**Advanced Material Characterization by Atom Probe Tomography and ElectronMicroscopy**

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**Week-04**

**Lecture-09**

Welcome to this class. Briefly, I will just go through what we discussed in the last class. We discussed the field of operation and how it differs from field ionization. We also talked about post-ionization effects, where atoms that get polarized at the tip surface may ionize if they are at the critical distance. Between the tip surface and the ionized ion, it may happen that post-ionization will occur.

This means that electrons can be drained out of these ions again, leading to the post-ionization phenomenon. This post-ionization is nothing but similar to gas imaging, where gas atoms get ionized near the tip surface, okay? So this is just similar to gas atom ionization, fine. So, briefly, I will go through it. In previous classes, we also discussed the appearance of poles, which are nothing but the projection or the stereographic projection of that particular element.

For example, these are the poles. These are the poles that correspond to pure aluminum. Pure aluminum. And these poles, you can see, are nothing but the low-density regions. Low-density regions.

And also, we see these zone lines clearly. Okay. So, in today's class, I hope that we will cover this part how these zone lines and the low density poles are observable during the field of operation. Okay. So, here this is a typically you can see that 1 dar 1 3 zone and you can see the symmetry which is exactly similar to what we observe in the film.

So, these particular images are nothing but Desorption images. Field desorption images. Okay. I will come to this terminology and this is nothing but a 0 to 2 pole of

Pure aluminum FCC, this is a 002 and you can see this 4-fold symmetry along this zone axis or the 002 or 001. So, we also discussed about the Kingman diagrams. So, we talked about the charge states that are directly depends upon the induced electric field. Okay? And that is directly related to the curvature, the local curvature.

Fine? And these charge states are a function of the electric field which is present near the field. And these charge states, depending upon the element and the charge, have different field evaporation or evaporation fields. Okay? Depending upon the charge.

So, these Kingham diagrams, it is nothing but you can see that on the x-axis, this is the field, okay, and this is the ratio of the charge, and you can see that these different colors correspond to different charge states. Okay? I have given you an example of the effect of curvature on the atom map. Okay, and which is related to the charge state of that particular element, okay. So, we described an aluminum-magnesium-silicon alloy where there are magnesium-silicon precipitates, okay, and depending upon the charge states F1 and F2 of those particular ions,

of those particular ions, then you can get the tomogram with respect to that, okay. So, due to the difference in the charge states locally, the curvature or the first, the electric field around that curvature will change due to which the evolution of curvature, the evolution of the tip, and that particular location will also change, which will have a direct impact on the the electric field, and due to this, the electric field can reach the evaporation field of one of the charge states like Mg 2+ or the aluminum 2+, then these ions get field evaporated.

Okay. So, this is a charge state for Mg 2 plus. Okay. So, that is why we see a different distribution of atoms even in the presence of a precipitate. You can see that there is a concentration of aluminum 2 plus.

Okay. So, now coming to the instrumentation part. The APT instrumentation is very similar to FIM. Okay. So, on the left side, you can see a very simplistic diagram.

It is a schematic diagram. Okay. So, similar to FIM, there is an ultra-high vacuum chamber which has a pressure of 10 raised to the power of minus 8 pascals, and the important One of the important points here is that the sample stage can be moved in three dimensions. So, you have X movement, Y movement, and Z movement, okay?

So, in front of this particular stage, on the stage, you can actually load several samples, okay? And at this moment, In the X, Y, and Z directions, this moment allows different tip surfaces to be positioned in front of the local electrode. This is a counter electrode. Okay?

Here, the temperature can go up to 20 Kelvin, and there is an application of a very high DC voltage. Okay? In the presence of this counter electrode, the counter electrode is also connected to a high-voltage pulser. We will come to this voltage pulsing, the high-voltage pulser. Okay?

This counter electrode is nothing but a hollow copper foil. A hollow copper foil. And this hollow has a diameter of 10 to 60 microns. Okay?

