Advanced Materials and Processes

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

Lecture – 28
Introduction to High Temperature Materials
(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. Last two classes, we have just started our discussion on Introduction to High Temperature Materials. We tried to look at or we have discussed two classes on various aspects of this high temperature materials, means the basic characteristic that are demanded for a material to be exploited as a high temperature or ultra high temperature materials.

And how to improve in terms of alteration of the microstructure, how to improve the high temperature capability of the materials, mostly like alloys, like precipitation strengthening, dispersion strengthening. And today, we would like to see that what are the alloy or material specifically used as high temperature material. And we would like to classify those material from the very beginning days where people try to explore material to be used as higher temperature or elevated temperature. Now, let us have a look at this diagram.

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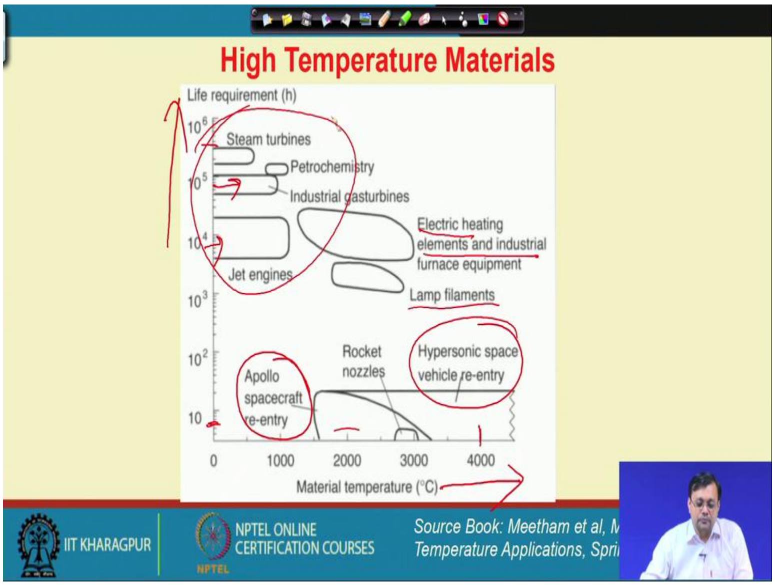

Here, we have plotted the demanded life of a component with the temperature or operating temperature of a material, you can see that around 10^6 hour required for using a steam turbine. Because repetitive times long time duration the steam turbine has to be used, very similar like petrochemical industries or industrial turbines and relatively lower life is expected in a jet engine.

On the other hand, for re-entry space camp, where we use those re-enter vehicles for maximum 1 or 2 times, means those vehicle which goes outside our earth atmosphere, go into the space and again re-enter into our atmosphere with a higher oxygen content and therefore, due to high friction and oxidation on the surface. So there are many other problems due to which we need to develop materials and here maybe maximum 2 or 3 times those similar material can be used. However, for these hypersonic re-entry vehicles he operating temperature is quite high like 4000 °C.

However at the very beginning we would like to start with the material that is exploited for this purpose means we need a very high life for very long time in a petrochemical industry or in a boiler, in a steam engine. So, where we can use or may be some of the heating elements that is used for furnace equipment, so these are like lamp filaments. So these are very important aspect of the material.

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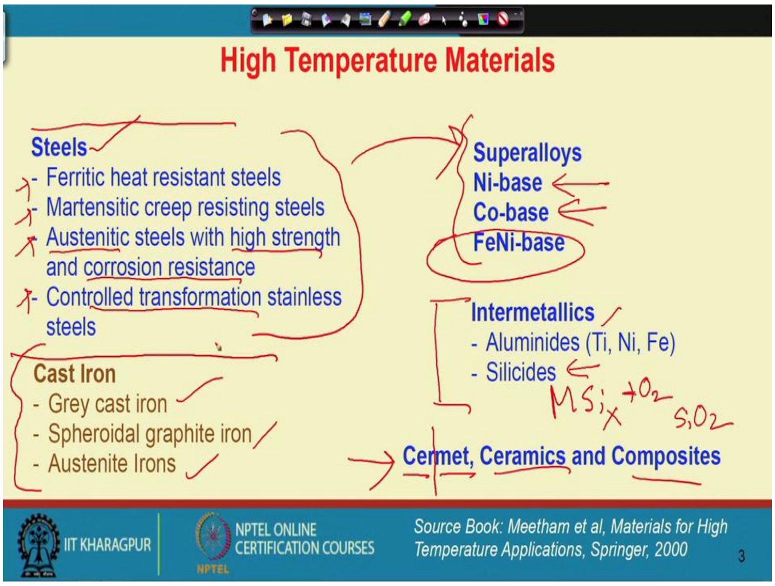

