Advanced Material Characterization by Atom Probe Tomography and ElectronMicroscopy

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Week-02
Lecture-06

Welcome to the fifth lecture of this course, and I will just briefly go through what we discussed during the last class. We described the MCP multi-channel plates, and we also talked about how the ions are converted to a range of secondary electrons by using these multichannel plates, okay. These channel plates are nothing but glass tubes which are negatively biased by a certain voltage so that the surface becomes highly charged, and these ions will go through these glass tubes and hit the surface, due to

which a large number of secondary electrons These secondary electrons again travel across these glass tubes and hit the phosphor screen, which leads to the emission of photons. Why are these converted to electrons? Because ions are heavy, and also the photons released when the ions hit the phosphor screen are very few compared to the electrons, which can produce photons after hitting the phosphor screen. These channels are actually aligned at a

5 to 15-degree angle with respect to the normal axis. This is just to increase the probability of the ions or the electrons hitting the glass tube surface, which is highly charged, fine. So, this is how it works. Once these secondary electrons come out of the MCP plate, they are again biased by a voltage where these electrons are converged to a spot. And at this particular converged spot, these electrons will hit the phosphor screen, producing the image of the atomic structure of the tip surface, fine. So, this is just a brief overview of the role of MCP plates. So, now we will briefly go through the interpretation of FIM images, field ionization microscopy images.

So, as you can see, in (a), (a) is the experimental FIM image, and (b) is the simulated one. Fine, and you can see that you can observe some concentric

rings appearing. In the images. These concentric rings are nothing but (a) showing major crystallographic planes protruding on the tip surface. Okay. And if you see the symmetry of these concentric rings, these are exactly similar to the stereographic projections. Okay. And each region where these concentric rings are present, these are called poles.

Okay, and if you see, these poles—the connection between these poles usually occurs by zone lines. We can refer to them as zone lines. So, in FIM images, you can actually see the crystallographic nature or atomic structure of the tip surface. Okay, so this is for a pure metal—the example of pure aluminum. If you think about an alloy or a tip surface, or your needle specimen, which is made from different species, okay, so these different species—their interaction with the imaging gas also differs, okay.

So, this leads to variation in the charge transfer, okay. So, this is the first effect we observe for an alloy, which has different species and is not a pure element. The second is the evolution of the local curvature of the tip. Because of the different species, they have different evaporation fields. We will come to the description of the evaporation field.

Based on this evaporation field, they will have different electric potentials. Different electric fields near the tip surface arise due to this difference in the electric field, which actually changes the evolution of the local curvature of the tip, okay. For example, if you have an alloy like copper-iron-nickel and a certain precipitate, if that precipitate's evaporation field is lower than the matrix's, Due to the difference in the local evolution of the tip's curvature based on the evaporation field and the electric field, The precipitate will appear dark in the film images, okay.

So, this is due to the low evaporation field, which can lead to the low electric field around the tip surface. Based on that, the local curvature of the tip will evolve. Due to this, it will appear as a dark precipitate. But in some cases, for some

alloys where the precipitates, phases, or species have an evaporation field higher than the matrix, they usually appear as bright regions.

So, here on the left side, I am showing an example of a T1 plate, which is a copper-lithium-rich plate appearing bright in the FIM image. On the right side, you can see this is a scandium-zirconium-rich precipitate. It has a higher evaporation field compared to the matrix or the aluminum. So, it appears bright on the fluorescent projector screen. So, this is how we can interpret the FIM images.

Now, FIM microscopy can also be used for some applications. Okay, and these applications are related to the crystallographic nature of the needle specimen. Okay, so by FIM, actually what we do in these high-end atom probes is, if you have FIM feasibility, then FIM can be used to clean the tip surface. Before actual atom probe field evaporation. Okay.

So after the clean surface, what you can do is actually get the crystallographic orientations. Okay, crystallographic orientations on the tip surface. So, actually, you can see the concentric rings, and based on that, you can determine which zone or which crystallographic direction that particular tip surface is in, okay. Similarly, you can also identify the grain boundaries and the precipitate phases, which have a different evaporation field during during field ionization, okay.

So, this is prior to the atom probe field evaporation, okay. So, this is one of the applications for orientation determination. Another important application is the radius of curvature. As you know, during field ionization, the radius of the tip evolves. Okay, so as I told you in the last slide, where the appearance of concentric rings, these concentric rings are directly related to the interplanar spacing of that particular atomic structure.

