Advanced Material Characterization by Atom Probe Tomography and ElectronMicroscopy

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Week-12
Lecture-44

Welcome to this class. In the last class, we showed the basics related to SEM, TEM, and other techniques such as electron channeling, contrast imaging, and transmission Kikuchi diffraction. Now, we will move to the application side. Mostly, I will focus on the structural material side.

So, in electron microscopy, I will briefly explain that in SEM, we can perform electron backscatter diffraction to obtain crystallographic information. You can perform crystal structure analysis. You can obtain the grain orientation map. Here, I am showing the inverse pole figure map where you can see that different colors correspond to different crystal orientations. In TEM, you can perform conventional transmission electron microscopy.

You can perform diffraction analysis. You can identify the phases, phase 1 and phase 2. You can determine the orientation relationship between the phases using conventional diffraction techniques. Also, in STEM mode, you can perform high-resolution scanning transmission electron microscopy to obtain contrast related to atomic columns. You can perform local structural analysis, examine interfaces and defects, and identify the types of defects or line defects present in the sample.

So, this information is all a 2D projection of volume, okay. And in transmission electron microscopy or SEM, you can actually perform EDS spectroscopy. EDS spectroscopy is nothing but the use of X-rays. These are used for the quantification of chemical species, and this accuracy depends on the Z number. The higher the Z number, the higher the accuracy.

EDS spectroscopy is not recommended for light elements due to poor energy resolution. It has an energy resolution above 130 electron volts, where in low-energy light elements, these energy peaks get overlapped. In TEM, you can perform electron energy loss spectroscopy, where you can obtain light metal quantification. However, it has a complex spectrum for heavy elements.

For heavy elements, there might be an overlap of specific edges, especially in these yield spectra, requiring deconvolution of the peaks. Correct. So, atom probe tomography has an advantage over these two techniques. It provides atomic-scale 3D compositional analysis. It has excellent mass resolution with an elemental sensitivity of 10 parts per million, irrespective of the element, and provides accurate quantification.

More important, you can visualize your specimen in three dimensions if you have some certain features which are having different compositions. However, as in atom probe tomography classes, I had told that there might be some reconstruction issues where the major drawbacks are low spatial resolution. This is due to the irregularity of the field of operation sequence due to the compositional changes and local bonding states. In reconstruction can be distorted. This is due to the predicting 3D electron field distribution is very difficult, especially in the near and the far field.

And there are also aberrations related to trajectory, which are related to the local magnification effects and due to local curvature in different precipitate and evaporation fields. So there might be the surface migration effects. So these are the major drawbacks in the atom probe tomography. But these drawbacks can be overcome by using the correlative microscopy. What is correlative microscopy?

It is nothing but a sample surface. A sample is examined in an electron microscope, either in a scanning electron microscope or the transmission electron microscope to get both the structural information from macro to atomic scale. Then the same specimen can be field evaporated in an atom probe to get the correlative chemical analysis. Here I am showing an atom probe needle where it is showing a certain features which corresponds to a stacking fault. And you can see the corresponding atom map where you can see that this corresponding

The fault has a different composition from the matrix. So, by correlated microscopy, you will get both structure and chemistry from the same region of interest. You will have a better understanding of the atomic-level mechanisms, and also you can improve the APT reconstructions, correct? This is to overcome the drawbacks related to atom probe tomography. Fine, here I am giving a very nice example where there is an EBSD pattern, and this is an inverse pole figure where all the orientations correspond to the different colors.

Especially, these are FCC copper, so you will have a red color for 001, blue color, and green color for the 111 and 101. You can pick up a grain. So, we picked up our 001 grain, which is red in color. You make an atom probe out-of-plane sample. You field-evaporate it.

This is a copper sample which has cobalt precipitates. These are coherent, and you can see that along this direction, this map shows cobalt clustering in the copper matrix. Copper is green in color, a golden color, and the red color is cobalt atoms. In the desorption image, we can see that the orientation of the needle specimen is near 001.

