1. ATOM PROBE TOMOGRAPHY AND NANOTECHNOLOGY
A general view of nanotechnology encompasses the design and fabrication of materials whose properties are controlled or influenced by features on the nanometer scale. Although nanotechnology often refers to semiconductors and other novel devices, the properties of many conventional materials and alloys are also controlled by features on the nanometer scale. In order to develop the full potential of these types of materials and understand their properties, their nanostructures must be characterized. A variety of state-of-the-art techniques are used to characterize different components of the nanostructure. Atom probe tomography (APT) and atom probe field ion microscopy (APFIM) have played important roles in the characterization of materials on the nanometer scale for more than five decades [1, 2]. Historically, the atom probe has been mainly applied to metals, alloys, and other high-conductivity specimens, but advances in both specimen preparation techniques and atom probe design have made the technique increasingly applicable to lower-conductivity specimens, with particular implications for semiconductor-based structures.

In this chapter, a description of the technique of atom probe tomography is presented. The main application of atom probe tomography is the characterization of the size, concentration and morphology of nanometer-scale solute fluctuations, such as precipitates, clusters and the levels of solute segregation to interfaces. The technique is generally referred to as atom probe tomography, since three-dimensional images of the internal structures of the specimen are generated from many slices, each
containing a few atoms. An overview of the various types of atom probes and the field ion microscope is given. The types of analyses that may be commonly performed with these instruments are also described. Some examples of the capabilities of the atom probe tomography technique are also presented.

2. INSTRUMENTATION OF ATOM PROBE TOMOGRAPHY

Atom probe tomography is a unique form of microstructural characterization that has evolved from field ion microscopy and its precursor field electron emission microscopy. The many different variants of atom probes that have been produced and have culminated in the state-of-the-art local electrode atom probe are described in this section.

2.1. Field Ion Microscope

The field ion microscope was introduced by Prof. E. W. Müller in 1951 as a major conceptual change from the field electron emission microscope [3]. In contrast to the negative voltage used in the field emission microscope [4], the field ion microscope used a positive voltage applied to the cryogenically cooled specimen in the presence of an image gas. The field ion microscope required significantly sharper needle-shaped specimens to enhance the field sufficiently for the electron tunneling process used to field ionize the image gas atoms. This new instrument produced the first images of individual atoms in a tungsten specimen.

The basic components of a field ion microscope are an ultrahigh vacuum system in which a cryogenically-cooled needle-shaped specimen is positioned approximately 5 cm from a phosphor screen. A small quantity of image gas, typically $\sim 1 \times 10^{-5}$ mbar of helium for the refractory elements and neon for most other materials, is introduced into the vacuum system and then a high positive voltage is applied to the specimen. Other image gases, such as hydrogen, argon and nitrogen, have also been used for a few materials with low evaporation fields [2]. The image gas atoms close to the apex of the specimen become polarized due to the high electric field. These gas atoms are then attracted to the specimen where they become thermally accommodated to the cryogenic temperature. If the field strength at the apex of the specimen is a few volts per nanometer, these image gas atoms are ionized and the resulting positive ions are radially repelled from the positively-charged specimen towards the phosphor screen. This field ionization process occurs over the entire hemispherical apex region of the specimen and produces the field ion image on the phosphor screen. An example of a field ion image of an iridium specimen is shown in Fig. 1a. The concentric rings evident in this specimen are due to the different sets of atomic terraces of the crystal lattice and the hemispherical nature of the apex of the specimen. The arrangement of the centers of the atomic terraces, i.e. the crystallographic poles, is close to a stereographic projection. The bright and dark regions of contrast evident in the field ion micrograph of iridium are known as zone decoration and their appearance is specific to the material. In contrast, field ion images of amorphous materials exhibit a random distribution of spots, as shown in Fig. 1b for a Pd$_{40}$Ni$_{40}$P$_{20}$ bulk metallic glass. Crystallographic features such as grain and twin boundaries are evident in the field ion micrograph as abrupt disruptions in the pattern of the atomic terraces, as shown in Fig. 1c for a...
grain boundary in NiAl. Dislocations that satisfy a visibility criterion and emerge near crystallographic poles are evident as spirals in the atomic terraces, as shown in Fig. 1d. Solute segregation to boundaries or dislocations can also be observed by the presence of bright spots, as shown for boron segregation to a grain boundary in molybdenum in Fig. 1e. However, the identity of the segregating species cannot be unequivocally established directly from the field ion image and atom probe analysis is required.

