Advanced Material Characterization by Atom Probe Tomography and ElectronMicroscopy

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So, welcome to this class. So, last class we went through the experimental protocols in atom probe tomography, and especially we also discussed the Z, how to find the Z. And that is based on the field evaporation, which takes place layer by layer. Okay. And that Z usually directly relates to the atomic volume.

Fine. So, in this class, I will show you some slides from some of my colleagues or friends who are actually scientists at BARC. And I would like to acknowledge them for these slides. So, Deepak Arya is a PhD student at HBNI, BARC. And Deodatta Shinde is a senior scientist at BARC.

Okay. So, coming to these slides, today's slides will briefly go through the information we get from the atom probe. Data and how this information is used to determine the reconstruction of the needle specimen. Fine. So, okay, we see in this slide, as you can see, there is a certain appearance of contrast, okay, and these are related to some kind of precipitates. Which are present in the matrix.

So, this is a matrix, and you can get this three-dimensional distribution of ions which are field-evaporated. So, this is a typical reconstruction. This is a typical reconstruction of the tip, which is field-evaporated. So, as I told you, most of the reconstruction is done by the reverse projection model. So, you will get the information of the x, y position and also the z depth.

And the color here—all the colors correspond to different species. So, here you can see there is a precipitate, which actually has a high number density of these yellow-colored precipitates in a matrix. There are another kind of precipitates, which are in red color. So,

this shows that they have different chemistry and are distributed in a matrix. Now, from the instrument, what information do we get?

Okay? So, the first thing we get is the sequence number. Okay? So, if you have a middle specimen, okay? So, the ions—the atoms which are polarized—travel along the field lines, and layer by layer, these are

Ions, these atoms get accelerated, or the ions get accelerated towards the detector. So, it is a layer-by-layer process. So, it means that there is a sequence. So, you can say that in the sequence, once the type of ion which is field-evaporated has a time of flight of about 200 nanoseconds. Okay, so these are the parameters which we get from the instrument.

Time of flight, the DC voltage which is applied, this is the pulse energy, We talked about the pulse energy. This is the xD position, yD position, and the number of ions per pulse, okay? And the pulse skipped, okay? So, these are the pieces of information which we get from a typical atom probe.

Now, if so, as it is a layer-by-layer process, there will be a sequence of atoms or the sequence of layers that get field-evaporated, like sequence 1, 2, 3, 4, and depending upon the type of ion, they have a different mass-to-charge ratio, and this mass-to-charge ratio is directly related to the time of flight. You can see that some species have a 200-nanosecond Some species have a 19.8-second time of flight, meaning the time of flight is much less.

So, they are moving much faster. Correct? So, this is related to their mass-to-charge ratio. Fine? And DC voltage, as I told you, increases with time.

Correct? As you know, in an atom-proof needle, the radius actually evolves. The radius increases as the experiment proceeds. So, if you want to keep a detection rate constant, you need to increase the voltage according to the detection rate for that particular needle specimen. Next is with this.

With this sequence and these parameters from the atom probe, we can reconstruct those ions. This means we can get the ion or atom map in three dimensions. For example, this is a particular material where you can see the distribution of yttrium, yttrium oxide as a

molecule, and even combine yttrium plus yttrium oxide to see their distribution. You can get the aluminum.

Fine? So, depending on the species, you can select what type of atom map you need in that three-dimensional volume. So, your needle specimen will be like this, and whatever the analyzed volume is, we can reconstruct it with these parameters. And to reconstruct, we need this data. Okay?

Heat sequence, time of flight, DC voltage, pulse energy, X heat and Y position, and Y heat position. Okay. So, briefly, With the one ion that is getting field-evaporated, we have a time of flight for that ion. We have an applied voltage at that time, and also we have XD and YD, which are the positions on the detector.

Okay, and what do we want to know? We want to know the identification of the ion and its original position at the tip, which is XY and also Z. Correct? We will come to that Z later. First, we will just briefly go through these slides. Okay?

So, we need a model. Okay, as I told you, this model is nothing but a point projection model, a point projection model. And the time of flight is to identify the chemistry or the chemical species, xD, yD, which can be converted to the XYZ of the position of those ions in the reconstruction. Okay, so this particular time of flight is just a revision.

You can actually model it. So, here there is a schematic where you can see that this is a needle specimen and these have certain atomic species. Atoms, different colors correspond to different types of atoms, okay? And this is kept at a very low temperature of around 20 to 80 Kelvin in an ultra-high vacuum chamber. And there is a distance, L, between the tip surface and the detector.

This is your local electrode, okay? This is a hollow local electrode. So, and when there is a timer. Okay. So, when you apply a pulse, either a laser pulse or a voltage pulse, one ion gets polarized, one atom gets polarized and it gets accelerated towards the field lines, towards the field lines.

