

**Advanced Material Characterization by Atom Probe Tomography and
Electron Microscopy
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Week-05
Lecture-14**

Welcome to this session. In the last session, we just went through the pulse fraction and the temperature importance during the field evaporation. So, basically, if you see the plot between the field and the temperature, you can see that the optimum condition should be such that there should be no preferential evaporation. And also, there should be no preferential retention. These are the two important things which we discussed.

So, your combination of pulse fraction and the temperature should be such that there should be no retention or there should be no... Now, we discussed four cases: first, second, third, and fourth. If you see for the first and the fourth condition, these are called optimum conditions or the best conditions. Why are these the best conditions? Because if you see the...

This is the F1 F2, the base DC voltage which is introduced by the voltage, the field, okay? And if you do a pulsing from this position to a position here in one, then you will get an optimum condition of field evaporation of different species. In this case, the species are A and B, which have different evaporation fields, and in the fourth condition also, for a particular evaporation rate, the condition from the field F3 to a point here will give you the best condition. The only issue will come with the second condition.

In the second condition, you can see that A... With a higher evaporation field. A has a higher evaporation field, correct? And B has a lower evaporation field. So, in condition 2, you can see that the pulsing of voltage doesn't reach the point of A, where it needs a higher evaporation field.

So, what will happen? Then A will be retained on the surface, right? Because the pulsed field is not enough to promote the field evaporation of A, as it has not reached the point

where A can be field evaporated. Similarly, in the case of 3, you can see that for B, The DC voltage in the field, which is introduced by the DC voltage, starts from this position F2. If you apply a pulse here, you can see

that the DC voltage is higher than this particular curve for the evaporation rate of B. So, what will happen? This will lead to the B atoms being provoked. During the DC voltage itself. It means that there is no need for a pulse electric field for the field evaporation of B species. So, this is the case of HV pulsing methods, but in the case of laser pulsing,

This graph is also valid. The only thing is the optimum condition should be in the horizontal condition, okay? So, all should reach the horizontal condition, but the arrows would be in the horizontal condition. This is the way we discussed in the last class, okay? Now, just briefly, we will We will talk about important points, correct? So, there should be optimal spatial resolution and composition, okay? And this depends on temperature and pulse fraction.

Which is a function of the material you are using, correct? So, you should avoid preferential evaporation, okay? So, it means that the electric field needed should be low enough, So that the specific loss of atoms will not take place. Correct?

The second thing is preferential retention. So, the electric field pulse should be high enough to exceed the evaporation field of that particular species. Okay? So, these are the two important points we need to take care of. Okay, now we will talk about the selection of pulsing mode—meaning under what conditions we can use HP pulsing and when we should use laser pulsing.

So, HV pulsing is not suitable for low-conductivity and brittle materials. Okay, but laser pulsing does not suffer from conductivity issues. Okay, so field evaporation takes place due to the temperature or thermal pulse—you can call it a temperature pulse. Okay, and the amplitude of temperature rise for a given pulse energy. The amplitude by which the thermal pulse increases for a specific pulse energy can be different for different specimens, okay, depending on the material.

Okay, so in this case, we can also use laser pulsing for highly resistive ceramics. But in HV pulsing mode, As I told you, low-conductivity materials or insulators cannot be used, okay? Why? Because of poor conductivity—because of poor conductivity, what will happen?

The shape Because of poor conductivity, the shape of the pulse—the HV pulse—will change, okay? So, due to poor conductivity, you know that the velocity of electrons will decrease. The limited velocity of electrons means that, due to this, the HV pulse usually broadens, okay. So, 'broaden' means the HV pulse broadens. Okay, so this is the problem when you use insulators or poor-conductivity materials.

Now, this can be minimized by increasing the pulse duration. Okay, so this can limit the broadening of the pulse, but it strongly degrades the mass resolution. Okay, so usually for low conductivity and insulators, we think about the laser pulsing method for optimum conditions. Okay, now, in the laser case, as you know, this also depends on the laser spot size, which is focused on the tip specimen. Okay, so the smaller the spot size,

the higher the mass resolution. This is due to the reduction in size of the heated zone at the apex. Okay. So this is the difference. So this is the way in which the pulsing modes can be chosen depending on the type of material to be analyzed.