And due to the presence of this counter electrode, if you have an atom tip needle in front of the counter electrode, the electric field lines will be highly concentrated due to which your Kf, it means that field factor becomes or decreases. Fine. So, this is the effect of counter electrode which in modern atom probes, they are regularly used. And specimen, as I told you, can be mounted on a substrate with the sharp needles and on application of voltage pulse or HV pulse,

these field evaporation of the atoms on the tip surface, they can get polarized and they can field evaporate and these field lines will be concentrated into the electrode, hollow electrode and these polarized atoms which are converted to ions, they will go inside, along the field lines inside the electrode. They will follow this particular path. This HV pulsing, this HV pulsing, it will last around few

nanoseconds okay with so pulsing means the if you have a voltage so hp pulsing means the voltage at a certain time it goes up and it goes down it goes up and it goes down okay and the time interval between up and up and down it can be the rise and decay time it can be between 0.5 to 5 nanoseconds okay so when your pulsing will be at the maximum point you expect that the evaporation of the atom, the evaporation of the ions from the tip surface will be maximum, okay? So, we will come to this discussion later.

But now, for now, these voltage pulses are few, lasting for a few nanoseconds. We can also apply, instead of HV pulsing—last class we showed that there is another type of pulsing called thermal pulsing. That is also called laser pulsing. What is laser pulsing? What do you do? You will apply the electric field.

The electric field will be constant, but you will increase the tip temperature. Okay? So, you will generate a beam—the laser beam or the light beam—onto the tip apex. So, you can see these are the mirrors. And if your beam falls on, and by using optical mirrors, this beam—the laser beam—is focused onto the tip surface.

Okay? And the wavelength or the laser spot is actually much larger than the tip—the radius of the tip diameter. Correct? And some of the photons—the photons from the, laser or the light—are absorbed on the tip surface, due to which there will be an increase in the temperature of the tip.

So, due to the increase in the temperature of the tip, what will happen? It will assist the field evaporation of the atoms on the tip surface. Okay? So, remember in the laser pulsing, it generates pulses of a few tens of nanoseconds. It can generate tens of

nanoseconds down to hundreds of femtoseconds. What is a femtosecond? We can say that a nanosecond is around 10 raised to the power of minus 9 seconds. A femtosecond is 10 raised to the power of minus 15 of a second. Fine?

So, this is the difference. So, we can actually generate a laser pulse or a thermal pulse which can last between tens of nanoseconds down to hundreds of femtoseconds. Okay? So, on the right side, it is a different image. It is different in different directions.

So, you can see that this is your atom probe needle. This is your counter electrode, okay? And while applying the voltage pulse or the laser pulse, these ions travel along the field lines. And this particular part is nothing but the detector, okay? This detector consists of two parts, as I told you last time. These are MCP multi-channel plates, plus there is a position-sensitive detector, or we call it a delay-line detector.

Delay-line detectors. So, a typical detector consists of these two important parts. Fine. So here, there is an optical image. It is an optical or camera image where you can see a very sharp needle in front of a local electrode. And this is a hollow electrode, fine? Around up to 60 microns in diameter, okay? And the back side of this electrode, you will have a detector

which is schematically shown on the right side, in the upper right side of the diagram. Now, we will talk about particle detection. So, how do these ions get detected by using this particular detector, which is composed of MCP and the delay-line detectors? Fine. So now, we will talk about particle detection. So, particle detection mainly involves the ions.

And these ions are typically collected by the detector. Okay. And this detector has two roles. One is that the detector provides the timing and also the position. Timing means the time of flight or the timing, and the position means at which position the particular ion has hit or impinged on the detector.

Position of the impact of each ion on the detector. Now, as I told you, this detector is composed of stacks of MCP plates. Plus delay line detectors (DLDs), and these MCP plates—these MCP plates—are in the chevron configuration. Chevron configuration. What is a chevron configuration?

You can see it in this particular image. This is your cross-section image, okay? And you can see that this particular region is nothing but this particular region, and this is called a chevron configuration. Okay. This chevron configuration is composed of two microchannel plates, which are arranged at a certain degree, which is 8 to minus 8 degrees. Why is this being done?

This is being done to increase the efficiency of the detection, so that, as in the last class, we told that the MCP plate is nothing but the periodic arrangement of the glass tubes. Okay, and these glass tubes are highly charged by the bias voltage. And when an ion hits this glass tube surface, it generates a large amount of secondary electrons. And these electrons, when they are in the chevron—the MCP plates are in the chevron configuration— these electrons can again strike the glass surface and generate thousands of electrons or a cascade of electrons.

