Advanced Material Characterization by Atom Probe Tomography and ElectronMicroscopy

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Week-05
Lecture-13

So, welcome to this class. In the last class, we introduced the parameters which are important for running an atom probe needle in an atom probe tomography during field operation, and we also discussed the resolution. So, we ended the last class by discussing some parameters which are responsible for determining the mass resolution. Now, those parameters are

As I told you, these are the pulse fraction, the second one is temperature, the third is voltage, and the fourth one is the tip geometry. So, if these parameters are not optimally used, it might be possible that even in laser pulsing, your mass resolution will be much poorer than in voltage pulsing or HV pulsing. So, this particular mass resolution can actually be modeled by a Gaussian function. And it can be written as m by delta m, which is equal to 1 divided by the square root of sigma v divided by v squared plus 2 sigma t divided by t whole squared plus 2 sigma l divided by l.

So, I will just briefly describe these three important terms. So, the first term is related to voltage. The second term is related to the time of flight. The third one is related to the flight path distance. Okay?

So, it is called TF, time of flight path distance. Okay? And there is another term which has to be added here: plus F of pulse with td. Okay? So, we will describe this term also.

So, this F pulse td is the function that accounts for the loss of resolution, loss of resolution associated with the pulsing mode and at any instant td, okay, of the departure of ion from the surface. Okay, we will explain this term a little bit more later. The first terms in all three are sigma v, sigma t, and sigma L. These are all standard deviations.

These are all standard deviations or the errors in the measurement of voltage, time of flight, and flight distance.

So, all three contribute to the broadening or affect the mass resolution. Okay. So, in the new APTs, In the new APTs, the accuracy of time measurement is now better than 100 picoseconds. Okay.

And the voltage—this is related to your time of flight. This is related to your time of flight. Similarly, the voltage supply stability can go up to a few volts per 10 kV. Okay. And related to the flight distance,

It is better than 1 mm in modern detection systems, which have a 90 to 250 mm flight path. Okay? And these effects are linked to the field evaporation. Okay? And this field evaporation and also this particular function.

Which is dependent upon whether it is HV, whether we are using HV pulsing or laser pulsing. We will talk about the HV pulsing. Okay, so in HV pulsing, as we also discussed before, not all the ions, not all the ions acquire the full energy. It means related to our energy deficits. Okay.

And this particular thing can actually induce a spread in the velocities of the ions, due to which there will be a spread in the time of flight. So, there will be a difference in the time of flight, and this can be corrected by energy compensation devices. Okay. In the laser pulsing, In laser pulsing, the spread in the time of flight is due to the cooling rate or due to the slow cooling of the thermal pulse.

How can we improve it? This can be improved by using different parameters. Okay, such as the wavelength of the laser used, pulse duration, and also the focusing. Okay, so for faster cooling, If you want to do cooling—for faster cooling—we actually need to make thicker specimens or use a high shank angle in the case of laser pulsing, correct?

This particular case is not for HV pulsing, fine? So, there is a difference between HV and laser pulsing, and this is how we can improve the mass resolution. Okay. So, in HV pulsing, mass resolution can be improved by energy compensation devices, and in laser pulsing, it is more dependent on the parameters —mostly the wavelength, pulse duration,

the focusing of the laser spot (we discussed this in a few classes before)—and also faster cooling by making the samples thicker or using a high shank angle.

Correct? So, the next topic we will cover is how an element is identified. Element identification means how we can determine the element or composition. Okay? So,

First, we will talk about element identification, then we will go to compositional measurement. Fine. So, in elemental identification, in the mass spectrum, it is nothing—you will get a relative number of atoms of each species present in the analyzed volume. This information you will get from the mass spectrum. Okay?

So, identification of these elements can be done by defining the ranges of that particular M or the mass-to-charge ratio which corresponds to each element. So now you have a mass spectrum, you have M, and you have a number of ions. So if there is an appearance of a peak, then you can range this particular region. Okay.

