Advanced Material Characterization by Atom Probe Tomography and ElectronMicroscopy

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Week-08
Lecture-25

So welcome to this class. In the last three classes, we described the sample preparation and also so basically sample preparation, which was divided mostly into electropolishing and also using the focused ion beam. We also discussed the basics related to the FIB column, the working principle, and how sputtering takes place. We also covered the principle behind the ion injection system and the manipulators.

So, how these three things can be used together to prepare the samples for the atom probe. Similar samples can be prepared even for TEM. Now, in this class, we will cover the analysis part. So, what information we get from the atom probe, how to analyze it, and what precautions must be taken during the analysis. So, in today's class, we will start with the analysis.

The basic thing we get from the instrument is the mass spectrum. It is the mass spectrum, and in the mass spectrum, we have given an example. It is nothing but the counts or the number of ions on the y-axis and the mass-to-charge ratio This is in the unit of DA, fine. So, you will have certain peaks.

At specific mass-to-charge ratios, you can identify the isotopes. We also discussed about that the resolution, mass resolution. So, if you have a certain peak which are very small, but if there is a large peak and which So, this particular case is called tail extension. So, it might possible that two or more ions can overlap along with this tail.

Even in this case, it might possible that some of the isotopes of different element can have a same or similar mass to charge ratio. So those peaks gets overlapped. So in the mass spectrum we have to be careful that it might possible that the two or more ions have a very similar or same mass to charge ratio. So you can have a peak overlap.

In the case of dilute alloys, dilute alloys means if you have a matrix which is a solid solution of aluminium or some other solutes and you have a solute of very dilute amount like zirconium less than 1%. So in dilute alloys it might possible that the peak can be can be obscured or can be hidden in the tail of that particular peak the large peak okay. So to analyze these two types of to reduce so first of all the whatever the mass spectrum you are getting it first thing we need to do is the noise reduction okay.

So we need to perform the noise reduction okay. Now, noise reduction can be done in two ways, step by step in two steps. So, noise reduction can be time-independent background subtraction. This is time-independent. Another step is time-dependent background subtraction.

So, this is the first step. This is the second step. Now, this first step is the simplest one. So, here's what we do: if you have a mass spectrum. If you have a mass spectrum, then you need to find a constant level of background, which should be identified and subtracted from the time-of-flight spectrum.

Okay, so here I am showing a slide where this is a mass spectrum, a typical mass spectrum with the counts and the time-of-flight. Okay, and you can see the appearance of peaks. Then you can see this red color. The red color is the estimated background. And it can be subtracted from the experimental mass spectrum.

So, this is the simplest method, which is the first step for background correction. In the next step, it is a time-dependent background subtraction, and it has to be done after the removal of time-independent background subtraction. So even though you can remove the noise, the time-independent background, you can remove the background, but there is a contribution of non-random contributions to the peaks. In the mass spectrum, okay, which has a direct influence on the composition, okay. So another important thing, what I described before, is if you have a mass, if you have a one particular mass-to-charge ratio peak, it might be possible that it may exist as a thermal.

And if you have a certain species which has a mass-to-charge at this location, it might be possible that this particular one has a contribution on counting the number of ions at this

location, correct? So, it will affect the overall composition of that particular alloy. This is the time. So, this is done in two ways.

This correction can be done in two ways, okay. So, here this is a mass spectrum where you can see that there is a peak at 14 DA and. There is a peak at 14.5 DA, okay, so you can see that this 14 DA peak, the background with the tail, this behavior, this behavior can be actually modeled, okay, by Constructing a line along the background and extrapolating into the range of interest. Correct?

So, extrapolated contribution from the tail. So whatever the extrapolated contribution is there, extrapolated contribution is there, that can be at the tail, that can be. Subtracted from the peak, okay, so basically for this purpose, you can see that after subtraction. After the removal of background, the peak at 14 and the peak at 14.5, you can see that the contribution from the background counts can be removed effectively. So, this can be done in the two process.