If you magnify along the Z direction, you can actually resolve these atomic planes. The golden color corresponds to copper, the green color corresponds to aluminum, while the cobalt atoms are red. And you can see that the resolution of these atomic planes is almost like the spatial resolution of the D-spacing of 001. And so, you can get the composition of each atomic layer,

fine, so you can get the cobalt and aluminum concentration on that particular atomic plane, and you can see that cobalt and copper are immiscible. So, wherever cobalt is not present, copper is almost zero in the reconstruction. Fine. So, this is another example of an aluminum alloy, and here you can see that This is a HAADF image of a TEM where you can see the different contrasts related to aluminum and also the precipitate of copper. And inside the aluminum crystal structure, you can also see the bright atomic columns. These bright atomic columns correspond to high-Z elements such as hafnium and tantalum in the matrix, and this copper has a higher Z than aluminum.

So, these bright columns correspond to the copper-rich atomic columns. If you see here, this is a zirconium-rich precipitate in the aluminum matrix. Since zirconium is a high-Z element, it shows brighter columns compared to aluminum. Fine. And in three dimensions, you can see that in the same sample, plate precipitates appear as green-rich regions and zirconium-rich precipitates as red-colored regions. So, with this introduction, I will just go through the case studies.

You know that we are surrounded by several engineering materials, especially steels, which are used in construction and also as stainless steel in our daily home appliances. So, steels are very important for construction because of their room-temperature strength, ductility, and very high tensile strength. So, there are special-grade steels which are used for construction and also for the transport industries. There are certain kinds of alloys which are called superalloys. These are high-temperature alloys that can sustain temperatures ranging from 1000 degrees Celsius to 1500 degrees Celsius, and these are typically used in turbine blade components.

In rockets, superalloys are also used, and there is a special class of copper alloys which are very important in rocket rocket-based systems where they are used for applications requiring high conductivity. Lightweight alloys, especially magnesium and aluminum, are the main critical alloys used for powertrain applications in automobiles, particularly in engine parts where temperatures can reach up to 200 to 250 degrees Celsius. So, a lot of work is being done on these alloys to improve their high-temperature capability up to 250 degrees Celsius.

Especially, these are used to construct to make pistons and piston heads. So, these are the main uses of lightweight alloys, and there are other applications of these alloys, such as utensils, wiring, electrical wiring, etc. Now, I have briefly gone through this introduction in this class about the importance of correlative microscopy.

Here, I will show you how these techniques can be used. First, here I am showing a location. This is a sample surface, and you can see there is a sample feature inside the sample. This is a rafted gamma-prime precipitate. We will talk about this later.

But if you identify a sample feature in FIB, actually you can mark this with the platinum. When you mark this platinum reposition with the sample features, then you can lift out this lamellar by using the manipulator and the platinum reposition by using FIB. And you can paste this lamellar on a half cut moly grid. And this half cut moly grid is nothing but the sharp tips are present. And these sharp tips have a certain cross section area about 2 microns, 2 to 3 microns.

And there you can actually paste the sample lamellar. by using the platinum deposition and you can use the fib ion beam for milling these lamellar samples to a sharp needle specimen. Now as the sharp needles are attached to the grid, this grid can easily go to the TEM holder where we can do the structural analysis from micro to the atomic scale and the same grid can be used for the atom probe tomography by using special correlative holders where you can get the structural information. Okay, so what we do?

The first thing is, we need to make the grids which are capable of holding the sample. This is a moly grid. These are cut in half, and you can see that this is the rough surface of the grid. And this rough surface is electropolished. So you are using a cathode and an anode.

Now, what you do is hold this cut moly half-grid with a crocodile lock pin. And another crocodile pin is held with a platinum wire which has a circular hole. And there is an electrolyte. Usually, we use sodium hydroxide, and due to the surface tension, this electrolyte hangs inside that particular hole. Now, what you do is move this particular grid up and down, and by this motion, the rough grid is polished into sharp, smooth needles.

And this is the needle, which is a moly post where the sample can be pasted using the FIB and can be milled to get the needle specimen with the sample of interest. Okay, now you have a moly grid with the sample. Fine. Now, what we do is place this particular moly grid directly into the TEM with a TEM holder where you can get the structural information. Now, this holder can be placed in a sample holder like this, which is also used in FIB systems for holding the copper grids, and we made special correlative holders which can hold these grids.

