

**Advanced Material Characterization by Atom Probe Tomography and  
Electron Microscopy  
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Week-12  
Lecture-46**

Welcome to this last class. So here I will give you a recent example which was done by my student Dr. Akshat and he has performed a correlative analysis on CMX4 alloy. This is a multi-component alloy which is having more than 10 components and these are used as a turbine disc turbine blade applications in a single crystal form and it contains a large amount of rhenium. It is around 3 weight percentage and the main task is to reduce the rhenium contents without affecting the properties.

So, to identify that we need to understand that what the rhenium actually doing during the high temperature creep deformation. So, he has performed correlative analysis of this alloy crept at different stress and temperature and on the defects which are produced and based on that we have identified solutes which can replace the rhenium by almost 50% without degrading the properties. Okay, then just I will go through this work and I hope that you will understand the crux how the atom probe tomography and electron microscopy can be used to actually for the better alloy design for high temperature applications.

So, if you see the S-cast microstructure, we have a interdendritic region, okay, typical interdendritic region and there is a dendritic region. Okay. And inter dendrite region usually we will found as a nickel, aluminum and titanium, where in the dendrites we usually form, we usually see that rhenium, tungsten, molyne, cobalt and chromium are partitioned. Okay.

So, this is a typical distribution of solutes, which we usually see in these alloys in the as-cast form. Okay. So, to remove these dendrites, it is a very difficult because these are very slow diffusing solutes. So, usually at DADO labs, what we do is they perform the

step heat treatment, okay, where these solutes or any segregations that are present can be removed subsequently. Overall, after aging, you will get a microstructure that has a very nice cuboidal shape gamma prime and the gamma phase, okay?

So, here there is a diffraction pattern where you can see that there are superlattice ordered spots okay, which correspond to, and show that these are all ordered structures, L1-2 ordered structures. If you take atom probe data across the interface, okay, Between the gamma and gamma prime, these red-colored atoms are rhenium, and these golden-colored atoms are nickel. If you take the composition profile, you can actually measure the partitioning at an atomic scale.

So, usually cobalt, chromium, rhenium, tungsten, and molybdenum go to the gamma phase, while aluminum, titanium, tantalum, nickel, and titanium go to the gamma frame. So, typically we say these solutes are the gamma prime stabilizers. This compositional partitioning is very important and crucial during free deformation. Based on the partitioning, these solutes can pin the dislocation movement, okay? So, they can act as a drag force while the dislocation shears the gamma thread.

So, I will go into detail about these mechanisms, okay? So, as I mentioned about the mechanism, You can see that a typical superalloy has an L12 structure. These are all 1 0 0 planes, and your triple plane, if you see in the Perpendicular to the plane projection, you can see these are the mixed atoms, okay?

If we call this A, then above this A, there will be another layer. There is a third layer, which we describe as a sequence of A, B, and C. This ABC sequence repeats, and this is a typical FCC or the L1 to FCC-based sequence, which we observe if you see the edge in the adjoint condition of the triple bond plane. Okay. So now, these superalloys with this structure, if you deform them at different temperatures and stress levels, different deformation mechanisms come into play, okay. So here, I am just showing you an example where it is a two-dimensional projection of gamma prime with a triple one plane and there is a soft gamma matrix. Here, I am showing you low temperature, intermediate temperature, and very high temperatures, correct. Now, if you deform the microstructure at low stress and low temperature, the gamma is a soft matrix, so you will produce

dislocations of the type half 101. These are perfect dislocations for FCC. They actually, at these stress levels—very low stress and low temperature—get pinned at the interface.

As I told you before, these interfaces are coherent, and there is a strain. And these dislocations at these stress and temperature levels cannot shear the gamma prime. So, they get accumulated and are restricted at the gamma-gamma prime interfaces. If you go to high temperature and low stress levels, due to the high temperature, they

These dislocations can actually shear the gamma prime along A by 2, 1, 0, 1 direction. And this  $A/2\langle 1\ 0\ 1 \rangle$  in the gamma prime is called super partial dislocations. Correct? And this creates antiphase boundaries. Now, while moving along this  $\langle 1\ 0\ 1 \rangle$ , you can see that they result in the creation of wrong aluminum-aluminum bonds.

