Advanced Material Characterization by Atom Probe Tomography and ElectronMicroscopy

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Week-03

Lecture-08

So, welcome to this class just briefly go through the in the last class we just discussed about the post ionization. So, post ionization it is nothing but the atoms which got ionized they can reionizes just near to the tip surface and this will happen at a very critical distance at which is called Xc and These ionization it totally depends upon how much time these ions will stay in the that particular ionization zone okay.so kellogg Kellogg adopted a model which involves which which takes care of which takes care of multiple stage post ionization multiple stage post ionization okay of during field of evaporation okay so

This model actually takes care of evolution of average charge, average charge of any particular ion, for example, tungsten ion, okay, evolution of the average charge during the field evaporation. okay so the relative frequency for each charge state was calculated and plotted as a function of electric field okay and these diagrams are called Kingham diagrams okay so these are so these Kingham diagrams are plotted versus the relative relative frequency of charge versus field, okay? So these were plotted for most of the transition metals, transition metals, okay?

So I will give you some examples related to these diagrams. So, I hope in the screen you are seeing some of the kingdom diagrams or the kingdom curves for different elements like in the left side you have a silver, in the right side you have a aluminium, arsenic and the gold. So, here the blue line corresponds to plus 1 charge, green corresponds to plus 2 charge, Red corresponds to plus 3 and violet corresponds to plus 4, okay.

So, depending upon the charge state, they have plotted the relative frequency of the charge states versus the field which is applied, fine. So, these are very particular for the different types of elements and that depends upon the field evaporation field okay so I will give you a brief example of aluminum magnesium silicon alloy this particular alloy This have a in an aluminum matrix they have a magnesium silicon rich precipitates So, in the next slide, you can see that on the left slide, you have a distribution of certain atoms. fine

So, the first distribution is of Mg^{2+}, the second is of Al^{+}, and the third is of Al^{2+}. Okay, So, in these reconstructions, each dot corresponds to the ions that are detected and reconstructed. If you see the evaporation field for magnesium, aluminium, and silicon, correct? You can see that for aluminium plus iron, the evaporation field is around 19, okay? So, F1 corresponds to a +1 charge, F2 corresponds to +2.

And F3 corresponds to +3. We will concentrate only on +1 and +2. So, magnesium with a +1 charge is around 21. You can see this value: 21 for 19, and for silicon, it is 45. Similarly, if you compare the +2, aluminium +2 is around 35, and magnesium +2 is around 25.

And silicon +2 is around 33. Okay? So, these are the evaporation fields for those particular charged ions. It means the evaporation field—just remember the definition of the evaporation field. It is a field that is required when your energy barrier QD is 0.

Okay? So, this is called the evaporation field. Now, for this particular alloy, you can see that when you do the reconstruction, Due to the difference in the evaporation field, there will be a local change in the tip curvature. Tip curvature.

And this change in tip curvature will induce a change in the local field. Okay? So, if your tip curvature changes—if your tip curvature increases or the R0 increases, or decreases—then what will happen is the local electric field lines will be more concentrated. Fine, so there will be a local increase in the field If your tip curvature reduces or the R0 increases, then your local field will get reduced

Okay? So, this is the change in tip curvature is a function of the evaporation field. Okay? So, the higher the evaporation field, they will induce local curvature variations—local curvature variation. Okay? And there will be a local change in the electric field. Fine. if you if you want to understand more schematically, I can explain that. If you have a needle specimen, fine, and if you have a precipitate sitting at the top, and this particular precipitate—assume this is a magnesium-silicon-rich—okay? So, based on the values, and this is a pure aluminum Okay, aluminum matrix now if you apply if you apply the voltage,

So, this particular needle specimen will evolve. So, after some time, what will happen is, as you know, Al+ charge is around 19, but Mg and Si+1 charge is more than 20. So, it is 21 and 45. Assume that if you have induced a local electric field around the tip surface is around 19 which is equal to the evaporation field of aluminum plus iron. So, what will happen?