Okay. Now we will talk about the pulsing rate. Pulsing rate. Okay. So usually for the good optimum analysis of atom probe specimens, the pulsing rates are usually kept high, okay? So, higher pulsing rates are desirable. But if you lower the pulsing rates, lower pulsing rates are necessary for larger molecular ions or heavier ions, because these larger molecular ions or heavier ions—okay—their time of flight will be very high since they move very slowly. So, these are heavy molecular ions, and your pulse rate should be

Enough so that during the detection window, these heavy molecular ions can be detected. Okay, so because they can be detected now, Otherwise, these ions will be lost or will contribute to the background. So, you will not get a definite peak or the mass-to-charge ratio peak of these heavy molecular or heavy ions. So, usually what we follow is if you

have a heavy atom, for example, rhenium or molecular ions, if you have these species in your sample, then we typically use a lower pulse rate.

So, heavier molecular time of flight may be too long to be detected within one of the detection windows. So, there will be a loss of these particular ions. So, we have to be careful with the pulsing rate. So, in HV pulsing, a higher pulsing rate means a longer time during which the specimen is held at a high electric field.

Okay? So, in HV pulsing mode, a higher pulsing rate means that you are putting the specimen at a high electric field for a longer time. Meaning if we calculate it as an average time. Okay. Therefore, what will happen is the departure of an atom from the tip surface leaves the neighboring atoms unstable.

Neighboring atoms very unstable. Okay, because they are in a very high electric field region, correct? Okay, so hence a large number of ions, so these atoms, so these particular neighboring atoms, these particular neighboring atoms are more prone or more prone to field evaporate during that particular pulse itself okay so during that particular pulse itself so they will get field evaporated they are more prone to field evaporate during that particular pulse itself so these atoms are more prone for the field of operation so because of this a large number of ions large number of ions

are detected on few pulses after one pulse has provoked the field evaporation. Fine? This is the case of HV pulsing. In the case of thermal pulsing, in the case of thermal pulsing, A high pulsing rate, high pulsing rate can be, can be an, it can create a problem, okay?

What problem? The problem is if it is a high pulsing rate, as you know in thermal pulse, you are actually heating the sample, okay? There will be a continuous rise in temperature and continuous drop in the temperature. Between the two pulses, the time between the two pulses should be enough such that the temperature should come down or otherwise the heat transfer should be high enough. But if the pulse rate is very high, the heat transfer will be very poor.

due to which there will be a continuously increase in the temperature of that particular tip. This has a direct consequence on the cooling rate, and also in your mass spectrum,

you will induce a large tail. Which can directly affect your mass resolution, okay. So, your pulse rate, your pulsing rate should be sufficient to ensure optimum heat transfer between the two pulses, okay, and also due to this, there will be an increase in the background. These are two important points.

We have to consider both HV and thermal pulsing, okay. So now, another topic we can cover or discuss is the detection rate. This we have discussed during FIM. So it is just a similar expression. So in APT, the detection rate—these experiments are conducted at a constant detection rate.

Okay? And this ϕD is proportional to the $\epsilon n D$ and atom exponential of, which is a similar expression to what we described during the FIM, KBT, okay? So, here the E , the $\epsilon n D$, is nothing but the detection efficiency, okay? And N at is the number of imaged atoms over a specimen surface, okay?

And this expression, exponential of this expression, reflects the probability of field evaporation, fine? So, this is the detection rate. So, ϕD , so ϕD is directly related to the detection rate, which is directly related to the electric field, okay? So, as the atoms field evaporate from the surface, the specimen usually blunts, okay? So, if you see a sharp needle, as time progresses, the specimen gets blunted, where the radius of curvature reduces with time, due to which, if you want to keep a

detection rate constant, then as time progresses, you need to apply higher and higher voltage with time, okay? So, this is called a typical voltage curve, which you will get during the field evaporation of any specimen, okay? So, this is called a voltage curve. So, it increases with time because the radius of curvature reduces, okay? So, the tip gets blunt.