Due to these wrong aluminum-aluminum bonds, they are usually high-energy. And due to this high energy, they are not stable. Typically, these antiphase boundaries are disordered structures inside the gamma prime, which are ordered structures. So, this is a high-resolution image where you can see a typical antiphase boundary. Okay.

Remember, these are high-energy with the aluminum-aluminum wrong bonds. Okay. Now, if you go to a slightly higher temperature at intermediate temperature and intermediate stress levels or high stress levels, these dislocations at the interface can actually shear the gamma prime with  $A/3\langle 2\ 1\ 1 \rangle$  dislocations. Okay.

So, what will happen by shearing these dislocations? They form an intrinsic stacking fault. Remember, these are low energy. It means that the nearest wrong neighbor violation did not happen. That's why these are low energy intrinsic stacking faults.

Typically, if you see a microstructure where you can see that these bright lines corresponds to this intrinsic stacking faults. At high resolution, it shows a Structure, which is an HCP based, which are typically DO19 based and intrinsic stacking fault means it is like removal of an extra triple one plane, which we see in the exon condition. So, this is a low energy intrinsic stacking fault. There is another case exists when the stresses are enough that on the two consecutive triple 1 planes,

the a by 6 1 1 2 dislocation can shear the gamma prime, due to which it forms a complex stacking fault with the wrong nearest neighbors. Due to these wrong nearest neighbors, it has a very high energy, but less than the antiphase boundary energy. This high energy can lead to the complex stacking fault to convert to the extrinsic stacking fault by a reordering step which was proposed by Colway long before in 1970s. Okay. And this formation of extrinsic stacking fault usually acts as embryo for microtuning mechanism.

Okay. So, during creep deformation, usually what will happen? The strain, the creep strain can be accumulated by the formation of Extensive stacking faults and microtwinning, and also the intrinsic stacking faults. So, now with this introduction, I will briefly come back to the unit cell, where I mentioned that ideally it is Ni<sub>3</sub>Al, correct?

Aluminum occupies the 0, 0, 0 positions, and nickel occupies the half, half, 0 positions. Now, if you see the generations of superalloys, which were developed from the early 1970s to the 2000s, the first generation does not have any rare additions or high-density elements. Mostly, these are concentrated in aluminum, chromium, cobalt, tungsten, titanium, and tantalum. But the creep properties of these alloys were very low, even though the densities were lower, around 7.8 to 8.1.

So, in the second and third generations, there was a significant addition of rhenium by 3 weight percent and 6 weight percent. Even though the creep properties have increased, increased two to threefold, the density of these alloys has become more than 9 grams. So, typically, now fourth-generation superalloys have a density of about 9.4 to 9.6 grams per cc. Okay, so it has increased the weight of the plates, and one more important point is that rhenium and ruthenium

these are all very costly elements. So, these cost approximately around \$10,000 per kilogram. And compared to tantalum and tungsten, these are almost 10 to 20 times more costly. So, with this background, what I want to say is, if you see a multicomponent alloy, you cannot treat it as an ideal antirion.

In a multicomponent alloy, some of the solutes go to the aluminum sides, and some of the solutes go to the half of zero sides. So, you will have a mixed number of atoms which are actually stable at zero-zero positions, but there are some atoms which are stable at the

half of zero positions, okay? This has to be remembered because, in the later stage, we will see how this is important to understand the cold base mechanism. Okay. And one more important point which I want to convey is the complex stacking fault, which I told you about the dislocations passing across the triple one plane in consecutive triple one planes.

Okay. Here, if you see that if there is a pure unit cell. The CSF energy is around 195 to 275, but if you have a mixed unit cell such as tungsten and tantalum occupying the 0, 0, 0 positions, then your complex stacking fault energy increases by almost 2 to 3 fold. This will have a direct consequence on the mechanism, deformation mechanism, which will happen during creep of these alloys.

So, with this, I just introduced that the experiments which my student Akshat has carried out are correlative use of tomography and electron microscopy to understand the solute defect interactions. These defects are interfacial dislocations, stacking faults, microtwins, and antiphase boundaries. And this led to the understanding of creep rate limiting solutes, which are other than rhenium. Now, based on this, we also generated diffusion mechanisms which were unknown until now before this work was done.

