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

# **Lecture – 35 Superalloys (Contd.)**

Welcome to NPTEL, myself Dr. Jayanta Das from Department of Metallurgical and Materials Engineering, IIT Kharagpur. I will be teaching you Advanced Materials and Processes. Today we will discuss the superalloys in case of cobalt base and mostly ironnickel base. In the earlier classes we have specifically discussed the nickel base superalloys and it is application. And today we will try to look at what are the benefit or disadvantages of these other superalloys means cobalt base or iron base superalloys, compared with the nickel one.

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So, there are few facts in case of a cobalt base superalloys because, one can always raise a question that cobalt has a hexagonal close pack structure. So, for designing superalloys mostly a matrix of FCC structure is preferred. So, in case of cobalt, we add chromium which stabilize the FCC matrix phase in cobalt base superalloys.

Now if you look at the composition range, you will see the chromium range is very high. So, there are two major type: one is the wrought alloy and another one is the cast alloy. So, wrought alloy was developed earlier and the cast alloys are more advanced alloys. Here also like nickel base superalloys, we add some solid solution strengthening element like molybdenum, tungsten or tantalum.

So, these alloys show quite a large or high amount of addition of tantalum and tungsten as well as molybdenum. However, here also nickel is added for the solid solution purpose and the strengthening effect mostly generated due to the presence of carbides. So, the cast alloys are mostly strengthened by the carbides and to form carbides we need consideration of adding carbon here.

So, please have a look at the carbon concentration here 0.3, 0.5, and 0.45, it will easily form some carbide with the refractory metals. Now niobium is one of the good refractory metal to form carbides and which is also prefer. However, the majority of the cobalt base alloys so far is under use they do not have any  $\gamma'$  phase. So, definitely you expect that if there is no  $\gamma'$  phase so, precipitation hardening is not really available in cobalt base superalloys.

So, strengthening part comes from the carbides or borides and therefore, the strength level of this cobalt base superalloys are relatively low than the nickel base superalloys. However, there are some very good advantages, because we can produce sheets out of these cobalt base superalloys because of their good weldability. And weldability is better because we need not to take care of this  $\gamma'$  phase in the matrix.

So, we apply basically these alloys in case of supercharger buckets and the major disadvantage of these alloys that hot corrosion which is quite severe. And also the cobalt as an element is very expensive in comparison with the nickel. And therefore, a common tendency has been observed that there is some diminishing trend of this use. However, there are some specific areas where we definitely need these cobalt base superalloys. Here one of the very common cobalt base superalloys are Mar M 509.

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In the left hand side, a typical microstructure of cobalt base superalloys is shown. The alloy name is Haynes 25, here you do not see any  $\gamma'$  phase, but what you see here is these kind of precipitates which are  $M_6C$  type of carbides along with some  $A_2B$  or let us say some of these a precipitates are A2B type.

If you compare the properties in terms of rupture strength for 1000 hour, here this is strength in mega Pascal with the temperature. So, if we compare other superalloy with one of the very famous cobalt base superalloy, the strength level is low. However, it can have a quiet a wide temperature ranges and the fall is not so sharp as the other base superalloys. So, this is one of the benefit of let us say the cobalt base superalloys.

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So, the typical application areas in cobalt base superalloys have relatively lower temperature and lower strength level than the nickel base blade alloys. So, like AiResist this is also one of these cobalt base superalloys where we produce sheets of tubing. And gas turbine engine combustors, or the flame holders, liner, some of the ducting. In case of Haynes 25 the microstructure is already shown earlier.

Here GTE combustor liner is often used, where the good formability is one of the property and high strength up to 816 °C is required and oxidation resistance is quite high. So, also for aggressive environment let us say sulfidation or resistance to wear this Haynes 25 is also a good alloy. Now in case of Mar-M 918, this is also another important alloy, where we can produce those kind of high temperature sheets and fasteners springs.

So, cobalt base alloys also occupy a quiet large region of application in gas turbine engine in several other components, where the stress level and temperature level is relatively lower than the disc and the blade application.

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Now, the third category of the superalloys I said those are iron base or let us say nickeliron base superalloys. So, here we need both iron, iron content is very high and nickel must also present there. So, nickel and irons are the main constituents and since nickel and iron has a FCC matrix.

And so, they are very tough and very ductile. So, by just looking at its property you could easily guess that; what are the purpose of using this alloy. So, we can use them in the disc alloy because, the formability is required for making the disc by forging or any kind of pressing operation. However, here besides only  $\gamma$ '-phase the appearance of other γˊˊ-phase has been observed. So, this is the Ni3Nb-type precipitate hardening is observed.

So, we have basically a presence of  $\gamma'$  phase or this  $\gamma''$ -phase. And we add niobium in order to enhance the precipitation of the  $\gamma^{\prime\prime}$  phase. At the same time, the solid solution strengthening element must be added and here too in the cast alloy, we need carbide in order to pin the grain boundaries. So, if you look at this nickel-iron or iron base superalloys, there are two major categories depending on the application areas. One alloy which has a very high strength level and it is used for a specifically precipitation hardened alloy.

