Advanced Material Characterization by Atom Probe Tomography and ElectronMicroscopy

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Week-05
Lecture-12

So, welcome to this class. In the last class, we just discussed about the experimental protocols related to field ionization microscopy. So, what are the parameters, important parameters to get a specially resolved FIM images. Now, in this class, we will discuss about the experimental protocols related to atom probe tomography. So, the first thing which we will introduce is the mass spectroscopy.

So, the time of flight of each detected ion. The time of flight of each detected ion is converted to mass to charge ratio. Okay? And this enables the identification. This enables the identification of the chemical species.

Of chemical species. Correct? So, With atom probe, actually you can do the detection from hydrogen to uranium and higher complexes. So we can detect up to uranium and also complexes.

Maybe it is in the form of ions or molecular ions. So as this experiment goes on, as the field of operation extends from the tip surface, The time of flight of each ion is recorded. Along with this, the position where the ions hit the delay line detectors is also recorded. Correct?

And these two pieces of information are used for the reconstruction. For the reconstruction. So, this particular data is stored in an electronic file with different formats that can be utilized for the reconstruction. So, first we will talk about the detection of ions. First, we will talk about

the detection of ions, as in the previous class—previous two classes—we introduced the two methods of pulsing, which are called HV (high voltage) pulsing and also thermal pulsing, which is also called laser pulsing. Okay, and these two, HV pulsing and laser

pulsing, can be applied sequentially. Okay. They can be applied sequentially. So each pulse, if you are applying each pulse, then a time measurement device is used. So, I will show you a schematic where you can see that.

So, these are the pulses that are applied. This is called detection window. Okay. And this is the what we can is the measurement of time of flight. Okay.

So, each pulse a time measurement device is started for a given duration which is called a detection window. So, detection window corresponds to this particular. So, you can see that if you project on the pulse time. So, when the pulse increases and it decreases during that particular time what a detection window corresponds with a time measurement device will get started.

Okay. And within that window, if any signal is detected, which is above the threshold, will be treated as ion generated. Ion generated. Okay. So, ion generated at the time of evaporation of the pulse.

Correct. So, you can see that, but it might be possible that even though the pulse has been applied, But there is no detection of ions on the delay line detectors. Okay? So even though the detection window is open, then there is still no detection of ions. So that particular case is called a blank event.

Okay, and if an ion is detected, that is called a single event. And if in that detection window, multiple ions are detected, that is called a multiple event. Okay, so we can say that with this, we will calculate the time of flight of the signal. Okay, note that in this particular region, you can see that when the pulse has started to increase, correct, at the highest point of the pulse. Correct. Now you can see that the detection window has started before the pulse has started, correct.

And the time between the highest voltage peak in that particular pulse and the starting time of the detection window is called T0 time. Okay, so this is the difference between the instant at which the time measurement started and the actual application of the pulse. Okay, so this particular shift, which we call the T0 shift, during the measurement of time

of flight, this has to be compensated. Okay, so it means time of scale. In time of scale, this has to be compensated.

So each pulse generates an associated event. As we know that the field of operation The field evaporation is actually a probabilistic phenomenon. So, all the pulses which are, not all the pulses can induce the departure of ions from the specimen. Okay?

So, there we also get blank events where no ion is detected. Okay? If a single ion is detected, it is called a single event. If multiple ions are detected, it is called a multiple event. Okay?

In some cases, what will happen is you can also get heavy ions or complex ions are detected, okay? And the detection window so sometimes what happens if these heavy ions and complex ions, okay? It might possible that when the detection window is open it might be possible that due to the heavy ions and the complex ions, these cannot be detected during that particular detection window. It means that whatever ions or complex ions go and hit the delay line detectors, they will generate and contribute to the background. Okay?

This is when your detection window, your detection window the time, the detection window, when it is open, then these ions will not reach and will not be detected on the delay line detectors during that particular time. So, those ions and complex ions will contribute to the background of the mass spectrum. So, if you see the mass spectrum, Now, we will talk a little bit more about the mass spectrum, which we get from the instrument.

So, as each ion is detected, the time of flight of that particular ion is converted into its m/z ratio. This is nothing but capital M, which is a unit of Dalton. For example, if we assume the ion leaving the surface of the tip has no initial velocity, then your potential energy is equal to n electrons and the voltage. If it travels along the field lines, then it has a half mv squared. Now you know the velocity of

is equal to the distance traveled divided by the time of flight. With this, if you equate these two equations and substitute V from this equation, you will reach a mass-to-charge

ratio equal to 2 electron volts multiplied by the time of flight minus T0 divided by Lf, which is the distance between the specimen and the detector. So, for each ion detected, you know the voltage, you know the electrons, you know the time of flight measured from the instrument, and you know this L, which is the distance between the specimen.