The magnification of the image is a function of the specimen to phosphor screen distance, \( d \), and the end radius of the specimen, \( r_t \), and is given by \( \eta = d / \xi r_t \), where \( \xi \) is a projection parameter known as the image compression factor. Since the typical end radius of the specimen is in the 10 to 50 nm range, magnifications are in the millions. The radius of the specimen increases and consequently the magnification decreases as atoms are destructively removed during the experiment. This process requires the application of an increasing standing voltage to maintain the same field strength for the field ionization process. The typical range of operation is voltages of up to \( \sim 20 \) kV.

In modern field ion microscopes, a microchannel plate image intensifier is positioned immediately in front of the phosphor screen to increase the gain by a factor of approximately \( 10^3 \) and also to use the more efficient output electrons to stimulate the phosphor rather than the helium or neon image gas ions. This higher gain enables the field ion images to be recorded on film or digital cameras.

Since the ionization rate is influenced by the ionization potentials, work function and sublimation energy of the specimen, microstructural phases generally exhibit different contrast in the field ion image. An example of nanometer scale precipitates in a nickel-based superalloy Alloy 718 specimen is shown in Fig. 1f.

If the field on the specimen is raised further, the surface atoms of the specimen may also be removed by field ionization. This process is termed field evaporation to distinguish it from thermal evaporation as it is generally performed at cryogenic temperatures. Field evaporation is used to smooth out any irregularities produced during specimen preparation and to remove surface contamination. Field evaporation is used to analyze the interior of the specimen by atomic scale serial sectioning thereby revealing the morphology of features present in the microstructure. Field evaporation is also used to remove atoms in the atom probe.

2.2. Types of Atom Probe

In 1967, Müller, Panitz and McLane developed the atom probe in order to identify the atoms that were imaged in the field ion microscope [5]. The original variant of the atom probe used a small hole in the center of the microchannel plate and phosphor screen assembly which served as the entrance aperture to a time–of–flight mass spectrometer, as shown in Fig. 2. The atoms were removed from the specimen at a well-defined time by the application of a short duration positive voltage pulse to the specimen. For many years, mechanical mercury–wetted reed relay based systems were used to produce these high voltage pulses at pulse repetition rates of between 50 and 200 Hz [1]. However, modern instruments now use solid–state devices that are capable of significantly higher repetition rates. The positive polarity high voltage pulse can be capacitively
Figure 1. Field ion micrographs of a) iridium, b) a Pd$_{40}$Ni$_{40}$P$_{20}$ bulk metallic glass, c) a grain boundary in NiAl, d) a dislocation in B2-ordered NiAl, e) a boron-decorated grain boundary in the heat affected zone of a molybdenum weldment and f) brightly-imaging γ” and γ' precipitates in Alloy 718. The dark circular region in the center of some of these images is dead region surrounding the entrance aperture of the mass spectrometer in the classical atom probe.
Figure 2. Schematic diagrams of the classical atom probe, the three-dimensional atom probe and the local electrode atom probe. Some of the different types of detectors used on the three-dimensional atom probe are illustrated.

coupled to the standing voltage on the specimen. Alternatively and equivalently, a negative polarity pulse can be applied to a circular counter electrode a short distance in front of the specimen. The magnitude of the pulse voltage and the specimen temperature are selected to ensure that all the atoms present in the specimen are equally likely to field evaporate on the application of the high voltage pulse. Typical conditions
are a specimen temperature 50–60 K for a wide variety of materials and ~20 K for aluminum alloys and a pulse voltage of 15 to 20% of the standing voltage. The correct parameters ensure that the more strongly bound elements are not retained on the surface and the less strongly bound elements are not preferentially removed by the standing voltage between the high voltage pulses thereby influencing the accuracy of the compositional determination. Calibration experiments are used to establish the correct conditions on new materials. A pulsed laser has also been used to momentarily heat the apex of the specimen to induce field evaporation on the standing voltage \[6\]. This pulsed laser method has been primarily used for the analysis of semiconducting specimens where the high voltage pulse would be attenuated before reaching the apex region of the specimen.

The field evaporated ions are detected on a single atom sensitive detector at the end of the mass spectrometer, as shown in Fig. 2. In the field evaporation process, the potential energy of the atom on the surface, \( nE \), just prior to field evaporation is converted into kinetic energy, \( \frac{1}{2}mv^2 \) when the atom leaves the surface. Therefore, the mass-to-charge ratio, \( m/n \), of each atom removed can be determined from

\[
\frac{m}{n} = \frac{c}{d^2}(V_{dc} + V_{pulse})t^2,
\]

where \( d \) and \( t \) are the flight distance and flight time from the specimen to the detector, \( V_{dc} \) and \( V_{pulse} \) are the standing and pulse voltages on the specimen, and \( c \) is a constant used to convert the mass into atomic mass units. Although contrary to Müller's original concept of the operation of the atom probe, this process is generally conducted in the absence of the image gas to reduce the background noise. In the original atom probe, the flight time was manually measured from an oscilloscope trace. This method has been superseded with computer controlled high-speed digital timing systems. A typical sample in this type of atom probe is cylindrical volume with a diameter of up to ~2 nm that is defined by the entrance aperture and that contains approximately 10,000 to 50,000 atoms. Nowadays, this type of atom probe is referred to as a classical, conventional or one-dimensional atom probe.