These sample holders can be fitted to the puck, which can then go to the atom probe tomography so that we can field-evaporate that particular needle specimen for chemical analysis. Okay. One more important point is that we can also make the needle specimen from TEM samples. Okay. So, if you have a TEM sample, you can carry out TEM analysis, both the atomic structure and the microscale analysis.

Then, by special FIB methods, you can actually extract that sample region of interest from the TEM sample. You can paste it onto the moly grid or moly grid, then you can use ion milling to sharpen the tip and to make the stacking fault present in the needle specimen or the sampled region of interest. So, you can make the needle specimen from TEM samples as well. These are the correlative experiments, which I will briefly explain through several applications related to materials.

Here, in electron microscopy, we can perform EBSD to obtain the grain orientation. You can get transmission Kikuchi diffraction for very thin samples, TEM or APT specimens. You can perform controlled electron channeling contrast imaging. I have briefly introduced this imaging technique, which can be used on bulk samples to quantify defects on the surface of any sample or deformed samples, and you can also use it for TEM and HR STEM analysis.

For example, the diffraction and atomic structure of these samples—if site-specific—can be prepared by FIB. So, FIB can be used for tip preparation, in-plane lift-out, and also TEM sample preparation. Correct. Once the sample is prepared, it can be analyzed in an atom probe by field evaporation, especially for site occupancy, composition, and segregation effects. So, I will give you brief examples related to applications in material science.

So, these are the different techniques I briefly introduced, which I will not go through again. These are the different techniques and steps we can perform for a specific investigative purpose. We can investigate defects. Twins, dislocations, stacking faults, grain boundaries—we can see the structure and the chemistry, and these are related to steels, magnetic alloys, aluminum-based, cobalt-based, superalloys, magnesium-based

alloys, where all the mechanical properties are critically governed or dictated by these microstructural features.

So, first, I will talk about the use of EBSD with site-specific sample preparation by FIB and atom-probe tomography. Here, you can see—I will give you a site occupancy example. Here, you can see there is a CO3Ti phase. This is a cobalt-titanium-based superalloy where a gamma-prime precipitate exists, which has an L1-2 ordered structure.

L1-2 ordered structure. It is an FCC-based ordered structure where cobalt occupies the face-centered positions, titanium occupies the corner positions. The face-centered position is a half of zero; titanium is at the zero-zero-zero positions. You can see that this is a typical cubic structure. The lattice parameter for Co3Ti is almost 0.36 nanometers. Fine—so remember that if this particular plane, the zero-zero-one plane, is a mixed plane because it contains both cobalt and titanium atoms. But this half of a plane, this particular plane—

But half the distance, it is a pure plane of cobalt atoms, and there is a mixed plane. So, there is a mixed plane, a pure plane, and a mixed plane. And you can see that the number of atoms of cobalt is a total of three in a unit cell, while titanium is one in the unit cell. So, stoichiometrically, these are called CO3Ti phase. Okay.

We prepared a sample from a 001-oriented grain. This is an EBSD map and inverse pole figure where the red corresponds to the 001 orientation. Once you field-evaporate the needle specimen from that orientation, you can get the gamma and gamma prime. In gamma prime, you can see that the titanium is enriched because it partitions, and at the interface, you can see that you can actually resolve the lattice planes of the cobalt or the CO3Ti phase. Now,

In our data analysis during atom probe tomography, I introduced the spatial distribution maps. This is a very powerful tool. Actually, it can be used to identify the site occupancy of any intermetallic compound at a particular orientation. So, just to revise, it is nothing but the average distribution of atoms in a particular crystallographic direction. The reference atom and the vectors are drawn in 3D and repeated for each reference atom.

All vectors are histogrammed in three dimensions. So, you will get spatial distribution maps along a particular direction or in two dimensions, the x-y dimension. So, here we will construct these spatial distribution maps along the z-direction, and the z-direction is near to the 001. Near to 001 means it is in this particular direction, and these are the 001 planes. Remember, the 001 planes are the mixed planes. These are the pure planes. If you get the spatial distribution maps of cobalt and titanium along the 001 direction, you can see there is a central peak.