Now, let us see that from a very common alloys how different high temperature alloys has evolved. We all know about steels. So, steel is basically an alloy of iron and carbon; however, the alloyed steels are used for very other important engineering applications. So, here there are four major category of steels that are exploited for let us say the higher temperature application. Like ferritic steels. Ferrtic means basically the microstructure contain ferrite, heat resistant steel, and martensite creep resistance steel, mostly we know here M_S temperature is close to room temperature.

And how we are talking about having a steel to be exploited something like 500 °C in a boiler and the microstructure should contain martensite by alloy addition we can do that, we will discuss today. Now, austenitic steels are very much well known with a high formability and we can refine those microstructure, tune the microstructure to achieve very high strength or in a very aggressive corrosion environment, or some of the steel with some transformation characteristic phase transformation, control transformation steels, there we can use.

On the other hand, for a very long time, use of an internal combustion engine that we all know where the cast irons are used, those are called as nickel hard and so on. High nickel containing cast irons are used, which lets say grey cast iron where friction is very less or spheroidal graphite cast iron or austenite cast irons.

So, cast irons are also used for a quite long time let us say something like 200-300 °C. Now, from a steel to a very advanced alloy like superalloys has been derived for this steam turbine. It does not necessarily mean that steels no longer used means high temperature steels are no longer used, it is used more day by day due to the development of alloy addition and so on. So these are also a class of advanced material along with the supealloys.

So, mostly these nickel base, cobalt base superalloys are often used; however, there are some derivative of iron nickel content superalloys and which are also used for higher temperature. Now, another important aspect here is a use of intermetallic for high temperature application, where titanium, aluminium containing intermetallic, where aluminium has a very low solid solubility or very limited range of solubility we call them as aluminide.

And you can easily understand, what is the purpose of using aluminium containing intermetallic? Because we expect at higher temperature those intermetallic has usually higher melting temperature. It will give us a good strength at elevated temperature. On the other hand aluminium will react with the surface oxygen and form alumina which is expected to provide a good oxidation resistance, so that is basically the purpose. Now, there are some speculative intermetallics people call.

And be more specific these are silicide, means some metal with some silicon containing compounds. So, here silicon and these intermetallics used for like molybdenum di-silicides used as heating element in furnace. And the purpose is that using these silicon containing compounds, if it react with oxygen then we basically get a silicon dioxide which is a glassy nature and protect the surface of those heating element, not only heating element, people are thinking about the silicide to be replacing a component for the superalloys or beyond nickel based superalloys. Along with that the other high temperature materials are like Cermet Cermets you know which is ceramic, 'cer' came from ceramic and metal the met. So, these are the material a like tungsten carbide and other metal matrix and so on are often used or high temperature ceramic and composites.

So, we will go step by step and we will try to look at what are those material which are very much important to discuss in this particular course. So, let us start with the steel which are called as the ferritic steels, so name itself says that the microstructure should contain the ferrite. But before going to that I said that the use are of these high temperature steel one of the large amount of the steels are produced for power plant.

