

**Advanced Material Characterization by Atom Probe Tomography and
Electron Microscopy
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Week-11
Lecture 32**

So, welcome to this class. In the previous lecture, I introduced the frequency distribution analysis, also called binomial analysis. Then we also covered cluster identification, okay? And briefly, I talked about the radial distribution maps, correct? And also, I talked about the nearest neighbor distribution. Fine. So, first nearest neighbor, second nearest neighbor, okay. So, based on that, how to identify the clusters in a given dataset.

Now, briefly, I will introduce the effect of detector efficiency. So, you know that detector efficiency, so— I think long before, we discussed this efficiency. It depends upon the ions collected at the MCP multi-channel plates, correct? And we know that these multi-channel plates are the glass tubes, and the area not covered by the glass tubes—usually those ions will be reflected back or lost.

So, there will be a detector efficiency, depending upon the design of MCP plates. So, it will not be 100 percent. It might be around—some instruments range from 40 percent to 75 percent, correct?—depending upon the instrument's design. So, this detector efficiency will also affect the cluster analysis.

Will also affect the cluster analysis. Okay, so first, we will discuss the nearest neighbor. First, we will talk about the k-th nearest neighbor and the effect of detector efficiency on KNN. So, it will affect in two ways. Limited detector efficiency induces, first, it will induce a peak shift

to the right in KNN nearest neighbor. Okay, why will it shift to the right? So, if you have a particular peak for the nearest neighbor distribution, then usually the peak will shift to the right side, okay, at larger distances. Correct? It means that fewer atoms, it means that the average distance, the average distances between the pairs are increased.

Okay? And the second thing is, it usually causes widening of the distribution. Okay? Why widening of the distribution?

Because the limited detection efficiency will actually remove a fraction of atoms which are in the nearest neighbour. Okay, so these are the two important things which usually affect the detector efficiency during the nearest neighbour distribution. So, I will show you a chart where you can see the solute nearest distance and this is the frequency. Okay, and you can see that the blue colour represents the simulated data. So, the blue color corresponds to 100% detection efficiency, red to 57%, and the green color to 37%.

Now, as the detection efficiency is reducing, Correct? From 100% to 57% to 37%. So, out of 100 ions, only 37 ions are detected at the MCP plates. Then you can see that there is a shift in the peak towards the right side, and also the width of the peak gets broadened.

Okay? So, the peak shift is due to the increase in the average distance between pairs. Okay, this is the peak shift. Next, the broadening or widening is caused by the fraction of ions or atoms being removed.

Due to which there will be an effect on the solute nearest neighbor analysis or the frequency distribution. Correct? Now, the next thing is how detection efficiency will affect the cluster characterization. Okay? First, we talked about the nearest neighbor.

The second is how it will affect the cluster characterization. Okay? So, the number of clusters, whatever is identified in an APT dataset, okay, will be less than the number that physically existed in the original specimen. So, if you have a real sample where certain clusters are present, correct? So, if the number of clusters, if the number of clusters is X ,

So now we will talk about the effect of detector efficiency on cluster characterization, okay. So if you have in a needle specimen, if you have several clusters, okay, and if there are X number of clusters which are actually present in your specimen, Okay, but after the field evaporation, due to the limited detection efficiency, the number of clusters will be smaller than X , smaller than X number of clusters. Okay, so the clusters that are identified within the APT data only contain a fraction of atoms, not all of them.

Okay, so for large clusters, if you have a large size cluster, then the limited detector efficiency reduces the measured frequency of clusters. So it will reduce the measured frequency of clusters. So here you can see that there is a plot, a simulated plot, where you can see that by increasing or decreasing the detector efficiency, actually you are reducing the size of the clusters.

Correct, the blue color is 100%, red is 57%, and green is 37%. Okay, so it reduces, it also reduces the frequency of these clusters. This is the effect of detector efficiency. So now we will talk about, again, we will go to the radial distribution. So radial distribution, last class I also introduced it.

So we will go a little bit into detail. Radial distribution is used to identify the structure in a material system. Okay, how to identify? This is done by examining the average local neighborhood as a function of distance. Okay, as a function of distance extended radially.

Outwards from each atom in the dataset. Okay, so this is used. Radial distribution is also used to identify the solute or dopant short-range order. In the system, okay? So remember, if you have a series of atoms which have been detected in a dataset, then radial distribution is the examination of the average local neighborhood as a function of distance, which is extended radially from a particular atom, and this is calculated for each atom position. Okay?