This can be done by the two process. One is the models which are used is we can use as a line of best fit. So, usually it is called a straight line model where A is equals to BM plus C. Here A is the number of counts with respect to the value of mass M. And B and C are the parameters which are used for fitting. So, this is a straight line model.

Another model which can be used is the exponential model which is also called a power law. Exponential model which is also called a In this the formula which is used is A is equals to B divided by M, M naught raised to the power P. Here the fitting parameters are B and P, okay. So with this you can actually subtract the background. In this case, in this image you can see that you can subtract.

So this is the background. And you can see that the contribution of number of ions to this peak is much higher. So, you will get an absurd compositional data. So, you can subtract the particular tail or the particular background from that particular tail so that you can get the actual number of counts inside that mass spectrum peak for the compositional analysis.

So now, another important aspect I just mentioned is that two or more ions can have a similar mass-to-charge ratio. It means that there is a peak overlap. So, how do you identify this peak overlap? By referencing the peak overlap, we can actually do the proper quantification. By comparing the peak contribution of isotopes with their natural abundance, okay.

The peak contribution of isotopes, which have a natural abundance, and there is a standard which is present for all the elements. Correct? For example, I have shown you a mass spectrum where you get a peak at 14, 14.5, and 15. Correct?

14, 14.5, and 15. So, the unit is Da. Correct? Now, if you compare So, 14 DA as per the periodic table, we can put it as a 14 DA can be sodium plus, plus 1 or it can also be silicon 2 plus.

Both these peaks can exist at the 14 DA, silicon 2 plus and nitrogen plus. So what we can do is as I told you the peak contribution of the isotopes can be related to the natural abundance. We can actually examine the neighboring peaks with respect to their natural abundance. So this is to estimate The fraction of peak that should be associated with the type of ion, okay?

So, if you have a peak, it might possible that at this peak, this is nothing but the number of ions, correct? So, this peak may contract. corresponds to Na plus and also the silicon 2 plus ions. Okay? So you will get only the number of ions at that particular mass to charge ratio which is a 14.

Correct? So based on the abundance, natural abundance, actually you can estimate the fraction of peak which can corresponds to either nitrogen or it can corresponds to the silicon 2 plus. Okay? So I will just briefly give you an example. So now we know that at the peak 14 and at the peak 15, we have two peaks, 14 and 15 and it might possible that

we can actually peak, we can identify, we can count, these are the number of counts and this is the relative fraction. Relative fraction means relative fraction of that particular data in that peak, correct? So you have a 14, you have a 15, you can see that the number of count is around, assume that it is around 30,122, this is 937. If you calculate the relative

fraction, it is around 97%, it is around 3%, correct? Now if you talk about the natural abundance of nitrogen,

If you talk about the abundance of nitrogen, it is isotope and the isotope abundance for nitrogen. So 14, it can exist in the 2 isotopes 14 and 15. From the standard table, you can see that the natural abundance is around 99.6%. But at 15, the abundance is around 0.4%, which is much lower. Okay?

But the thing is, from your actual experimental data, you can see that at 15, the relative fraction of that particular is around 3%. The experimental data, the number of counts, which is much higher than the natural abundance of the nitrogen, which can present at the abundance of the 15 isotope, which is only having a 0.4%. Correct? So, based on this, if you talk about that, so this is one case. In another case, similarly, if you identify the three peaks, one is at 14, 14.5 and 15.

If you talk about the silicon 2+, correct? Silicon has a 2+, then based on the counts, this is 14 has a number of counts of 30,122, 14.5. If you count from the mass spectrum, it is around 1378. And at 15th, it is around 937. Same figure, correct?

Now, if you calculate the relative fraction, then you will get this is around 92.9, 4.2 and 2.9. If you compare this with the silicon abundance for the three isotopes, you can see that the three isotopes belongs to 27.98, silicon 2 plus we are talking. So 27.98 divided by 2. Then another isotope 28.98, 29.97.