This cascade of electrons will come out from the rear end of the MCP plate. And these, by the application of a bias voltage between the delay between the detector—between the delay cross delay line detector or the phosphor screen—and the rear end of the MCP, then these electrons will accelerate towards this particular delay line detector. Okay, so this chevron configuration is for effective ion-electron conversion and signal amplification. Okay?

And the detection efficiency of a particular detector is between 55% to 65%. Why is it very low? Why is it not 100%? This is due to the fact that, if you assume this particular glass tube, what will happen is—if you see the cross-section—you will have a glass tube like this. And this particular area,

The electron cannot pass through it. The electron can pass only through the hollow area of the glass tube. So when an ion hits this, the non-glass tube area, the non-tube area, Then what will happen? These ions, when they hit the non-tube area of this particular region, generate secondary electrons.

But these secondary electrons cannot penetrate through the glass channels. Okay? So, it gets reverted back. So, ions strike the intra-channel. So, this non-tube area is called the intra-channel or the web region, or we can call it the web region.

So, these secondary electrons do not enter the glass tube. So, it will not pass through and will not reach the delay line detectors. So, that is why the efficiency becomes 55 to 60 percent. But to improve the efficiency or the gain of MCP, usually what we do—what can be done—is that these particular designs The design of these glass tubes can be made as a flared entrance.

Flared entrance. What we see on the left side of the image. This decreases the inter-channel region. Due to this, the probability of ions traveling through the glass tube increases significantly. So, it goes up to 65%.

These ions strike the glass surface and convert into a large number of secondary electrons. Additionally, what you can do is, One more technique to increase detection efficiency is to coat a layer on the MCP side with a conductive layer. Usually, it is a micron. So, what will happen when and placing a mesh just ahead of the front end of the MCP. This mesh, along with the front end, has a negative bias voltage, and when an ion travels When an ion travels and gets trapped in the inter-channel region, what will happen? These ions or the secondary electrons generated by that strike will go to the mesh, and due to the negative bias voltage, they will rebound into the glass tube channels. This is how you can reduce the loss of these electrons.

To the outside of these MCP plates. So, this is where you can actually increase the efficiency of the MCP or the MCP plates. Okay, so I hope now I understand how the design of these MCP plates leads to higher efficiency of detectability, or we can say how we can generate a large amount of cascade electrons by multiple hits of these ions on the MCP plate. Okay.

The next thing is behind this MCP there is another detector which we call the delay line detector (DLD). At the start of the class, I just mentioned that DLDs provide timing and also position. Okay, so these delay line detectors are particle detectors. These are particle detectors that use the time difference. The time difference between the arrival of any signal at different points.

On the delay line, okay, and you can see here on the right side a schematic diagram of this delay line detector, you can see these delay line detectors are nothing but a continuous wire, this blue-colored continuous wire, which has an endpoint at x1 and another point at x2. So, this is the x2 point, and this is the x1 point. These are the two endpoints.

Now, similarly, this is the x position. Similarly, for the y, this is a y end point, y1 end point, and this is a y2 end point. Okay? So, you can see this delay-line detector will be like this. Okay?

So, you will have two, X1, Y1 and X2, Y2. Fine? So, this is, and these are nothing but continuous delay-line wires, conductive wires. Okay?

So, when the electrons come from the MCP, the rear back end of the MCP, these electrons will hit this mesh. Of x1, x2, and y1, y2. Okay, so what will happen? These electrons, which have a certain spread, will generate an electrical pulse on those particular wires. Okay, so schematically, if you see that if you have a continuous wire, assume that this is an x1 position, this is an x2 position. When an electron cloud hits the wire, the conductive wire, so what will happen? It will generate an electric pulse on the conductive wire. And this electric pulse can travel in this particular direction or in this particular direction.

Fine, so you will have a one-pulse electric pulse that can travel along x towards x1 or towards x2, and measuring the time difference. For the pulse to reach X1 and to reach X2, actually, we can estimate, we can find out the heat position of that particular electron cloud. Fine. So, this is how we can measure the XD, which is the position at which the electron cloud hits the tiller line wire or the conductive wire. Fine, so okay, now we will talk a little bit about the delay line detectors. Okay, so as I told you, these are typically particle detectors that use the time difference of an electrical pulse.