This particular region can be ranged so that the number of ions can be calculated from this particular spot to this particular spot. So, there is an increase in the peak, the start of the peak or onset of the peak, and there is also an onset at the back, correct? So, this way, from the mass spectrum, we will get the relative number of atoms of each species which In the analyzed volume, and this can be defined as the range of m for each element. Okay? So, identification involves—identification involves—the first is the position in the mass spectrum or at which mass-to-charge ratio the peak is appearing, position in the mass spectrum.

And the second important point in identification is the distribution of its isotopes. Distribution of its isotopes. Okay? And remember, as I told you, these isotopes have a certain abundance in nature. Correct?

Based on the abundance, these isotopes—so the isotopic ratios are usually maintained, with some exceptions, okay? So these isotopic ratios are maintained. So, for identification, these are the two important things which we need to take care okay? So the peaks which are associated with the minor isotopes—so if, as I told you, if some of the isotopes in abundance have very low values, like 0.2% or 0.1% it might be possible that

that particular peak can be hidden in the background, can be hidden in the background, or overlap with the larger abundant or the larger abundant peak of the isotope, correct?

And the charge state in which an element is detected, the charge state in which that particular element is detected depends upon two parameters. The first is the evaporation field for that particular isotope. The EF value, evaporation field, and the second is the curves of the relative abundance of different charge states, different charge states, okay? And this is derived from the post-ionization theory, okay? So this is nothing but what I told is abundance, so they will maintain certain isotopic ratios and the charge state, which is the charge state of the element which is field-evaporated, depends upon the evaporation field and also the curves of the relative abundance of each charge state, which is according to the post-ionization theory.

Okay. Sometimes, you will also get complex ions. Okay, and these complex ions, these are actually ions consisting of consisting of a number of different atoms, the number of atoms that are encountered in the AP atom probe analysis. Okay, it might be molecular ions, it might be complex, or it might be cluster ions. Okay.

So, these are the complex ions. So, this may involve one. So, it means this particular statement means these ions may involve one or more species, or you can tell as an atomic species. Okay. And also, we need to understand that the elements

The elements with several isotopes can form molecular ions. Several isotopes. Elements with several isotopes can form a molecular ion. These ions comprise combinations of individual isotopes. Okay.

So, it means that two types of isotopes can come together and form a molecular ion, which can be field-evaporated and detected. Fine? As an example, this is a very good example of Sb. Correct?

You can see that there is an appearance of a peak at 121. So, Sb 121 plus 1, and also there is a peak which is a contribution from Sb 242 plus 2. Correct? And there is an additional peak which corresponds to Sb 121 plus Sb 123.

2 plus which corresponds to this particular peak. Okay? So, it appears at 122 Da. This particular peak occurs by the combination of the two different isotopes of the same element, which are field-evaporated as one molecular ion.

One molecular ion. Now, the next topic we will touch upon is the range files. Just briefly, I will introduce the range files. Okay, so range file—as I told you, these range files, if you index them on the mass spectrum, if you index this

if you index these range files, these range files are populated, and the lower and upper limits of each mass range are taken care of, okay? And each mass spec is labeled with that particular element isotope, ion, or cluster ion, okay? So, these are the range files, okay? Once we index them, then we need to find out the composition, correct? Now,

The composition—so we will talk about the measurement of composition. So, after identifying the element—first, we have identified the element by the mass range. The composition is actually computed from the proportion of atoms of each species. So, usually, it is a proportion of of atoms of each species.

Okay. So, if there is a J element, okay, which is a part of a multicomponent, multicomponent alloy. Okay. or material containing I different species or elements. Okay?

So, if there is a J element which consists, which is a part of a multi-component material or alloy where these are the I, with the I different elements. So, the composition can be given by C J in atom percentage is given by Minimum to maximum NAT divided by summation of all the elements with their minimum mass totalization minimum to mass totalization maximum of NATM. into 100 which is nothing but a you can put it as a n atom percentage of that particular element j element divided by n total number of atoms into 100 okay so this is how the composition of that particular element j element can be measured okay so here the nat is the number of atoms

At that number of atoms or the ions at the mass-to-charge ratio of M in the mass spectrum. Okay, and I is each element by its range, each element between the range of M mass-to-charge ratio minimum to the mass-to-charge ratio maximum. Fine. So, this

composition is nothing but the atomic ratio. Okay, so now there is a volume, there is a particular volume which is analyzed, and you are measuring the composition of a J element. In an alloy which has I number of components or I number of elements.

