

**Advanced Material Characterization by Atom Probe Tomography and
Electron Microscopy
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Week-07
Lecture-21**

Welcome to this class. In the last classes, we have discussed the field ion microscopy, atom probe tomography, and field desorption microscopy. We also covered the instrumentation, the basics related to field evaporation, and the parameters important for reconstructing the needle specimen. This is equivalent to how it is present in the tip specimen, okay. So, to replicate the exact atomic structure, we need to understand the parameters and their influence on the reconstruction. Now, in this class, we will start with sample preparation, which is very important for conducting the experiment, okay. So,

sample preparation. We know that sample preparation is a very crucial step. The sample should be optimal enough so that the atoms get polarized at a definite voltage and can field evaporate. Fine. For the needle specimen, there are some conditions for sample preparation. The tip dimension, or the radius of curvature, should be between 50 to 150 nanometers.

Okay. This is the optimum range where the radius of curvature should be maintained. Okay. If there is a larger radius, a larger R , then it becomes very difficult for the atom to polarize and get ionized. Okay. So, if it is a large R , you will require a higher voltage.

To induce the field evaporation such that locally the electric field lines are concentrated enough that these atoms get polarized, ionized, and accelerated. Okay? So, you need a higher voltage. If it is a very small radius, then your electric field distribution will be very complex, and the ion trajectories may distort. Ion trajectories may distort. Okay, this will have a direct implication on the reconstruction of the needle specimen.

So, the optimum radius of curvature should be between 15 to 150 nanometers or up to 100 nanometers. Okay, the second condition for the needle specimen. So, you have a

sharp needle. The second condition for the needle specimen is that the surface should be smooth. It should be smooth.

Okay. Meaning free from any protrusions, grooves, and cracks. Okay, so because of these protrusions, grooves, and cracks, it might be possible that the needle specimen will fracture very easily. So, the yield will be very small. Correct, and usually in the reconstruction, whatever reconstruction we are doing, it is based on the assumption that the tip surface is actually a hemisphere.

Hemispherical cap. Based on this, we are doing reconstruction. So, what is the reconstruction? By the reverse projection model. Okay?

So, your reconstruction is based on the assumption that the tip surface is a hemispherical cap. Any deviation from the hemispherical cap might lead to artifacts in the reconstruction. Okay? It may be due to the geometrical discontinuities, stress concentrations—it may arise from stress concentration, such as cracked tips, grooves, or protrusions, okay?

This generates the artifact. The third condition is that the tip surface should be of circular cross-section, okay? We have assumed that these are hemispheres and there is a circular cross-section, truncated shape. Correct? But if it is not a circular cross-section, it might be possible that the electric field distribution is very erratic.

Okay? This may lead to inhomogeneous field evaporation from the needle specimen. Okay, so then you will not exactly replicate the needle specimen during the reconstruction. Fourth is the feature of interest. The feature of interest should be within 100 to 200 nanometers.

Okay, so if you have a needle specimen with a certain precipitate, that precipitate should be between 100 to 200 nanometers in distance. Okay, this is one more condition. The fifth condition is sufficient specimen length. Specimen length. Okay, and also the absence of secondary tips.

Okay, so I will go through the sample preparation by focused ion beam or electropolishing, but before that, I need to discuss this secondary tip. Usually, what will

happen during sample preparation is, if there is your main needle specimen, it might be possible that there will be a small protrusion developing on the sample surface. So during field evaporation, it might be possible that your voltage is enough to cause field evaporation from these tips. So, you will get extra ions that are not from the exact specimen surface we want. So, it will generate a wrong reconstruction or artifacts in the sample.