For this the relative abundance is isotope. These are isotopes and abundance is 92.2, 4.7 and 3.1. And if you match these relative amendments to the relative fraction of these isotopes, of these isotope peaks, you can see that it actually matches well whatever the present. Okay? So it means that the 14th peak, the 14th peak is dominated by silicon 2+.

It is not dominated by nitrogen. Okay? Correct? So, this is how we can identify the species. Now, how to deconvolve?

So, actually, we can get the composition based on the relative fraction and abundance data. So, if you consider these three peaks, DA, and the number of ions, if you consider these three peaks, Assume that X Na plus is the nitrogen ions, Na plus, and X silicon 2

plus are the silicon ions. Okay. So, from the total number of ions and compared to the isotope abundances, we can write it as 0.996 X N plus 2.

plus 0.922 X silicon 2 plus equals the total counts, which is 30000, 1, 2, 2. This is the first equation. This is for the peak 14 DA, correct? For 14.5 DA, okay, we have only contribution from silicon. Correct?

So, we can directly write as per the abundance as per the abundance 0.047 X silicon 2 plus is equals to 1378 number of ions. This is for the 14.5. For 15 mass to charge ratio It can have a contribution from the both nitrogen and silicon. So, based on the isotope for this nickel, you can write 0.004X nickel plus 0.031.

This is the isotope. X silicon 2 plus is equals to 937 nickel. number of ions for the 15 day. So, we have three equations. Equation 1, equation 2, equation 3.

So, with the equation 2, actually we can get the X silicon 2 plus can be written as 1378 divided by 0.047 which is equal to 29319 ions. and this can be substituted back to the equation 1. It can substitute back to the equation 1 then you can actually get X n plus is equals to 30122 minus 0.922 into silicon 2 plus divided by 0.996. If you substitute this particular value in this X silicon 2 plus then you will get Xn plus has 3102 ions okay.

So this is the contribution the number of nitrogen and number of silicon peaks. which is present in the sample. Correct? So based on the total number of ions detected actually you can now get the composition of nitrogen and composition of silicon with respect to whatever the mass spectrum you have obtained it. So this is how we can do the deconvolution or we can estimate the compositions which is having a peak overlap.

Okay? And for validation what we can do is you can actually use this equation 3 for validation and you can see that you will get a Xn plus nitrogen plus nearly same as 3102 which is around 2263 and X silicon 2 plus you will get a values of 30000 to 226 ions. So, you can see that it is similar to the values which is obtained by the equation fund means it is consistent. We cannot tell it is the same but it is consistent.

So this is how we can actually sort it out, the peaks in the mass spectrum if they have an overlap. Now one more way to identify the peaks is if you have a mass spectrum which is

14.5 and 15, you can see that For the nitrogen, the peak should come at 14 and 15. But for silicon, it comes at 14, 14.5 and 15 as per the abundance. Correct?

If in your sample, you can see that you have all three peaks from the silicon. But if it is nitrogen, this 14.5 extra is the additional peak with respect to the nitrogen. So in this way, we can actually identify what type of species may be present in your system. And more importantly, another key aspect is the ratios. The relative abundance ratios are very important for the peaks.

So the ratio is usually maintained. For example, how is it? So if you have a silicon 2+, which has a ratio of, as I told you, 92, 4, and 3. 92, 4, and 3%. So in the mass spectrum for your sample, you can get this at 14, 14.5, and 15.

So you should get peaks as per the abundance with decreasing number of ions with the charge, okay? So if you have an abrupt peak like this, then you can estimate—so then there is a contribution from some other ion to that particular peak other than silicon 2+ at the mass-to-charge ratio of 15. So this is how, by seeing the trend of intensity of the peaks or their abundance, we can identify these elements—what type of elements are present and what type of isotope is present.

So with this, I will end this class now. So, in this class, we briefly described the mass spectrum and the initial corrections, which are very important. And if the peaks are overlapped with the two isotopes, how we can deconvolute them and examine the abundance of these peaks in nature, which can help us identify the exact atomic species present in the sample. In the next class, I will discuss the quality of the mass spectrum and how it relates to your atom probe reconstruction, which we will cover in the next class.

Thank you.