There is an appearance of peaks, consecutive peaks at a certain distance. Similarly, for titanium also, at a certain distance, there appears a peak. Now, if you see the distance, you can see that at 0.18 cobalt appears, again at 0.36 cobalt appears, and again it will appear at 0.36 plus 0.18. So, at equal intervals of 0.18, you see that there is a presence of cobalt atoms. Now, if you see the unit cell, you can see that if you assume DC has a zero position, which has a cobalt here, then at each 0.18, you will see a peak.

At each, so from here to 0.18, there is a cobalt. From here to 0.18, again there is a cobalt because of the mixed nature. So, you will see the cobalt presence at both halves of 0 and 0, 0 positions. In the case of titanium, you do not see this. In the case of titanium, there is no peak at 0.18.

Always, the peak appears at 0.36, 0.72. It means that the distance between the two titanium atoms, the minimum distance, is 0.36. With this, what we infer is titanium occupies the 0, 0 positions, but cobalt occupies both mixed and the pure planes, correct? So, this is how we can actually determine. No, the site occupancy of the specific elements.

Now, what is the application for the site occupancy? So, if you see this particular alloy, if we alloy molybdenum with cobalt-12 titanium, you can see that the molybdenum also goes to the titanium positions, which are at 0.36 nanometers, fine? And this is all present in the Mixed plane means titanium sites. If you add additional chromium and molybdenum together, both chromium and molybdenum go to the titanium positions, which are the 000 positions.

Now, if we increase the chromium content, we see that chromium actually occupies the titanium position, but the molybdenum site occupancy shifts from 0.36 to 0.18. So, there is a change in the site occupancy of the molybdenum atom. With the shifting, with the increase of the alloying addition. So, it has a direct—the alloying addition has a direct consequence of shifting the site occupancy of any solute atom, either it is in a 0-0 position to the half-half of 0 positions. This will have a direct consequence on the lattice parameter of this particular gamma prime.

Because the lattice parameter depends upon the interatomic potentials, correct? The bonding between the two atoms. So, if there is a change in the site occupancy, it will definitely have an impact on the lattice parameter of the gamma prime, which is coherent with the gamma phase. So, the strain between these two phases will change. And due to the change in strain, there will be an effect on the overall mechanical properties.

So, one example I will give you is another cobalt alloy where you can see that this is a cobalt-nickel-aluminum-molybdenum-tantalum-titanium alloy. And if you increase the chromium content from 2% to 8%, you can see that the gamma prime morphology changes from cuboidal to spherical. So, definitely, there is a change in the local lattice misfit between the gamma and gamma prime, fine. If you do the spatial distribution maps of the chromium atoms in gamma prime, you can see that for the two-chromium alloy, the chromium occupies all the 0.36 points. 0.36 means these are occupying the 0, 0, 0 positions of the L12 unit cell.

However, if you increase the chromium up to 8%, you can see that the lattice site occupancy is also at 0.18. It means that due to the change in the chromium site occupancy, it has a direct impact on the lattice parameter of the gamma prime. Due to this, there is a change in the lattice misfit from plus 0.48 to plus 0.19. It means that the lattice misfit decreases. Due to the decrease in the lattice misfit, you can see that there is a change in the morphology.

If there is a change in the morphology, this will have a direct impact on the creep properties of this particular alloy, which is used in high-temperature stress applications. So, this is how we can use the site occupancy to correlate with the microstructure

obtained, which actually governs the overall creep property of that particular alloy. Now, I will give you an example of site-specific preparation of a needle specimen from the grain boundary, and the use of transmission Kikuchi diffraction and how atom probe tomography helped us to understand the grain boundary character. Okay.

So, now, and this is a combined use with the transmission EBSD, which is transmission Kikuchi diffraction, as I explained before. These are nothing but patterns you can actually obtain from the transmitted inelastic electrons from the specimen, after the interaction of the beam with the specimen. Okay, so you can get the pattern. Here, the spatial resolution is down to two nanometers. The sample is electron-transparent, and the diffraction pattern originates from the bottom surface of the sample on a scale of the same smaller diffraction source volume.

