, may induce fracture before the analysis is completed. Typically, metals and alloys are strong enough to withstand voltage pulsing, but laser pulsing, which field-evaporates ions at lower stress levels, is often used with weaker materials.

In an ideal world, all APT experiments would extract data with maximum quality and minimum analysis time. However, each sample is unique and so operators need to define the optimum conditions for each analysis (Table 1). This is particularly important when planning experiments with types of samples not previously analyzed.

For certain samples, analysis speed has to be sacrificed. Slower pulse rates may be required for samples containing high-mass elements with slow TOFs or elements with low thermal diffusivity, as a fast pulse rate can produce spectral peaks with long tails. Similarly, high detection rates maximize data quality for most samples, but not when the analyzed material is prone to field-evaporating multiple ions at the same time, or if the sample is weak and prone to early failure.

In most cases, lower temperatures provide better data quality, by reducing the impact of residual gas present in the analysis chamber and harmonizing the fields required to evaporate different elements, which in turn reduces spectral background. Some samples, however, provide better yields at higher temperatures; for example, aluminium alloys perform better at temperatures of around 20–40 K, whereas steels are typically analyzed at 50 K.

Acquisition parameter	Variable	General trend	Metrics	Comments	Primary trade-off
Pulse rate ↑	*f (Hz)*	++ – – –	Background *m*/*n* range Wrap around Base temperature offset effects (laser)	Faster is better Exceptions: high mass ions with long TOF or extremely poor thermal diffusivity materials in laser mode	Almost none except for practical considerations for TOF of all potential ion species
Base temperature ↑	*T (K)*	++ – – – – – –	Analysis yield MRP Background Heat flow (laser) Surface diffusion	Lower leads to better spatial resolution Higher leads to better yield	Data quality versus analysis yield
Detection rate ↑	*DR (ions/ pulse)*	++ – – –	Background Analysis yield MRP Multi-hit performance	Faster is better Exception: poor yielding materials and materials prone to multi-hit behavior	Data quality versus analysis yield
Pulse fraction ↑ (voltage mode)	*PF (%)*	++ + – –	Compositional accuracy Background Potential for PF decay High cycle fatigue	Higher is better Exception: extreme PF may limit MRP and pulse amplitude is hardware limited	Data quality versus analysis yield
Laser pulse energy ↑ (laser mode)	*LPE (nJ or pJ)*	+++ ++ + + – – –	Analysis yield Background MRP Effective pulse fraction Complex ion generation Surface migration	Higher leads to better yield Lower leads to better spatial resolution	Data quality versus analysis yield

Table 1. General experimental parameter considerations, data quality trends and trade-offs (parameter increases ↑, trends improves +, or worsens – the metrics)

Peak overlaps between elements at different charge states are possible. In most cases, overlaps can be distinguished based on the other isotopes present. A classic example is steel. If a particular steel alloy contains chromium (Cr), this element shares a common isotope with iron (Fe): ^{54}Cr and ^{54}Fe. As both Cr and Fe also have three other isotopes, it's possible to analyze the ratio of each isotope in the steel alloy and compare them to their natural abundances, using this isotopic information to identify the fraction of the peak that corresponds to ^{54}Cr and to ^{54}Fe.

With APT now being used in fields beyond metallurgical analysis, data interpretation is becoming increasingly complex – particularly in samples containing complex organic molecules, where elements may field evaporate in conjunction with hydrogen, carbon or oxygen. This can produce a complex mass spectrum that is difficult to interpret. Nevertheless, even though it may not be possible to identify single atoms, high-quality 3D reconstruction can still produce valuable information at the molecular level.

One of the most intriguing aspects of APT is its ability to create a 3D map of a sample at nanoscale resolution. The calculations used to produce these maps are based on a number of assumptions, including the hemispherical surface of the tip. In homogeneous samples, this is a good assumption, as it's natural for the sample to become approximately hemispherical to minimize its surface area as atoms are evaporated.