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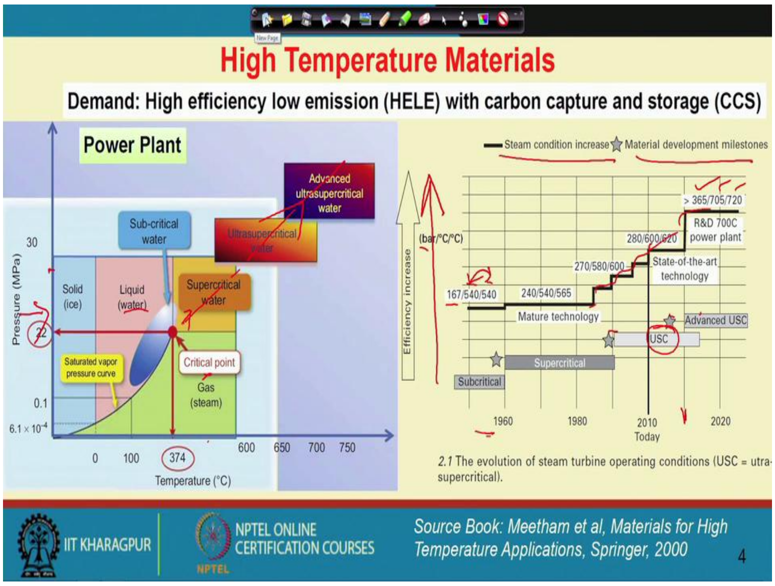

In a power plant what we really do? We basically increase the temperature or above the vaporization temperature and boiling temperature of a water and we use these steams and send it to a turbine which generates the electricity. Now, from our very basic thermodynamic concept, you would realize the more and more higher temperature of the steam, will give us a better and better efficiency of the Carnot cycle, means, we can extract more amount of energy out of that energy input. And on the other hand what will be the benefit of that? If we can extract more energy then we will automatically have for a particular power output lower carbon dioxide content generation.

So, at the very beginning, the demand is basically higher efficiency means Carnot efficiency and lower emission of the carbon dioxide, which is called as HELE. However, these days another supportive technology has been developed in order to reduce the carbon dioxide from the atmosphere which came out of a power plant, so this is called Carbon Capture and Storage, CCS technology.

Now, to understand the mechanism of a power plant, we must look into very basic of the pressure versus temperature diagram of the phase diagram of ice water and steam. And you must have noticed that there are some critical point exist in this diagrams. Please have a look, this is a saturated vapour pressure curve of a solid ice with the gas and this is the liquid and the critical point here is defined as that beyond this temperature, where the water and steam you cannot really distinguish.

So, we have a chance to go into the super critical region where we will get a higher temperature, we need higher pressure. So, if you want to boil water at high temperature you have to input a higher pressure, means the vessel itself should contain higher pressure. So, material should survive such higher pressure, means you in one hand have steam which may corrode the material at the same time you have higher temperature and higher stress.

So, all these three corrosive environment, higher temperature, higher stress all are involved. So in this case a higher corrosion and higher creep resistance steel is required and now the efficiency will increase if you go along this direction. Now, let us have a look from 1961 during this time here are some digits are shown where 167 is basically the pressure in terms of bar and this is the temperature range which is operated. So, we can go into this higher side actually and day by day people develop material to go into higher operating temperature side. So let us say during this time we use mostly the upper or ultra-supercritical critical technology.

So, here the steam condition increases and material development milestones are shown here, where we expect and we need to develop material which can be used as a much higher temperature. So that the efficiency of the Carnot cycle will increase or we can extract more amount of heat or more amount of power or more amount of electricity out of that cycle. So therefore, the demand of the material is very clear at this moment.

Now, to discuss about this material, we need to understand what are the alloying addition to be done in a steel, usually any alloy addition or alloying element can be classified into two major categories. So, one element could stabilize the ferrite, ferrite is α phase, which is a BCC in structure or the element which can which can stabilize the austenite phase which is a FCC structure.

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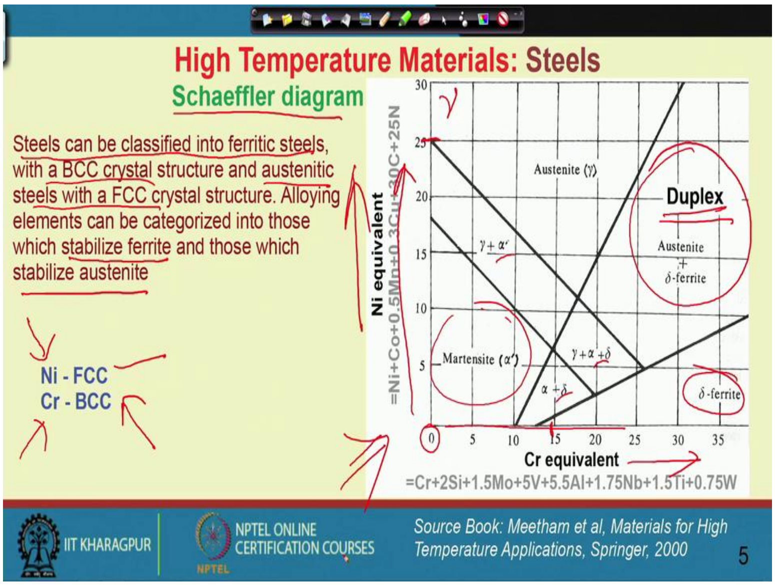