You can actually calculate the mass-to-charge ratio, which is unique for a different ion or different isotope of that particular atom. Okay, so this particular M, whichever you have calculated, It is your mass spectrum, which consists of a histogram. This will be a mass-to-charge ratio in the unit of Da, and these are the number of ions. Okay? So you will have a background, then you will have a peak depending upon the mass-to-charge ratio that is detected.

Okay, so we will come to the shape of these particular peaks in the coming time. So, you can see that here in this case, the number of ions is on the y-axis and the mass-to-charge ratio is on the x-axis. Okay? And you can see there are peaks coming from W4+ and W3+. And as we know, the atoms... Different elements have different isotopes depending upon the charge state.

Correct? And these isotopes, depending upon the charge state, have a relative abundance in nature. Okay? For example, the tungsten isotope with a molecular weight of 182 has a 26% abundance. The maximum is 184.

So, based on these isotopes and their abundance, you will also get peaks, the intensities correspond to that particular abundance. Okay, so the highest will be at 184, the lowest will be at 180. Okay, so that is why you see multiple peaks corresponding to the tungsten. Correct, so here we can see that there are two series of peaks which correspond to W4 plus and W3 plus. Okay, and W4 plus ranges from 45 to 47 while W3 plus corresponds to 60 to 62.

Okay, and in each the individual peaks within each charge state, You can see that there are 3 peaks here, there are 4 peaks here. These 3 and these 4 peaks correspond to the stable isotopes of that particular atom. Isotopes of tungsten which have a definite proportion. Definite proportion.

And this can be distinguished between different isotopes combined with the mass-to-charge ratio. Okay. So, with this we can identify the chemical species or the isotope. Identification can be done associated with each mass peak. So, we will briefly go through how the formation of mass peaks occurs.

Okay. Now, we will talk a little bit about the formation of a mass spectrum. Now, as I told you, these are the set of mass peaks in the mass spectrum on a background. Okay. So, in this

What will form is, if you see a single peak, there will be a background, a sharp rise in the peak, and then a decrease, followed again by the background. Okay? So, the sharp rising edge is followed by a decline. This results from the ions. Okay?

So, This sharpness is exactly related to how you are doing the pulsing, correct? So, this sharp rise means that the ions are detected at this particular mass-to-charge ratio. With the same mass-to-charge ratio, you can see that there is a decline, okay? And this inclination or declination is related to the ions.

That have not acquired the full energy, especially in the HV pulsing. As I told you, when your HV pulse is ongoing, it might be possible that at these locations the atoms get field-evaporated and can be detected. Because of this energy deficit, we call it an energy deficit. Because of this energy deficit, you can see that there is a broadening of the mass spectrum peak. Okay? This is the case of HV pulsing.

It means that these ions are field evaporated later because they did not absorb the whole energy. Correct? This is in the case of HV pulsing. So, in HV pulsing, the tail, what we call it is this particular tail, the tail is of the peak is mainly due to the contribution from the energy deficit.

Okay, so the mass peaks appear similar across the, so in this case, the mass peaks are, appears almost similar across the mass spectrum. While in the case of laser pulsing, where you introduce the temperature or it is called a thermal pulsing, The tail of the spread, the tail of the spread, this particular tail of the spread is due to the finite duration

of thermal pulse. It means that the atoms or the ions, the atoms... they will, they feel evaporate during the decay of the specimen temperature, base temperature at the surface.

Okay, so this is related to the cooling time. So when you give a thermal pulse to a needle specimen, the temperature will increase, and depending upon the parameters and also the tip surface, the decaying temperature you will get a tail in the laser pulsing of that particular peak. Okay, so this is this particular tail—the appearance of a tail—therefore, the tail will distort the peak shape. That depends upon the specimen geometry.

I think in the last class, we just talked about this particular case. How specimen geometry is affecting the rate at which the tip gets cooled down. Correct? So, and also the thermal properties. Thermal properties of the material.

Okay? So, this is the case of laser pulse. So, here the ions which are flying. So, there is one more issue: the ions. So, you have an atom probe tip needle, okay, and you have a detector screen here.

Now, if you see this particular axis. The atoms which are traveling from this tip to this tip and the ions which are traveling from here, we can see the distance traveled by the ions. Those hitting the center of the screen and those traveling and hitting far away from the axis of the screen both have a difference in the time of flight. Same mass-to-charge ratio. So, ions flying toward the center of the detector,

they have a shorter distance. And the ions arriving at the edge of the detector have a longer distance. This causes a spread in the time of flight for that particular mass-to-charge ratio or the ion. Okay? So, this causes a difference in the time of flight of the ions with the same

mass-to-charge ratios. Okay? So, this also contributes to the broadening of the peak. Okay? So, this particular correction can be taken care of by using the Pythagorean theorem.

Okay? You can correct the particular estimate of the actual flight distance. To measure the actual flight distance of an ion. Okay? This improves the mass resolution while correcting.

