## **Advanced Materials and Processes Prof. Jayanta Das Department of Metallurgical and Materials Science Engineering Indian Institute of Technology, Kharagpur**

# **Lecture – 33 Superalloys (Contd.)**

Welcome to NPTEL: myself Dr. Jayanta Das from Department of Metallurgical and Materials Engineering IIT, Kharagpur. I will be teaching you Advance Materials and Processes.

Last two classes, we have started our discussion on nickel base superalloys. Along this direction, we tried to explore the various microstructures that are available in these superalloys, and we have seen that from a different type of strengthening mechanism that are available in these nickel base superalloys. So, today will be discussing on the physical metallurgy in terms of microstructure and property relationship in this nickel base superalloys.

(Refer Slide Time: 01:13)



So, if we like to see the wide range of microstructural constituents that are possible in nickel base superalloys; they are like from the left hand side we have a FCC γ-nickel matrix. Where there are different elements which causes solid solution strengthening.

Now, here the dark color region is the  $\gamma$ -nickel phase with some other alloying elements and these precipitates, in case of nickel base superalloys, are  $\gamma$ -phase. So,  $\gamma$  is a Ni<sub>3</sub>Al phase. Now if we consider the strengthening by precipitate, so, there are two different type of precipitation strengthening in nickel base superalloys. As I said earlier, one is the γˊ phase which is Ni<sub>3</sub>Al, another is  $\gamma$ <sup>''</sup>phase which is Ni<sub>3</sub>Nb phase.

So, in one case, it is an ordered FCC structure which is called as  $L1_0$  and Ni<sub>3</sub>Nb is D0<sub>22</sub>. Specifically, in case of nickel base superalloys, we only get Ni<sub>3</sub>Al. However, if it is ironnickel superalloys, let us say Inconel series where a substantial amount of iron is present inside, we get this γˊˊphase, which is an ordered BCT; Body Centered Tetragonal structure.

Now, here you can look at the structure of these Ni3Al here this is an ordered FCC structure means the position of the atoms are fixed. Here, this empty bubbles represents aluminium which is sitting at the corner of the cell and all the face centered positions are occupied by nickel atoms. However, very close to its melting temperature  $\gamma'$  phase means Ni<sub>3</sub>Al become disordered.

So, any position either nickel or at aluminium can be found. So this is a typical Ni<sub>3</sub>Al structure. In case of Ni3Al phase here we get an ordered body centered tetragonal structure.



(Refer Slide Time: 04:06)

And these are the position of the niobium atom which is the corner of the cell. The nickel atoms are sitting at the face center positions and this cell is quite large. And definitely there is a body center atom and body centering translation. So, this is a body centered tetragonal structure.

Besides precipitation hardening, I also explained about the grain boundary precipitate which causes grain boundary strengthening. Because at elevated temperature any grain will try to grow because of the diffusion of the atoms and some specific carbide and boride helps to stop that, which assist nickel base superalloys to survive at higher temperature.

Here, MC stand for a Metal Carbide and this represents the stoichiometric of the compound  $M_6C$  or  $M_{23}C$  and  $M_7C_3$ . These are the stoichiometry, where M stands for chromium or molybdenum or titanium or tantalum or hafnium. So, these are the possibilities.

There are also some borides, which have a stoichiometry of 3-2, let say  $M_3B_2$  and they usually appear at the grain boundary region of the nickel base superalloys. Here you can see these are the precipitate of  $\gamma'$  or let say  $\gamma'$  phase. So, here these are the precipitate at the grain boundary region.

However, these two type of phases which are very much important in case of enhancing the high temperature properties of the nickel base superalloys. Now, there are also some undesired phases evolved due to improper composition selection or some sort of heat treatment of the alloy.

So, these are that topologically close pack phases, we call it as  $A_xB_y$ , this represents that A and B are two different elements and x and y are their stoichiometry. So, these are topologically close packed phases and they are very much undesirable and they mostly from at the grain boundary and causes cracking during service life. So, due to improper selection of these elements like chromium, molybdenum, tungsten, rhenium, if the stoichiometry is not proper, then instead of forming any carbide or going into the solid solution or going to the precipitate they form this kind of new phases or sigma phases.