The classical atom probe is very inefficient in the number of atoms collected from the specimen due to the small effective size of the aperture. Therefore, several variants have been developed to improve the collection efficiency. The 10 cm atom probe or imaging atom probe (IAP), designed by Panitz, had a significantly larger field of view \[7, 8\]. This variant used a pair of spherically curved channel plates and phosphor screen so that the flight distance from the specimen to all points on the detector were identical. The detector could be momentarily energized to record only the ions of a given mass-to-charge ratio. Therefore, a two-dimensional map of the solute distribution could be obtained. However, these data were difficult to quantify and alternative approaches were developed.

These newer variants all feature an analysis chamber housing the field ion microscope and mass spectrometer, a specimen storage or preparation chamber and a fast entry air lock to load interchangeable specimens. The base pressure in the analysis chamber is
achieved with either a turbomolecular, diffusion or ion pump supported with a titanium sublimation pump (TSP) or non-evaporable getter (NEG) pump and is typically less than $1 \times 10^{-10}$ mbar. These designs differ primarily in the type of position-sensitive single atom detector that is used, as shown in Fig. 2. All the detectors are based on a stack of two (in a chevron configuration) or three (in a Z configuration) microchannel plates providing a gain of more than $10^6$ times. However, different types of position-sensing elements are used. In these instruments, the active area of the detector together with the flight distance defines the area of analysis on the specimen’s surface. Typical flight distances are smaller than the 1 to 2.5 m used in the one-dimensional atom probe and are typically between 0.45 and 0.62 m. These variants include the optical atom probe (OAP) that uses a phosphor screen and a CCD camera [9–11], the position-sensitive atom probe (PoSAP) that uses a three anode wedge-and-strip detector [12, 13], the tomographic atom probe (TAP) that uses a $10 \times 10$ square array of anodes [14], the optical position-sensitive atom probe that features a primary detector with a phosphor screen and a pair of secondary image-intensified detectors consisting of an $8 \times 10$ array of anodes and a phosphor screen and a CCD camera [15], and the optical tomographic atom probe (OTAP) that uses a combination of a linearly segmented anode and a phosphor screen and a CCD camera [16]. These types of instruments are collectively referred to as three-dimensional atom probes (3DAP). A typical sampled volume in a three-dimensional atom probe has an area of $\sim 10 \times \sim 10$ nm to $\sim 20 \times 20$ nm and contains approximately $10^5$ to $10^6$ atoms. The typical time required to collect this number of atoms is of the order of 20 h. In both the classical atom probe and the three-dimensional atom probe, field ion microscopy is almost always performed at the start of the experiment. A region of the specimen is then selected for analysis by rotating the specimen about its apex until the field ion image of the selected region covers either the probe aperture or the single atom detector. The image gas is then removed from the system and the specimen is field evaporated until a sufficient number of atoms are collected or the specimen fails.

A new variant of three-dimensional atom probe known as a scanning atom probe (SAP) or a local electrode atom probe (LEAP®) has been introduced recently [17–20]. This instrument uses a small aperture or local electrode positioned extremely close to the apex of the specimen, as shown in Fig. 2c. A photograph of the local electrode atom probe is shown in Fig. 3. Nishikawa’s original concept of the scanning atom probe was that the local electrode could be scanned across the surface of a rough specimen and a natural protrusion could be selected for analysis thereby extending the type of specimen that could be studied. However, the analysis of natural protrusions is limited to simple compositional analysis since the non-uniform end forms of these types of protrusions do not permit reliable reconstructions of the positions of the atoms. In addition, surface contamination and surface diffusion can have a serious influence on the reliability of the analysis. It is also possible to analyze traditional needle-shaped field ion specimens with this variant. In addition, in-situ analyses may be performed on many individual microtips in two-dimensional arrays of microtips that are fabricated from the surface of flat specimens by focused ion beam based techniques. An integral part of this instrument is a nano-positioning piezoelectric stage to accurately align
the aperture in the local electrode with either the apex of a traditional needle-shaped specimen or a protrusion. The alignment of the specimen with the local electrode is performed while viewing the process with a pair of orthogonal high resolution video cameras attached to long working distance microscopes.