Of an electrical pulse between reaching the two positions X1 and X2, which is connected to the conductive wire. So this is used to determine the position of heat and also the timing. Okay, so if you see the stepwise function of this, the first will be the signal generation. Signal generation, so when a particle, ion, electron, or photon strikes the detector, it generates a charge pulse. You can call it a charge pulse or electrical pulse.

The second is the signal which is generated has to propagate or has to travel. Okay, so the signal propagates along the delay line. Typically, this delay line is a conductive wire, and towards the two ends of that particular delay line, X1, X2 or Y1, Y2. Okay, then the third function of this delay line detector is the measurement of time, measurement of time. So that signal, as I told you, if there is an electron cloud, it hits the delay line detector and generates a pulse.

travel towards X1 and Y1, correct? The signals at different points on the delay line arrive at different times. Okay, so like this, an electron cloud arriving at this position after a certain time, or at the same time, it is possible that an electron cloud is also arriving at a different position. Okay, at a different position at the same time, or it is possible that at different times, these electron clouds E1, E2, and E3 can arrive at different positions of that particular delay wire. So, depending upon the particle impact positions. So, the time taken for that electrical pulse to reach X1 and X2 will depend upon where the particle has hit the detector at that position.

So, how can we measure it? So, the fourth point is the, the fourth important function is it measures the position of It calculates the position. So, this is by measuring the time difference between the signals that are arriving at different positions. Different points, we can tell.

Different points. Okay. With this, you can, the detector can detect the particle's position. So, usually what we measure is if there is a delay line wire, if there is an X1, there is an X2, okay? Consider the total length of this delay line wire is LX, fine?

So, the position, if an electron cloud E1 hits this position P1. Then, that position P1 can be calculated by the formula of XD. XD is equal to tX2 minus tX1 divided by 2tX whole power LX. Okay? So here, the tX2 is the time to reach the endpoint. Similarly, tX1 is the time to reach the endpoint x1.

Okay, tX is the total time along the line. And LX, as I told you, is the physical length of the wire. Okay, usually, this particular Okay, so I can write the formula again. So, usually XD is equal to tX2 minus tX1 divided by 2tX equal to LX. Okay?

So, this is the position of the head of that particular electron cloud on the wire, on the conducting wire. Correct? So, this is the position calculation. The position calculation. The fifth function is the timing information.

Okay, so these DLDs provide the timing information and can be used to determine the time of arrival of the particle. Time of arrival of the particle. Okay, so this is how it provides an excellent way of timing resolution and also the position of the head of that particular electron cloud. So I talked about only in one direction, xD. Similarly, you will have a yD.

So you will have a two-dimensional position. So you will have coordinates of xD and yD at the cross section. Correct? So, this is how it is measured. DLDs are used for the measurement.

So, the timing information, the t, the average time of flight can be given as tX1 plus tX2 plus tX3, tY1 plus tY2 divided by 4. Okay? So, this is the time which is measured. So, there are two time pairs we can tell you. tX1, tX2, and there is another time pair, tY1, tY2, for each of the XY line configuration. Okay?

So, schematically, what we can see is we will have a mesh. So, you will have an X1, X2. Similarly, you have a Y1, Y2. Okay. So, one of the drawbacks of these DLD detectors is multiple heat capacity.

What does it mean? It means that there is a limitation which is imposed when different electron clouds or different electrons or the ions arrive very close either by time or position. So, it will identify them as the same type of electron cloud or ion. So, this is imposed as a multiple heat related to the multiple heat capacity. So, the total time of propagation of any signal along the lines imposes this particular constraint.

Okay. And to separate out the signals for each single ion. Correct. And this particular phenomenon, which we call, is an ion pileup. And usually, in most of the atom probes, this is the main detection limit for the capabilities.

Okay? And this particular phenomenon can also be described as if more than one ion hit is detected during a single pulse. Okay? This can also be termed as This can be defined as if more than one ion is detected in a single pulse.