So, one should be careful of selecting an alloy composition and proper treatment to avoid the topologically close packed phases which deteriorate the properties of the nickel base superalloys. So, these are the wide range of microstructural constituents that are possible in nickel base superalloys.

## (Refer Slide Time: 07:27)



Now, specifically if we look at the  $\gamma'$  phase, what is the role of aluminium that always comes to our mind? Why we are so interested about aluminium? Is it only because aluminium form alumina scale, is it the only thing? However, if you look at the formation of the enthalpy of nickel and aluminium you can observe some interesting things.

So, let us have a look at the diagram here which is represented here with the X-axis with atomic fraction of aluminium and here is the enthalpy of formation of various phases. So, the dotted line represents the  $\gamma$  nickel solid solution phase. And the solid line is joining different stoichiometry compound that formed in nickel aluminium systems. The first one is of our interest that is the  $\gamma'$  phase-Ni<sub>3</sub>Al.

Now there is a binary composition aluminium nickel. You can see that up to 0.2 and close to that, the formation enthalpy of the solid solution phase is preferred and whereas, just beyond this composition range the  $\gamma'$ -Ni<sub>3</sub>Al phase is preferred.

Now, if we consider that if we add an aluminium to a nickel lattice, whether nickelaluminium bonds are more preferred or aluminium-aluminium bond is more preferred or nickel-nickel bond is preferred? So, in that case you will find that inside that crystal structure nickel-aluminium bonds are more preferred than the nickel-nickel or aluminiumaluminium bonds.

Therefore, there is a very strong degree of chemical ordering displayed by this nickel and aluminium system. So, this is the nickel side and this is the aluminium side. Now, on the other hand, there is a complete mutual solubility is expected because nickel has FCC structure and aluminium also have a FCC structure.

So, we should have a complete range of solid solubility, but it is not in reality. Because they form a wide range of different compounds. And there is some sort of a directionality of the bonding even though they are metallic, but because of this little directional nature of the bonding and covalent bonding.

So, many stoichiometry compounds exist in case of nickel-aluminium system. But, we try to understand the role of aluminium in the  $\gamma'$  phase.

(Refer Slide Time: 10:32)



Now, if you look at the composition of these nickel base superalloys, many different alloying elements has been added so far. Now, let us think about what are the addition of the different alloying elements like cobalt. Cobalt is always alloyed with the nickel and chromium is here molybdenum and tungsten etc.

So, now we should not consider only on nickel-aluminium, but we can call it as a NiAlX, X is basically one of this metal. So, one can always ask if we add a ternary element to a to a system whether that will go into the solid solution or it will go to the precipitate or it will from some other phase. What will determine? So, we can have a look at the ternary phase diagram that will be very much useful and what are the individual role of this elements. Now we can simply think about the 3 cases. So, let us say a cobalt and platinum, if we consider this 2 element they basically expand this  $\gamma'$  phase field parallel to nickel X. What does it mean?

Let us say here, I had nickel on one of the side and here this is the X and in this side aluminium is going to increase. So, please try to read the ternary phase diagram. if you go from this side to this side then basically nickel atoms are replaced by X. So, if you look at cobalt and platinum, so, the phase field of the  $\gamma'$  phase which is sitting at the Ni3Al. So, that means basically around 25 % aluminium is here, because if you look at the atom ratio. Now from here it basically expands to this direction.

(Refer Slide Time: 13:03)



So, the cobalt platinum and also copper they basically extend this phase field towards a direction of the nickel and X this side. So, it is simply said that the aluminium concentration or addition of cobalt and platinum do not replace the aluminium. Now, if you look at titanium and tantalum what I want to mean that this set of elements if you see they expand these phase field of  $\gamma'$  towards aluminium X axis. So, here this is the aluminium and X-axis and nickel remains constant.

