Advanced Material Characterization by Atom Probe Tomography and ElectronMicroscopy

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Week-12

Lecture-45

Welcome to this class. In the last class, I briefly went through the application of APT and transmission Kikuchi on the grain boundaries and how the structural and chemical information is used to identify the root cause of the mechanical properties or the corrosion properties. Now we will go further. into the details of the defects, which are very important during the creep deformation of high-temperature alloys. Coming back to the application of atom probe tomography and electron microscopy.

So now, I will briefly go through the electron channeling contrast imaging of the defects from the bulk samples, site-specific specimen preparations and using conventional and high-resolution TEM, as well as the use of atom probe tomography to get the segregation effects. So here, I will briefly give you an example of a superalloy. So, this is a turbine engine, and this turbine engine usually provides the main thrust for the aircraft and airplanes. It has a certain cross-section consisting of an air inlet, compression, combustion, and exhaust.

The air inlet allows air to enter, which is compressed under high pressure. When it reaches the combustion zone, there will be ignition of the fuel, and due to this, the combination of air and fuel will cause the temperature to rise up to 1500 degrees Celsius, resulting in a large amount of heat and pressure at the components in the combustion zone and the exhaust zone. Usually, the materials used for the components of this combustion zone are called nickel-based superalloys, and they are used in the form of single crystals.

So, usually, they avoid using the grain boundaries because grain boundaries are the major source of creep deformation at high temperatures. So, these are a special class of materials called superalloys. They break down after a certain service life, and this breakdown happens due to a certain amount of stress and strain accumulation and defects. If these defects increase beyond a certain critical value, then failure takes place.

So, to understand these defects, it is very crucial to understand the nature of these defects so that we can control over the service life of these super alloys because during creep deformation, these defects are present throughout the microstructure, okay. So, typically super alloy microstructure, there is a cuboidal gamma prime phase, the bright lines corresponds to the gamma phase and these gamma prime precipitates are the L1 to ordered precipitates. If you take a composition profile across the gamma-gamma prime, you can see at the gamma phase, there is an enrichment of cobalt, chromium, rhenium and tungsten and partitioning.

And while in the gamma prime, there is an enrichment of aluminium, titanium, tantalum and niopium. This shows that these green color, aluminum, titanium, tantalum, niobium are the gamma prime stabilizers, correct? And as a cobalt, chromium, rhenium tungsten are the gamma stabilizers, okay, across the interface, fine? So, you have a compositional partitioning between the two phases and the volume fraction of these gamma prime is usually kept at 65 to 75 percent, okay, to get the both high temperature and the room temperature strengthening properties.

Now, we will go to the basics related to the defects present in these structures. Now, this is an FCC gamma-disordered unit cell. Here, All the elements are in the solid solution and occupy both 0, 0, 0 positions and also half-half 0 positions. But in the L12 gamma prime, this is an ordered FCC-based L12 structure.

0, 0 positions are occupied by one set of atoms, and half-half 0 positions are occupied by another set of atoms. Usually, aluminum, titanium, niobium, and tantalum occupy the 0, 0, 0 positions, while cobalt, iron, or cobalt, nickel, chromium occupy the FCC half-half 0 positions. So, in any unit cell, there is a vector called the Burgers vector, and for FCC, the perfect Burgers dislocation is a/2 $\langle 1\ \bar{1}\ 0\rangle$. This is defined as the smallest vector from one lattice point to another lattice point where shear can occur. Okay, this is the smallest vector where one atom can transport to another atom.

This is called a/2 $\langle \bar{1}\,\bar{1}\,0 \rangle$. But in the case of an ordered lattice, this is not the smallest vector. The smallest vector is from this position to another lattice position of 0, 0, 0. So, it means that $\langle 1\,\bar{1}\,0 \rangle$ is the smallest lattice vector for the L12 gamma prime. However, you can see that the a/2 $\langle 1\,\bar{1}\,0 \rangle$ from the red to this golden-color atom half-half 0 position—this vector is called a superpartial dislocation. So, the perfect dislocation in FCC gamma is a superpartial dislocation in the ordered gamma prime unit cell.