So, these are some of the typical series of names of the alloys like Inconel. So, here let us say the iron content is very high and you could easily understand if in an alloy iron content is higher, then we expect a lower cost. So, this is a big advantage of this nickel iron or Inconel alloys. The second types of nickel-iron alloys are used for a low thermal expansion coefficient. Means, I may have a component or let us say a blade which is rotating inside a casing and the gap between casing and the blade has to be reduced. Now temperature will increase, the casing will also increase. So, in that case one should specifically look at a low thermal expansion coefficient so that the gap will be minimum between a blade and a casing.

So, this is a very specific purpose that a smaller clearance between a rotating wheel or a non-rotating component should be considered. So, it basically increases the overall engine efficiency and for this specific purpose we like this nickel-iron base alloys in some specific composition range where it shows a low coefficient of thermal expansion. And this is also a big advantage and since these alloys are very tough and ductile, therefore, we can have a good control over the grain size and the morphology of the microstructural constituents.

So, mostly we use these alloys in wrought or other condition in the form of turbine disc, some of the forged rotors or let us say, some of the compressor blade or in relatively low temperature not like the single crystal nickel base superalloys. But in some areas where we do not need such extremely high one, but formability is the higher priority.



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So, this nickel-iron base superalloys also exist in large composition range. So, I show you some of the composition ranges of various nickel base alloys. Here, there is a series of Incoloy, these are quite a large. And if you have a look at the niobium concentration which is added purposely to get  $\gamma$ <sup>"</sup> phase, the concentration is quite high in several alloys.

Now here the iron content is ranging between 66 let us say to 42 % and even in some cases it reaches to 60. So, the iron content is much higher than the nickel contents. So, if you have a look at these nickel and iron content of the alloy so, please have a look let us say Incoloy 800 H which is also very famous alloy here we have 45 % of iron and 30 % of the nickel.

And then we add some of these refractory metals like molybdenum and tungsten along with some niobium, and here too we need carbon, and boron in order to specifically get some carbide strengthening effect. So, by looking at the composition chart one can easily understand the purpose of the various alloying elements and their role.

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So far we have discussed three major types of superalloys, as I said that one is the iron or nickel-iron base and another one is a nickel one, third one is the cobalt base. So, the advantage and disadvantage if I summarize so far we have discussed the iron base or let us say I would say nickel-iron also because we have a high content of nickel too.

So, they have relatively low cost and a very good workability. So, forming operation is much higher. On the other hand, it has a relatively low environmental resistance and a higher propensity for getting these kinds of TCP phases which are not desired. But since iron is a BCC element, we need the assistance or help of nickel so that nickel goes and stabilizes the face center cubic phase. And therefore, we need the FCC stabilizer.

The typical application areas are the turbine casing and the disk and suitable high toughness application areas are commonly dominated by the Incoloy series. In case of cobalt, we have the highest incipient melting point of pure cobalt. However, here also we have to add some chromium to stabilize the FCC matrix. However, they have also very good corrosion resistance, but there is no strengthening comparable to  $\gamma'$  and  $\gamma''$  phase.

And therefore, we only need actually the carbide and borides in order to strengthen the alloy. However, here also we need a FCC stabilizer, because this is a hexagonal close pack structure. In case of nickel superalloys we have discuss here this forms. Basically, these  $\gamma'$  phases or sometimes  $\gamma''$  phases and there is no requirement of the FCC stabilizer.

And there is always have lower propensity of the TCP phases which is avoided by some sort of ruthenium and other element. So, they have a large application area in case of gas turbine engine, the blades, where there is no other superalloys, which can compete with the nickel base superalloys. So, this the summary of all the different superalloys so far we have discussed.



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And if we look at some of the average composition ranges of various alloying element that I have summarize here where iron base, cobalt base, and nickel base alloys are present. The different alloying element including the ruthenium and aluminium, titanium and chromium are also added. So, the refractory metal and carbide formers are also added in some extent in all these alloy compositions. Whereas, iron content could be in average something like 43 % in case of iron base superalloys. And carbon and boron are all added to get basically the effect of carbide in most of the cases.

So, in general, at the composition ranges, some elements have been preferred for some specific alloy addition and stabilization of some phases. So this is all about the superalloys. However, we further improve the properties of the superalloys by adding some coatings on it. So, in the last week, we were discussing about different types of coating and we apply coating in case of the superalloy blades also. So that the performance of the blade can be enhanced or let us says the failure life of the blade or time to rupture that can be enhanced further.

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And there are three major types of coating that has been developed; one is the diffusion coating, another one is the overlay coating and the third one is the thermal barrier coating. And each of the coating has their own specific purpose. How? If you have a look at the diagram we have plotted here, the relative improvement in the coating life. So, the life increases along this direction and this is the temperature enhancement. So, relative temperature enhancement or increment is in that direction.