Okay. As I told you, we have extensively used the electron channeling contrast imaging in SCM. To identify the defects at the macro scale. Then, we performed sample preparation from those locations. We confirmed it by using high-resolution electron microscopy in TEM, and subsequently, we performed the chemical analysis locally at the atomic scale on the same samples by using atom probe.

Okay. So, If you see the creep deformation, I have divided it into two important parts. One is intermediate temperature, and one is high temperature. First, I will talk about the intermediate temperature.

Okay. So, at intermediate temperature, you can see that after the creep at 800 degrees Celsius and 800 MPa, in this gamma-gamma prime structure, the gamma prime interfaces are serrated. But you see that we don't see any contrast related to the faults. Actually, we should see it. So, what we did is we went to...

Bragg's condition, in a two-beam condition, and at that particular condition, 0, 0, 2 bar, by using electron channeling contrast we can see that the appearance of bright lines occurs exactly at the same location, which indicates the shearing of these gamma prime precipitates. Okay? And with the stereographic projection, we identified that these correspond to the one, one bar, one bar plane. Along which the shearing of gamma prime has taken place.

So, we have identified at the microscale and also at certain locations that the creep strain is accumulated by the formation of multiple micro twins. In one way, we also obtained evidence that these extrinsic stacking faults, which are very thin here, are converted into twins during the creep. Okay, so this is the evidence of how these extrinsic faults are converting into twins. They act as an embryo. So now what Akshat has done is he has macro-scaled, he has identified those faults.

He has made an in-plane lift-out method, atom probe tip, where you can see this is a bright-field image. You can see these dark regions. And in this particular region, he has identified that these are all extrinsic stacking faults. Now, the same atom probe tip, what he has done is he performed tomography where he has identified the stacking fault by plotting. Chromium 3.2 atom percentage isosurface.

If you take a composition profile, what we see is there is an enrichment of chromium, enrichment of cobalt, while depletion of nickel and depletion of aluminium. We do not see any significant composition fluctuation of other solutes. What he has done is, then again, he has plotted a two-dimensional profile perpendicular to the viewing direction. And what we observed is there is an aluminum-depleted region across the foil plane while there is an aluminum-rich region across the foil plane. So, there is a variation in aluminum composition.

Similarly, the nickel also varies. So, wherever the aluminum is depleted, there nickel is enriched and tantalum is enriched. Wherever aluminum is enriched, there nickel and tantalum are depleted. Okay. So, similarly, what he has done is he has performed a correlative analysis of a region where he has obtained the twins across the tip.

Okay. And this is a typical diffraction pattern. On the atom probe tip, there are twinning spots, and he has taken a dark field from 002 bar where he has shown that these bright regions correspond to the twin boundaries, and we have identified them as T1 and T2. On the same atom probe tip, he performed the atom probe for the chemistry, and you can see this gamma-gamma prime interface, which is exactly at the top, and these planar interfaces

are reconstructed with two different isosurface values, okay? And this planar interface corresponds to the twin boundaries of one particular twin, and these were marked as T1a and T1b. If you take a profile perpendicular to these regions, at these two regions, we see that Along the twin boundary, there is a variation in composition. At certain location, there is an enrichment of nickel.

At certain location, there is a depletion of nickel. Wherever there is a nickel enrichment, aluminum is depleted and tantalum and tungsten is enriched. Wherever the nickel is depleted, Aluminum is enriched while the tungsten and tantalum and cobalt get depleted while the chromium is enriched. So, this behavior was not seen before in these typical alloys, why the variation in composition is taking place along the twin rings.

For more understanding, what he has done is he has plotted a two-dimensional composition map of aluminum. across these twin boundaries perpendicular to the viewing direction and you can see that the aluminum concentration at this region is less and while going towards this direction it increases. Now, he has plotted a composition profile across this twinning plane and what he has observed is from X to Y, there is a continuous decrease of aluminum composition while there is a continuous increase of aluminum composition and continuous decrease of nickel composition. With these profiles,

We need to remember that as per the coal-based mechanism, he has proposed in a ideal anitrile lattice, correct? Either ideal anitrile lattice means aluminum, only aluminum is occupying 0, 0, 0 positions while nickel occupying the FCC position. So, he has assumed anitrile lattice. So, based on the coal-based mechanism, the formation of extrinsic stratum fault by shearing along the 112 bar direction in two consecutive planes will lead to high-energy CSF.