Due to this ordered nature, it produces different types of defects on the 111 plane. So, this is your top view of the 111 plane, and you can see that the black corresponds to A and the the white color, the uncolored, corresponds to B, and different sizes of these circles correspond to the positions A, B, and C, okay? And these are the different directions projected on the triple one plane, and based on the direction of movement of the dislocation, you will get different types of stacking faults or planar faults, okay?

So, if you move half 1 bar 0, 1 position, Okay, you can get the anti-phase boundaries, and these have a very high energy of 100 millijoule per meter square because they usually violate nearest neighbors. So, this means the nickel-aluminum bonds are converted to nickel-nickel bonds or aluminum-aluminum bonds. And if the dislocation shears by 2 bar one one dislocation, then these may form intrinsic or extrinsic stacking faults.

Here, there is no nearest neighbor violation, so they have very low energy. So, the propensity of forming these stacking faults will be very high. If they shear by A by 6, 1 bar 1 bar 2, this is a small vector, then it violates the nearest neighbor violation similar to the anti-phase boundaries and has a higher energy, which is around 250 millijoule per meter square. So, depending upon the shearing direction, you will get different types of faults.

And these shearing directions are governed by the temperature and the stress conditions of that particular alloy. With this example, I will give you a multi-component cobalt nickel based super alloy which have been heat treated by these steps and followed by water quenching and this shows a very uniform distribution of gamma prime precipitates in the gamma matrix space. However, if you see after the tensile creep at 850 degree

Celsius with 400 MPa of stress, you can see that These gamma prime cuboidal precipitates converted to a

rafted structure. So, the gamma prime precipitate in the sample gets rafted along a particular direction. So, these are the positive misfit alloys where the gamma prime is a positive lattice misfit. So, if your loading direction is in this direction, your rafting also takes place in the same direction. Okay.

And this is a controlled electron channeling contrast image of the deformed sample, and these gamma prime precipitates are rafted. If you see in these gamma prime precipitates, you can observe that there is an appearance of bright linear features. These bright linear features are nothing but the planar faults in the sample. If you magnify the particular region, you can see that these bright features correspond to different types of variants at different triple one planes. So, this is an ECCI image.

You can see the gamma matrix is dark, gamma prime is relatively brighter, but these features are much brighter than the gamma prime. So, these are in the channeling condition. So, you have made the 002-bar diffracted beam channeled through the sample, and due to the presence of defects, it got Bragg diffracted and produced higher backscattered electrons from those regions. And those electrons are used for imaging purposes, so you will get bright intensity areas at these locations.

Now you have an orientation of this particular grain, so you can map out these crystallographic planes by stereographic projection. If you see, there are four variants of stacking faults: A, B, C, and D, and these A and D are actually showing bright, dark, bright, dark contrast, which is exactly similar to what we see of the bright, dark, bright, dark contrast of the stacking fault in an electron microscope, in a transmission electron microscope. Okay? So, with the stereographic projection, you can actually calculate the angles; for A and D, these are 36 degrees and 38 degrees with the sample surface plane.

Okay, so these are at angles that are cutting through the sample set. That's why you see a bright-dark contrast for A and D. However, B and C are nearly edge-on. You do not see that type of contrast. These are nearly around 80 to 81 degrees from the sample surface.

Okay, so the appearance of these bright straight lines or bright areas inside the gamma prime precipitates are characteristic of the stacking faults.

Now, you have identified these stacking faults. As you know, in the STCI, we can also perform the G.R analysis invisibility criteria, similar to what we do in the transmission electron microscope. So, here the displacement vector is R, which is plus minus 1 by 3, 1, 1, 2. Usually, this displacement vector corresponds to the planar faults. Now, you know the stereographic projection of that particular plane.