The aluminum atoms at the surface will get field evaporated, okay? Will get field evaporated but the Mg silicon atoms are present at the tip surface will remain as it is due to which what will happen due to this field evaporation of this particular region your atom probe tip will involve in such a way that it will get sharpened at the region of magnesium silicon region okay because your aluminum gets field evaporated. So there is a change in the tip curvature so your the tip the radius of curvature increases

It means your R0 decreases at this location of the precipitate, a magnesium silicon. Due to this change in the radius of curvature, what will happen is the electric field lines . near to the tip surface will get more concentrated. So your local field will increase. If the local field increases up to a value of 21 or 45, then what you will get is Mg plus and silicon plus ions will get field evaporated.

So that is why you will see the difference in the field evaporation sequence of these depending upon the charge state, depending upon the charge state and this charge state So, the number of one charge state, the number of either aluminium plus or Mg plus 1 ions, it is totally the number of, it depends upon your, the evaporation field for that particular ion. Now, if you go back to your image in the presentation, you can see that These are Mg2 plus ions. These are aluminium plus ions.

Okay? So, during field evaporation, as I told you that the aluminium has a value of 19, aluminium plus 1. So, that is why in this particular aluminium plus ions, you can see that the most of this blue colour dots are corresponds to aluminium plus. And you can see that the locations wherever the precipitates are there, There is no aluminium plus 1 ions.

Correct? So as the tip will evolve by the time, what will happen at this region, the tip surface, the tip due to magnesium and silicon evaporation fields are much higher than aluminium. Due to which at these locations, your tip radius will decrease or the curvature will increase due to which you will get a local electric field, local electric field due to the concentration of the field lines much touching to the evaporation field for magnesium and silicon.

So, you can see that in the case of Mg2 plus okay and in the case of aluminum 2 plus. If your local electric field lines, local electric field is near to these values, then what will happen? Mg2 plus and silicon 2 plus gets the field evaporated. That is why you see these precipitates are concentrated. like magnesium 2 plus and also the there is some charge of aluminum 2 plus fine I hope this correlation has been understood between the evaporation fields

which is different for different charge states and as your field evaporation is taking place you are actually depending upon the evaporation field the curvature of tip changes depending upon the evaporation field of the precipitate whether it is higher or lower than the matrix the curvature can become higher or less. Based on this local electric field concentration local electric field concentration lines also will change due to which they may reach to a value where it is equivalent to the plus 2 or plus 3 charge state of the ions correct. So, this is how we can correlate the evaporation field with the tip curvature which is evolved during the field evaporation.

Now, in the next part, what we will describe, what we will discuss is the imaging atoms. Okay. So, in this part, we will just go through the how to analyze, how to analyze atoms one by one or we can also tell that atomic layer by atomic layer. atomic layer by atomic layer, okay? So, similar to FIM as we discussed in the previous classes for microscopy where we require a very sharp needle.

So, for APT, atom probe tomography also we need a very sharp needle and subjected to a very high potential or the voltage, okay? So, exactly similar to FIM, we have a field which is equals to V divided by K, F and R, okay? I hope you remember KF is nothing but a field factor, is a field factor. R is the radius of the needle specimen and V is the applied voltage.

Okay, so Kf actually this is a constant which accounts for the tip shape and it also accounts for the environment or we can tell it has a electrostatic environment around the tip surface. So, this is exactly similar equation which we have seen in FIM. So, based on the nature of the tip or the nature of the needle. If it is a metallic, if it is a metallic sample or a metallic needle, then the electric field the electric field penetration is within the range of atomic distances, okay? So, it is very, very small

it means if you have a needle specimen of a metallic sample, the penetration of the electric field on the tip surface is very small. It is on the order of atomic distances. So, it is mostly less than 10 raised to the power of minus 10 meters. What does it mean?

It means that when field evaporation is taking place, you are actually removing atomic layers one by one, layer by layer. This is due to the electric field penetration. which is at a very small distance, very tiny distances. It means effective screening occurs at a distance much smaller than the size of an atom. Fine?