Correct? So, this is one of the drawbacks of the DLD detectors. So, now we will move to another topic: what is the difference between field desorption microscopy and atom probe tomography? Okay, as the name suggests, it is related to the field desorption of a polarized ion from the tip surface that is directly detected on the fluorescent screen. Correct?

So, usually before these MCP plates and position-sensitive detectors came into use, atom probe tomography was termed field desorption microscopy. It means that due to the application of the DC voltage, whatever polarized ions are present, those direct ions actually hit the fluorescent screen. So, there are no position-sensitive detectors. So, it means there is no conversion of these ions to secondary electrons to be detected. But in the new atom probes, we usually convert these ions to a cascade of electrons.

that are then impinged on these position-sensitive detectors. So, an image is formed by formulating the ion impact positions on the detector. Okay? These images are also called desorption images. Desorption images.

Okay? So, desorption images—what are these called? These are the images formed by the field-induced field-induced desorption of atoms from the specimen. Okay.

So you can call it a desorption image or desorption map. Okay. So if you take a desorption image, if you compare an FIM and the desorption image, it looks very similar, but there is a difference in the electric field. There is a difference in the field ionization of these atoms when you use gaseous imaging gases or imaging ions or when you use the desorbed image, desorbed atoms, or desorbed ions.

So they have certain differences in the images. The first image of a field desorption image, the field desorption image, was shown by Walco and Mueller in 1972. Okay? They called it an FDM image. Then, these FDM images—what Mueller's student, Dennis, whose name is Panitz, did—he attached time-of-flight spectroscopy to these two FDM.

So, this was related to your atom probe. Okay? So, this is the just a time scale. So, we call it FIM, we call it FDM.

FIM uses the imaging gas, and these get polarized or ionized at the ionization zone above the tip surface. Now, in FDM, this is not the case. In FDM, the surface atoms of the tip are ionized. Surface atoms of the tip get ionized, and due to the potential difference, voltage, and electric field, these ionized surface atoms get desorbed. That's why these are all called field desorption images or field desorption microscopy.

So, the trajectory of ions originating from the surface atoms of the tip will be slightly different from the trajectory of imaging gas ions accelerated along the field lines. From the ionization zone ahead of the tip surface. Okay? So, there is a difference in the trajectory. So, therefore, there will be a difference in the projection parameters.

Projection parameters between the FIM and the FDM. Okay? So, usually in FIM and FDM, If you see an image of an FIM and an FDM image, what we see is this is the left side, this is a film image. On the right side, it is an FDM image.

Fine? So, you can see that this is from the same material, tungsten, and you can see these concentric rings which correspond to the atomic terraces. Atomic terraces in both images. So, this is an FIM, and on the right side, it is an FDM, field desorption. If you see properly these concentric rings, the size of these concentric rings, you can see that in the FDM, the size, the concentric ring diameter is lower than in the FIM.

So here the size of the concentric rings is larger. Here these are a little bit smaller in size compared to the FIM image. This is directly related, as I told you, to the trajectory difference of ions projected from the tip surface. So in FIM, usually the imaging gas ions Imaging gas ions get ionized near the ionization zone ahead of that particular atomic terrace.

But in the case of field desorption, the atoms which are actually attached to the lattice of the tip surface get polarized and these atoms get field-evaporated. Okay, so there is a difference in the trajectory of these contrasts which we see on the detectors. Okay, so in the case of comparing A and B for FIM and FDM, you can see that So in the case of the difference between FIM and FDM, you can see that it might be possible that the contrast gets reversed. Meaning the concentric ring which appears bright can become dark.

Why is it so? This can be understood by the density, the atomic density which is projected on the FIM or FDM image. Okay? The first case, A, is related to FIM.

The second case is FDM. Okay? So, you can assume that. So, first we will describe the FIM. Assume there is a tip.

Assume there is a tip, which has a local curvature. Again, there is a local curvature. Okay? Fine? And okay?

Yeah. So, assume there is a tip, okay? And it has a local curvature. You can see these atoms are arranged on the tip surface, okay? And you can see there is a local curvature.

