Advanced Material Characterization by Atom Probe Tomography and ElectronMicroscopy

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Week-08
Lecture-26

Welcome to this class. In the last class, we discussed the mass spectrum and how to deconvolute the two isotopes which have similar mass-to-charge ratios. In this class, we will discuss the quality of your atom probe data. Okay? So, the first thing that comes to mind is the detection efficiency. Okay, this detector efficiency completely depends upon the physical means of MCP detectors.

Okay, multi-channel plate detectors, as we have described long before in the classes, when you use these MCP detectors, a large fraction of the field-evaporated ions are not detected, meaning they get scattered from the area, from the solid area of the MCP plate, okay. So, you will have plates that have a hexagonal shape, and the solid area not covered by these hexagonal glass tubes can actually scatter a high fraction of the ions. Okay, so usually in straight ion-path atom probes, the fraction of ions that get scattered is around 40% in a straight-line path. But in reflectron-based atom probes,

the fraction of ions that are scattered is actually more—around 60%—because by using the reflectron, you are increasing the flight path, increasing the flight distance, correct? So, you will have more and more ions getting scattered in the main chamber, especially when using the MCP detectors, okay? However, even though the detection efficiency is 50% or 60%, correct? However, with the atom probe, you can actually get a large number of atoms or ions accumulated. It means that on average, they can provide good statistics, composition statistics.

So, which can enable good compositional statistics. So, usually the number of ions detected is around 10 to the power of 6 to 10 to the power of 9. So, if you have a needle specimen and a detector, you can see that the number of ions In this, all the ions contribute to the net field evaporation of the specimen. Net field evaporation of the specimen.

It means, what is it? All the atoms, all the atoms are field evaporated. However, due to the efficiency of the MCP or the detector efficiency, not all the atoms are detected, or we can say that not all atoms are imaged or detected. This is due to the MCP design. So, this is one factor we need to take into account when talking about the quality of the atom probe reconstruction. So, here you can see that I will show you a two-dimensional.

So, this is the actual atomic structure of your specimen, correct? And you can see that If you, this is a two-dimensional cross-section. This is a 2D cross-section. It is not a 3D cross-section. And different colors of atoms, different colors correspond to different atoms or different chemical species.

Okay. And you can see that these are all arranged in a crystallographic way. So, in a crystallographic fashion. With a specific d-spacing, or we can call it the distance between the two atoms. And you can see that most of the points, most of the lattice points, are occupied by different kinds of atoms.

Correct? But in the case of B, this is the reconstructed. And you can see that there are certain locations where the atoms are not present. It means that during the detection event, due to the inefficiency of the multichannel plates, these locations—the atoms, the fraction of these ions—are not detected, so these are empty. So it is more or less not exactly similar to the crystal structure. So you will get a 2D cross-section. You are actually disturbing

the spatial resolution, okay? But as I told you, we are detecting a large number of atoms, up to 10 to the power of 8 to 10 to the power of 9. So, your actual composition will not be affected much due to this large number of atoms detected, correct? Now, the second thing is, we discussed the spatial—I just introduced the spatial resolution, correct. So the second is spatial resolution, and I think in a few classes before, we have just gone through the spatial resolution of atom probe.

In the Z direction, it is 0.04 nanometers, but in the XY direction, in a 2D section, it is much less—it is around 0.2 nanometers, okay? However, the resolution Here, whatever you are getting in the atom probe is comparable to the high-end TM instruments where we can get high-resolution imaging. Correct? So, in a crystalline material, usually atoms

in the reconstruction are not distributed. So, if you talk about the 2D section, XY, you have a needle specimen.

If you cut this 2D section, this is your Z direction, this is your X, this is your Y. If you cut this section, And if you see along the Z direction, the atoms actually are not occupying the exact lattice position, okay. So, they do not occupy the exact nodes or the lattice positions which are expected. In a typical crystalline material, rather, they are slightly offset from the actual sites due to which, in a two-dimensional projection or in the two-dimensional projection, the resolution is poor.

than in the Z direction, okay? So, usually the DHKL or the distance between the atoms in two dimensions is usually much less than the spatial resolution in XY. This leads to the loss of crystallographic information. in two-dimensional projection in that plane. Just now, I have shown you an image where you can see that this particular image

You have this, which is actually a two-dimensional reconstruction, and you can see that by comparing A and B. You can see that the crystallographic information is mostly missing or not comparable to the actual lattice in a two-dimensional projection because the resolution is much poorer in the XY direction as compared to the Z direction. There are certain reasons for this. We have briefly covered it before, but here I will just go through that. The resolution, the spatial resolution, is less. This is due to one of the most contributing factors: trajectory aberrations. We have covered this in a few classes before.