The primary advantage of this local electrode configuration is that the voltage that has to be applied to the specimen is significantly reduced from traditional atom probe configurations. For example, only \(~50\%\) of the voltage is required for a 30 \(\mu m\) aperture positioned \(~10\ \mu m\) in front of the apex of the specimen compared to the 5–10 mm diameter apertures placed 4–10 mm in front of the specimen in the conventional three-dimensional atom probe. This lower voltage not only extends the range of the instrument to blunter specimens but, more importantly, allows the instrument to be operated at significantly faster repetition rates that are possible due to the correspondingly lower pulse voltage. The repetition rate currently available commercially for generating these high voltage pulses is 200 kHz and the limit is likely to be in excess of 1 MHz. In order to take advantage of these high repetition rates, a different type
of position-sensitive detector is used. Therefore, the local electrode atom probe uses a chevron microchannel plate with a crossed delay line coupled to an ultrafast digital timing system. Unlike other types of atom probe, the close proximity of the local electrode with the specimen dictates that the design uses a vibration isolated cryogenerator to minimize any change in the field due to small changes in the alignment of specimen to the local electrode. This local electrode configuration also enables the single atom detector to be positioned significantly closer to the specimen without the normally associated degradation in mass resolution. As this configuration has a wide field of view, the design and operation of the local electrode atom probe can also be simplified by eliminating the goniometer that is normally used to rotate the specimen to select the region of analysis. A typical sample volume in the local electrode atom probe contains $10^6$ to $3 \times 10^7$ atoms and datasets containing over $10^8$ atoms have been collected. Due to the faster high voltage pulser, detector and electronics, the analysis time has been reduced by several orders of magnitude ($\sim 300X$) compared to the traditional three-dimensional atom probe. Typical collection rates in the local electrode atom probe are $5$ to $10 \times 10^6$ ions per hour. This high collection rate enables many specimens to be characterized in a day.

Since a time-of-flight mass spectrometer is used in all of these instruments, the atom probe is able to detect and has equal sensitivity for all elements. Unlike some other techniques, no pre-selection of elemental species is required to perform an analysis. The mass resolution of the atom probe is limited by small deficits in the energy of the ions. These energy deficits arise due to the full magnitude of the pulse not being transferred to the ion as it leaves the specimen. The initial method to improve the mass resolution in the one-dimensional atom probe was the addition of a Poschenreider lens to the mass spectrometer [2, 21]. This lens is a section of a toroid with matched length field free regions. Ions with different energies take slightly different length paths in the lens and are isochronally focused on the single atom detector. One additional advantage of the Poschenreider lens is that it can filter out any residual image gas and other impurity ions that are field evaporated on the standing voltage before they strike the detector thereby improving the background noise level in the analyses. Unfortunately, the Poschenreider lens configuration cannot be used in the three-dimensional atom probes due to their large acceptance angles. Therefore, reflectron lenses or energy mirrors have been used in three-dimensional atom probes [2, 22]. In this type of lens, the ions enter a region of increasing field and are reflected back to the detector. Ions with lower energy do not travel as far into the lens as ions with the full energy and are isochronally focused on the detector. However, the reflectron also reduces the detection efficiency by $\sim 10\%$ due to a field defining mesh at the entrance/exit of the lens. These energy-compensation devices improve the mass resolution so that the individual isotopes of the elements can be resolved. Due to the close proximity of the counter electrode, energy compensation is not required in the local electrode atom probe to resolve the individual isotopes. However, further improvement in the mass resolution can be achieved with a method based on post acceleration [23]. This post acceleration method can also increase the field of view.
2.3. Specimen Preparation

As with many techniques, the quality of the specimen is one of the most important parameters in the success of an experiment. The aim of specimen preparation is to produce a needle-shaped specimen with an end radius that is less than approximately 50 nm. In addition, the taper angle of the shank of the needle should be no larger than $10^\circ$ as this parameter defines the maximum number of atoms that may be collected from the specimen. Most atom probe specimens are produced by either electropolishing or ion milling techniques depending on the material, original shape and the type of specimen [1, 2].

In most metallic specimens, the bulk sample is reduced into square or cylindrical shaped bars that are $\sim 0.25$ mm across by $\sim 10$ mm long usually with the use of a diamond wire saw or diamond impregnated cutting wheel. Other starting forms of material such as wires or whiskers are also suitable. The bar is generally crimped into an annealed copper tube to facilitate handling in subsequent stages. Electropolishing is generally performed in two stages. In the first stage, the specimen is suspended in a 5 to 6-mm-thick layer of electrolyte floated on top of a dense inert liquid such as a polyfluorinated polyether. The electropolishing cell is configured with the specimen as the anode and a wire or circular cathode made of gold or platinum. Since only the middle portion of the specimen is in the electrolyte, a necked region is formed in the central region of the bar. For some materials, the electropolishing process is continued until the necked region is too narrow to support the weight of the bottom half of the bar and two atom probe specimens are made. However for many materials, the process is normally terminated before this point is reached so that a second stage with more controlled electropolishing conditions may be used. Since the necked region has been formed in the first stage, the specimen may be transferred to a simpler cell without the inert liquid and electropolishing continued until separation occurs. A list of suitable electrolytes for a wide variety of materials may be found elsewhere [2].