Okay, so, you can actually see that each concentric ring acts as an atomic terrace, acts as an atomic terrace. Okay, which is directly related to your dhkl of that particular spacing, d-spacing of that particular orientation, correct, of that particular zone. So, assuming that, and these poles, you can see there are several poles appearing, these poles actually poles which are surrounded by

these concentric rings, the spacing between the concentric rings is directly related to your interlamellar spacing, okay? So, now if you know the material, for example, this is tungsten, so if you know the material, then actually each concentric spacing can be calibrated to the spacing of

the d-spacing of that particular tungsten material, okay? So, you can have several poles and the symmetry, okay? So, based on this interlamellar spacing, actually you can estimate the R0, which is the radius of curvature, fine? So, the interlamellar spacing, you can actually calibrate the dimension of the reconstruction by using the interlamellar spacing. Okay? And you can see that several poles are readily identified. Okay?

So, these concentric rings, as I told you, they are also linked to the local geometry, local geometry of the tip surface, okay, and which can be used to determine the R0. local curvature of the needle specimen evolution, okay. So, as I told you, each successive terrace, so you can, this is a schematic where you can see that each successive terrace is each successive terrace is nothing but can be calibrated to the d-spacing of that particular material, interlamellar spacing. Okay? So, if you see that based on this, what we can do is we can also measure the angle between the two crystallographic planes. Fine?

So, this can be done as you can see: if you have the nth terrace and join it up to R0, this is called R0. So, depending on the nth terrace, from the first to the nth terrace, it can be given as N dHkl. So, based on that, this particular value is R0. Now, this particular angle can be related to your cos theta. So, you can write cos theta equals R0 minus theta.

And dHKL divided by R0. So, this particular equation can be rearranged to measure R0 or the curvature of the needle specimen. So, this is one of the applications where we can use FIM for measuring the evolution of the radius of curvature. Another important measurement we can do is the shank angle. The shank angle is nothing but the half-angle of the tip.

So, the evolution of R0—you can see that when field evaporation is taking place in the needle specimen, the radius of curvature evolves from R1 to R2. Based on the triangular symmetry, and knowing that each terrace of the concentric ring corresponds to n times the dhkl, you can measure the shank angle of the needle specimen, which is given by sine alpha equal to (R2 minus R1) divided by (R2 minus R1 plus n dhkl). Okay. So, this is how we can measure the shank angle alpha. FIM can also be used to accurately measure the image compression factor.

In the previous classes, I just explained the image compression factor. This is related to the compression of field lines toward the axis of the needle specimen. Okay? And this image compression factor is given by xi, which is equal to theta crystallography divided by theta observed. Okay, which is estimated by theta observed. This theta crystallography is the actual angle between the two crystallographic planes, which is measured crystallographically. Okay?

So, this can be measured by cos theta, okay, for any two crystallographic planes. And theta observed can be measured by using the FIM image with the formula, if you assume that the distance between the two crystallographic poles is D, and the distance between the needle specimen and the fluorescent screen is L. As L is much greater than R, you can assume that the tan inverse R10 is equal to D by L, which is actually related to your theta observed. Based on this, you can put this value in theta observed, and you have a value of theta crystallography, which is a standard, a constant between the two angles of the planes.

You can actually measure the image compression factor for that particular needle specimen, okay? Which is a function of the field and also the shank angle, fine? So, these are the basic applications of FIM, which can be used prior to the actual field evaporation during atom probe. So with this, I will summarize the field ionization microscopy concepts. As I told you, Professor Müller first developed FEEM, which is a field emission electron microscope. Okay?

So the difference is here he has applied a negative DC voltage on the needle specimen. Where the electrons are used for the imaging purpose, and these electrons travel along and accelerate along the field lines and hit the fluorescent screen. Later, he has applied a positive DC voltage on the needle specimen. There, what he has done is he has injected the imaging gas atoms, for example, like neon, argon, or hydrogen, and these gas atoms when they reach near the tip surface, near the ionization zone, these gas ions get polarized.

Due to which there will be a tunneling of electrons, or the electrons will drain into the tip surface while these gas atoms will be converted to ions due to the Then, based on the local electric field, a very high electric field, these positive ions, gas ions which have information of the atomic structure of the tip surface, will be projected on the fluorescent screen. Okay, I talked about the Heisenberg uncertainty where you can see that by the projection of ions on the fluorescent screen, you can actually mimic the atomic structure. However, based on the electrons, you can get a resolution up to a maximum of 2 nanometers.