This is for the metallic sample. So, therefore, the only atoms affected by the electric field are the surface atoms. So, you can actually remove atoms one by one, or we can say it has an atomic layer by atomic layer, as we had described, okay. So, if you have a non-metallic sample, if you have a non-metallic sample, actually in these samples, the electric field penetration is very high, okay. So, it penetrates to the specimen tip surface.

A few atomic layers, okay. So, what is the impact of this? The impact of this is you can generate complex ions. It means that if the atoms in the non-metallic sample If they are stable between 4 or 5 atoms together, then what will happen? This particular group of 4 or 5 atoms can field-evaporate at a time. So, it will generate complex ions. So, here the field evaporation does not take place layer by atomic layer.

So, this is the difference between both the metallic and the non-metallic samples. So, in non-metallic samples, due to the penetration of the electric field, the depth resolution is very poor as compared to the metallic samples. So, I hope you understand that we have first described the field around the tip surface. We have also described the difference between the metallic and the non-metallic. How the electric field penetration is different for these two, which results in the generation of complex ions in the non-metallic samples.

Okay, so now we want to understand atom probe tomography, correct? So, the basic thing to understand for atom probe tomography, which is different from FIM, is that we are applying pulsed field evaporation. Okay, it is nothing but pulsed field evaporation. Pulse field evaporation means that you are applying a pulse. The field can happen in two ways—two ways, I hope you remember. In the last class, we described the field-temperature calibration curve.

field temperature calibration curve okay so if you have this temperature, this is your field. means F relative field F by FEVAP, okay? So, this particular value will be 1 here. Assume it is around 0.9 fine and here, you can assume the temperature is around 40 Kelvin, 80, 160, and so on, okay? So now, in the last class, we derived an equation where that equation is related to the field, the relative field versus the temperature calibration, okay? So, I have shown it for tungsten, okay?

So, if you, and that field calibration, the slope, for a particular metal or element, it goes like this, fine? So, these are the 0.9. So, there are two mechanisms to be controlled. There are two mechanisms which can be controlled for inducing the pulse field for the vibration. Correct?

The first thing is to increase the electric field at constant temperature. Okay? So, by increasing the electric field at constant temperature. The second thing is to increase the temperature at constant field.

Okay? Both these conditions can induce field evaporation of the surface atoms. This is how we can do it? In the first case, assuming that you have a tip and the tip is kept at a base temperature of some 40 Kelvin. Okay?

So I can mark a dashed line which is at the 40 K, okay? And assume that you are applying a potential which generates a field of a certain value say 0.9 relative field, okay? Or you can say that it is 0.6, so you will have a relative field. I can draw a horizontal line, okay? So this is a base temperature which is 40 Kelvin. This is a base field, relative field, which is around 0.6.

Fine? So, for the first case, where I told you that the temperature increases, to increase the electric field at constant temperature. Okay? So, we keep the base temperature the same at 40 Kelvin, and if you increase the field, this is called field pulsing

meaning you are increasing the field at the surface of the tip. This is what we term as HV pulsing, okay? The second case is to increase the temperature at a constant field. So, you keep the base field around 0.6, and if you increase the temperature from 40 Kelvin to a certain other temperature like 80 Kelvin or 100 Kelvin, this is called thermal pulsing. So, most atom probes use these two types of pulsing for the field evaporation of atoms from the tip surface. So, I hope you understand the two basic mechanisms: increasing the electric field at constant temperature or increasing the temperature at constant field.

If you increase the field pulse, those are called the HV pulsing method. If you increase the temperature of the tip surface at the base field, you can perform thermal pulsing. So, in recent atom probes, like the latest version, the 6000, we can perform both types of pulsing. Both types of pulsing together. The older versions of atom probes, like the 5000 or 4000, cannot perform both pulsing methods together; we must choose either voltage pulsing or thermal pulsing.

So, there are certain advantages, which we will cover later, to using these two mechanisms together. So, we can perform controlled field evaporation based on these two mechanisms, and most atom probes now have these two techniques and most of the atom probe now have these two techniques or the two methods. So, after introducing the two pulsing modes, we must now consider two important terms frequently used in atom probe tomography. One is the evaporation rate.