The resulting needles are then carefully cleaned in a suitable solvent to remove any traces of the electrolyte. Specimens are generally examined in an optical microscope at magnifications of 100 to 200X to check the quality of the surface finish, taper angle and the end radius before insertion into the atom probe.

Specimens that are either too blunt for further analysis or had fractured during analysis may be resharpened. This micropolishing method may also be used on freshly made or corroded specimens to remove any damaged regions or surface films. In this method, the specimen (anode) is carefully positioned in a drop of electrolyte suspended in a platinum loop (cathode). The electrolyte is held in place in the $\sim 3$-mm-diameter loop by surface tension. A voltage is then applied to the cell to electropolish the region of the specimen in the electrolyte. The position of the specimen in the electrolyte may be adjusted with the use of a micromanipulator and is generally monitored under a low power ($\sim 30X$) microscope. A desired taper angle may be sculpted by adjusting position and the time spent polishing in the electrolyte.

Thin film specimens such as surface, bi- or multi-layer films are generally fabricated into the needle-shaped specimens with the use of a focused ion beam (FIB) miller.
The aim of the fabrication process is to position the area of interest in the apex of the needle. One common method is to use a silicon substrate that has been Bosch etched into an array of \( \sim 5 \times \sim 5 \mu m \) square or rod posts [1, 24]. The resistivity of the silicon should be less than 0.05 \( \Omega \cdot cm \) to ensure that the pulse voltage is not attenuated in the specimen and thereby rendered ineffective. Alternatively, posts may be cut with the use of a dicing saw [25]. The multilayer film is then deposited on the surfaces of these posts. A 2- to 3-\( \mu m \)-thick platinum cap is deposited on top of the region of interest, i.e. the center of the post, to protect the underlying region from gallium implantation during milling. In specimens without this cap, concentrations of up to 30\% gallium has been measured. The post is then ion milled with an annular 30 keV gallium ion beam where the outer diameter is slightly larger than the extent of the post and the inner diameter is \( \sim 2 \mu m \). The inner diameter is progressively reduced to \( \sim 0.06 \mu m \) during milling to produce the desired taper angle and end radius. Milling is terminated when the end radius of the specimen is less than \( \sim 50 \text{ nm} \) and the last remnant of the platinum cap is removed. Examination or monitoring of the specimen should be performed with the electron beam rather than the gallium ion beam to minimize gallium implantation, and therefore instruments featuring ion and electron columns within a single system are preferred.

In the case of the local electrode atom probe, this milling method may also be used to fabricate specimens from a specific location on the surface of a specimen by placing a platinum cap or marker at the desired location and then milling a wide moat around that cap before preparing the microtip as described above. This milling method may also be used to fabricate specimens of fine powders. For this starting form of material, an individual powder particle is attached to the end of a relatively blunt needle with either a conducting epoxy or a platinum bridge deposited in the FIB.

3. BASIC INFORMATION

The raw data from the instrument, i.e., the pixel coordinates in the case of the CCD camera based detectors, the charges from the anodes, or the times measured at the ends of the crossed delay lines, are first converted into true x and y distances on the detector. These distances are then scaled by the magnification to obtain the atom coordinates in the specimen. The accuracy of these positions is limited by small trajectory aberrations due to interactions with the neighboring atoms as the atom leaves the surface of the specimen. Consequently, the spatial resolution in this x-y plane is approximately 0.2 nm. The third or z coordinate is estimated from the position in the evaporation sequence taking into account the detection efficiency of the mass spectrometer, typically \( \sim 60\% \), and the atomic density of the material under analysis. The spatial resolution in this direction is typically 0.05 nm. Additional corrections are required to take into account the hemispherical nature of the specimen and the orientation of the volume of analysis relative to the main axis of the needle-shaped specimen. These resolutions only permit the reconstruction of atomic planes if their orientation is close to a suitable direction and their lattice spacing is sufficiently large, and are not sufficient to place the atoms on their atomic sites in the crystal structure.
The elemental identity of each ion is interpreted from the mass-to-charge ratio. Fortunately, the time-of-flight mass spectrometer has sufficient mass resolution to distinguish the individual isotopes of all the elements, generally produces only one or two different charge states for each element, and produces a limited number of complex molecular ions. Databases of these charge states and molecular ions have been compiled for almost all elements [1]. Therefore, most peaks in the mass spectra can be readily assigned to the correct element. In cases involving more than one possibility, tables of natural isotope abundances may be used to distinguish the elements and deconvolute overlapping peaks for concentration estimates.