Because it is a right-angle triangle. Okay? So, we also talked about the time of flight. T0. Correct?

So, for example, in a mass spectrum, the TOF correction Means the T0 correction has to be done. It means that for aluminium, the two peaks appear at 13.5 and 27. Okay? But in the actual case, if it is not corrected, there will be a shift in the peak.

And this shift in the time of flight, T0, has to be corrected. So, there should be proper calibration. So, this is related to the calibration of the instrument. So, this is called T0 correction, which we usually do during the calibration of the instrument. And this particular shift, T0 shift, is also contributed by the delays

Induced by the cables and devices. Okay? So, this correction also, this T0 also includes the delays induced by the cable and the devices. Okay? So, now coming to the background.

What does this background consist of? Okay? So, I hope that you now understand the peak. The mass spectrum peak and the difference between the HV pulsing and the laser pulsing. HV pulsing is related to your energy deficit.

Laser pulsing is what we call a thermal tail, which is related to the rate of cooling when the pulse is going down. Correct? So, these two generate different shapes of the peaks. So now we will talk about the background. Earlier, I just talked about the complex ions and heavy ions.

So, if the detector window is not sufficient to detect these heavy and complex ions, then these will contribute to the background. So, the first thing which contributes to the background is the residual gas atoms or molecules from the chamber. Second contribution is from the, you can call it as a pollution absorbed material. at the specimen surface. Okay?

Also, the MCP, the multi-channel plates also generates noise. Generates noise. And this contributes to the background. It means that this noise is related to, as I told you, in the MCP plate, these are the glass tubes. which are charged, highly charged surface, which

has a highly charged surface and as I told you the ion is hit to this charged surface and generates a cascade of electrons.

It might be possible that without any hitting of these ions, because of the highly charged state, it may generate electrons. That also contributes to the background. Okay, so that is related to your noise, the generated noise. Now, the next parameter is the definition of mass resolution. How will we define the mass resolution?

In focused field ion microscopy, we talked about the image resolution, correct? So here also, first, that is related to the position of hit, correct? And now we will talk about the mass resolution. So, mass resolution always degrades when there is poor calibration, especially related to T0 and flight L flight. Okay, so these two parameters are very critical for the mass resolution. Mass resolution is defined as M divided by delta M. Okay, so M divided by delta M means if you have a peak, delta M is the distance, is the width of the peak. It is the width of the peak at different levels of that particular height.

At different heights of that particular peak. Okay? So, this corresponds to the width of the peak. And you can define the mass resolution as you can put it as 50% of FWHM. What is FWHM?

It is nothing but the full width of Full width half maximum. Okay. It means that at exactly the middle portion. We also call it 10.

It means that FWTM. Full width tenth maximum. And also the 1%. 10%, 50%. Which is the 1% of the maximum peak.

These are the three things which we usually use to quantify the mass resolution. So the appearance of a tail directly influences the resolution. So the resolution will be degraded or lower when there is a lower height of the peak. Okay, so for HV pricing, the typical value for the FWHM, mass resolution at half maximum, is around 500. Okay, and FWTH, 10th maximum FWTM, is 100.

This is for the direct flight path, direct flight. Paths if you use the reflectron, which we talked about in the last class, that these are used as energy compensation devices, then your FWTM can increase up to 400. Okay, so remember this is an energy compensation

device. It means that during pulsing, the higher energy ions, the higher energy ions get deflected at a later stage while the low energy ions get deflected early. Okay.

And they reach the detector approximately at the similar time of flight. Fine. So these are the high energy. These are the low energy. Fine.

So we use the reflectron. Okay. So this is just nothing but an electric field distribution across these planes, which is increasing from position 1 to position 2. Okay, so these reflectrons can improve the HV pulsing resolution up to 400.

Now, in the laser case, the resolution we get is around FWHM, which is more than 1000. Okay? So, for a straight flight path, as compared to a lower value of HV pulsing. So, mass resolution usually depends upon, first, the pulse fraction; second, the temperature. Third is voltage, and fourth is tip geometry, especially in the case of thermal pulsing.

Okay, so sometimes if these parameters are not optimized, then even in laser pulsing, in laser pulsing, you will get a poor, very poor mass resolution as compared to HV pulsing. So, these four parameters are very important to get an optimum mass resolution for any specimen. Okay, so with this, I will end this class now. So, we have briefly gone through the parameters.

So, with this, I will end the class now. So, we have discussed the parameters which are important to run atom probe tomography for the samples, and we also discussed the mass resolution. correct, and what is the difference between how to improve the mass resolution between HV pulsing and laser pulsing. And in the next class, I will start with this particular modeling of the mass resolution with an equation where all these parameters are inbuilt into the equation. next class, I will start with this particular modeling of the mass resolution with an equation where all these parameters are inbuilt into the equation.

Thank you.