Okay. So, this creates aluminum-aluminum high-energy bonds. These aluminum-aluminum high-energy bonds will reshuffle to form nickel-aluminum bonds, which converts the high-energy complex stacking foil to a superlattice extrinsic stacking foil. This particular extrinsic foil has a DOE two-force structure, which is an HCP-based structure.

Okay, this has to be remembered now. And this particular extrinsic stacking fault, while shearing of 1, 1, 2 dislocations along consecutive planes, will convert to twinning. Okay, so this is how Kolbe has proposed that from extrinsic stacking fault, from complex stacking fault towards extrinsic stacking fault and how the twinning is taking place while accumulating the creep strain. Now, coming to our multi-component alloy, as I told you, ideally these are multi-component,

and aluminum sites are occupied not only with aluminum; tungsten and tantalum can also occupy these 0, 0, 0 positions. Due to this composition, the multi-component nature, what we propose is that If you remember previously, I also talked about the CSF energies. If there is tungsten in the alloy in Ni<sub>3</sub>Al, the CSF energy is much higher compared to the ideal Ni<sub>3</sub>Al. Similarly for the tantalum.

Okay, so based on this data, what we propose is if you have a Ni<sub>3</sub>Al tungsten tantalum gamma prime lattice and if a dislocation shears the gamma prime, okay, you can see shearing of the gamma prime along the 1, 1, 2 bar direction, then you will create a high energy aluminum tungsten, aluminum tantalum bonds, which is different from aluminum-aluminum bonds. And these have much higher energy than the Ni<sub>3</sub>, which are aluminum-aluminum bonds, fine. Now, what we propose is that

There is an additional step which is happening of reordering where the aluminum tungsten tantalum bonds are replaced by aluminum-aluminum bonds to get a low energy CSF. After getting low energy CSF, as these are also wrong nearest neighbors which is having a higher energy, these will convert to a NIL forming an extrinsic stacking fault. As I told you, these extrinsic stratum falls has a locally DO<sub>24</sub> HCP base structures. So tungsten and tantalum prefers to occupy these structures. HCP-based structure because in the phase diagram, they have an equilibrium structure of CO<sub>3</sub>W or CO<sub>3</sub>TA.

So, they want to reside on HCP-based structure. Then, they will segregate back to these extrinsic stratum fault and with this, the deformation proceeds by twinning process. That is why you will get a aluminium depleted region, aluminium enriched region and whatever the atom probe tomogram has able to capture it, it is at the intermediate stage where these composition fluctuations are going to happen. So, this is how we have modified the coal-based mechanism by an additional reordering step, which is an aluminum-aluminum low energy CSF formation from aluminum tungsten and titanium.

So, this I talked about the intermediate temperature. Now, if you go for high temperature at 1000 degrees Celsius, which they have a nearest neighbor violation and higher energy. These, during and after creep deformation, you can see that these gamma prime precipitates have been sheared by these antiphase boundaries, okay? And even at the gamma-gamma prime interfaces, we see a large amount of dislocation network, okay? These antiphase boundaries are typically bent if you observe them in the cubic 001 directions.

And if you clearly see in the high-angle annular dark-field image, you can see there is a significant change in the Z-contrast across these antiphase boundaries. If you take high-resolution microscopy, these antiphase boundaries are actually a disordered gamma phase. of a structure, correct? The effect is shown from APB and gamma prime; you can easily see that these are disordered structures. If you take a composition profile in TEM, you can see that we actually observe a slight enrichment of rhenium and all these antiphase quantities.

So, what Akshat did is he performed tomography at the interfaces, and at the interfaces, he located these interface groups which correspond to the interfacial dislocations, okay? And if you take the composition profile across these groups, you can see there is an enrichment of rhenium, molybdenum, and also tungsten at the interface. This shows that if this particular dislocation If given enough time, it can shear the gamma prime, and these rhenium, molybdenum, and tungsten might possibly drag this dislocation.