So, thermal barrier coating is always better than other coating, you can see in terms of service life. However, we cannot apply thermal barrier coating alone. why? We will discuss later on. However, the question is how this coating looks like and how they are processed? Let us say after finishing of a blade how we put some coatings there.

So, there are some specific advance technique like pack aluminization technique, by which we can produced this diffusion coating. Mostly this diffusion coating is aluminium containing alloys where it is rich with nickel-aluminium and β-phase mostly dominating. So, in the right hand side, one such coating is shown has been developed on a  $\gamma$ - $\gamma'$ matrix.

So, this is  $\gamma$ - $\gamma'$  nickel superalloys and then we have coated aluminide on that like; nickel aluminide by pack aluminization process. Now, if we simply put a coating then it does not give us a good strength in terms of bonding between the coating and the base alloy. So, there is an inter diffusion zone that is beneficial in some way after some heat treatment process.

So, some alloying elements will come here and they will develop basically a diffusion zone or inter diffusion zone. Therefore, it will have a better one. Now the second type of coating; are the overlay coating that we said earlier that MCrAlX So, this is basically a basic composition of this overlay coating. We basically put such coating by APS, APS means, Air Plasma Spray or let us say physical vapor deposition technique. So, these both techniques could be available for producing this overlay coating.

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However here these MCrAlX, here M basically means it could be nickel or cobalt. So, this is also sometimes often called as a bond coat.

So, this bond coats are always preferred below a thermal barrier coating why? We will come, but here I show you one schematic where thermal barrier coating is done on the base alloy in between there is a MCrAl coating.

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So, in case of these X, X basically stands for yttrium or some other elements. Now along the direction of this TBC technique there is a growth of these grains of the thermal barrier coat and here mostly we prefer some zirconium dioxide as a constituent for this thermal barrier coating.

The morphology of the grain structure could be of different types depending on the processing condition. So, it could be columnar type or laminar type. However, there is an oxide film in between this two coating that forms. So, here is a substrate, a substrate means the alloy made of  $\gamma$ - $\gamma'$  phase. And then on the top of it we can give an overlay coating and on the top of it we will go for some sort of thermal barrier coating.

So, here in the blue color the different techniques that are available for preparing this kind of coating is shown. So, electron beam physical vapor deposition is a very common technique for producing thermal barrier coat, but one should remember that, if we take a base alloy then one after another layer to be given and like first we will go for some overlay coating then we will go for thermal barrier coating.

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Now we can think about why a thermal barrier coating has a better life so, why do not we choose only thermal barrier coating, and why we always look at the microstructure that a thermal barrier coating is associated with another bond or overlay coating. So, the problem with thermal barrier coating even though it increases the service life is that the expansion coefficient is very different compared to the base substrate alloy. So, if we take a  $\gamma$ - $\gamma'$  alloy and then if we apply only thermal barrier coating so, let us say this is a thermal barrier coating.

The mismatch between the thermal conductivity and expansion coefficient is very high. And therefore, we need another overlay coating or bond coating in between; so, that we will get a barrier coating. However, thermal barrier coating has the highest thickness. So, purpose here is that the thermal stresses that basically generate during thermal cycling and that leads to the failure of this thermal barrier coating.

And therefore, it basically spalls from the substrate and to get a very good adhesion with the thermal barrier coating and the base substrate we always prefer a bond coat, overlay coat is always preferred and to avoid this kind of a problem, as I said that some form of diffusion or overlay coating must be used.

Now the second question will come that there are so many different ceramic coating we can give as a thermal barrier coating on the top of a superalloy. Why we preferentially choose zirconium dioxide? There is also a reason. Please have a look at this plot. Here I show you a temperature versus thermal conductivity plot and if you look at different ceramic material, alumina, nickel oxide, thorium and beryllium oxide.

The zirconia has a very stable thermal conductivity level on a wide temperature range. This confirm us that there will be less spallation. If thermal conductivity is very uniform over a temperature range, it always gives us a better service life. So, less spallation and less stress will be generated in between the substrate and the coat.



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So, there are a several coating that are commonly used today and you will see it here and a summary of them. So, like these are the manufacturer like general electric GE, Siemens, ABB, and Mitsubishi; there are various model of their turbine engine. And they have the vane and blade and the coating so, let us say Rene and Udimet; let us say Mar D S, these are directionally solidified alloys. And here is also a Mar series, this is directional solidified alloys. Here, you will see that we often use or they often use the thermal barrier coat along with several other kind of overlay coating or let us say bond coating.

So, this is a typical composition of the electron beam physical vapor deposition of MCrAlY type of coating. So, for all these industrial and gas turbines, we have seen the role of various nickel base alloys and their specific purpose and also in competition with cobalt base superalloys, iron base superalloys.

So, this three major category of the superalloys is used. However, for very high temperature application; we preferred not only the development of processing technique like single crystal production by some sort of a directionally solidification and crystal selector use. We also need to apply some coating in order to achieve a better performance of these superalloys.

So, with this we complete the discussion on let us say high temperature material and superalloys. And in the next week we will start a new discussion topic.

Thank you very much.