So, if we add indium and tin and tantalum and vanadium and titanium, they will replace aluminium. So, this is very straight forward matter. Now look at the chromium iron and manganese. So, let us say the elements lying here in this region, they usually show some sort of mixed behavior. Now we can understand that these are the element if we add then simply it will go to this a  $\gamma'$  phase and they will extend the phase field. So, they have some solubility in the  $\gamma'$  phase and you can see this is a quite a heavy amount something around 32-40 % solubility existing here. In case of these set of element it has something like 22 to 23 %.

Now, there are also some other behavior we should see because if we add an element and if it reduces the melting temperature of the hard intermetallic phase. Then also it is not useful for making a good alloy. So, this  $\gamma$ -phase ordering and their ordering temperature decreases. That means if you look at the pure Ni3Al phase. They have an ordering and order disorder transformation temperature which is very close to the liquidus temperature. So, there is very little gap. So, from let us say something like 1375 °C to close to 1400 °C.

Now, I like to show the case of iron, it basically makes the ordered phase as a disorder phase and decreases the ordering temperature. So, here I have an ordered phase and here I have a disordered phase. So, ordered phase is preferred because we will see later on they are quiet linked with the strength of that particular precipitate.

(Refer Slide Time: 16:23)



Now, let us look at some other aspect of this  $\gamma$ -phase. If we keep on adding element to a  $\gamma'$  means Ni<sub>3</sub>Al, we expect that the lattice parameter will change. And if lattice parameter changes then definitely there will be a difference between the lattice parameter of the matrix γ-nickel phase and the order  $γ$ -phase.

So, we can mathematically calculate and experimentally we can also estimate the amount of the mismatch. So, here this is represented by the δ. where

$$
\delta = 2 \times \left[ \frac{a_{\gamma'} - a_{\gamma}}{a_{\gamma'} + a_{\gamma}} \right]
$$

a is lattice parameter of the  $\gamma'$  phase and γ-nickel matrix.

So, this particular solid solution phase means the γ-nickel phase shows a greater sensitivity to the solute if you take a solid solution. If you keep on adding different alloying element, then the lattice parameter will change. However, the lattice misfit, which depends basically on 2 different parameters therefore, because if we add a ternary alloying element then there will be a partitioning. So, it will prefer either to go to a γ-nickel phase or to  $γ$  phase. So, the partitioning of the solute between the γ-nickel and  $\gamma'$  phase. Now influence of a particular solute on the lattice parameter that is a defined by the Vegard's law that how much percentage of the solute or concentration of other alloying element to with the change of the lattice parameter that basically explain the Vegard's law.

So, now we can also look at the coarsening of the  $\gamma'$  phase that loose the coherency and increases the misfit. What I want to mean that if you look at the microstructure, if you look at the morphology of this γˊ phase, we can get a rough estimate whether the lattice misfit has increased or decreased. Means, if you look at these 100 projection of a  $\gamma'$  phase, in a  $γ$ -nickel matrix this is  $γ$  phase in a gamma matrix. Then if it is circular then misfit strain or lattice misfit is less, but if lattice misfit increases they will tend to make a cuboidal type of shape and this is something very much interesting to notice.

So, the degree of ageing if you increase then the lattice misfit is also increases. This is just a (111) projection of the same particle from a different direction. So, if we increase the degree of ageing in a nickel base superalloy then lattice misfit will also increase. And we must think about why this lattice misfit is linked with the strength of a particle, because we all know the strengthening mechanism.

### (Refer Slide Time: 19:57)



So, there are many different type of defect also available in this  $\gamma'$  phase. So, definitely point defect will arise and it depends on the temperature of the application. However, stacking fault is one of the very important major defect in  $\gamma$  matrix also. So, in case of  $\gamma$ matrix we find that the for high temperature application this stacking fault energy is one of the important consideration because of the screw portion of a perfect dislocation.