Okay, so this is just an example of an orientation map of aluminum where you can see the grain structure inverse pole figure by using transmission EBSD. So, we will see how transmission Kikuchi can be used in correlation with other electron microscopy techniques. So, grain boundaries play a very important role, especially in the corrosion properties of this austenitic stainless steel A316. This is an industrial-grade steel where the major constituents are chromium, nickel, and molybdenum, and the minor constituents are silicon, phosphorus, and sulfur. These have excellent properties, corrosion resistance, and creep resistance.

But at high temperatures, these are prone to intergranular corrosion. And usually, corrosion occurs because of high diffusion of chromium along the grain boundaries. And this chromium depletion occurs along the grain boundaries near the carbides. And due to the presence of carbides, due to the precipitation of carbides, the localized corrosion increases because These carbides act as cathodes, and the chromium-depleted regions act as anodes.

So, there is a potential difference. So, usually, the corrosion preferentially attacks these boundaries. It was found that some of the CSL boundaries, such as sigma 3 and sigma 1, are less prone to corrosion. But It was not always true.

Okay. So it was also shown that by increasing the fraction of CSL boundaries, they can prevent carbide precipitation and also provide better corrosion resistance. But the evidence is not so clear. Correct. So now the task is to understand how the grain boundary character controls the corrosion behavior of these alloys.

Okay. So this is a typical microstructure backscattered image. where you can identify the sigma 5 and sigma 7 type of boundaries in a solutionized condition and after sensitization this is nothing but annealing at 700 degrees celsius for 10 hours you can see that sigma 5 and sigma 7 boundaries are present now if you do the corrosion If you put this sample in the 10% volume HF solution, you can see that at 2 hours there is no change

but at 5 hours you can see that the sigma 7 boundary gets corroded heavily while sigma 5 boundaries remain intact. So, there is a change in the corrosion behavior of these two types of boundaries, and definitely, it is due to the grain boundary character. Correct. Now, if you see the fifth cross-section of this area, we can see that at the sigma 7 boundaries, there are several examples, there is a high presence of chromium and moly. So, it hints at the formation of carbides near the sigma 7 boundaries, but we should understand why only at the sigma 7 boundary and not at the sigma 5 boundaries. To do that, we did the correlative analysis.

First, to get the composition profile of the solutionized alloy for sigma 5 and sigma 7, what we do is lift out the sample from the sigma 5 in-plane lift-out and perform transmission Kikuchi to confirm that the obtained boundary at the tip surface needle specimen is a sigma 5 boundary. Okay, so we proved from TKG that it is a sigma 5 boundary. Then, the same needle specimen was field-evaporated. Interestingly, we see that at the boundary, the molybdenum segregation increases; however, the molybdenum segregation is uniformly distributed across the boundary.

This is a very important conclusion, which I will explain later. If you take the composition profile across this particular boundary along with the molybdenum, there is segregation of silicon, carbon, boron, and phosphorus, okay? Also, chromium increases while iron and nickel get depleted at these sigma 5 boundaries. A similar analysis was

done for the sigma 7 boundaries. Interestingly, we found that the molybdenum segregation is not homogeneous. The molybdenum segregation occurs in a linear way.

Like these, it is as if the molybdenum segregation occurs in a linear fashion. If you take the two-dimensional map of that particular region, you can see that the molybdenum is segregated at certain intervals. So, we termed this a faceted type of molybdenum segregation at these facets. Also, there is an increase in silicon. Now, if you magnify this particular sigma 7 boundary,

Similarly, we also did this for the sensitized samples, and you can see that at the sigma 7 boundary, these linear features segregated by molybdenum are still intact, and we have also seen that there are chromium-depleted regions. Okay, so there is an enrichment of molybdenum, and there are also chromium-rich depleted regions. Now, if you see a higher magnification of this sigma 7 boundary, it appears that there is a faceted structure, and in this faceted structure, you can see that one facet is bright. Another facet is dark.