And they give the radial distribution map. Okay? So here, the volume around each atom is divided into a series of shells, or we can call them concentric shells. Okay? So each shell is centered around an increasingly large radius R and has a thickness of ΔR . So here

So here, this is an image where you can see that these are the atomic positions, okay? And if you see this particular atom, this particular atom at a radius r radially, and you can see that these are the concentric shells which have a thickness of Δr . Okay, so each shell is centered around an increasingly large radius R and has a thickness ΔR . Now, this algorithm, this radial distribution algorithm, builds a histogram of the number of atoms in each of these shells. Okay, and this algorithm repeats the process, centering on each atom.

Okay, so this is the histogram which plots the number of atoms in each cells and this process is repeated at each atom for each atom. okay, every atom on the data set. So, what we call as a RDF which is given by $\frac{1}{\rho} \frac{nRDF}{4 \pi R^2 \Delta R}$ divided by $\frac{1}{\rho} \frac{r^2 \Delta r}{2 \pi R^2}$. So, this particular value denominator is the volume of each shell, and ρ is the average atomic density of the data set.

And $nRDF$ is the number of atoms in the shell at a distance r around each atom. Okay, so this is the function where this algorithm calculates the RDF for each atom. of the data set. So, based on this, there is another term which is called, we call it a partial radial distribution. What is partial?

So, it is nothing but PRDF, which is the average chemical distribution. So, what does it mean, average chemical distribution? It is nothing but the RDF analysis confined to the distribution of a specific element in the system, not all the elements. Only if it is specific to a single element, then these are called partial RDFs. Normally, if there is an RDF, you can consider that you are calculating for each atom.

But if you are calculating for a specific element, these are called partial RDFs. Okay. So, it means that these are combined distributions. You can call it a combined distribution of elements. A and B reference with respect to both A and B. Okay?

This is the combined distribution of elements A and B with respect to both A and B. Now, Another terminology is the pair correlation. This is also a type of radial distribution for RDF analysis. This pair correlation is more specific. Okay, so this characterizes the distribution of atoms of a particular element,

say B, or a group of elements, B and C like that, in the vicinity of atoms of a different element, say A. Okay? So, this is given by $\frac{1}{\rho_B} \frac{M_{AB}}{4 \pi R^2 \Delta R}$ This is the same term which is the volume of that particular shell. Okay? So, this RDF can be used as a partial RDF, partial radial distribution, or you can also use it as a pair correlation function.

So, here the ρ_B is the density of B atoms, and M_{AB} is the average number of B atoms. in the shell at a distance r around an A atom. Okay? It means these have certain

meanings. So, if your $GAB(r)$ is 1 for all values of r , it indicates that there is no correlation.

By the occurrence of that particular element. If your $GAB(r)$ is greater than 1, it means that there are a higher number of B atoms than expected at r , at a distance r from the A atom. Okay? So, this is the GAB.

So, now, with this introduction to the radial distribution map, we will—so this is one dimension, correct? So, we are talking about one dimension. Now, similarly, as the radial distribution maps, we have spatial distribution maps. Okay, so this spatial distribution map is nothing but a modified three-dimensional RDF. It means that it examines the average distribution of atoms in a particular crystallographic

In a particular crystallographic direction. So, these are called spatial distribution maps. Now, these spatial distribution maps can be done either in one dimension or analyzed in two dimensions. So, if you have a needle specimen and this is your Z axis, You can generate these spatial distribution maps along this particular Z axis, which is one dimension, okay?

And if you are generating spatial distribution maps in X and Y , then these distribution maps are called two-dimensional spatial distribution maps, okay? So, we call it an SDM. Usually, these SDMs are very helpful in characterization, in the characterization of atomic planes in depth through reconstruction. So, these atomic planes mean you can actually calibrate the DHKL value along the Z direction by using these HDMs.

So, I will give you some brief examples of the utilization of HDM. So, you can see that this is a desorption map, and you can see these zones which are appearing on the desorption maps. As I told you, these zones are nothing but the crystallographic poles, similar to those in the stereographic projection. Now, you can take this particular region. Or this region or this region, and if you plot, you can actually, by using SDMs, get the lattice planes.

Lattice planes of that particular pole. So here we can see that these are called 002 planes. which can be resolved, and the distance between these two lines is the interatomic

distance, the interplanar spacing of that 002. And if you plot this particular region in the dataset, you can actually get these low-density zones of each pole. which can be indexed for crystallographic poles.

Similarly, you can also reconstruct the atomic planes of 113 and 111 planes. So, these are the reconstructions in one dimension. Now, in two dimensions, you can also get the two-dimensional spots. Those spots actually correspond to the diffraction patterns you are getting. Correct?

So you can see that this is in the z direction, whatever you have plotted. So if you have a desorption map and a needle specimen, if you take the SDM along this particular direction and reconstruct it, you can actually image the atomic planes. But if you do it in two dimensions, in X and Y, you can get the spots which correspond to the diffraction spots. Correct?