Actually, you can perform the G dot R analysis at different vectors by ECCI. So, as I explained to you, the Z and the X, you can actually get the X and Z values where you can tilt, you can reorient your Kikuchi pattern such that your G vectors are in the Bragg's condition. So, in 1 bar 1 1 condition, you can see that the B is invisible. In 1 bar 1 1 bar condition, you can see that C is invisible. In 2 bar 2 0 condition, you can see that both A and D are invisible, right?

So, this is exactly the same in TEM, where we can perform the G dot R analysis. Now, we have identified the location. So, what we do is prepare a needle specimen from this particular region where we can cover the C-type stacking fault. We made that needle specimen by in-plane lift-out. You can see that this is the bright-field image of that atom probe needle.

You can see that most of the electrons are transmitted across the sample. Okay, so this is the bright-field image, and it is near the 110 direction. However, due to the presence of the stacking fault, you can see that—or due to the presence of a stacking fault—these electrons get diffracted. Okay, and due to this, you will see a dark contrast, and these dark contrast linear features correspond to the stacking faults.

Now, you are in it—you are in—this is your, this is in the bright-field mode in the TEM. Now, the same analysis can be performed—the g·R analysis—in TEM also. And you can see that in the condition of 1 bar, 1 bar, 1, 1 bar, you can see that both faults become invisible. It means that if you compare it with the bulk analysis, this particular fault corresponds to the C variant of the stacking fault. And you can claim on which triple one plane it is localized or present.

Okay, so you can actually use both TEM and atom probe. They can be used to identify the crystallographic nature of these faults. Now, you have a needle specimen with a stacking fault. You can go to the high-resolution microscope and see this is a HAADF contrast image. As I told you, this is a high-angle annular dark-field image where the brighter areas correspond to high-Z elements.

Okay, it means that the electron beam is scattered at a greater angle in those areas. If you magnify these regions, you can see these are the atomic columns taken along the 110 cubic direction. And you can easily see that at the fault plane, there is an increased intensity. which corresponds to more scattering by a larger scattering angle. And that is why you will get a strong signal in the dark field, high-angle annular dark field detector.

And it shows that heavy elements might segregate there. So, there is a hint of that. If you examine the structure of these stacking faults, you can see these atomic columns, and in this region, there is a change in the sequence of the atomic structure. So if you map the ACB, ACB, you can see there is a missing A plane at this location, and this missing A plane indicates an intrinsic fault within the L12 unit cell.

That's why these are called superlattice intrinsic stacking faults, or SISF. The structure of SISF is called the DO19 structure, which is an HCP-based structure and is coherent with the surrounding L12 unit cell. If you take the intensity profile across this structure, you can see that the intensity increases. This suggests that heavy elements in the sample may segregate at these stacking faults. Now, you have a complete structural analysis of one particular fault.

Okay, this is a schematic to show the presence of the DO-19 structure. Now, with the same tip needle specimen, we did the field evaporation, and you can see the distribution of cobalt atoms. If you draw a chromium isosurface, you can see there is a linear feature. at the same location where there is a stacking fault. Now, this linear feature—if you concentrate on the region near the linear feature and plot a two-dimensional composition plot in YZ, XZ, and also in the YX plane, and project it on cube planes, you can see that there is a continuous depletion of aluminum.

and which exactly stops at this linear feature. If you visualize, this is nothing but a stacking fault which exactly stops at the partial defect. So there is a partial dislocation, and there is a stacking fault behind the partial dislocation. So this is the first time we have shown that the chemistry of the stacking fault and the partial defect is different. So here, this linear defect is a partial defect which is chromium-enriched, while the stacking fault is aluminum-depleted.

Now you have a complete picture of the three-dimensional composition analysis of this particular defect. If you do the YZ projection of the chromium atoms, you can see that the chromium atoms are enriched at the partial defect. So, these are nothing but the Cottrell atmospheres. So, in textbooks, we must have learned that the solute segregation to the dislocations is called Cottrell atmospheres. They are responsible for the drag effect of those dislocations.

If you see the stacking fault plane, you can see there is an aluminum deficiency along the plane. And this aluminum deficiency along the plane is nothing but Suzuki segregation. Okay. And Suzuki segregation corresponds to the stacking fault. Fine. So, we have evidence of both Cottrell atmosphere and Suzuki segregation, and the composition of these features is different, which was not known before.