So, here the curvature is Here the curvature is small, here again the curvature is large. And these are the gaseous atoms on the tip surface, on the ionization zone. Now, in film, the region of high curvature will appear bright. So, the region of high curvature will appear bright and because this is due to the, directly related to the high density of hits on the film image.

So, you can see that the atomic density here, It is very high as compared to atomic density here. Fine? So, these regions appear very bright due to the high density of heat on the film image. And remember that these gas atoms are just in the ionization zone ahead of this tip surface.

Fine? And this gets polarized based on the distance, like XC—if it is less than XC or more than XC, then these gas ions get polarized and, depending upon the curvature, there will be a high density of heat on the film image. So, this particular region will appear bright. But this particular region will appear dark.

But in FDM, the case is different. Here in FDM, Assuming that this is a tip surface, okay? So, there is a local curvature. So, here there is a local curvature.

So, here there is a high curvature. Here there is a high curvature. This high curvature leads to a high electric field ahead of the curvature, okay? So, a high electric field, and this induces A local magnification effect.

Magnification effects. What is this local magnification effect or the trajectory aberration? These occur when these atoms get ionized or polarized, actually, due to the local curvature and electric field; these particular ions get repelled. Okay? So, this ripple between the ions.

Okay? So, these local magnification effects are directly related to the ripples of the ions at that local curvature or to that higher curvature due to the electron density. So, due to this local ripple nature, these atoms will get—these atoms will lead to the trajectory aberrations, and these trajectory aberrations lead to a very low density just ahead of the curvature but a very high density at the terraces or the atomic terraces. Okay, so these will appear bright. Fine? So, this is the difference between the FIM and FDM images. So, using the data from APT, atom probe, actually, we can replot these, we can replot these FDM images. Okay?

So, these FDM images are nothing but desorption images. Okay? And in these desorption images, wherever there is a low density of atoms, those appear dark, okay? Wherever the high density of these regions is, they appear bright. So, there is a difference in the appearance of desorption images and FIM images, okay?

Usually, these low-density regions are related to the poles, okay? and zone lines. Okay. This is due directly to the trajectory aberrations. As I told you in previous classes, the electric field around the tip surface is also directly related to the crystallographic axis, whether it is 100, 110, or 112.

Depending on this, you will observe trajectory aberrations which are related to the appearance of low-density regions and high-density regions. And these regions are directly related to the poles or the zone lines which appear on the desorption images. Okay. So one more point which I want to clear is the in the last class we discussed about the post ionization. Post ionization it is nothing but the atoms from the lattice which are get ionized and

and which are near to the ionization zone at a critical distance of Xc, these ions can reionize. Okay? So, the electrons can drain out from those ions again. So, this is called reionization, due to which you will get different FD images, field desorption images. As we know that the local charge state

The charge state of the ions is directly related to the electric field, the local electric field in the vicinity of the tip for a given species. Correct? So, here I am showing you an example of tungsten. Fine? And this is a typical field desorption image.

You can see that by plotting W3+, you can see that the zone lines, zone lines and also the pole has low-density regions, while for the tungsten 4+, you can see that near the zone lines, these tungsten 4+ ions get accumulated Okay, so these are nothing but trajectory aberrations, as tungsten 4+ needs higher potential; they have a higher evaporation field. Okay. Similarly, this is the case of magnesium.

This is Mg+ and this is Mg2+. And you can see that in between these poles, there is a bright region appearing. These bright regions are nothing but the trajectory aberrations related to Mg2+ ions. And it shows that due to the large curvature or higher curvature, the electric field near the tip surface also becomes more concentrated.

If the local electric field reaches the evaporation field of that particular charged-state ion, you will get a high density of those ions in those regions. So typically, we can use these field desorption images to locate the poles, to get the zone lines, and also to explain how the charge state is distributed along these low-density regions. So, with this, I will end this class now. In the next class, we will discuss the pulsing methods in a bit more detail. As I mentioned two classes ago, there are two pulsing modes: voltage pulsing mode and thermal pulsing mode, or laser pulsing mode.

Voltage pulsing mode is when you change the electric field at a constant temperature. But in thermal pulsing, you keep the electric field constant while increasing the temperature. So, there is high-precision (HP) pulsing and thermal pulsing. We will meet in the next class to discuss these two important points for this course. Thank you.