And the sixth is the appropriate shank angle. Appropriate shank angle. This we will discuss during the reconstruction. so these are the six conditions which are very important for a optimum specimen for the needle specimen for the atom probe tomography or the field ionized microscopy so now we will go to the some of the basic polishing methods some of the basic polishing methods the most common method which was used now also it has been used it is the electropolishing

This is the most conventional method and the property of the material should be having a good electrical conductivity and it is suitable for electrochemical cell. okay and the material so this electropolishing it is nothing but a you have a you have a rectangular blanks this we call as a blanks of some mm size then by electropolishing actually you can thin down this specimen to a needle specimen by removal of this material okay so actually you are doing the removal of the material is removed by electro polishing from the surface from the surface of the specimen okay or the protruding protruding parts of a surface profile

is dissolved okay so what is the basic to the electropolishing this is a very basic thing where what we do is simply we need a DC power supply which applies a positive charge to the specimen which acts as a cell anode okay and this particular sample or the specimen is emerged in an electrolyte liquid electrolyte okay and together with a cathode together with a cathode okay so basically With this process, when, then when you apply the electric, when you apply the voltage, when you apply the voltage, there will be a passage of current across this specimen, anode, electrolyte and the cathode. Then the specimen gets started dissolving.

Okay. So, if you see this schematically, you can have a bathtub. Okay. You have a bathtub. You have a specimen.

Okay. You have a cathode. This is the cathode. This is the anode. Okay.

And this is connected to a negative and positive. Okay. So, Just wait. Okay.

So, basically, if you see this, it is a very simple cell which has a container, okay, which contains electrolyte. Okay, you have a cathode. You have an anode, which is a specimen. This is a cathode. Then, this particular anode is connected to the positive.

The cathode is connected to the negative. Correct? And this is a specimen. Correct? And it is dipped into the electrolyte.

Okay? When you pass the current, when you pass the current, the electrons will travel along in this direction, and the electrons will travel in this direction towards the positive. Correct? So, with this process, what will happen is, at the surface of the specimen, at the surface of the specimen, the metal gets converted to metal ions, and these metal ions start moving towards the cathode, okay?

And whatever the electrolyte or the acid that is used, it moves toward the anode, okay? So, at the cathode, A reduction reaction happens. A reduction reaction happens at the anode, where usually hydrogen gas evolves. So, if you magnify this particular region, magnify this particular region, assuming that this is the surface of the specimen,

then usually the metal will dissolve as ions into the electrolyte, so there will be a dissolution of the specimen. Okay, and the electrons will travel toward the metal surface or the specimen surface, where they may form oxygen or hydrogen gas, and it gets released into the electrochemical cell. So, in this way, over time, you are dissolving the specimen. in the electrolyte, so that your specimen will be removed and converted into a sharp needle. Okay.

So, usually during the process, during the etching process, there are three reasons, or during electropolishing. Okay. So, this is your current density. Okay. And this is the specimen voltage applied, in volts.

So, here we can mark four positions: A, B, C, and D. So, the best polishing conditions occur between B and C. Okay, this is the optimum condition where the current density does not change drastically with the increase in voltage. This is the optimum condition. While in A to B, usually the current density changes drastically with the voltage. So, usually etching will happen, and in C to D, spitting occurs.

So, your voltage should be such that the optimal condition is in the range between B and C. And the shape of this particular curve depends on the material, electrolyte used, temperature of electropolishing, and the geometry of the cell. So, these are the four conditions which can change the shape of this particular curve. And in this B to C position, where the current density does not change with the voltage much, that is the optimum condition. Now, what are the steps to prepare for electropolishing?

The first is, if you have a bulk material of larger dimension, If you have bulk material of larger dimension, this bulk material has to be converted to blanks. Blanks means these are very small rectangular slabs of a few mm dimensions, with a length of a few centimeters, okay, in few centimeters. So, the cross section. is around a few mm.

So, these are called blanks, which can be made by either slow-speed saws or cutting with EDM cutting machines. Okay, so the cross-section of this particular blank is around 0.3 mm square, okay, and the length And the length is a few centimeters. It is about 225 mm, around 2.5 centimeters long. Okay, so you can use the precision saw, a slow-speed saw, for cutting the blanks from the bulk samples.