So therefore, the steels also classified into ferritic steel with BCC structure or austenitic steel with FCC crystal structure, it is very clear. Now the alloying element also can be categorised as a ferrite stabilizer or austenite stabilizer. However, to understand this, we need the help of a diagram which you already have learned in a physical metallurgy classes, which is called as Schaeffer diagram.

What this diagram said here this is the nickel and this is the chromium content and we can get at what chromium content or what nickel content which phase is stable. However, only nickel or chromium is important? No, there could be other alloy additions which may be expressed in terms of nickel equivalent or chromium equivalent, means it has the same effect as addition of nickel.

And nickel is a FCC structure and chromium is a BCC structure. So from here itself it is clarified that if you add chromium then ferrite will be stabilized and if we add nickel then austenite is going to be stabilize. So, here from starting from 0 if we go along this direction, you will see above 25 % of addition of nickel here everything is austenite.

On the other hand, along this side if we go above 15 % of chromium, then I will also get the ferrite. However, here what we call it as a ferrite is the δ ferrite means that high temperature ferrite we are talking about means, a higher lattice parameter; however, in the lower side we will get the martensite.

And these are the domains which overlap between two different phases, where a particular domain at high nickel and high chromium containing steels are often called as a duplex steel. This is a diagram which are often used for stainless steel, because stainless steel is a heavily alloyed steel.

Now, so from here if we need to design a ferritic steel we could easily understand that we need a chromium equivalent, which can be higher or if we need to develop austenitic steel for higher temperature application then we have to go into this side. Now, let us see what are the alloys so far has been developed and where those domain actually exist.

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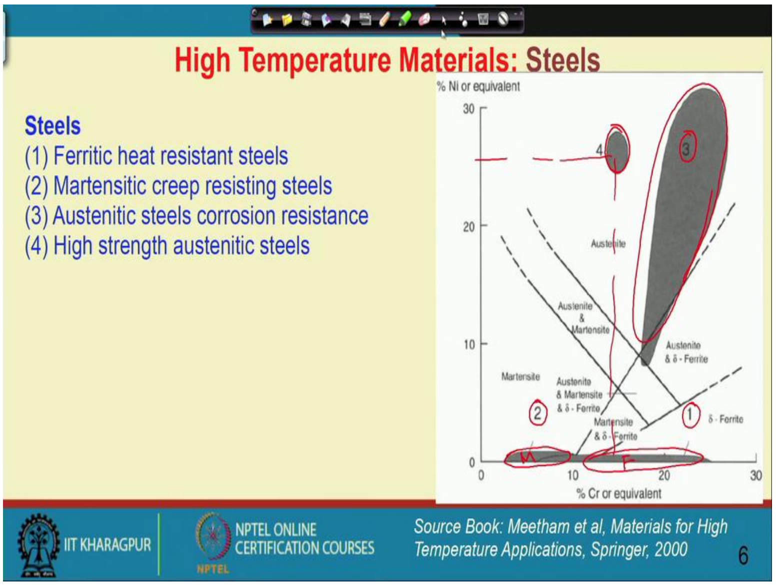

Now, here you see I show you 4 major types of heat resistant steel and their domain of the composition where they are stabilized. So, the 1 stands for the ferritic, this is the ferritic steel domain, which is shown here as 1 and the 2 is the martensitic grade steels. This is the martensitic and this is the ferritic and for austenitic a grade corrosion resistance steel the domain is here. So far, has been developed and this is the very special high strength austenitic steel, which has relatively high nickel and high chromium content. So, let us now start our discussion with the ferritic heat resistant steel, what is expected and what we have developed so far.