Okay, so this difference is due to the Heisenberg uncertainty. Electrons, because electrons have a large spread. And because of their lower mass. But however, ions have a very low spread because of their heavier mass. Due to which the uncertainty is much less for the ions case.

So that is why we see that there is an atomic structure we can resolve the atomic structure of the tip surface by using the ions. In the case of electrons, we can get a resolution of a maximum of 2 nanometers. Okay, so just to note, the image from the FIM is not strictly an image of the surface of the tip surface. But rather, it is an image of the ionization zone, which is located just ahead of the atoms on the tip surface. Okay, so the ionization zone we have described as the main delta zero, which is the core for the resolution.

Okay, so as we described the resolution in FIM, which is related to the spot size, fine, and this will have a contribution. From different factors, lateral velocity—we talked about lateral velocity. Then Heisenberg and similarity, so they have a

contribution, so they will put up a spot. The second important point is the ionization zone directly relates to the surface itself. Okay, but this distinction is enough to potentially introduce bias in the measurements and observations, fine. So, these are the two important points which we need to keep in mind for the FIM analysis in FIM, okay.

And in the last slide, I have explained how this FIM can be utilized to get the orientation, shank angle, radius of curvature, and also the image compression factor, fine. Now, The next thing is from field ion microscopy, we will now move to the field evaporation microscopy. Okay? So, usually the field evaporation is nothing but what we call field desorption microscopy, and how it has evolved towards atom probe tomography. Okay, to understand this, the field evaporation—consider this is an atomic structure. Okay, this is the atomic structure of a needle specimen near to that, and you can see that there is one atom protruding on the tip surface.

It is kept under high vacuum. Now, if you apply a very high field or a high DC potential to this tip surface, then what will happen? An intense electric field will be generated just near the surface. Okay, so what will happen? These electrons—the first thing that happens is field ionization.

Okay, so this is under the field. Okay, then what will happen when you apply a high DC voltage? These electrons from this particular atom will drain inside the tip surface. Due to this, the particular atom gets ionized. So, the first process is called field ionization, which happens to the atom bound to the tip surface. Remember, we are not putting any imaging gas into the chamber.

near the tip surface, fine. We are talking about field removal of an atom from the tip surface or from the lattice positions of the tip needle specimen, fine. So, if you apply a field, the first thing is the electrons will drain toward the surface, then this particular atom will be converted to an ion, depending on the number of electrons drained into the surface. Due to the voltage, there will be field lines ahead of the

tip surface, and this ion will accelerate along these field lines toward the projector screen.

So, there will be a projector screen, and this particular ion is projected on it, giving the actual ion coming from the lattice of the tip structure. So, this is field evaporation. Now, as we understood, field evaporation is nothing but a field-induced removal of an atom from its own lattice. And this has, if you apply an intense electric field, two important steps. First, ionization takes place.

Second is desorption. Desorption means the removal of that particular ion, which is converted and projected toward the screen. For ionization, there should be a sufficient electric field. The next thing is the electrons will drain off to the tip surface. That will induce ionization of the atom, and based on the electric potential and the electric field lines near the tip surface, these ions

get accelerated toward the projector screen from the surface of the atom. So, remember, we are not using imaging gas here. So, to understand this field of operation, we can use simple thermodynamic considerations. The most popular model used to understand the field of operation is the Muller model. Here, Muller proposed that the atom is fully ionized at a critical distance from the tip surface.

before escaping from the surface. This was the assumption Muller made to simplify the understanding of the field evaporation process. So what he has done is the atoms, so he has proposed that he has assumed that the atoms first get ionized at a critical distance before escaping from the surface, and this particular model is called image hump model.

This particular model is called the image hump model. So, here the field evaporation takes place when there is a thermal contribution or thermal agitation. or thermal agitation energy that allows the atom to overcome the energy barrier. So, we will come to this barrier, how to understand this energy barrier. So, during field evaporation, there will be a thermal agitation energy.

which is provided to the atom, and this atom, so if there is enough energy for thermal agitation, then it can overcome the energy barrier. So, this is also possible that without any thermal agitation, it is also possible that the ion can actually tunnel through the energy barrier. And this tunneling process is related to the temperature. So, usually this happens at very low temperatures. So, tunneling can also happen.