Okay. Along the field lines and hits the detector at a position of XD and YD. Okay, similarly, with another pulse, you will have another atom which moves much faster,

meaning it must have a low mass-to-charge ratio, and it hits the detector. Fine. If there is another pulse, then in this way, you can measure the time of flight by using the time. keeper where we can distinguish these chemical species or the atoms on the detector. Fine?

Okay, so as I told you, the velocity of the ion traveling directly depends upon its mass-to-charge ratio in the electric field. Okay, so how to identify? So, this is the basic equation, assuming that the atom leaves with an initial velocity of 0. So, it has a certain potential energy on the tip surface. Okay, and that can be given by qV.

And there is a total kinetic energy, and you know the velocity is L by t, where t is the time taken, and with this basic equation, you can evaluate the mass-to-charge ratio of that particular ion. So, in this way, we can actually identify the chemical species. So, We have discussed the mass spectrum. So, this is a typical mass spectrum.

These are the counts, and this is the corrected time of flight in nanoseconds. Correct? So, these are the identity. So, you can see that these corrected time of flight, each peak corresponds to a single ion, single type of ions. single type of ions, okay?

And we can range this, we can index it based on the time of flight which can be converted to the mass to charge ratio, okay? So, if you calculate the mass to charge ratio based on the time of flight, you can see that for a single element like chromium, you have a different charge ratios, correct? So, for coronium, you have 1+, 2+, 3+, for iron, you can appear for 1+, 2+, 3+. So, you can have a different charge to mass to charge ratios for each species, okay?

And the width of this particular mass spectrum The width of the mass spectrum which is m divided by delta m. This is related to your mass resolution. Okay. And the number of ions can be count by ranging this particular peak. Okay.

So, in this way we can identify different types of ions. So, these three peaks corresponds to chromium and these three peaks corresponds to iron. Correct? In this way, we can arrange the mass spectrum. Now, once we have talked about the identification of the chemical species, we will see the position X and Y. Correct?

So, the XY position of atoms. So, in this, we can see that after field evaporation, that particular red atom gets polarized and ions and heat to some detector which is at XD. Along the field lines, okay? So, ion trajectories will be independent of mass charge and applied voltage, okay? And they, geometrically, are shown as hyperbolic in nature, okay? So, in the last class, we also talked about the reverse point projection model, okay? Here, the geometry So, usually in the last class, I told you that if any atom is present on the surface at the near field, usually they

will feel a force perpendicular to the surface and as it moves away from the near surface, it gets compressed. Towards the axis of the specimen, correct? So, with this, what point projection was the Baas ETL method? You can assume that what the position is. So, as we discussed in the last class, if any atom is present on the surface Which is present on the surface by the reverse projection model, it appears that this has to go along the field line perpendicular to the tip surface and hit the detector. Fine?

Usually, this is not the case. Usually, in the near field, it might appear that the initial travel of that particular ion is perpendicular to the surface. But as it goes towards the detector, these get compressed. Okay. This is bent and compressed towards the specimen axis.

Okay. So, the final position will be these positions, not these positions. Based on this, what we can do is a simple reverse projection model. It was assumed that the final hit position of that particular ion can be regarded as a straight line which passes through that particular atom on the tip surface and crosses to a position which is away from the center of that hemisphere.

Correct? So, you can put it as a center of the hemisphere; that point is called P. Okay? So, a point P exists which maintains the same spatial relation between the tip and the detector. So, this is the basic assumption in the reverse point projection model.

Okay? Now, this particular distance from the tip surface to P is related to the xi r, where xi is called the image compression factor. Okay? Okay, so with this, we also talked about how the detection is happening and how it is converted to the positions of x, d, and y, d.

Usually, xi, the image compression factor, is 1 for the radial projection, which shows that it is perpendicular to the surface.

If this is a stereographic projection, it usually has a maximum ICF value of 2. Okay, so based on the simple geometry, you can see there is another assumption that the particular atom which is located at the tip surface, which is going to be ionized,it actually it is assumed that it is projected on the plane perpendicular to the the tip axis. Okay? Based on this triangle symmetry, you can get as a d. By xi r, it is related to your magnification, okay?

So, d by d is magnification, which is given by L by xi r, okay? L is the distance between the tip surface and the detector. So, your magnification becomes this formula, okay? So, for each position, x d and y d, we can actually measure the x actual by x d divided by m and y d divided by m. So, this is how the two coordinates, x and y, can be obtained with this reverse point projection model.