Now, based on the composition profiles, what we propose is a new type of deformation mechanism which is happening here. So, here is an example of gamma and gamma prime. Okay. Gamma is a disordered lattice. Gamma prime is an ordered lattice.

These are the triple one planes. And if the dislocations come near the gamma-gamma prime interface, they can actually shear the gamma prime precipitates. This is due to the application of temperature and stress conditions. Correct. Once these dislocations shear, what will happen?

It will develop a quadral atmosphere around the partial defect, which we see as chromium segregation. If you take the composition profile, you can see that both chromium and cobalt are segregated while nickel and aluminum are depleted. If stress is applied further with time and at high temperature, this partial defect will shear further and transform the L1-2 structure behind into a DO-19 SISF structure. This DO19 SISF structure is an

HCP-based ordered structure in the sample. This has a certain different composition other than the linear defect.

Now, if you take a composition profile across this particular SISF structure, you can see that there is a depletion of aluminum and enrichment of cobalt and tungsten while the nickel content So, here there is a Tungsten enrichment shows that it usually tries to transform to Co3W, which has a DO19 structure. The bright contrast in a HADAP image corresponds to the tungsten segregation, which is a heavy element—a high-Z element—compared to other elements present in the alloy. Interestingly, if you know the three-dimensional composition profile, we took a composition profile along the plane.

Along the plane, you can see that at the partial dislocation where chromium is enriched, aluminum is depleted, but aluminum is enriched just ahead of the partial dislocation. There is also an increase in the nickel concentration. It shows that the diffusion of solutes plays a very important role, and what is happening is due to the applied stress. As per the applied stress, as the resultant applied stress on the triple one plane, the diffusion of solutes is happening in the plane, okay. So, with this, we

the enrichment of aluminum ahead of the partial, we show that tungsten and cobalt diffuse towards the DO19 phase from the adjoining gamma prime L12 unit cell, while aluminum and nickel actually diffuse towards the gamma prime L12 from the DO19 phase. So, tungsten and cobalt occupy those positions while aluminum and nickel leave those positions. So, this is how we generate a new diffusion mechanism which is operative during the creep deformation of this particular alloy.

Here, tungsten is the rate-limiting solute of this particular alloy, and these defects are continuous or homogeneous across the sample. So, the mechanism of diffusion is happening throughout the cross-section of the sample during creep deformation, and that is why the creep rate-limiting solute is identified as tungsten in this particular alloy. So, The next example is also on a superalloy.

It's a cobalt-nickel-based alloy with aluminum, molybdenum, tantalum, and titanium. These are all directionally solidified, and based on the composition, temperature, and stress conditions, you can see that this alloy can contain different types of defect structures. Fine. So, this particular alloy was directionally solidified along the 001 direction.

This is the cross-sectional collage of an optical image where you can see the dendritic structure. If you take the EBSD map and IPM map, you can see that these are all near the orientation of 001. And this is a typical gamma-gamma prime microstructure with cuboidal precipitates of gamma prime, with a volume fraction of around 72%. This sample was tested at different stress levels and temperatures: 800, 850, and 950 degrees Celsius. These are the creep curves, and the TEM analysis was performed after the creep deformation.

Based on the curves, what we plotted is the minimum strain rate versus stress. So, here what we do is, if you increase the stress levels, you can see that there is a transition in the slope from a lower value to a higher value. For example, at 800, it goes from 3.1 to 6.8. At 850 degrees Celsius, it goes from 2.3 to 7.4, while at 900 degrees Celsius, it goes from 3.2 to 9.5.

So, there is a transition in the slope. This is called the stress exponent, which is n. And with an increase in temperature, you can see that the transition happens at lower stress levels. So, it means that at different stress exponents and temperatures, there are discrete mechanisms that are occurring. We also calculated the activation energy.