Based on this, what we found is we were able to capture antiphase boundaries in the atom probe, where this is the planar feature, and if you take the composition profile across this

planar feature, we see that the molybdenum, rhenium, and tungsten, which we observed at the interface, were significantly segregated along this APB plate. It shows that during creep deformation, high temperature along with the rhenium, molybdenum, tungsten, and hafnium play a very important role.

Interestingly, if you take the hafnium profile, usually now hafnium is in the alloys around 0.1 to 0.2 percent and nowadays in the latest generation of alloys, the hafnium content has increased up to 0.3. So, The literature doesn't talk about hafnium, but it was shown that the creep properties are enhanced by the addition of hafnium. So, this time we have shown for the first time that hafnium actually drags the dislocation during

the formation of APB antiphase boundaries while shearing the gamma prime precipitates. So, this shows that hafnium plays a very crucial role in high-temperature creep deformation. Okay, so based on these two data sets, which are at intermediate temperature and high temperature, we got to know that at intermediate temperature, the creep rate-limiting solutes are tungsten and tantalum. Okay, and at high temperature, the creep rate-limiting steps are tungsten, molybdenum, and hafnium, other than rhenium.

Okay, whether we can do the alloy design based on these solute segregation phenomena which are happening. So, the next part was to explore how we can modify the composition of CMX4 by replacing the rhenium with the segregating solutes. It is expected that by reducing the rhenium, the creep properties will definitely deteriorate. Based on this, my two students, Shashi and Poonam, designed two alloys: CMX4W and CMX4WT. Okay.

And here are the creep plots. which shows the difference in creep with time, okay? This is the creep strain, and this is the time. As you see, for the CMX4 base alloy, within 10 hours, the creep strain reached 3%, and the sample fractured. It means the creep rate is very high for this particular ideal CMX4 alloy, a polycrystalline alloy, okay?

But with the addition of tungsten, CMX4W, which is a B1 alloy, the creep life increased up to 40 hours, and the creep strain reached 5% with a lower creep rate. Now, if you add tungsten and tantalum with the replacement of rhenium by 1.5 weight percentage, the B2 alloy did not fail; it fractured after 145 hours. And it even shows only 3% strain without

fracturing. So, this shows how compositional analysis across defect features can be used to fine-tune the composition to reach a reduced

uranium content while achieving good creep properties. Okay. So, for these alloys, we now have detailed microscopy and tomography underway, which will be published soon. With this, I will end my talk. I have shown how atom probe tomography can be used to understand solute-defect interactions,

and how deformation mechanisms can be revealed. I have also shown that we have proposed a modified cold work mechanism by using an additional step of reordering during creep at intermediate temperatures. And also, based on the segregation behavior, we have reduced the uranium content by almost 1.58 percent. Okay. And we can come up with a composition that

as per the solute segregation behavior with improved creep properties. I hope that you have understood this last lecture where Akshat has shown how we can replace the rhenium with tantalum and tungsten, with a higher amount of tungsten and tantalum, to get better creep properties without affecting the lower density, lower mass density, and cost. And this is the last class. I hope all the students, faculty, or industry experts who have listened to these lectures have gone through and have got

basic idea about the use of atom probe tomography I have not gone into detail in electron microscopy basics and also scanning electron microscopy because okay I hope now you understand what Akshat has Okay, so I hope you have understood the basic crux of this work, where we have replaced the tungsten and rhenium with tungsten and tantalum. The main thing is the use of atom probe tomography and electron microscopy to get the structure and chemistry of these defects and how these defects are correlated with the diffusivity of these solutes. So this is the last class, and I hope all the students, faculty, and industry experts who are attending have enjoyed this course.

And I hope you got a feeling of how these techniques can be used in a correlative way to understand better mechanisms, especially in metallurgy and structural materials. These have huge implications on semiconductor industries, even though I have not covered some examples because there are several works, correlative works, which are very

important to understand the semiconductors, especially the interfaces. With this, I will end this course now, and I thank NPTEL provides a great platform where this course was executed successfully.

We have also given a brief introduction to the practicals of sample loading in atom probe tomography, as well as FIB preparation, which is crucial for any student using FIBs for sample preparation. With this, I thank you all for listening to me throughout this course. Goodbye.