They are dissociated into the Shockley partials and must constrict locally if they are to cross slip and this is a very common mechanism which obstacle such a precipitate can be circumvented. It means that a widely spaced partial arising from a low value of  $\gamma$  that basically stacking fault energy are advantages for the high temperature application. If the stacking fault energy basically increases, then the distance between 2 partials will increase. This is a let us say low stacking fault energy example and this is let us say high.

Because they have a higher line tension and so, they can they can attract each other more. And here these are the 2 parameter that is the stacking fault energy value and here is the creep strain rate. So, here these are the diffusivity and shear modulus burgers vector with the temperature and here we have the shear modulus and the burgers vector. So, aluminium has a higher stacking fault energy, we all know about it and you see that the creep strain rate is also higher. So, this is let us say in case of aluminium and let us say this is in case of copper zinc which has a very low stacking fault energy something like 14 to 18 mJ/m<sup>2</sup>

So, pure nickel is lying here and we add chromium and all other alloying element to reduce the stacking fault energy as well as to reduce the creep strain rate. And this is the purpose of the stacking fault energy in the matrix of the superalloys.



(Refer Slide Time: 22:36)

Now, before going to this precipitation strengthening mechanism, we must try to recapitulate what is possible. So, you must have heard about that 2 different type of concept or particle nature that people considered like a particle reinforcing. In a matrix there are two different feature either it is deformable particle or it is a non-deformable particle. If it is a deformable particle, then the strengthening arises due to coherency or let us a misfit strain and due to stacking fault energy, due to ordered structure, due to modulus effect because dislocation if it has to pass through a lattice. And let us say like a GP zone.

So, coherent precipitate basically fluctuates the local strain field because of the modulus fluctuations and interfacial energy and morphology and also the lattice friction stresses. So, due to all these effect basically a deforming particle strengthen an alloy. However, in case of oxide nitride or other borides if these are ceramic nature particle which are considered as a non-deforming particles, there we know about mechanism by bypassing and we have a very typical an equation that says that the stress is linked with the spacing between the particle.

So, if the spacing is higher the increment of the stress will be less. However, if the spacing is very close then we can increase the strength. So, here this is a burgers vector and let us say g is a shear modulus. In case of a deforming particle, the strengthening is linked with the anti-phase boundary energy.

(Refer Slide Time: 24:40)



Now, if we consider specifically for an order structure. Let says this is an example of an ordered structure where we have a-type of atom b-type of atom. And then you see that this is a boundary between an anti-phase means here I have another b and then I have a.

So, this is a boundary between let us say a phase and an anti-phase. So, this anti-phase boundary energy is important because if one dislocation passes through this phase then we need another dislocation in order to make an anti-phase into the phase. This is the phenomena of phase and anti-phase in an ordered structure. So, in that case when dislocation basically passes a through a particle then we need to consider this mechanism of strengthening, whereas, in case of a non-deforming particle this  $\lambda$  or the spacing between these 2 is rather important.

So, first what will happen, dislocation will obstruct by the particles. And then they will try as the stress will increase and they will leave a loop and then they will bypass the particle.

So, this is typical Orowan mechanism of a widely separated obstacle.

## (Refer Slide Time: 26:07)



Now, very similar situation people have observed in case of a superalloy when we consider  $a \gamma'$ -phase Ni<sub>3</sub>Al strengthening. So, you can see that the dislocation they basically pass and cut through the particles. So, here these are the sheared particle of 140 nm in size and they have almost round like shapes.

So, you understand that the misfit strain is less and now the order strengthening it basically appeared when this dislocation travel into the matrix to form an anti-phase boundary in the  $\gamma'$  phase. These anti-phase boundary is removed by passing another dislocation which was mentioned above. Now, the anti-phase energy represents a barrier which must be overcome if the particle cutting has to occur.

Now, the anti-phase boundary ordered strengthening can reach up to 400 MPa, which is much higher than the strengthening by let us a modulus stacking fault energy, interfacial energy or let us say Orowan mechanism, because of these order nature of the precipitate of this γˊ phase. They provide the much higher strengthening effect than any other kind of mechanism. However, if I considered a dislocation, the dislocation need basically 2 dislocations to make an anti-phase into a phase as explained above. Now you consider these are the particles and one dislocation passes and then I have anti-phase.