So, this is the minimum strain rate versus 1 by T temperature. You can see that at higher stress levels, the activation energy is very high, which is around 400 MPa. At lower stress levels, the activation energy is around 200 MPa. 351.8 kilojoules per mole. So, these are the activation energies.

Now, to identify the deformation mechanism, we selected three samples. One is at lower temperature and high stress conditions, another at low stress and intermediate temperature, and the third at high stress and high temperature conditions. First, we will talk about the lower temperature and high stress, and lower temperature and intermediate stress conditions. Under these conditions, what you see is that the gamma dislocations are not able to shear the gamma prime precipitates. They are actually pinned at the gamma-gamma prime interfaces.

If you take an atom map, from an interface, you can see that there is—this is the gamma phase, this is a gamma frame phase, which is identified by tantalum partitioning—and there is an appearance of a groove. This particular groove indicates that there is pinning of dislocations at the interface. If you take a composition profile across this groove, you can see that there is segregation of molybdenum at the groove. So here, what we learn is that molybdenum solute diffusivity might be the rate-limiting factor for the dislocation climb process, and it has a low-stress region.

If you go for low stress, low temperature, and high stress conditions, you can actually see that these dislocations can shear the gamma prime precipitates. It means that you are seeing the presence of a large amount of extrinsic stacking faults. Again, this is a HAADF image where you can see that there is Z-contrast. The atomic columns are brighter, meaning the intensity is larger compared to the surroundings, and these are coherently embedded with a locally DO24 structure. If you see the composition profile, the EDS profile, you can observe an enrichment of molybdenum and cobalt while depletion of nickel and aluminum, with changes in tantalum and titanium.

Similarly, if you increase the stress levels, you see a large amount of micro-twinning in the samples. Usually, micro-twinning occurs when extrinsic stacking faults act as an embryo for the micro-twinning process, okay? So, we prepared an atom probe needle specimen, and this is the needle specimen. You can identify T1, T2, and T3, okay? This particular sample was field evaporated. After field evaporation, you can see this atomic structure where it is around 17 layers thick, with a twin boundary surrounded by TB1 (twin boundary 1) and twin boundary 2.

The same sample was field evaporated, and we were able to capture TB1. We were not able to capture TB2 because the sample fractured, but you can see that with the isosurface of 7 at% molybdenum isosurface, we can identify this TB1. If you take the composition profile and the two-dimensional projection, you can see there is aluminum depletion while molybdenum is enriched at the twin boundary plane. So, remember when the dislocations are not able to shear, the molybdenum is enriched and pinned at the gamma-gamma prime interface at the dislocation. Once the stress levels increase, the dislocation shears, and you can see that the molybdenum is also segregated along the twinning plane.

Now, coming to the high-temperature and high-stress conditions. Here, we see that a large amount of deformation is happening by antiphase boundaries, and these antiphase boundaries are curved in nature. It means that they are on the triple one plane because of the wrong nearest neighbors; they have a high energy. So, they will transform to the 1 0 0 plane, which is at lower energy. So, there is a curvature-induced antiphase boundary.

If you see the atom probe map, Clearly, as expected, there is a curvature inside the gamma prime precipitates. You can see that the cobalt isosurface shows that these antiphase boundaries are curved in nature, meaning they are actually the transition from the triple one to the 1 0 0 plane. Okay? And you can see that it is also associated with the partial defect. If you take the composition profile across the partial defect and also the antiphase boundaries, you can see that in both regions, the Moly is desegregated.

So, there is a depletion of Moly and enrichment at the antiphase boundaries of gamma prime interfaces. Correct. So, with these conditions—with the three conditions—we see that there are three different types of defect structures with three different types of atomic structure and also the chemistry. And we can conclude that the Moly solute diffusivity plays a very important role and is the rate-limiting creep deformation. Based on that, schematically, we have shown that at low-stress conditions, these dislocations are pinned at the gamma-gamma prime interfaces, and the Moly is enriched along that particular dislocation. And at high-stress conditions, you can see the diffusivity plays a role; diffusion takes place along the path when the gamma prime is sheared by dislocations.