Problems may arise in complex heterogeneous samples, such as those containing interfaces and precipitates that result in heterogeneous evaporation. When the sample contains materials with different compositions, they can require different strength fields to evaporate, which means the assumption of a hemispherical sample is no longer valid.

This is the case for precipitates with a higher melting temperature than the surrounding matrix. When they reach the surface of a sample, the tightly bonded ions in these precipitates will be the last to evaporate, creating a bump on the surface with a higher magnification than other regions. In this case, assuming a hemispherical surface will result in scaling errors during the reconstruction process, although an accurate reading of the magnification can often be obtained by complementing APT with a correlative analysis like TEM.

WHAT'S NEXT?

The company CAMECA, headquartered in France with facilities in the UK and USA, and a business unit of the global instrument company AMETEK, is now the sole producer of commercial APT systems, and is still actively working to improve the technique by increasing throughput, efficiency, acquisition times and resolution.

One of the last areas to resist automation is sample preparation. This is because, with APT being applied to an ever greater variety of materials, more demands are being placed on the methods for producing a needle shape. At the moment, all these methods require multiple instruments to achieve this shape, with heavy involvement from the operator. The future for sample preparation includes developing methods that can produce such microtips rapidly, accurately and automatically. This would allow for the preparation of identical and uniform samples in large volumes, generating comparable results for each analysis.

Another area where researchers would like to see improvements is in the efficiency of ion detection. At the moment, ion detection efficiencies of 50–80% are the best that can be expected with modern instruments. The problem starts at the microchannel plate before amplification. As this plate is composed of thousands of channels arranged close together, there is always a chance that an ion will hit the space in between two channels and get lost. New designs for microchannel plates are envisioned, using thinner and stronger materials covered by a secondary electron-emitting layer made from a metal oxide such as aluminium(III) oxide, silicon dioxide, zirconium dioxide or magnesium oxide. Researchers are also testing new superconducting materials for this application.

Further improvements to the 3D reconstruction algorithms would also be desirable. As described earlier, the most common reconstruction method assumes a hemispherical end, but this cannot be applied to all samples. One way to overcome distortions would be to determine the exact trajectory for each ion, but there is a large computational cost associated with such analyses at the moment. Other options include developing new algorithms that can more accurately describe a particular sample, and combining APT with TEM to obtain information on the dimensions and angles of the sample, as well as information about any interfaces and precipitates that are present.

At the moment, combining APT and TEM on the same sample volume can be time consuming and complicated, requiring samples to be transferred from one instrument to the other under UHV and/or cryogenic conditions. As there are many advantages to this combination, including more accurate magnification and reconstruction, researchers are considering ways to physically combine both instruments or to more easily integrate the information provided by each of them. One idea is to place a TEM on the side of the APT to obtain information in an easy and convenient way, as well as to allow the development of a more automated system.

After its expansion into non-conducting and geological materials, some scientists are now trying to apply APT to biological samples, but that raises the problem of how to produce a needle shape in soft biological material. One solution is to freeze the sample and prepare a needle tip with FIB, but this process still has many difficulties. Efforts are underway to make it possible to transport frozen samples between instruments under UHV conditions.

Finally, APT also has the potential to become a metrology tool. To do so, analyses would need to be completed within a certain time, with the results used as feedback during further processing. This approach would require a considerable amount of effort, but no more than other metrology tools already available.

Conclusion

Since the turn of the century, the user base of APT has expanded from just a handful of researchers to thousands who now use APT on a regular basis, and is predicted to grow rapidly in the coming years. The rapid increase in the number of publications featuring atom probe work is a testament to its increasing popularity.

This is not surprising since, despite still struggling with certain limitations, the ability of APT to determine the elemental composition of samples in three dimensions at the nanoscale level is too appealing to ignore. And this appeal should only grow, as APT systems become more automated, and their resolution and sensitivity gradually increase, until scientists really can determine the identity and position of every atom in any material they desire.

FURTHER READING

Atom Probe Tomography user's website, run by CAMECA. (http://www.atomprobe.com)

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