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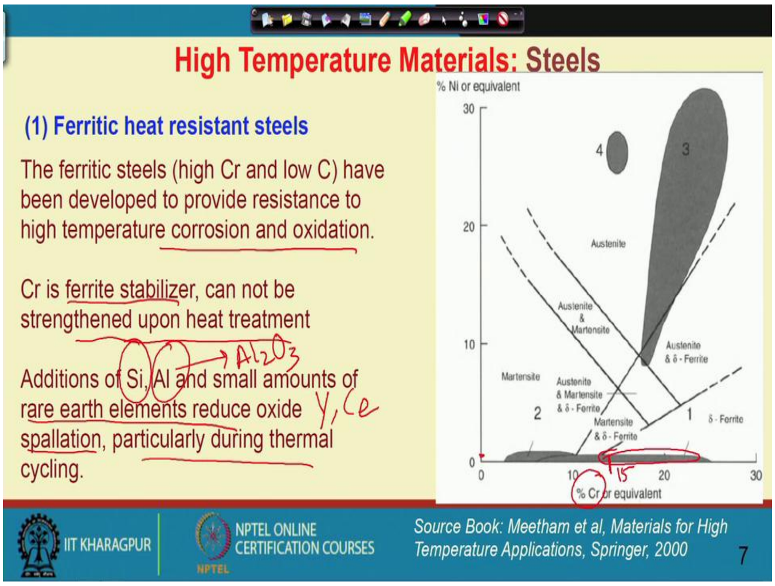

Now, the ferritic heat resistant steel are basically high chromium and low carbon containing steels.

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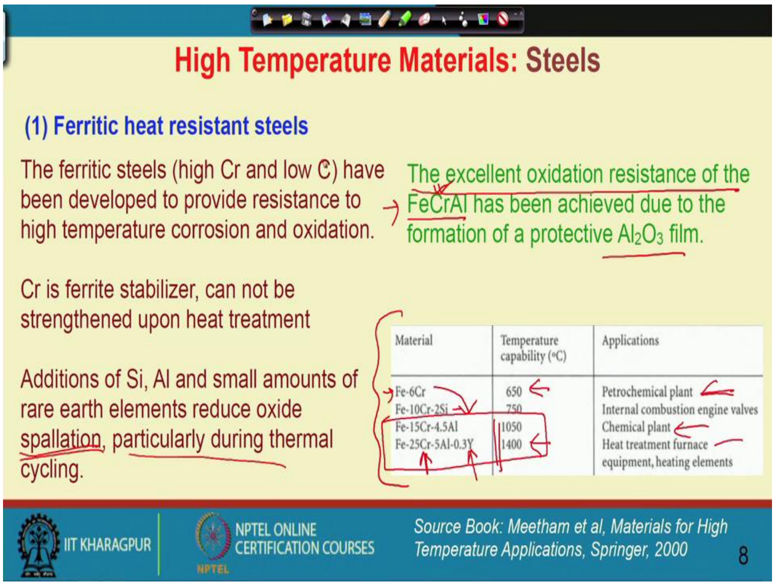

Here these alloys are developed to provide a resistance to high temperature corrosion. So, the high temperature corrosion and oxidation they must be coupled with, we are talking about the alloy addition here. So, from the diagram or the Schaeffer's diagram itself one can assume that the chromium percentage should be somewhat around 15 % and there the nickel is very less.

So, since chromium is a ferrite stabilizer and therefore, we basically stabilizes the ferrite which is a low temperature phase at higher temperature, because the application temperature is higher and we are talking about ferritic heat resistance steel; that means, that the during the operation itself the ferrite phase should get stabilized. And therefore, the strengthening by heat treatment is not really possible; however, we can go for addition of silicon and aluminium, small amount of some rare earth element which reduce the oxide spallation, you have already discussed that about yttrium and cerium.

They have some pegging effect or mechanical keying effects, which give a good adherence of these alumina which appear at higher temperature on the surface of the material and give us a good protection for high temperature exposure and therefore, these addition can be done with silicon and aluminium. However carbon content is very low and therefore, the excellent oxidation resistance we can achieve which we have also discussed in iron chromium aluminium alloy this is also a ferritic heat resistant steel, because chromium content is high and aluminium is added so that we get alumina scale on the surface.