These are called trajectory aberrations in the flight path of the ions. Why do trajectory aberrations occur? This is due to the local geometric and compositional variations on the surface of the specimen. This is the first reason—the first important reason—why the spatial resolution in atom probe is poor as compared to the Z direction. The second reason is thermal agitation, the agitation of the atoms at the specimen surface, okay.

Third is the roll-up process, the potential roll-up process, or you can call these surface diffusion-related effects. The fourth is the model we adopted for the reconstruction. It is a very simplified projection model so that we can actually predict or reconstruct the evaporation geometry. Remember, in 3D reconstruction, remember we talked about Kf, θF, okay? Image compression factor, field factor.

So these are all estimated by assuming some distribution of field lines in the near and the far field. And so it has been estimated by using a simplified model, which is a reverse projection, point projection model. Correct? So these four things, these four reasons are... responsible for the poor spatial resolution as compared to the resolution in the z direction, okay.

So, the first which I talked about is the detection efficiency plus the spatial resolution in XY. These both are related to this particular figure B, okay? So it leaves the crystallographic information to go away in the XY direction because of these two effects, okay? So here you can see that If you... So, I talked about the detection efficiency.

Second is the spatial resolution. If they both contribute, you will have the atomic distribution. as shown in the figure at C. This is a contribution from both issues, okay. So, you will lose the actual crystallographic information and also the resolution in the two-dimensional section, in the two-dimensional section, fine, okay.

Now, we just talked about mass resolution. I think we have discussed enough about the mass resolution. So, we have discussed mass resolution related to HV pulsing and laser pulsing. Okay, we discussed the energy deficits. We discussed We discussed the thermal tails.

Okay, that directly affects the mass resolution. Tails in the peak, so due to the thermal tails, it might be possible that peaks get overlapped with the thermal tail. So, you will not get the actual composition. These two effects directly relate to what limits the mass resolution. Okay, this is the third point.

Fourth is background noise. So, in APT experiments, in the last class we discussed the background noise. So, the mass spectrum usually contains the time-independent background noise. Okay? So, these are the four important points which have to be taken care of during your quality of the atom probe, which determines the quality of the atom probe data you are getting.

And another, the fifth point, also an important point, is the volume. So you know that the atom probe needle is an analysis of a very small volume from your big bulk sample.

Correct? So if your microstructure has a heterogeneous microstructure, then the representation of this particular atom probe data cannot be related to that particular sample.

Okay, because the atom probe provides very localized information from the sample region unless it is homogeneous throughout the microstructure. So these are the five important points which determine the quality of your reconstruction or the quality of the atom probe data. Correct. So, once you get a needle specimen, your reconstruction is done. Okay, and you have a distribution of atoms across the needle specimen. Correct. Now, to count the number of atoms in the reconstruction, this is done by grid-based counting.

which is called grid-based counting, okay. So this means that the atom probe needle, if you consider this particular volume, the needle space, the area of the reconstruction, is divided into voxels. Okay, it is divided into voxels, or we can call them cubes or small rectangular cubes. Each cube has a certain volume, and dividing the needle reconstructed data into these voxels is called voxelization. Okay, so voxelization involves partitioning three-dimensional data into grid-based discrete cubic or rectangular blocks.

Or we can call it as a voxel. Okay. So depending, so the size of the voxel, the size of the voxel chosen actually depends on the type of analysis to be done. The size of the voxel chosen depends upon the type of analysis which is to be done. And the distribution of these voxels or the definition of these voxels can be determined by two important quantifications.

One is volume and another is population. What is the volume? It is nothing but a geometric dimension of the ith block. It means that the length of length in x direction into length in y direction into length in the z direction is equals to volume. And another way is the population, so it is nothing but the number of atoms occupying the ith block, okay, which is related to Ni, okay.