Okay, so these blanks, individual blanks, are used as the anode in an electrochemical cell where the material is removed. from the tip surface, from the cross-section, so that it will become a sharp needle. Okay? So, in earlier days, the most popular method used for electropolishing is a multi-step process. Multi-step process.

Okay, in this multi-step process, the first step is rough polishing, and the second step is fine polishing. Okay, rough polishing—this is nothing but, we can say, it is due to the formation of a neck. Fine polishing After the neck formation, it is sharpened into a needle specimen, into a tip. Okay? So, based on the material, different types of electrolytes can be used.

Okay. For rough and fine polishing, we can also change the concentration levels of the electrolyte. Based on the concentration levels, you can either do rough polishing or fine polishing. Okay. So, in the multi-step process, these two are the methods used.

Okay. What is rough polishing? Usually, these are called the double-layer method. Double layer method, okay. So, here, this is just a general view showing the blanks which are made from the bulk sample.

You can see these blanks are nothing but rectangular cross-section rods of that particular sample, which have around 0.3 mm square cross-section and a length of around 25 mm. So, these are the blanks. Now, what is the double layer method? This is called the double layer method. In this method,

Usually, the first step is rough polishing, and the second step is fine polishing. Okay. So, in rough polishing, what we do is this is a one blank. Okay. So here, this acts as an anode.

And this is a cathode. This is your electrolyte, and this is your inert. So, in this, the specimen—specimen means the blank—is repeatedly dipped into the layer of an electrolyte, which is placed on the top of an inert layer. Okay. And this inert layer is nothing but a perfluorinated polyether.

Which is also called PFPE. Okay? So, in this, the blank is repeatedly dipped into a layer of electrolyte on the top of an inert liquid. Okay? With this, and the current is the DC voltage.

The DC voltage is applied simultaneously. So, it is moved up and down. Okay? This up and down motion is This up and down motion allows control over the taper which forms as a neck region.

So, this is called the neck region, and you can see that the material is being removed from this neck region. So, this is done until these blanks become thin enough to be at the few-micron level. Once these are thin enough, it might be possible that they can break away. So this can be monitored by the current. So the polishing will be continuing when the current is still showing some value.

When the current becomes zero, it means that it is near to the breakaway of these blanks. Then once the sample cross section becomes a few micrometer square, then what is done is the second method is followed which is called fine polishing. In fine polishing, what we do is we don't use any, so inert layer is not used. The complete electrolyte is used with a different concentration. This is your cathode.

This is your anode. Okay, so this polishing is again repeated by up and down motion of that particular specimen, and it is done until these two—these two The blank separates into two pieces, and the cross-section of this particular area where the necking has formed is in the nanometer range, a nanometer-square area. Okay, so this is called final polishing, and this final polishing also removes the damaged On the surface, protrusions.

Okay? So, this is how we prepare a needle specimen. And the needle specimen will be sharp, with a radius of approximately 50 to 150 nanometers. Okay? So, this is how electropolishing is done.

So, this is a double-layer method. But now, this is the old process that we use. Nowadays, the rough polishing—usually the first step, rough polishing—is directly carried out in the electrolytic cell where there is no inert layer. It is just a beaker. We put a beaker, add electrolyte, and the rough polishing is done directly in the complete electrolyte.

Okay. Then, Okay, so it means that once this rough polishing is done in this particular step, once the rough polishing is done, then you will have a needle specimen, which has a few micrometer square area. Okay.