Okay, so it is actually related to a statistical distribution. Statistical distribution. Okay. Or statistical distribution. So, it may, it will induce a statistical variation, statistical variation like sigma j for that particular element in the composition.

And this statistical variation can be given as sigma j is equal to the root of c j, 1 minus c j divided by the total number of atoms. Okay, so this is called, this is, this is nothing, this is, this is just related to statistics, or we can say it is a statistical variation. Correct? Fine? So, I hope now the composition measurements, now you understand how composition is measured for that particular element in a multi-component material with different.

with the total number of elements present or the different types of elements present. Okay? So, the next thing is the detectability. Correct? We will talk about detectability.

So, it is nothing but the ability to detect a given atomic species. Okay? So, this depends upon the statistical variation. Okay? So, it is nothing but to measure the composition of an element.

So, for example, if you are measuring the composition of an element, composition of an element which is at a concentration of 200 ppm with a precision of 50 ppm, okay? Then for this particular thing, you need to collect more than 100,000 more than 100,000 atoms should be collected. Okay? So, this depends upon the statistical variation.

So, that is why in very dilute systems, dilute systems, you need to have a total number of atoms which are detected to be very high. Fine? Another thing is the detectability depends on mass resolution. And the signal-to-background ratio. Okay?

So, why is it important? Because in a mass spectrum, if you have a certain background, And if your peak is small enough—this is your mass peak, and the peak of this particular mass spectrum—if it is equivalent to the background, then the composition cannot be detected. Okay? So, a peak can be distinguished only if its amplitude is greater than the background level.

Okay, so these are the two important things which usually affect the detectability. There are other parameters which also affect the detectability. One is the flight path. Okay, so the flight path. So, some of the APT, some of the atom probes, actually allow us to vary the distance between the specimen and the detector.

This particular distance can be varied. So due to which actually we can get a higher mass resolution. okay, due to which we can increase the mass valuation by increasing the actually time of flight. The only thing is if you reduce, if you increase the flight path larger enough, then you are inducing the lowering of field of view. So, it has to be at an optimum distance, lowering of field of view.

Okay? So, this is the importance of the flight path. Now, we will come to the two important parameters which is related to your pulse fraction and temperature. Pulse fraction and temperature. So,

The electric field which is required to induce the field evaporation at a given rate of evaporation rate at a given evaporation rate is critically depends upon the temperature of the specimen surface. Okay, so the amount, the intensity of the electric field which is required to induce the field evaporation for a particular evaporation rate at a constant rate, then it critically depends upon the temperature. Okay, and this influences, this influences the micro analytical capabilities of APT or we can tell it as a micro analytical capability.

Capabilities of an atom probe, okay? So, when the specimen contains atoms—so, this means that if you have a needle specimen with different components or elements, with different elements having different evaporation fields, So, the temperature should be chosen in such a way that you can actually detect all the ions together. Correct? So, the required electric field totally depends on the temperature.

This can be understood by the stabilization curve. So now you can see that—if you see this particular graph, okay—so In this graph, this is your field—let's take field—this is your temperature. This is nothing but a calibration curve, correct? So, this is the field temperature.

Okay. So, for example, in this condition, you can see that the field evaporation should be directly triggered by HV or the laser pulse. Either you apply HV or you apply the laser pulse. And the time of... Okay. So, you are applying a DC voltage to the needle specimen. Fine?

So, this DC voltage should be enough to avoid field evaporation between the pulses. Correct? So, you are applying a pulse. So, the DC voltage should be enough to avoid field evaporation between these two pulses. Okay?

So, the two important parameters are the base temperature and the amplitude of the pulse field. For the HV, in the case of HV, it is a voltage. In the case of thermal pulsing, it is the temperature. So, first we will describe the case of HV pulsing. First, we will talk about HV pulsing.