One facet is white. So, periodically, there is a bright phase, a dark phase, a bright phase, and a dark phase. Correct? And this is not present in the sigma 5 boundaries. Now, for further investigation, what we did was perform EDS mapping.

You can see that these bright regions are molybdenum-rich. And if you see the crystallography, these are found as laves phases. These are molybdenum-rich laves phases. If you find that this dark phase, this particular phase, and if you see in the TEM, these are actually carbide phases which have a cube-on-cube relationship with the exterior grain boundary. So, you have two types of phases.

The bright phases, which correspond to Laves phases because moly is enriched; moly has a higher atomic number. Carbide phases, which are carbon-rich, are the dark phases. Now, So, there is a distinct corrosion behavior between the sigma-5 and the faceted structures. You can see here that this is before corrosion, and this is after corrosion.

At sigma-7 boundaries, you can see that corrosion has already started taking place. And you can see that before corrosion, these facets contain a periodic presence of Laves phases and carbide phases. Correct, and if you go for higher magnification, this is clearer,

and you can see that in some areas where the carbide phase is present, at very high magnification, if you increase the exposure to HF, you can see that there is severe debonding or severe corrosion of that particular Okay, so, precipitation of Laves and carbide phases is linked to the faceting and anisotropic segregation of sigma-7 boundaries.

So, remember in atom probe, we see that moly is segregated in a periodic, faceted way. This segregation of moly leads to the formation of Laves phases at those locations, and wherever the precipitate-lean regions are, there it forms the carbide phases, and due to this, there is an electrochemical potential difference, and corrosion takes place at a very high rate. So, by texture analysis or texture engineering, you can actually lower these sigma-7 boundaries and increase the fraction of others.

Sigma or CSR boundary such that you can minimize the corrosion of the steel. So, this is how atom probe tomography in conjunction with TKD can be used to identify the cause for the corrosion of the steels. I will give you another example of a grain boundary. So, you can see that this is a superalloy with a gamma-gamma prime microstructure. And you can see that if you add 0.005 boron of that particular composition at the boundary, the yield strength increases significantly by 200 MPa compared to the boron-free alloy.

However, if you increase the boron content beyond 0.04, the strength also reduces, correct? So, the boron is doing something at the grain boundaries. Usually, boron strengthens the grain boundary, but you can use atom probe tomography. To get the details, this is the transmission Kikuchi diffraction of that particular boundary. You can see the presence of a boundary between the two orientations.

If you take the APT reconstruction, you can see that at the grain boundary, the boron atoms are segregated, reaching up to 0.15%, along with the cobalt. So, due to the enrichment of boron, it strengthens the grain boundary and increases the yield strength of the alloy. Similarly, in another superalloy where you add 0.06 boron, the creep properties of this particular alloy increase significantly. You can see that the other alloys and the creep rate for this particular alloy are much lower. As compared to other cobalt-based or nickel-based alloys.

So, the current study shows that the density is very low, the solvus temperature is high, and these are much better than other tungsten-free and tungsten-containing alloys. So, to find out the reason, you can see there is an atom probe map. Here, you can see these are the gamma prime secondary precipitates. This is the grain boundary, which is located as a boron, and boron is homogeneously distributed across the grain boundary, while it is also present across the gamma prime precipitates and the gamma matrix phase.

If you take the composition profile across the boundary, you can see that both niobium and boron are segregated along the grain boundary. So, there is a tendency to form niobium boride. But if you cannot increase the boron beyond 0.06, what will happen if you do? All the gamma prime stabilizing elements will be segregated, so you will get a lower volume fraction of the gamma prime. And the boride fraction will increase, which will degrade the creep rate of that particular element.

Okay, so with this, I will end this class now. You see that I have given you an example of the grain boundaries and how atom probe tomography. In conjunction with transmission Kikuchi diffraction, can be used to identify the segregation behavior or the nature of the boundaries that control the overall creep properties. In the next class, I will cover electron channeling contrast imaging, the use of electron channeling contrast imaging to identify the defects. Site-specific preparation, the use of conventional high resolution and atom probe to obtain. Both the structure and chemistry of those defects, and these defects are formed or produced during creep deformation.