So, I need another dislocation to pass and then only it become a phase. So, if this is a weakly couple dislocation then  $\lambda$  will increase. So, the effective distance between two particle increase. So, strengthening will be less, but in case of a strongly coupled dislocation, the strengthening effect is very high because here  $\lambda$  is smaller. So, you need to consider an effective coupling of the dislocation also. So, here these are just some of the micrograph that says that 8 nm size of pair that gives an effective strengthening.

(Refer Slide Time: 28:39)



Now, very similar situation that I explained above that we have a weakly couple pair. And we have a strongly coupled pair. Now people have measured the increment of strain, and a people observed that the mean particle radius is somewhat in the range of 15 to 20 nm, where we get a more effective strengthening where there is a transition between these 2 different mechanism.

So, a higher level of ordered strengthening can be possible in this  $\gamma'$  phase strengthening.

## (Refer Slide Time: 29:17)



Now, if we considered that temperature dependent strengthening of  $\gamma'$  phase and role of  $\gamma'$ phase we have to see this plot and these are quite interesting plot. Usually if you take any alloy and expose at higher temperature and put some stress on it then the strength of the alloy always decreases with temperature that is already understood.

In case of a  $\gamma'$  phase, you see that these are some single crystals superalloys tension tested around let us say [001] directions where the strength increases; let us say 800 °C. Please remember this temperature and then it decreases. So, there are several example like CMSX series, which is a single crystal superalloy and single crystal means it is basically processing method.

So, people try to understand why this strength increase is coming from whether they are from the matrix or from the  $\gamma'$  phase? To look at they have taken a single crystal Mar alloy and single phase Ni3Al. You can see the increment of the strength is higher in case of single phase Ni<sub>3</sub>Al  $\gamma'$  phase.

### (Refer Slide Time: 30:44)



So, γˊ phase is responsible for such kind of strengthening at higher temperature level. So, this is explained with this Kear Wilsdrof lock that the cross slip segment act as a micro structural lock. Because just a minute ago I explained about anti-phase boundary energy. So, if we have a APB; Anti Phase Boundary, then a dislocation movement is restricted, means if cross slip has to occur they always stick to this anti phase boundary which is behind them and they become immobile. And therefore, we get an increase in the strength of the of a γ-phase.

Now, there are 2 zone, 1 zone here, there is an increase and then there is a decrease why such phenomena occur.

## (Refer Slide Time: 31:41)



Here, I show you one of the schematic that up to 1000 K or let us say something like around 800 °C the dislocation in  $\gamma'$  phase become immobile because of this KW configuration Kear Wilsdrof configuration. So, here these are the dislocation and there is a cross slip and I have a APB here and if has boundary and they become immobile because of this cross slip. So, these are the cuboidal plane and dislocation is moving in the (111) plane.

So, this Kear Wilsdrofs configuration act as a barrier and increases the flow stress; however, above 1000 K, then again you have seen that the stress decreases. So, these stress decrease is linked with that the slip in this cuboidal plane, here these are the cuboidal plane increases means cube planes are activated at higher temperature which are not the primary slip system in a FCC. We all know that (111) are the planes of the major slip system of the FCC at room temperature, but at higher temperature this cube plane activated. And therefore, the flow stress begins to decrease above this temperature. Edge and screw dislocation on the cube plane move without any cross slip and therefore, the effective strengthening from the APB decreases.

So, these are all about the KW configuration. Here also I show you one of the stacking fault and these 2 stacking fault due to 2 different partial. They are lying on this plane of (111) and I have another configuration of this kind of KW lock. So, this is a typical KW lock on a cuboidal plane. So, we can see that there are many different reason and mechanism involved in the strengthening in detail.

Thank you very much. We will continue the discussion in the next class.