First, we will talk about it. So, the pulse fraction has to be adjusted in such a way that you should avoid the preferential departure or retention of any given species in the specimen. So, if you have a specimen, correct? And in these specimens, if you see that some species have different evaporation fields,

So, your HV pulsing or the pulse fraction should be such that you should avoid the first preferential departure and also preferential retention of any species during the HV pulsing. Okay? This will have a direct impact on the composition of that particular volume which is to be analyzed. Okay? So, if you see the plot, you have a y-axis where there is a field It is the temperature. Okay? And F1, F2, and F3 are the DC fields, the minimum fields which are applied on the tip surface.

Okay? So, if you talk about condition 1 and condition 4, okay, you can see this dark region. So, if you see that when you apply an HV pulse, okay, this is called pulsing. You are increasing the HV pulse, then, okay, so you can see that it covers The Phi 1, Phi 2, Phi 1, Phi 2 are the evaporation rates.

Okay. So, the first and fourth cases are the best or good analysis conditions where both A and B species have avoided preferential departure or preferential retention. So, both the A and B species can be field evaporated at a specific evaporation rate. Okay.

So, this particular curve shows that if you apply a pulse from F1 up to this level, then you can see that you are covering both A and B. This is B and A during that pulse event, where these can be field evaporated at that evaporation rate. But if you see the second one, you can see that the field required for A is much higher. Okay, for the field evaporation to take place. So, you are applying a pulse from F2 to a level where only B can be field evaporated.

So, actually, you are enabling a preferential departure of B atoms. Okay, so what we can tell is that in the second case, you are not reaching the field required to field evaporate A species. to field evaporate A species. So, actually, what you are doing is preferentially retaining A atoms while getting B atoms field evaporated more and more. So, your composition will change accordingly.

Correct? Now, in the third case, you are applying a pulse from F2 to a level higher than A. But what you can see is that your main F2, the base DC voltage, is more than F2, okay? And you can see this particular line, B, is lower than the base DC voltage. It means that without any application of a pulse.

Pulse, actually you are continuously field evaporating the B atoms. It means that you are doing the preferential departure of, you are provoking or the preferential departure of B atoms for the condition of 3, where your base DC voltage is more than the field evaporation. evaporation field of the B atoms if you want to make a phi 1 evaporation rate okay so I hope this you understand that how pulse fraction pulse fraction and the temperature are very important So that you can get and how it is controlled, how it can affect the composition or we can tell is the detectability of these different species which is having a different evaporation fields.

So in this only the case 1 and 4, these are the optimum conditions where actually only on application of pulse, These A and B species are field evaporated depending upon their evaporation field values at that constant or the evaporation rate. Similarly, in the thermal pulsing, similar thing can be understood, but only thing is in thermal pulsing, you are actually changing the temperature. you are increasing the temperature as a thermal pulse. So, the only difference will be in this direction, in horizontal direction.

Fine? But the conditions will remain same as for the HV pulsing. Okay? So, for thermal pulsing, the condition will be the same scenario Same scenario but the arrows would be horizontal.

Okay, so with this, what we described is the role and the importance of pulse fraction and the temperature. Which can directly affect the composition of that particular alloy, which has components or species with different evaporation fields. Okay? So, the correct analysis condition should be an equilibrium point. An equilibrium point means the combination of pulse fraction and temperature.

It should reach that all... evaporation fields and temperature. Okay? So, in thermal pulsing, the DC field is lower than in HV pulsing. Okay?

And usually, the DC field required in thermal pulsing is lower than in HV pulsing because you are inducing the temperature, increasing the temperature. So, it makes preferential evaporation less likely. So, the problem with the composition or the preferential evaporation or retention is found more in HV pulsing than in thermal pulsing. Okay, so with this, I will end this class now.

I hope you got a good feel for the importance of the pulse fraction and the temperature and how this affects the composition. So these are the parameters which are important during the running of the atom probe for that particular sample. So, with this, I will end this class. In the next class, we will cover more parameters which we can fine-tune for better analysis. Thank you.