Now let us have a look at some of the very important ferritic heat resistant steel. Very initially Fe- 6Cr was developed. And the temperature capability was 650 °C which still now used for petrochemical, but the derivative of those elements of those alloys came like 10Cr2Si and these are somewhat very important alloys.

You have seen that it has been derived from those basic grade steels, which used for heat resistive treatment furnace equipment or let us say some of the chemical plants or like petrochemical plants, today which can survive at such a very high temperature around 1000 °C or even we can go for 1400 °C because steel is cheaper and we only need some heavy alloy addition.

So, 25 % chromium to be added; however, it require very special attention during the alloy processing itself, so that the chromium should be in the alloyed condition not as a chromia or other carbide formation should be avoided and very little amount of rare earth elements are added so that we get a good pegging effect and avoid the spallation of the scale. So, this is one of the very important category of the steels of the ferritic category.

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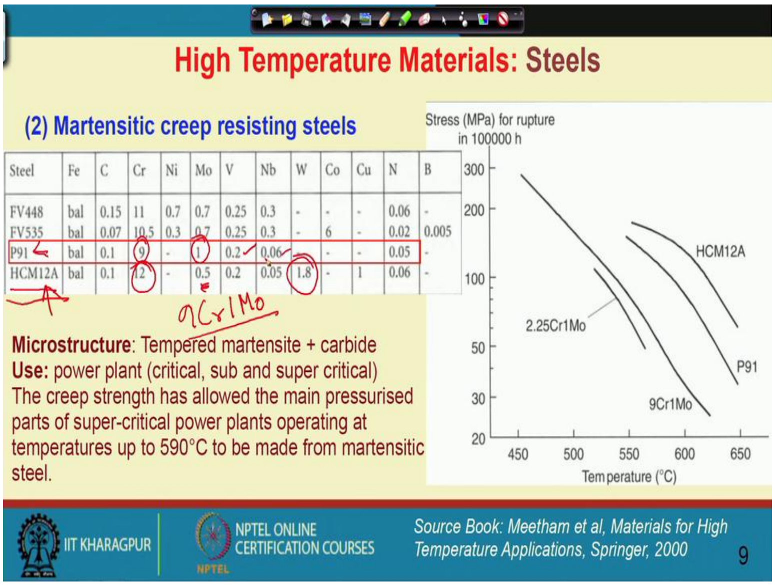

Steel	Fe	C	Cr	Ni	Mo	V	Nb	W	Co	Cu	N	B
FV448	bal	0.15	11	0.7	0.7	0.25	0.3	-	-	-	0.06	-
FV535	bal	0.07	10.5	0.3	0.7	0.25	0.3	-	6	-	0.02	0.005
P91	bal	0.1	9	-	1	0.2	0.06	-	-	-	0.05	-
HCM12A	bal	0.1	12	-	0.5	0.2	0.05	1.8	-	1	0.06	-

Now, let us talk about the martensitic creep resistance steel, so the name itself said again that they contain martensite microstructure. And now what is the operating condition of the steel yes it should be a minimum something like 500 or 600 °C, so the martensite phase should be stabilized, but is it possible or not that is another question, but let us look at what is desired out of the steel.

The microstructure contains tempered martensite means before application the martensite is tempered and during tempering operation we get some carbide precipitates. So alloy addition should be done in such a way that, we get a good distribution or homogeneous distribution of very fine carbide which are not at all soluble in the matrix even at a very high temperature.

Now, the use here is the power plant that I said and this power plant means either it could be critical, subcritical, or supercritical temperatures. And the creep strength has been allowed the main pressurized part of this supercritical power plant where, the temperature rise even something like 590 °C or 600 °C in a the martensite steel which is the expectation. And with time people have derived so many different steels, you can see that chromium content herein the martensitic steel should be lower than the 15 % so here it is expected that we have somewhat like less than 12 %. And those steels has little niobium content you can see and nitrogen is not really very good compound because it form nitride and brittle cracking so a nickel is somewhat like 0.7 to 0.3.