And the information is collected from the reconstruction. by using these voxels. Whatever the information which you get from the voxels are actually used to create frequency distribution statistics. So, based on this volume and population for each voxel,

the ith voxel, you can get a frequency distribution statistics for these two volume or population. With the volume, actually what we can get is the

atomic density density distribution and with the population of ions or atoms you can get the concentration okay so these are the two attributes which we can get by the voxelization based on the volume and the population and the selection of block size the selection of block size or voxel size is the critical parameter okay and it should be balanced between one is positional error And another one is the statistical error. It should be balanced.

What it should be balanced? The size of the voxel chosen for the analysis. It should be balanced with the position error and the statistical error. the positional error but smaller very smaller size can have a very high statistical error which have a direct influence on the your analyzed composition profiles. For example, if you have a dilute solution in the grid mesh, so if you have a very dilute solution, then if

the voxels are very small, it might possible that in your reconstruction if your voxel size is very small, It might possible that the dilute element or the atom is not detected in the number of voxels, in the very high number of voxels. It means that the most number of voxels do not contain those atoms. This can lead to a very poor statistical error. If the voxel size is very large, actually we can miss the fine details from the sample or it will be lost.

For example, clustering information can be lost. These two factors can lead to misleading results obtained from the needle specimen. Correct? So, the block size or the voxel size is a very crucial or critical parameter for the analysis of the reconstructed data. And it directly depends upon the type of material you are investigating.

Another important point is the density. Okay, so what is density here? We talked about volume. We talked about the population. Volume is related to your atomic density.

Population is related to the concentration. So, how is it measured? The density is nothing but the distribution of... the atomic density of that particular element. So, sigma I is equal to Ni divided by Vi.

So, Ni is nothing but the number of particles, the number of particular atoms, the number of those particular atoms in each voxel. So, for each voxel, you can actually measure rho I. And it can be distributed in three dimensions. So, this is called the density distribution. Here, the volume of the block or the voxel is kept constant throughout the reconstruction.

So, you have a needle specimen; you remove this analysis area, and you can set a definite voxel size. And from each voxel size, you can actually estimate the distribution of density, the atomic density of that particular species. Okay, this is the density distribution. Now, coming to the concentration. Similarly, the concentration of a given element A with respect to the voxel number I can be given as X AI equals NAI divided by NI.

NAI is the number of A atoms, while Ni is the total number of atoms in that particular voxel or block, fine. So, these are the two important things. We can construct in three dimensions or two dimensions the concentration and the density in one dimension, correct? You can actually get the distribution of these attributes, okay?

And this is done by the distribution of the reconstruction in three dimensions. Of voxels, the distribution of voxels with a definite size, keeping the voxel volume constant. In your reconstruction, if you have any number of ions or atoms that are segregated in certain regions, okay? So, the number of B atoms in these locations is much higher compared to the A atoms, which is a different phase. So, if you have a number of B atoms segregated, then what we can do is use the reconstruction by using the visualization tool.

For visualization, we can use the reconstruction tool, which is called iso-density plots or iso-concentration plots. What are these? So, for plotting these two—iso-density and iso-concentration—the first thing is you have to interpret the APT. And you should know that if, in this particular needle specimen, there are certain species that would like to segregate together and

form a compound or the beta phase, or the B number of atoms coming together, you can actually cover this particular area with a surface that can be either an iso-density or iso-concentration surface. So, it gives a three-dimensional boundary. We can call it as a three-dimensional boundary or we can call also the interface, three-dimensional interface

along the segregated B atoms. And these iso-concentration plots and iso-density plots, they have a certain value, a definite value.

Okay? So, the construction of these iso-plots, actually what they do is they isolate the blocks or the voxels with a specific concentration or density. Okay, so they create a surface by isolating the blocks which have a certain concentration or certain density, correct? And these iso-plots are usually used to identify the regions of different phases, grain boundaries, and precipitates, okay, in a specific analyzed volume. Okay, so here I am giving an example.

So, this is just an example where you can see that this is for an aluminum-magnesium-zinc alloy, where this particular tomogram reconstruction shows that there are certain species which are actually agglomerated. And if you divide a certain block of this particular voxel of a certain size of this reconstructed data, then if you magnify this particular region, you can see that the green and orange-colored atoms corresponding to magnesium and zinc, you can see that there is a high number of these magnesium and zinc atoms but the atoms which are from the matrix region here, the density or the number of atoms of magnesium and zinc are very low, while aluminum atoms are much higher.