So, to compensate for the constant detection rate, your voltage should increase as your tip radius is consumed, okay? So, If you keep $5D$ large values, your detection rate—if you keep it at very high values—then your electric field also increases. Because it needs more and more electric field, an intense electric field, to remove the high number of ions or atoms from the tip surface per unit time, okay? So that is the detection rate, but if you

increase Phi D to a very high value, then the first drawback is the fracture tendency increases, okay? Also, the case of multiple events

the tendency of multiple events also increases. These have two consequences. So, that is the enhanced probability of correlated field evaporation at higher field, okay. So, this means enhanced probability of correlated field evaporation at higher field, and B is molecular dissociation.

The tendency of molecular dissociation also increases due to the high electric field, okay? This is when you keep your detection rate at very high values, okay? So, now we will talk—we will just briefly talk about the fracture. Specimen failure—specimen failure is nothing but these are as 2-3 classes before we talked about the fracture or the specimen failure occurs due to the intense electrostatic pressure, okay? Due to the applied electric field.

For field evaporation. So, this is called a rupture or what we refer to as a flash. Okay. Sometimes what happens is the needle specimen does not fracture catastrophically. Sometimes there may be micro fractures on the tip surface.

So, you have an atom probe needle; it might be possible that it can fracture from this region as a micro fracture. Correct? So, the specimen is still intact. Okay?

So, this particular part, the shadowed part, will get micro fractured. So, due to which, what will happen? The position of the tip or the highest radius of curvature will change from this position to this position. Okay? So,

Due to which there will be a change in the position of ions hitting the delay line detectors, correct? So, these micro-fractures usually will induce if you are plotting time and the voltage curve. What will happen? When you increase your voltage with time, there will be uniform field evaporation, but suddenly if there is a fracture, then what will happen? The voltage curve increases drastically.

Again, it continues. This increase in the voltage curve drastically is due to the 5D, the detection rate being kept constant. For example, if in your experimental part, you keep

5D as 5%. So, at this location, if the fracture occurs, then the number of ions detected on the phosphor screen will reduce drastically. Okay?

So, it will fall off. But you have to maintain a constant detection rate. So, what will happen? The system will try to increase the voltage. Okay, so there will be a sudden drop.

So, usually what will happen is there will be a sudden drop and again there will be an increase in the voltage. This particular phenomenon we usually see in different materials. So, you will have a. You will have a continuous voltage increase, there will be a micro fracture, again there will be a voltage increase, there will be another micro fracture, and again a voltage increase. So, this is related to your micro fractures to maintain the constant detection rate, okay.

So, with these events, actually your desorption maps, your desorption maps also get disturbed. So, it means that they are not homogeneously filled with the ions and it is also with the ions. Now, we will just briefly go through the mass spectrum again. What are the conditions which we need to take care of for a good or quality mass spectrum? The first thing is peaks.

So, as your ions being detected the number of peaks actually forming within the mass spectrum dictates or shows the quality of the data okay and these peaks shows that these atoms are being field evaporated as you as you are increasing the as you are putting the pulse but sometimes what happens some in some material in some material at initial stage when you are applying when you are not applying a pulsing you are you just applying a DC voltage what will happen there will be in the mass spectrum there it will not appear any peaks because it is that is the constant evaporation

constant field evaporation of atoms without pulsing okay so you will not get any peak you are just getting a increased background with time I am talking about with time in this Increased background with time because your number of ions increases as your time progresses. So, the DC, this is called a DC field evaporation. Okay. And this usually occurs at a very early stage of the experiment.

Okay. Then once it gets stabilized. Once you get stabilized with time, actually you can then you can see the appearance of peaks. At the initial run, whatever the peaks you are observing, those are not from the material, those are from the adsorbed ions. So on the tip surface, you will get some adsorbed species.

Okay, these are mostly hydrogen or hydroxides. So, hydrogen mostly these are H_2 plus, H_3 plus which appear at 1, 2, 3 dA. Okay, and in the case of hydroxides, you will get oxygen and also the hydroxide. Oxygen, you will get at 17 OH+, these are hydroxides. At 18, you will get H_2O^+ , and at 19, you will get H_2O^+ .