However, for this creep resistant steel we really do not need nickel at all. The next generation steels or advanced steels which has been developed as a martensitic creep resistance steel at the P91 grade steel. Where this is a 9Cr1Mo steel this is a very famous 9Cr1Mo steels. So here a molybdenum has an effect on solid solution strengthening and we added also for forming some carbides. So here you do not see except niobium and vanadium other carbide formation; however, this is another advanced steel HCM 12.

Here 12 is basically the 12 chromium and molybdenum is slightly reduced; however, tungsten is added. Tungsten is added here so that we get actually the good use of these tungsten carbide or maybe other Laves phases. So, if you look at the applicability of the steel and the rupture time of 10^5 hour.

So, here the temperature of application of these low 9Cr1Mo steel is somewhat here where P1 grade steel P91 grade steel has been improved from the 9Cr1Mo this is a modified grade steel actually then the simple 9Cr1Mo. And this HCM12A can be operated at much higher temperature range because this is a very advanced material or advance steel that has been used in this power plants.

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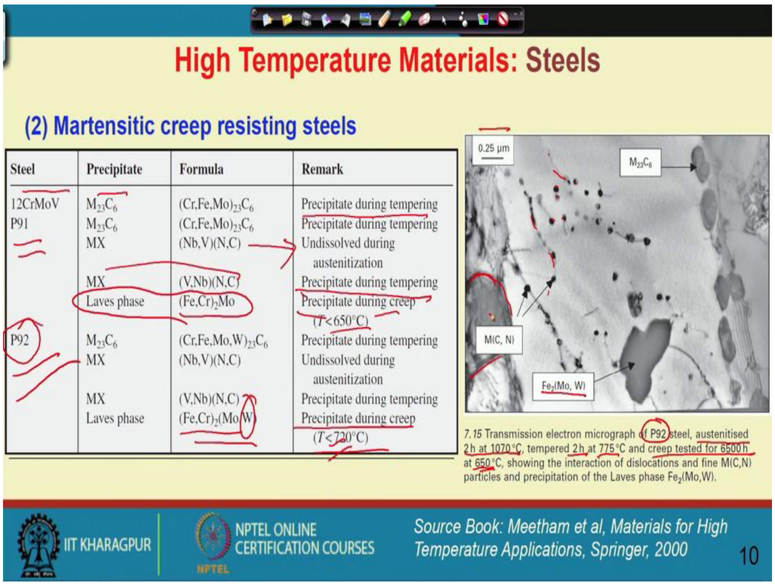

So, the other purpose that we must discuss that what are the precipitate expected from this P91 or this advanced steels. So if you kindly have a look at the 12CrMoV here there are $M_{23}C_6$ carbide and this is a precipitation hardening alloy, due to tempering of the martensite. Whereas, P91 has these Laves phase, which has been precipitated during creep itself, where as some of these nitride or carbo-nitride precipitate that occurred during tempering.

And what we really do? There are some solution treatment in the austenite field, means we take the steel, we go to austenite phase field, we quench it, we get martensite, we then temper it. So, that we get the desired precipitate type in order to strengthen the steel. P92 is also another derivative where we purposely add tungsten so that we get this precipitation strengthening effect. So I show you one of these microstructure of such martensistic creep resistant steel so this is a transmission electron micrograph where you can see the precipitates and these are the dislocations.

So, how the interaction of the dislocation and precipitate occur and this is a steel after use means this is a P92 grade steel which is this one which has been austenitised, this is the heat treatment schedule I am talking about like 1000 °C, tempered for 2 hour at 775, so means we should expect some Laves phase inside. And it has been creep tested for 6500 hour at 650 °C and then you see this microstructure. So this is a length scale of 250 nanometre and you can see that the precipitates are very fine the Laves phase is also in the nanometre scale.

So, this is a Laves phase which contain Fe2MoW-type laves phase and you can see the finer microstructure, how fine the grains are of 250 nm, which is the typical tempered martensite microstructure. So, one hand we have the controlled nanostructured or precipitate which gives us and retain the strength at high temperature as well as we get very good creep resistance at higher or elevated temperature.

So, martensite phase itself can be exploited as high temperature application and people are using for power plant for very long time even for a very long rupture time. And then the third category of this heat resistant steel has austenite microstructure.