Okay? And the other term is the detection rate. And these two terms are different. Okay? Evaporation rate—remember, in FIM, we have described the evaporation rate.

It is nothing but the number of atoms evaporated per second. Okay but the detection rate is the average number of atoms or ions detected in a single pulse. Okay? Just now, we have introduced the pulsing methods, so you can now correlate: the detection rate is nothing but the average number of atoms detected in a single pulse. Fine? And these two are different things.

So, it is not necessary that the detection rate is proportional to the evaporation rate. Okay? So, in the coming time, we will describe the equations for this. So, this evaporation rate, as in the last class, we have derived—we have shown—is equal to the frequency of atomic jumps on the tip surface perpendicular to the surface, exponential of minus θ_F, which is an energy barrier, K_B T.

This is an Arrhenius-type equation, correct? You can see that the first term, second term, third term—the first term is nothing but the vibrational frequency, the frequency of vibrating atoms at the tip surface, okay? The second term, θ_F or Q_F, is the energy barrier, and the third term, temperature, is the base temperature. So, in FIM, we have just applied the DC voltage.

So, you are applying a voltage continuously. But in an atom probe, as we described the pulse, we should incorporate the pulse in this term. And as you know, this pulse is time-dependent. So, this pulse is time-dependent. So, assuming that

The frequency of vibrating atoms is constant and remains the same at that particular field and temperature. We can write the expression for field evaporation rate as a function of time to account for the pulse, given by μ_0 exponential of minus θF as a function of T divided by KB. Temperature as a function of time. Okay, so you can see that here the term comes as a function of t, which is a pulse, a time dependent process. okay so this is the equation for the evaporation rate. Now we will come to the detection rate. Okay, so detection rate can be defined as the

integral of this particular term, field evaporation rate as a function of time. Fine, so the integral of evaporation rate over a duration of time. So here, there are two important factors which need to be considered for the detection rate. The first one is, it is not necessary that all the atoms are detected or all the ions are detected. Okay. This can be directly related to your detection efficiency, which is termed as ED, called detection efficiency.

Okay. The second thing is the number of atoms that can potentially field evaporate is not finite, is not infinite. Okay. So, that has some finite number of atoms which can be field evaporated from the tip surface. So, which type of atoms?

Only the atoms at the surface of the small tip can be field evaporated. Okay? So these two factors have to be incorporated into this integral of evaporation rate to actually know the detection rate. Okay? And if you assume, if you make two assumptions—assume that N A T—these are the

number of atoms across the entire surface of the specimen that can be field evaporated. The second is the probability of evaporation is equivalent. for all the atoms, okay? Which is a very hypothetical case, but based on these two assumptions, what we can write is the detection rate pi D is equals minus infinite to plus infinite evaporation rate as a function of time DT into detection efficiency detection efficiency into the atoms which are present across the tip surface which can be field evaporated.

So, this is the equation for the detection rate. So, until now, we have just gone through some important terminology: evaporation rate as a function of pulse. which is a function of time, okay? We also talked about the detection rate, which is not necessarily is a function of evaporation rate, okay? And this is the final expression for phi D, which is a detection rate, okay?

So, now I will briefly go through the meaning of pulse fraction. Pulse fraction. In the case of HV pulsing, HV pulsing you remember HV pulsing means it is a change in field or the increase in field at constant temperature that is called HV pulsing. In HV pulsing the pulse fraction is defined as the ratio between the amplitude of the HV pulse

to the DC voltage, okay? So, pulse fraction in the HP pulsing mode, we can define it as a ratio between the amplitude of the HP pulse by the DC voltage. If there is an atom probe needle and if you see with time, with the field of operation, the radius of curvature R evolves with time, okay? So, your tip radius will increase as your field evaporation taking place.

So, the tip gets blunted and blunted, your R increases, okay? And to maintain this pulse fraction constant, which depends upon the amplitude of the HV, this has to change continuously, okay? continuously to maintain the pulse fraction constant with time because as your field of operation taking place your radius of curvature decreases or increases. due to which the amount of field required to field evaporate the surface atoms will also increase. And to maintain this pulse fraction, your amplitude of the voltage pulse should increase to make the PF as constant.