These are the common peaks which usually form at the initial stage of the experiment, okay? With time, So, these peaks actually progressively disappear as these adsorbed species get ionized until they all become ionized, okay? So, one more important point to consider is if you have a needle specimen, You are applying a very high electric field, okay? So, these adsorbed ions tend to travel along the surface towards the tip, okay?

And at the tip, I have shown you that there are, if your material has some atomic structure, okay? Or the poles, correct? So, they have certain terraces, correct? These are the terraces, okay? So, at these terraces, as I told you, these terraces correspond to, if you see the cross-section, very high-intensity electric fields. Due to this, whatever adsorbed atoms

are laterally going towards those terraces will suddenly undergo field evaporation—sudden field evaporation. Due to this, along these edges, you will see high intensity—high density—of these ions on the reconstruction or on the detectors. So, these residual gas atoms migrate towards the tip axis due to the intense electric field, and wherever, due to the terraces, there is a presence of high electric field, you will get a high density—high intensity—high number density of these species at those locations. Okay, so the second important point is your signal-to-background ratio should be high because it has a direct impact on mass resolution.

Okay, and this mass resolution, as I told you, usually comes from the difference in the time measurement, error in the time measurement, or error in time measurement. So, if in HV pulsing, a decrease in time of flight at high voltage usually occurs, that directly

influences the mass resolution. Okay, so at the initial point when you are field is your voltage is lower, your mass resolution is better than when the field is very high. This is due to the impact of voltage on the decrease in the time of flight, so it induces time-of-flight spread. Thus, your mass resolution degrades as your voltage increases, for example, in the aluminum case.

Up to 3 kV of voltage, it has a resolution of 675 FWHM. But if you go for 6 kV, as the voltage increases, you get 330 FWHM, which is lower. This is due to the fact that if you have a needle specimen with time, you are actually increasing the radius or decreasing the radius of curvature. In the case of a laser, it directly depends upon your specimen geometry, your laser type, the laser wavelength, and also the thermal conductivity. That determines—that is, that affects—the mass resolution drastically, then

we can talk about composition. We just described that composition is affected by poor mass resolution because peak overlap will take place, so you will not get the accurate composition. Poor mass resolution, if it is a low signal-to-background ratio, then your composition will not be accurate. Then we also talked about the pulse fraction, the importance of pulse fraction and temperature, which directly affects the composition or alters the composition information, correct? So there is another point: we just briefly talked about the multiple events, the tendency of multiple events. This is when a single pulse

When a single pulse results in the detection of more than one ion, that leads to multiple events. So, the number of detected ions from a single pulse is referred to as event multiplicity. Event multiplicity, okay? So, these multiple events, as I told you, can also be increased by molecular ions that get dissociated and can be detected during a single pulse. Okay, so, ions detected in multiple events tend to arrive closer in space and time, which reduces detectability. Okay, so, it will have a direct consequence on the composition.

Okay, so, based on this, what we can conclude is that there should be an optimal balance, an optimal balance of different parameters, okay? So, your signal-to-background ratio should be very high. It can be done by lowering the temperature, which will have a direct

influence on the electric field, okay? You will get a high spatial resolution, high spatial resolution,

Okay, so, here I am showing you a radar plot. where this is the case of aluminium, copper, magnesium, okay, and this is operated during HV pulsing mode okay, and here you can see that there are different parameters which have been plotted as radar axes, okay? Different parameters, and this grey area is termed as the optimum area to get a good combination of mass resolution plus composition for the

An aluminum-copper-magnesium alloy during the HV pulsing mode, okay. So, with this, I will end this class now. With this, we have completed the main parameters which are important during field evaporation in an atom probe. We discussed the different modes: HV pulsing and laser pulsing, pulse fraction, and the importance of temperature. And how they overall control the mass spectrum or the mass resolution of the analyzed specimen, okay? These parameters not only control but also the specimen geometry. Specimen conductivity, the type of specimen—whether it is brittle or ductile, whether it is an insulator or conductive—all these things contribute to choosing the optimum pulsing mode.

Whether it is HV pulsing or laser pulsing. In the next class, we will go through some topics related to sample preparation, which is very important for making the needle specimens. Okay, so we will discuss different types of sample prep methods. Thank you.