This particular needle specimen again goes to a second step where we use a rig. Okay. So, in which the electrolyte is suspended by using a loop of that particular cathode or the cathode. So, this is the second step after preparing a needle specimen by using the electrochemical cell. This rig is nothing but a you have a platinum wire and this particular wire is bent in such a way that it looks like a at the end it looks like a

circle or you can tell as a wire loop and at this loop due to the surface tension actually you can actually deposit the an electrolyte okay so this is the this is your loop of that platinum wire and there is a electrolyte and there is a electrolyte which is held on that

particular loop due to the surface tension. And your needle specimen, which was prepared previously by the rough polishing in an electrolyte, is kept into this particular loop and it moves up and down. And while moving this up and down,

What you see there will be a polishing of this particular needle and this micron meter square needle can convert to the some few nanometer square cross section needle. Okay. So this is the this is the fine polishing. This is your fine polishing. And this method now it is used most popularly everywhere in several labs where the rough polishing is done by simply an electrochemical cell with the electrolyte.

Once these needle specimens become sharp enough in micrometer square range, the cross section, then you can prepare a loop by the platinum wire and due to the surface tension effect you can deposit, you can suspend the electrolyte on this particular loop. And by this arrangement, you can do up and down movement into this particular electrolyte so that until that this particular tip surface becomes in a few nanometer square cross-sectional area. And the DC power supply is continuously applied across these needle specimen. Fine?

So, and this, and usually it is not only in vertical direction, you can actually also do this particular thing in horizontal direction. And the electropolishing—if you put it under a microscope, an optical microscope, a high-resolution microscope—the thinness of this needle specimen can actually be observed live. So, this is the basic procedure that people usually carry out for electropolishing. So, here the only difference is that the needle specimen is repeatedly pushed through the loop. This is your loop.

This is your platinum wire loop that holds the drop in the electrolyte due to the surface tension effect, and the tip becomes sufficiently sharp. So, this is an optical image of a sharp tip. It has a few nanometer-square cross-section. Sometimes, as this is a destructive technique, the field of operation—once your tip surface becomes fractured or the voltage increases enough that the tip becomes blunt—this final polishing method can also be used to sharpen the tip sufficiently for further analysis.

So, what do we need for this purpose? We need a power source. We need some beakers to hold the electrolyte. We need an electrolyte, which depends on the material to be polished. You need an inert material.

Usually, we use a platinum wire, which is formed into a loop. And there is a binocular or optical microscope. These are the four or five important things which we need for electropolishing to be done. The only disadvantage with electropolishing is that you cannot prepare site-specific samples. For example, if you want to do field evaporation across a grain boundary,

Across interfaces, which control your overall material properties, you cannot prepare the site-specific methods by site-specific electropolishing samples. Okay. So, by trial and error only, you can somehow prepare these samples from the grain boundaries or interfaces. Fine? So, typically, as I told you, this is a setup where it is in the ISC.

Okay? So, this is your microscope—an optical microscope—and this particular one is a small, fine, polishing electrochemical cell. Okay? So, here you can see that this particular region, if you zoom in, Okay, you have a crocodile clip.

This is a crocodile clip, which is holding the specimens here. This is called a specimen, which has several tips. Okay, and this particular wire is called a platinum wire. And you can see that there is a loop, and you can see there is an electrolyte suspended on the loop. And the crocodile pin is moved up and down such that these tips will go into the electrolyte, which is suspended on the loop, and get electropolished.

And a DC voltage is applied continuously across the electrolyte and the platinum inert wire. Okay, so this is how we usually do the electropolishing for the specimens, and the electrolyte depends upon the material which is investigated. Correct, so this is the most versatile method for preparation of atom probe needles or field ion microscopy needles. But the only disadvantage is that we cannot make site-specific needles wherever the precipitates or interfaces are needed. Okay, so with this, I will end this class now.

In the next class, we will discuss how to prepare site-specific methods. Recently, there has been huge development in focused ion beam microscopy, where you can use heavier

elements, heavy liquid elements, or ions which can be focused. Through lenses, those heavy ions can actually be used to remove the material or to trench the material in such a way that you can make the needle-shaped specimen site-specific. So, we will meet in the next class with the second type of sample preparation method. Thank you.