The concentration, \( c \), of a solute in a small volume is determined in atomic fraction from the number of atoms of each type, \( n_i \), in the volume, i.e., \( c = n_i / n \), where \( n \) is the total number of atoms in the sample. The accuracy of the concentration and the minimum detection level are therefore functions of the number of atoms in the volume sampled. The standard error of the concentration measurement, \( \sigma \), is given from counting statistics by \( \sigma = \sqrt{c(1 - c) / n} \).

4. DATA INTERPRETATION AND VISUALIZATION

The initial data produced in the three-dimensional atom probe by the reconstruction process described in the previous section are the x, y, and z coordinates and the mass-to-charge ratio of each ion. These data may be investigated in a variety of methods that involve either the examination of pairs of atoms, shells of atoms surrounding an atom of interest, one-dimensional strings of atoms, and one-, two- and three-dimensional arrays of blocks of atoms. The methods may be considered as being naturally divided into two main categories: the visualization of solute inhomogeneities, such as precipitates and solute segregation, and the quantification of the magnitude of the solute inhomogeneities. These methods are generally applied after the experiment is completed although some simplified versions of these methods can be performed as the data is being acquired.

Due to the three-dimensional nature of the data, most visualizations are performed interactively so that the data can be viewed rapidly from different perspectives. When the first generations of three-dimensional atom probes were developed, expensive graphically-oriented workstations were required to visualize the data. Nowadays, modern personal computers generally have sufficient processing and rendering power to perform these visualizations in real time on datasets containing many million ions.

4.1. Visualization Methods

The basic and most intuitive method used to visualize the solute distribution is the atom map. In this representation, a sphere or dot is used to indicate the position of each type of solute atom, as shown in Fig. 4a for a distribution of \( \sim 3 \)-nm-diameter copper precipitates in a model pressure vessel steel. Different colors and sizes of spheres may be used to visualize multiple types of solutes simultaneously. The atom map is normally used to view the distribution of the solute atoms rather than the solvent
Figure 4. Atom maps of the copper atoms in a model iron-0.8% copper alloy that was annealed for 7,200 h at 290 °C to produce ultrafine copper precipitates. All the copper atoms are shown in a), whereas only the copper atoms within 0.6 nm of another copper atom are shown in b). 60 ~3-nm-diameter copper precipitates are detected in this volume. These ultrafine copper precipitates have been shown to be one of the main features responsible for the embrittlement of the pressure vessel of nuclear reactors during service.

atoms. This method is most effective in cases where there is a large difference in solute concentration between the feature of interest and the surrounding matrix and the solute level in the matrix is relatively low. Therefore, atom maps are frequently used to detect small precipitates and segregation to interfaces, grain boundaries, dislocations, etc. The significantly larger area of analysis and orders-of-magnitude larger number of atoms in the sample in data from the local electrode atom probe imposes additional visibility criterion and consideration of the longer rendering times. For higher concentration solutes, displaying only a fraction of the solute atoms or subsampling the volume can
Figure 5. Isoconcentration surfaces in a Pd$_{40}$Ni$_{40}$P$_{20}$ bulk metallic glass. a) A fine-scale isotropic interconnected network structure of two amorphous phases is evident after annealing for 80 min at 340 °C.

Improve the visibility of features. Alternately, the background or matrix atoms can be eliminated from the display through the use of the maximum separation method, as shown in Fig. 4b. This method is based on the principle that the solute concentration in a precipitate is significantly higher than in the surrounding matrix and therefore the solute atoms are closer together. Therefore, a maximum separation distance between solute atoms can be defined that will encompass all the solute atoms in the particle and eliminate those in the surrounding matrix.

The morphology and size of features present may be visualized with the isoconcentration surface. This method is the three-dimensional equivalent of a contour map. In this representation, the compositions of a finely spaced (~0.5 to 1 nm), regular three-dimensional array of volume elements are estimated. The composition array may be smoothed with a moving average to minimize the influence of the statistical fluctuations due to the relatively small sample size in each composition determination. Then, a surface is constructed at a selected solute concentration generally with the use of an applied marching cube algorithm [26]. The concentration level used for the isoconcentration surface influences the volume fraction of the phases and may change the degree of interconnectivity in complex structures. An example of a highly interconnected, percolated, network structure of amorphous phases in a Pd$_{40}$Ni$_{40}$P$_{20}$ bulk metallic glass that was isothermally aged at 340 °C are shown in Fig. 5.