So, it is just to generate the electric field required to evaporate ions and to keep the PF constant. Now, in the case of laser, In the case of laser, there is no defined term for this. Because in laser, it is nothing but a thermal pulsing. It is nothing but a thermal pulsing and in thermal pulsing, the energy of the laser is kept constant throughout the experiment.

It means that here the pulse fraction varies with the change in the specimen shape or with the change in the evolution of the tip. Unlike in the HV pulsing where the pulse fraction is kept constant. In the laser mode, usually we will do the energy of the laser as a constant. This energy of the laser depends on the wavelength or the direction of polarization of the light which is used. So these are the two important differences regarding the pulse fraction in the HV pulsing mode and in the laser pulsing mode.

Remember HV pulsing it is nothing but change of field as at constant temperature but in the laser at constant field you are changing the temperature by using the laser and this laser the energy of the laser directly depends upon your lambda of that particular light and also the polarization. In HV pulsing, the pulse fraction is kept constant. So, the amplitude of the HV pulse has to increase over time.

However, in the laser, the pulse fraction changes continuously. And the last topic I want to cover is the most important part of the APT: the time of flight. So, whatever ions are field-evaporated from the tip surface, those have to be identified. Correct?

And this pulsed field evaporation actually gives precise control over the time of flight or the measurement of the time of flight. So, the time of flight is nothing but the time taken by an ion or atom from the tip surface to the detector. Okay, so if you have a tip surface and a detector, the distance between them is taken as L. If an atom on the tip surface gets ionized and travels to the detector, the time taken by that particular ion to reach the detector is calculated with respect to L. For example, if you have a needle specimen with two or three kinds of atoms,

one kind of atom is heavy and another is lighter. What will happen is that during travel along this distance, the lighter atom will travel the distance L much faster, but the atom with a higher atomic mass will travel more slowly. So, by measuring the time of flight, you can identify the chemical species. So, how is it done? It is a very simple equation.

The time of flight is related to the kinetic energy of that particular ion. So, as we know, ions get accelerated along the field lines. So, if they are at this position of the tip surface. Assuming that the kinetic energy or the initial velocity is 0, initial velocity V initial is 0, then it has a certain potential energy which can be given as EP is equal to NEO, V. V is the applied voltage, N is the charge, and E is the total charge.

So, this is the potential energy when the atom is at the tip surface. Assume that the ion leaves with an initial velocity of 0, then the kinetic energy EC is given by half m V squared. V is the velocity of that particular ion, and m is the mass. Now, as I told you, this time of flight is measured by the atom probe. The time taken for the ion to travel from the tip surface to the detector is the distance L. So, we can express the velocity as L divided by the time of flight.

If you equate these two equations, the initial and the final condition, you will have n electron volt which is equal to half m V squared. If you substitute V in these terms, you will have n electron volt which is equal to half m L divided by the time of flight squared, fine. Now, if you rearrange this particular equation, you will have m divided by n which is equal to m, which can be called the mass-to-charge ratio, mass-to-charge ratio. of the ion, then it can be, if you rearrange this one, then you will get an expression of 2 electron volt multiplied by T flight divided by L whole squared. So, in this particular equation, you can see that the...

By performing atom probe tomography, the L is constant. You will measure the time of flight. You know the voltage. You know this is constant. Then, actually, you will get the mass-to-charge ratio, which is different for different chemical species.

Okay. So, based on this, you can actually identify the chemical species and determine which element it belongs to. So, with this, I will end today's class, where we have gone through the different aspects, such as pulse field evaporation. we also talked about the importance of HV pulsing and thermal pulsing, the difference between both of them, and how pulse fraction is maintained constant during HV pulsing. In laser pulsing, the pulse fraction varies with the field evaporation.

also briefly gone through the identification of chemical species by the time of flight. So, with this, I will end today's class, and we will meet in the next class which will describe more about the instrumentation part of atom probe tomography and how it differs from FIM or field ionization microscopy. Thank you.