I will just briefly go through, even though we have explained the determination of ICF and the radius of curvature. So, ICF can be obtained by using FIM or by using pole figures, correct? So, here there is an ion map. which shows the distribution of ions that are hit on the fluorescent screen. Okay, and you can see there are several terraces, and you can see the concentric rings which correspond to the poles.

Actually, from the stereographic projection, you can measure these poles. Okay? So, in the field desorption image, This is a field desorption image. You can see that the appearance of these poles as low-density regions. Okay.

And these are called zone lines. This is exactly related to your Kikuchi pattern, or you can create or the stereographic projection. Fine. So, you can index these poles as per the symmetry. Okay.

And these zone lines correspond to these lines. Now, You can say that if there are two poles, P1 and P2, okay, and the distance between these two poles on the detector is D, so the angle between these two is related to the theta P projection. But you know that P1 and

P2 have some crystallographic orientation and they have a certain definite angle, crystallographic angle, correct? That can be deduced mathematically by cos theta, okay?

So, So, this theta P, with the triangle, we can assume that it is related to the D by L. Okay? And we already know the theta C, which is the crystallographic angle between these two poles, which were indexed. Correct? By cos theta.

Fine? And so, the difference, the ratio between the theta C and theta P is equal to the ICP. Image compression ICF, image compression factor which is xi. Correct? This is how we measure the image compression factor.

Now, how to find the radius? Okay. So, here you can see that the radius, as in the few classes back, as I told you while the field while the field evaporation is taking place, actually your radius is evolving, and the radius is increasing from R1 to R2. Okay, so, to make the detection rate constant, you need to increase the voltage as well.

Okay, so, this is just an SEM image where you can see that the radius is not constant. It increases as we move away from the tip surface. Okay? So, based on the radius, you can see that initially, the voltage required to maintain a constant detection rate constant detection rate is lower, and as the tip radius increases, your required voltage also increases. Correct?

So, your tip will be very sharp here. It will be blunted. It will be blunt; the bluntness will increase as your radius increases. Correct? And you know that if you assume that the electric field

The electric field of the tip surface, if it is equivalent to the evaporation field of that particular atomic species, Actually, we can find the radius at that particular moment by putting the voltage divided by the Kf, which is the field factor. Okay, and remember, the voltage for HV pulsing will be the DC voltage plus the pulsed voltage applied. Okay? So, this is how we can assume—we can actually calculate the radius of curvature if we know the field factor.

Okay? So, now the next thing is how to find the K factor. Okay? So, K actually is a geometrical factor. As I told you, it relates the strength of the field at the tip to the voltage applied.

Correct? And it depends upon the tip radius, shank angle, counter-electrode distance, detector distance, and chamber shape. Okay. So, if there is a small sphere of radius R and L, the field factor is actually 1.

Okay. And for K, it usually varies from 2 to 8 in the needle specimen. So, how do we estimate K? For the estimation of K, I will go into more detail later in the class. So, this is just an example of an iron-chromium alloy.

Okay. So, where they will get the alpha precipitates, alpha prime precipitates. Okay. These are all BCC precipitates, and they know that these are spherical in nature. By using alternative microscopy techniques,

they know that in the iron matrix, these are spherical precipitates. Now, if you perform the field operation on this particular alloy, what will happen? You can actually reconstruct with different K values. So here, you can see that with 3.7, 4.7, 5.7, 6.7, and 7.7, at 3.7, these precipitates are actually compressed along the Z-axis. That is different from your image or the expected precipitate shape.

So, at 6.7 and 7.7, you can see that these are elongated along the Z-axis. Okay, so the k-factor from here—we can, from the microscopy image, we know that these are spherical. It should be between; it should not be so low as 3.7, and it should not be so high as 7.7. And with the 5.7 k-factor, you can see that these precipitates appear as spherical precipitates, which is most near to the expected one. So, this is how the field factor can be estimated. There are other methods also to estimate the k-factor that will come into the later class. Okay, so this is how we can estimate the k. So, now...

What do we know? We know the voltage. We know the path length. We know the evaporation field of that particular species or your tip surface. You have an ICF.

You know the k-factor ICF from the crystallographic axis, crystallographic angles. We can measure the k-factor by using other microscopy techniques, and we can measure the

k-factor. Now, we calculated the radius evolution, the tip. Radius of all time, which is related to the voltage, k, and F. Okay. We have magnified.

So, we have calculated the magnification by using a definite R value, which is xi and L. So, magnification is related to L by xiR. Also, we have detectors. The delay line detectors are used to determine the XD and YD positions. But, we need to find Z, correct?