They form antiphase boundaries, stacking faults, and twinning, and they are based on the atomic structure. Usually, the segregation and desegregation of molybdenum happens along the fault planes. Okay, so here is another beautiful example where we predicted the mass transport during creep deformation. You can see this is a grafted gamma-gamma prime microstructure, and if you go for higher magnification, you can see there is a large amount of planar faults which are shearing, appearing to shear these grafted gamma prime structures.

If you do the—we prepare a needle specimen, and you can see that in the needle specimen, you can see the appearance of dark regions which correspond to the gamma pockets. Okay. And near the gamma pockets, you can also see a planar feature which is a gamma prime. A planar feature which corresponds to a stacking fault present in the gamma prime, and this stacking fault shows a bright Z contrast. It shows that there might be an enrichment of a high-Z element.

The same needle specimen—what we did was perform field evaporation and exactly expected these gamma pockets to be cobalt-enriched while the stacking fault is depleted in aluminum. If you take the composition profile, you see that tungsten is enriched along the fault plane, while aluminum is depleted. So the dark regions are found to be cobalt-chromium with respect to the gamma prime and tungsten-tantalum with respect to the gamma phase. Based on this compositional analysis of the gamma pockets, we also introduced the concept of mass transport during

and how this mass transport leads to the rotation of these gamma prime rafted structures along the {111} planes. So, assume that these are the {111} shearing planes. And if you apply compressive stress, you can see that the dislocations will shear along these planes. If you go to higher magnification, you can see that the dislocations can carry the mass. Mass flows from this particular region and transports to the B region, from the A region to the B region.

Similarly, the dislocations carry elemental transport from the C position to the D position. After some time, these two regions will merge. And there will be a continuous flow of these fault planes across the precipitate. And with time, these will develop as raft structures along the triple bond planes and the formation of shear bands during creep deformation. So, this is how we identified the mechanism based on the segregation behavior of these faults.

That are responsible for the transport of solutes from one side to the other side of the rafted structure. Okay. So, with this example, I have shown you the use of electron channeling contrast imaging by FIB, and now what I will do is give you some brief examples of site-specific preparation of FIB samples and the direct use of atom probe tomography to get more information related to the microstructure, okay. So, we will talk about interface segregation.

So, Here you can see that there is an alloy where rhenium is added, and here these are not perfect cuboidal-shaped precipitates. These are round-corner-shaped precipitates. Okay, now, if you do the atom field evaporation, you can see the distribution of rhenium atoms and the niobium atoms. Rhenium is partitioned to the gamma phase, while the niobium is partitioned to the gamma prime phase.

If you take the composition profile, interestingly, what we see is there is an enrichment of moly and rhenium at the interface. This enrichment actually causes a change in the local lattice misfit and may cause the lowering of the lattice misfit. If there is a lowering of the lattice misfit, definitely the coarsening resistance will increase. And if you keep this sample at 50 hours and 1000 hours of exposure, the gamma prime microstructure remains stable. Otherwise, without the rhenium alloy, these gamma prime microstructures phase transform into the equilibrium needle-like specimens or the TCP phases.

Okay. So, Due to the interfacial segregation of rhenium and moly, these microstructures get stabilized even at 900 degrees Celsius for up to 1000 hours of exposure. Similarly, in aluminum alloys, we do novel alloy development. So, usually...

Aluminum copper alloys are the major source of aluminum alloys where the copper forms a theta double prime, theta prime precipitates. These precipitates are room temperature strengthening, but they are very poor in high temperature beyond 200 degree Celsius. So, what we did is we added zirconium, tantalum, and mahafnium. These forms L1 to L3 ZR type precipitates. You can see it and it is governed to a novel two stage heat treatment process where the coupling of copper rich and L1 to press plate takes place.

So here you can see that in the microstructure, the bright plates corresponds to the copper rich and the round press plates corresponds to L3ZR. If you see the hardness curve, presence of zirconium and tantalum, you can see that the hardness does not drop while without zirconium tantalum, the hardness drops drastically. So, this is a HUD off image where you can see that the atomic number contrast as I told you and you can see that these L12 has a zirconium. That is why it is a high atomic number. So, you will get a higher contrast and these are coherent with the aluminum and also the plate precipitates.