Fine-scale concentration variations may be visualized with orthogonal or arbitrary slices through the sample. As in the previous method, a three-dimensional composition array is constructed from the data. Then, the concentrations of a two-dimensional plane through these composition data are exhibited as different levels on a grey or color scale, as shown in Fig. 6. This plane may be swept interactively through the entire volume to highlight different composition regions and to examine their morphologies.

The presence of small precipitates can also be visualized with the x-ray tracer representation. As before, a composition array is constructed from the data. Then, one of the primary axes—usually the x or y axis—is chosen. The maximum or minimum concentrations of the columns of cells perpendicular to this selected direction are exhibited on a two-dimensional intensity map, as shown in Fig. 7 for the copper
Figure 6. Arbitrary slice through a Pd$_{40}$Ni$_{40}$P$_{20}$ bulk metallic glass showing regions of high and low phosphorus corresponding to the crystalline phase and the matrix, respectively.

Figure 7. An x-ray tracer representation of the maximum copper concentration in a model iron-0.8% copper alloy that was annealed for 7,200 h at 290 °C. The ~3-nm-diameter copper precipitates are evident by the high contrast regions.
precipitates in the model pressure vessel steel. This method is most effective in cases in which the volume fraction of the features of interest is insufficient to produce image overlap of those features along the chosen direction.

4.2. Quantification Methods

Atom probe tomography data may be analyzed to quantify the size, composition and some topological parameters of the microstructure [1, 2]. In this section, some of the more common methods are outlined.

Several methods have been developed to determine the size of nanometer-scale features. In the previous section, the maximum separation method was applied to visualize the atoms that belong to individual features. This method yields the position of all the solute atoms in the features. Since the atom positions are known, the center of mass and the radius of gyration and the related Guinier radius can be calculated directly from standard formulae. In particles where there are multiple elements present, these parameters may be estimated for each element individually. An alternative statistical method to evaluate the size of feature is the autocorrelation function either in one or three-dimensional forms [1, 2]. The size of small particles is estimated from the position of the first minimum in the lags.

For spherical particles, radial concentration profiles may be constructed from the centers of mass of each particle into the matrix. These radius concentration profiles are constructed by calculating the compositions of thin spherical slices of increasing radius centered at the center of mass. This information may be used to estimate the extent of any interfacial segregation or solute inhomogeneities within the particles.

The number density of the features may be estimated from the number of features in the analyzed volume. The volume of the analyzed region is generally estimated from the number of atoms, detection efficiency of the mass spectrometer and the atomic density of the sample.

The original method to determine the composition of features in the data was the selected volume method. In this method, a small spherical or cuboidal volume is defined to match the size of the feature of interest and the numbers of atoms of each solute within the volume are determined. The composition of the feature is then estimated, as described above from the number of atoms of each solute. In practice, this method is extremely time consuming to perform for a high number density of small particles and is usually only applied to coarse particles. Alternative automatic methods are generally used for other cases.

One of the fastest methods to estimate the individual compositions of a high number density of small particles is the envelope method [1]. This method uses the atom positions defined by the maximum separation method to define the extent of each particle by marking the cells in a fine three-dimensional grid. The typical grid spacing is 0.1 to 0.2 nm. The composition of the particle is then determined from all the atoms in these marked cells.

In materials where there is a high volume fraction of more than one phase, as in the example of the bulk metallic glass shown in Fig. 5, the compositions of the
coexisting phases can be estimated from the statistical analysis of concentration frequency distributions. The frequency distribution is constructed from the concentrations of equiaxed blocks of atoms typically containing 25 to 250 atoms. The frequency distribution is the number of blocks with each solute concentration. Phase separation is detected if the measured frequency distribution deviates statistically from a binomial distribution with the average solute content. The extent of the phase separation and the compositions of the coexisting phases can be estimated from the sinusoidal based Pa method or the Gaussian based Langer-Bar-on-Miller (LBM) method [27–30].

The co- and anti-segregation behavior of the solutes in a volume containing different phases may be examined with the use of contingency tables. The contingency table for the two solutes of interest is created from the compositions and may be regarded as a two-dimensional frequency distribution [31, 32]. The correlation between the elements is determined by comparing the numbers of composition blocks containing high or low concentrations of the two elements with those expected from a random distribution.