Okay, so this is called a grid-based analysis of the reconstructed volume. So, here I am showing a distribution of—first, we will see the left section. So, here you can see that these small spheres correspond to different atoms distributed in an aluminum alloy. The red or orange color corresponds to aluminum. The green-colored atoms correspond to zirconium.

And you can see that in these locations, the zirconium atoms are actually agglomerated. The zirconium atoms are agglomerated. And if you draw, you can draw the iso-composition. Iso-composition or iso-concentration surfaces around these agglomerated regions, and you can specifically identify these zirconium-rich regions, and these are nothing but what we call a secondary phase or a beta phase, or we can call them zirconium-rich precipitates.

Okay. Once these iso-concentration surfaces identify these volumes, Actually, you can create a one-dimensional profile analysis. It is nothing but making voxels of definite size and taking the composition of each voxel along a particular direction across the precipitate. So you will get a one-dimensional compositional analysis. You can see that this is X, and you can see that the zirconium concentration goes up at the precipitate and goes down, reaching up to 25 atom percentage.

This is your aluminum plot. Okay. So you are taking a composition profile across these voxels, and each data point corresponds to the composition of each voxel. And that voxel size can be optimized or can be an easy input parameter from our side for further analysis. Okay. So this is the one-dimensional compositional distribution. Now, in an atom probe, you can also do the two-dimensional projection.

Okay, if you take up one particular agglomerated precipitate, And actually, you can—this is the y-direction, this is the x-direction. Actually, you can make a two-dimensional plot of zirconium distribution in x and y, so that you can get an actual distribution of zirconium in a two-dimensional projection. This is a two-dimensional projection in this particular direction, perpendicular to this. Okay, and this concentration scale you can use for the identification of how much zirconium

is located at each point on this two-dimensional map. Fine? So, you can generate both one-dimensional and two-dimensional projections. Now, there are certain interfaces where these are not straight. If you have a needle specimen—for example, if there is an alpha face and a beta face—if you calculate a composition profile across this using the one-dimensional profile,

you can plot the composition of each voxel across this particular interface, correct? Now, this plane, this surface, or the interface is planar. If the interface is curved, it has a certain radius of curvature locally, and if you plot a one-dimensional profile across this curvature, due to the curvature, your one-dimensional profile will not be exactly true to what is present in the sample across the interface. For those purposes, what we use is called the proxigrams.

Proxigrams are nothing but the measurement of composition in three dimensions. Across any interface that has curvature. Okay? How is it done? Imagine that this is a reconstruction volume.

You are creating an isoconcentration surface of that particular phase or precipitate, and you can extract this particular isosurface from that region. Now, what you are doing is at each location of the interface, you are measuring the composition normal to that interface at that location. Okay? And the distance between the measurements you can actually control by the beam size.

Okay? So, at each location of that interface, you are measuring the composition perpendicular to the local interface. So, actually, you are nullifying the curvature effect, okay. So, this is nothing but the local atomic neighborhood adjacent to the interface which is examined and has curvature, and atomic positions are corrected with respect to the distance of the local normal of the isosurface.

So these are called proxigrams, which we regularly use if the precipitate has a curvature. Okay, and because of this—actually, it is because of this algorithm—this is independent of geometry. Okay, so these proxigrams—actually, it is a choice. And it is with reference to the iso-concentration surface, which is generated or the iso-concentration that was created. Depends upon high beam. Okay?

And this is superior to the one-dimensional profiles where the curvature effect plays a role. It gives the full compositional analysis. Okay. So, with these proxigrams, actually, you can also—this is also used to measure the interfacial axis. Okay.

So, these are called proxigrams. So in this class, we have covered—so I will end this class now—and I think we have briefly gone over the attributes which we get from the atom probe data: the voxelization, the basics related to voxelization, and how the compositions can be measured. How the composition—the quality of the mass spectrum or the quality of the data—can be optimized, and I have briefly gone through the one-dimensional and the two-dimensional profiles across the interfaces, also the importance of proxigrams.

So with this, I will end this class now, and we will meet in the next class.