This is a three-dimensional view of this particular alloy where you can see that the red color corresponds to the Al3ZR while the plate corresponds to the copper which are actually touching each other. So, means these are heterogeneously nucleated on the copper rich precipitates are heterogeneously nucleated on the prior present Al3ZR precipitates. If you see the interfaces, the coherent interface, you can see there is an enrichment of zirconium at the copper rich precipitates. at the interface of the copper precipitate and the alpha matrix.

This shows that the diffusivity of copper is hindered by the zirconium segregation. Also, at the incoherent interface, you see these bright-colored atomic columns. These correspond to the presence of hafnium and tantalum. That also restricts the growth of the precipitates by the ledge mechanism, and this has a direct consequence on the high-temperature properties where

the high-temperature strength can go up to 250 MPa, while for the 2 to 198 temper, it is around 150 to 160 MPa at 250 degrees Celsius. So, this is how, in correlation with the microscopy and also the tomography, we can get the actual reason for the high-temperature properties. This is another example of interfacial segregation in an aluminum-nickel alloy. Usually, aluminum-silicon cast alloys are used for piston applications in automobiles. But nowadays, due to fuel efficiency requirements, the temperature capability must also increase.

So, what they are doing is they want aluminum-silicon alloy, but it cannot sustain beyond 200 degrees Celsius. So, we are looking—these researchers are looking for an alternative to the aluminum-silicon eutectic alloys. Here, there is a class of alloys which are aluminum-nickel based. Here, it forms a eutectic of alpha aluminum and Al3Ni. But these have very low ductility and low strength, even though they are stable at high temperatures.

To improve the strength, what we did was add zirconium at 0.15 to this eutectic structure, and you can see that this zirconium addition leads to very fine precipitates inside the alpha aluminum. We made the atom probe needle, where we have covered both Al3Ni and the matrix, and you can see that there is a homogeneous distribution of Al3Zr precipitates inside the alpha matrix, and also there is a presence of Al3Ni. If you take the composition profile across the Al3Ni, you can see there is a significant segregation of zirconium. Okay, and this segregation of zirconium stabilizes the interface of alpha aluminum-Al3Ni, lowers the interfacial energy, and stabilizes it at high temperature,

so that you can get a very high-temperature stable and very high yield strength at room temperature, and also higher yield strength than the binary alloy at 250 degrees Celsius, around 200 MPa. Okay, these exceptional mechanical properties are related to the interfacial segregation of zirconium at the interface. I will give you another example of a grain boundary. This is related to the grain.

This is related to the segregation. This is related to the compositional partitioning across the reaction front. So when any alloy is cold-worked and recrystallized, a recrystallization process occurs by the movement of the grain boundary. And if this is a multi-component alloy, there must be a solute transport mechanism across the reaction front, which governs, and actually controls, the driving force for this particular movement.

So, my student Nitin, what he did is, he has taken a multi-component alloy with aluminum content, nickel, cobalt, chromium, and aluminum. where aluminum has a tendency to form L12 precipitates with the nickel-cobalt-chromium matrix. Okay, so these form a lamellar structure. So, the lamellar structure is due to the movement of the grain boundary, and it happens due to discontinuous precipitation. While during the movement of the grain boundary,

And there are also non-recrystallized grains. So, this recrystallized grain, this grain boundary moves further so that this lamellar structure develops during movement. So, this is typically discontinuous precipitation. And he has identified a reaction front where this reaction front goes further and forms a compositional precipitation of the gamma prime precipitates behind the reaction front.

So, he has taken a lamella from this reaction zone. You can see this is a reaction zone, and what is, he has prepared the sample by in-plane lift-out by these regions, okay, on the moly grid. And here he is showing a bright-field and a dark-field image from the reaction front. And here you can see that the bright-field image contains an A grain and a B grain. And if you orient the A grain to a zone axis, you can see that the B grain is out of the zone axis.