So, as I told you, this is a sequential process, correct? So, in this sequence, you can see this table, which I showed in the first slide, where we are getting all the information from the atom probe, correct? So, here the time of flight is for the identification of chemical species. Your DC voltage is for the reconstruction and evolution of the radius, correct? And the backseat and Y-way positions cannot be used for Z. Your pulse energy and number of ions also cannot be used for the determination of Z, correct?

So, now the only remaining factor is the sequence number, which is very important for Z. Okay, so in the last class, we discussed in detail how the atoms are field-evaporated sequence by sequence. Correct. So, with this sequence, we can actually assume and calculate the evolution of Z during the field evaporation. Okay, so this is a schematic where you can see a needle specimen. Okay, and the color corresponds to different chemical species.

So if you apply the pulse then the atoms are polarized and get accelerated towards the detector in a sequence way. So you can see that in the first sequence the atoms got field evaporated first then after that the second sequence. Correct? So, it does not appear that the third sequence will feel operated first and before the first sequence. Okay?

So, with this assumption, we can actually calculate the Z. Okay? So, the position of heat detector can determine the X and Y. Correct? So, if the top layer has 10 ions, so if we count this number of ions which are present, then I will be knowing that what is the 11th ion which will be from the next layer. Okay?

So, first all these ions or the atoms has to field evaporated. Then only there will be a second set of atoms which are sitting gets field evaporated. So, this is called sequence 1. This is called sequence 2. Okay?

Now, So, for each, this is your reconstructed. So, now you can see how the relationship between the delta Z and the sequence of ions will go, okay? You can see that in the first, there are four ions, okay? And these four ions which get field-evaporated first, after that only there will be a second sequence, then a third, and the fourth sequence, and these can be filled, correct?

So, This is in three dimensions. Okay? So, you have a needle specimen. Okay?

This is actually an area. Fine? This is actually an area. Area related to X and Y. Okay? So, by determining the atomic volume, we can actually relate

to the xy and also the cross of delta z which is equal to delta v. It is noted that the number of ions into the volume of each ion. Okay, so with this atomic volume, we can easily estimate the delta dz means the depth increment during the field evaporation. And in the last class, we have derived some of the basic equations which are directly related to the atomic volume, correct. Now, this is a schematic of a wooden specimen, and you can see that

based on the sequence, you can see that the red color will evaporate first, yellow is second, and third is the green color. So, with this way, your depth is increasing correct. With this way, we can measure so this delta z is nothing but the area of xy into delta z, which means the number of ions into the volume of each ion, correct. So, this delta z equals to N into atomic volume divided by the area of X and Y, that cross-sectional area. And this area of cross-sectional area, if there is a detector here, it corresponds to the demagnification 1 by M square of that particular area, detector area.

So, it is nothing but the area of the detector divided by the M square, which is the area of the XY, which is the analyzed volume. Correct? So, this way we can measure the analyzed volume. You know that the magnification is given by L by xi R. R can be given by V by kF. So, with this equation we can actually estimate the delta z with this particular equation, which we have also shown in the last class.

Okay? So, now here one more variable has to be added: efficiency, because not all ions that are field evaporated are detected. So, there is a detection efficiency associated with

that, which is related to your detection efficiency, and that comes into the picture of 1/ξ. Okay, so this is just a revision of how z is determined, along with the x position, y position, and the chemical identity of the particular species from the needle specimen.

Correct? So, This is one slide where I want to show you how these reconstructions are so powerful. So, actually, we can resolve the atomic planes by this reconstruction protocol, which we described just now. So, here you can see that this is a small volume of a big data set.

where you can see that each ion is actually arranged in planes, correct? And these planes are nothing but the atomic planes, which have a certain d-value. Remember that this particular d_hkl is larger than the penetration depth of the electric field, which is around some picometers. This is much less than the spacing of that crystallographic plane, correct? So that's why we can actually resolve the atomic planes and get the composition of each atomic plane in the z-direction. This is what we can call it as a

It is a resolution along Z, or we can call it lateral resolution. Okay. So, With this, I will end this class. So, in this class, I have briefly gone through the different types of parameters and also briefly revisited Z with some schematics

where you can understand how the reconstruction is done based on the data we get from field evaporation in an atom probe. So, here the time of flight, position of X and Y, the voltage, evolution of the radius and also parameters such as pulse energy—all these are used to reconstruct Z, which is calculated based on atomic volume. Okay, assuming that field evaporation occurs sequence by sequence. And based on conditions like temperature, pulse, HV, or all pulsing conditions, you can resolve the atomic planes.

The resolution of atomic planes is possible because the electric field's penetration depth is a few picometers. So, you can resolve the distance between atomic planes based on the reconstructions, okay. So, I hope in the next class, I will go through the calibration procedures which are very important to calibrate during field evaporation and also during reconstruction procedures, okay.

We will meet in the next class.