The early stages of phase separation, clustering and chemical short range ordering may be investigated with methods based on the analysis of Markov chains. For this type of analysis, the three-dimensional data is converted into a one-dimensional string or chain of atoms. The chain is usually taken along the z direction as it has the highest spatial resolution and is typically the longest dimension in the data. In this type of analysis, B refers to the solute of interest and A is any other type of atom. Two main methods of examining the chains have been devised. The Johnson and Klotz method is based on the examination of pairs of atoms, \( n_{AB} \), \( n_{AB} \), and \( n_{BB} \), and comparing the results to the numbers expected for a random solid solution [33]. If \( n_{AB} \) is higher than expected in a random solid solution, then the data exhibit short range order. Conversely, if \( n_{BB} \) is higher than expected in a random solid solution, then the data exhibit solute clustering. The Tsong method compares the number of sequences of \( ABA \), where \( n \) is the number of consecutive B atoms [34]. If the number of \( ABA \) \((n = 1)\) chains experimentally observed is larger than expected, the data exhibit solute clustering. If the number of \( ABBA, ABBBA, \text{ i.e., } n \geq 2 \) chains experimentally observed is larger than expected, then the data exhibit solute clustering.

The amount of segregation at interfaces and grain boundaries may be quantified directly from an analysis that contains an interface with the use of a method based on the Gibbsian interfacial excess [35]. The Gibbsian interfacial excess of element \( i \), \( \Gamma_i \), is defined as \( \Gamma_i = \frac{n_i}{A} \), where \( n_i \) is the excess number of solute atoms associated with the interface and \( A \) is the interfacial area over which the interfacial excess is determined [35–37].

The three-dimensional data obtained in atom probe tomography can also be analyzed for topological parameters. Topological analysis has been used to determine the degree of interconnectivity of the microstructure. In order to quantify the interconnectivity, the number of loops per unit volume or “handles” is determined. The handle density may be regarded as a similar parameter to the number density of isolated precipitates. One such measure is the Euler characteristic, \( E = n_n - n_e + n_f \), where, \( n_n \) is the number of nodes, \( n_e \) is the number of edges and \( n_f \) is the number of faces in a
structure [38]. The data may also be examined to determine whether a continuous path can be traced within the second phase from one surface of the volume to another i.e., the microstructure is percolated. Other topological parameters such as the fractal and fracton dimensions can also be determined [39].

5. SAMPLE ANALYSIS OF NANOMATERIALS: MULTILAYER FILMS
The characterization of the atomic chemical composition of nanostructured materials is important in applications such as magnetic data storage and semiconductor thin film devices. The performance-defining properties of these multilayer films and devices are sensitive to the nature and quality of the inter-layer interfaces. Some atom probe tomography results are presented from a multilayer film comprising of 40 layer pairs of 2.2 nm Ti/3.3 nm Nb that were sputter deposited under UHV conditions at ambient temperature onto a n-doped Si [100] wafer (resistivity = 5 Ω-cm) [40, 41]. The atom probe specimens were prepared by the focused ion beam process described previously. The niobium and titanium atom maps and the isoconcentration surface depicting the interface between the niobium and titanium layers are shown in Fig. 8. The interface between the niobium and titanium levels was relatively smooth. Niobium and titanium concentration profiles oriented perpendicular to the plane of the interface, shown in Fig. 9, indicate that significant solute interdiffusion of niobium had occurred in the titanium layers. The niobium interdiffusion into the titanium layers has facilitated the titanium phase to grow in a pseudomorphically body centered cubic form rather than in its bulk equilibrium hexagonal closed packed form [40, 41].

![Figure 8](image-url) Niobium and titanium atom maps and isoconcentration surface from a sputter deposited niobium (3.3 nm) -titanium (2.2 nm) multilayer film.
6. SUMMARY AND FUTURE PERSPECTIVES

Atom probe tomography is a powerful tool for the characterization of the size, morphology and composition of ultrafine features in a variety of materials. With the development of new forms of specimen preparation especially with focused ion beam milling systems, atom probe tomography should be extended to a wider variety of applications in nanotechnology.

The local electrode atom probe is a major advance in atom probe design and has greatly simplified the operation of the instrument. There is considerable scope for its continued improvement through increases in the area of analysis, mass resolution and overall data acquisition speed. New, more efficient and automated methods to analyze the three-dimensional data should be also forthcoming as the user base for atom probe tomography increases.

7. ACKNOWLEDGEMENTS

The author would like to thank K. F. Russell for her technical assistance, and Profs. G. B. Thompson and H. L. Fraser of Ohio State University, Drs. R. B. Schwarz and T. D. Shen of Los Alamos National Laboratory, Prof. G. R. Odette of the University of California—Santa Barbara, and Prof. T. F. Kelly and his colleagues at Imago Scientific Corporation, Madison, WI for the results of the collaborations featured in this chapter. Research at the Oak Ridge National Laboratory SHaRE Collaborative...
Research Center was sponsored by the Division of Materials Sciences and Engineering, U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

8. REFERENCES