Now, you can see that with this, if you plot—so these are the planes, atomic planes. And if you take SDM across these planes, you will get sharp peaks at certain defined intervals. And the distance between these two is nothing but the d-space, d_{hkl} of that particular 002 plane. Correct? You can see that this is the 1, 1 bar 5 plane.

Similarly, if you plot, this is in the z direction, only one direction. Correct? One-dimensional. If you take it in two dimensions, then you can actually see these spots. Similarly, you can see these as diffraction patterns.

Correct? So, this way, these SDMs are very useful. Now, I will give you a very brief example of how these SDM maps are helpful to locate the site occupancy. Now, here you can see there is an EBSD map, and the color on the EBSD map is nothing but these differently oriented grains. Okay, and the red color corresponds to near the 001 direction.

Green color corresponds to near 101. Dark blue corresponds to near 111. Now, if we identify a grain which is around 001. Okay, so as I told you in FIB, we have seen how to make atom probe samples. Now, if I make a sample from this red region.

And if you see the reconstruction and the desorption map, you can see this exactly is a four-fold symmetry. And this shows that this is along the 001 pole direction. You can see that. Correct? And these are the precipitates which are present in pure copper.

Now, this particular region, if I take the SDM maps along the Z direction, And if you reconstruct along that particular pole, then actually you can get the 001 planes. You can see these golden color atoms, which have a constant distance of D spacing, which corresponds to the interplanar spacing of the 001. And this red color corresponds to cobalt atoms. And with this resolution along the Z, actually you can get the composition of each plane.

Okay, so this is how powerful it is—these SDM maps, which we can use to reconstruct the atomic planes and get the composition of those atomic planes. Okay, so one more example—it is very useful to understand the site occupancy. So, you know that in any unit cell, if there is a solid solution, the atoms can be randomly arranged. But if it is an ordered structure, the atoms have certain lattice points or lattice positions. So, by generating spatial distribution maps,

As I told you, these are nothing but the average distribution of atoms in a particular crystallographic direction. Okay? And for each atom, it is being measured. Now, here you can see that there is a unit cell which is an L1-2 ordered structure, and this unit cell has two lattice positions. One is 0, 0, 0.

Another one is half, half, 0. These are the two lattice positions. And at these two lattice positions, you have different atoms. At 0, 0, 0, there are titanium atoms. At half, half, 0, there are cobalt atoms.

You can see here. So, at this particular plane, if you see in this direction, this is called a mixed plane. Why a mixed plane? Because it has both titanium and cobalt atoms. But if you see this particular plane, it is a pure plane.

Okay, a pure plane means only cobalt atoms. And here, it is titanium plus cobalt atoms. Now, if you take the distance between this unit cell, it is 0.36. And this pure plane is at 0.18 nanometers, at the center of this 0.36. Now,

I will reconstruct the atom probe, and you can see that these are the lattice planes. Fine? Now, if you plot an SDM map along this particular direction for this unit cell, you can see that this is the distance: 0, 0.4, 0.8, and you can see that at each 0.36, This is at 0.36. This is at 0.72.

You can see that the titanium peak appears. It means that the titanium atoms are located at 0, 0, 0 positions, which is at a distance of 0.36. But if you see the cobalt distribution, you can see that each peak appears at 0.18, 0.36, 0.54, 0.72. So, because one peak is mixed and one peak is pure. So, you will get the presence of cobalt atoms at each 0.18 distance.

So, from here, From these SDMs, what you can find out is that titanium is occupying the 0, 0, 0 positions while cobalt occupies the half, half, 0 positions. So, this is how these spatial distribution maps can be used to identify the site occupancy of any unit cell. If it is an ordered structure, you will have a different element sitting at different atomic positions if it is an ordered structure.

If it is a solid solution, what you will see is a titanium peak even at 0.18 or 0.54. So, you will get a solid solution because titanium can occupy any of these positions, either 0-0 or half of 0 positions. Okay? Okay. So, with this...

In this class, what we have taught is about the effect of detector efficiency. Then we talked about the radial distribution maps, radial distribution, RDF analysis, and radial distribution frequency. Then, this radial distribution frequency is along the radial direction, correct? And if you want a 3D representation of this, we have spatial distribution maps. These are very useful to find out what type of atom is present at what site of the unit cell.

Okay, so with this, I will end this class today. Now, most of the atom probe topics have been covered. So, in the next class, I will start with basic electron microscopy. After covering electron microscopy, it will include not only transmission electron microscopy but also electron channeling contrast imaging and SCM. I will show you how these three techniques, in the last few classes—maybe two or three—will be applied in a correlative way.

We will cover some correlative microscopy by giving real examples and demonstrating how these techniques can identify mechanisms or problems in materials. Thank you.