So, there are two things. One is thermally driven or thermally agitated energy, and the other one is due to the tunneling of ions, which can tunnel through and cross the energy barrier. Okay, so, to be ionized and repelled from the surface, the atom must cross the Schottky hump. This is called the energy barrier, which is associated with the atom. Okay.

So, This particular hump or this particular energy barrier is directly related; it is directly related to the field which is applied, the electric field which is induced or which is present near the tip surface, okay? So, this energy barrier is termed as QF, okay? This energy barrier is also called the activation barrier.

for field evaporation, okay? So, this is the energy barrier. Now, we will talk about the energy barrier, okay? Energy barrier means QF. So, in the Muller model, the atom to be evaporated is considered to have the same energy, the atom so

If you have a tip surface which is having atoms arranged in a crystallographic way, if there is a protruding atom on the tip surface, In the Muller model, it was considered that the atom to be evaporated The atom to be evaporated is considered to have the same energy as the atom adsorbed on the surface of a metal. Based on this assumption, what we can do is draw a potential curve with respect to the distance, okay? Now, Okay, so, assume that this is the distance x, okay? This is your potential V, fine. If there is an atom which is bound to the tip surface,

it means it is occupying the lattice position. So, it has a certain binding energy, fine? Based on that, the potential energy curve for that particular atom which is

on the lattice position can be given as, okay? And this particular value is called the binding energy. This is called binding energy.

Okay, so, initially, when an atom is located at the lattice position, it is bound to the neighboring atoms. Okay? So, the potential energy curve will look like this. As per Muller, if the ion, if that particular protruding atom is ionized and near the tip surface, Okay? And due to the ionization, what will happen?

The potential curve for that particular ion will shift upward. Okay? And for that particular case, we can draw it like this. Okay? So, how much shift is it from the lattice position?

So, this is for an ion which gets ionized. Okay. Remember that till now, there is no field applied. No field applied. Okay.

So, this is the potential energy curve for an ion. which is near the tip surface, and this is the potential energy curve for the atom which is bound to the neighboring atoms in the lattice, fine. So, if there is an ion, then there is another term which we call sigma In minus n phi, okay? Here, In is the ionization energy, and phi is the work function of that particular material, okay?

Remember, during this ionization, Due to this ionization, remember that the electrons which are lost from the atom get drained into the surface. So, it gets certain electrons in the tip surface. That is why it has a negative term, and n is the number of electrons. Okay, so that is why it is a negative term.

So, the energy barrier can be written as sigma i, and n can be 1 to that number of electrons minus n work function of that particular material. Okay, So, the total energy barrier we can call is theta 0. This can be given as theta 0 equals binding energy plus summation of ionization energy depending upon the number of electrons, number of ionizations, minus n work function. So, this is the total energy barrier for an atom to get ionized. Now, the next part is

If we apply an electric field, okay, if we apply an electric field, your total ionization curve, this ionization curve will get distorted, okay. So, this ionization curve gets

distorted. How is it distorted? Okay. So, this is just a schematic in the PowerPoint, what I explained while writing.

So, you will have a binding energy, you will have an ionization energy, and you will have a work function. Okay. And so, if there are n electrons, this is under a field—you are applying an electric field, an under field. Okay. So, electrons will drain out, and the atom gets ionized.

Okay. Then, what will happen is your ionization curve—this is your ionization, the potential curve for the ion—will get distorted in this way. Okay? So, when an electric field is applied, the ionic energy states are affected. So, ion states, ionic states of equivalent or lower energy than the atomic state can be accessed because previously, the ionization curve was like this, and it gets distorted to this position on application of the electric field. Now, you can see that there is a hump here. This particular hump is nothing but the energy barrier, and the value of this is given by theta F. Fine?

So, this is your energy barrier, and this energy barrier can be By thermal activation, any atom, any ion can overcome this energy barrier and accelerate towards the fluorescent screen. As I told you, it can also tunnel. The ion can also tunnel through the energy barrier, but this process usually happens at very low temperatures. Okay. So, we will assume that the tunneling process—most of the models assume that the tunneling process is not occurring—all are thermally activated. Fine.

So, this is under the field—how the distortion of the potential curve for the ion takes place—and there exists an energy barrier which is related to your theta F. So, with this, I will end this class, and what we will do in the next class is derive some equations to understand this field evaporation. Okay? So, some important equations we will derive based on how you can understand that field temperature and DC voltage will affect the field evaporation process during field desorption events.