It shows that we have actually captured the reaction front with different zone axis values. Now, in the A grain, if you take the diffraction pattern, you can see there is an appearance of L12 spots. Similarly, for the grain at the sea, you can see that the appearance of L12 spots is at a different orientation. He has taken the dark field from these aluminum spots to differentiate between the non-recrystallized grain and the recrystallized grain.

Interestingly, at this location where there is a dark region, if you take the diffraction pattern, there is no superlattice spot. It means that there is a precipitate-free buffer zone which is formed just near the reaction front. If you take a bright-field image which is out of zone, you can see that there is a reaction front. There is a precipitate-free buffer zone, and between the precipitate-free buffer zone and the non-recrystallized grain, there is a boundary called the PFG boundary. The same atom probe needle was field-evaporated.

And as expected, you can see that in region C, there are discontinuous precipitates of L12 order. In non-recrystallized grains also, because of aging, you can see that spherical precipitates appear. But between these two, there is an appearance of a precipitate-free zone ahead of the reaction front. Now you have a three-dimensional composition profile. If you see the profile across the reaction front in the gamma prime, there is a nickel enrichment.

However, if you see the boundary between the PFZ and the non-liquefied grain, you can see that there is a change in composition. If you do the top section, then you can see there is a chromium enrichment. And in between the chromium enrichment, you can clearly see that there is a dissolution of precipitates happening. This dissolution of precipitates is happening exactly at that particular plane. And if you take the composition profile, we see that, similar to the nickel, there is a nickel segregation.

And along the chromium-rich part, you see there is an enrichment of chromium while depletion of nickel, and nickel and cobalt and aluminum are almost the same. Based on these composition profiles, he has also taken the composition profile perpendicular to the reaction front. You can see there is an increase in the nickel and a decrease in the chromium. So, based on the composition profiles, what we did is identify a local solute diffusion mechanism which is happening, and the main controlling factor is the diffusivity of the nickel, because of which there is a formation of a precipitate-free buffer zone.

And the thickness of the zone depends upon the inter-diffusivity of these solutes across the boundary. So, here the nickel diffusivity plays a very important role during the recrystallization of this particular alloy. So, this was revealed by the combined usage of microscopy and tomography. Another example is interesting example is from the Tata Steel where they have provided a ferritic steel which are very prone to the hydrogen embrittlement and in this ferritic steel they can induce the carbide precipitation.

And it was shown in the literature that the carbides are prone to being trapping sites for hydrogen or deuterium. But they don't know whether hydrogen or deuterium is trapped at the carbides or at the interface, so they have given this sample. These are the precipitates that are present. This is the dark field image, and you can see the appearance of these precipitates. This particular sample is charged chemically. By the D2SO4 deuterium charging, where the deuterium diffuses into the matrix. And due to the presence of ferrite and precipitates—actually, wherever the precipitates are present, which are niobium carbide precipitates—

deuterium is partitioning to those precipitates inside the unit cell. Okay? So, this is how they have identified that niobium carbides are effective for the trapping of deuterium. And based on this, they can actually improve the processing such that the volume fraction of these precipitates increases, so that they can trap more and more deuterium, thereby preventing or increasing resistance to the hydrogen embrittlement effect. Okay. With this, what I have shown till now are several examples related to defects, grain boundaries during recrystallization,

and also deuterium trapping or hydrogen trapping on the precipitates. And these are not only related to structural materials. These microstructural features are also responsible for the properties of magnetic alloys, bond codes, etc. Aluminium-based alloys, okay? Even functional materials. So, the interfaces play a very crucial role in the structure and the chemistry.

So with this, what we get to know is that the structure and chemistry are interrelated. Depending upon the local structure, the composition may change, and the diffusivity of those solutes—the rate-limiting solutes—governs the overall properties of the alloy, okay. So, with this, I will end this class now, okay, and I hope that you have got a good picture of how to use electron microscopy and tomography for this analysis. Thank you very much.