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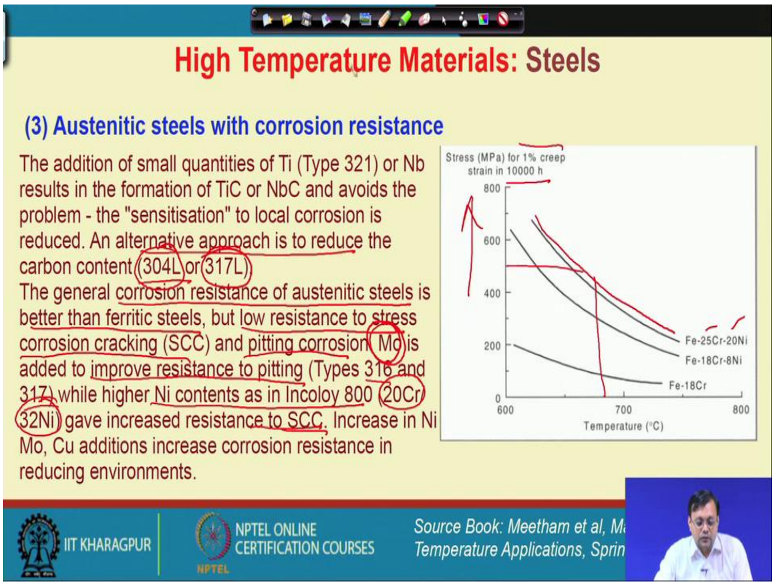

So, austenite itself you understood that austenite fails to stabilize we need high nickel content and high chromium content, so the steel itself contain alloy addition to be higher or whereas there is a phenomenon called as sensitization. You probably heard about which occur due to some of the precipitation at the grain boundaries; however, we can avoid precipitation at the grain boundary where we get the carbide precipitate inside the grain boundary, so that it can be avoided.

So alternative approach here to reduce the carbon content, L stands for low carbon content. However, the general corrosion resistance of austenitic steel is much higher than the ferritic steels that is already well proved, but the low resistance to stress corrosion cracking or pitting type of corrosions. And here molybdenum is used so that we added to improve the resistance to pitting like 316 or 317 type or higher nickel content like Incoloy 800 with let us say 20 chromium and a 32 nickel.

So, higher nickel and higher chromium is desire in order to avoid the stress corrosion cracking and that is why you see those composition range why is that been selected. So, only to avoid a general engineering problems. And it is for sure that for 1 % of creep strength for let us say 10^4 hour this 25Cr20Ni that gives us a higher strength level as well as a higher operating temperature. So, this austenitic steel with a high corrosion resistance are also important for this high temperature application.

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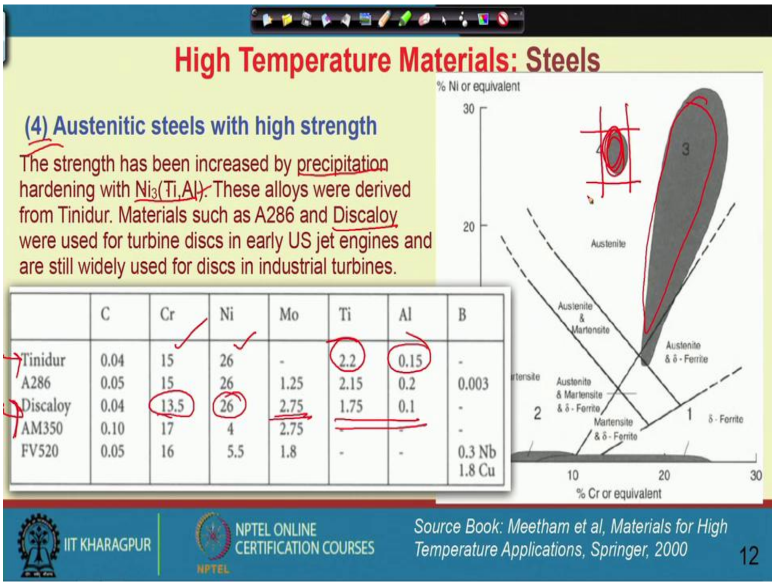

And since I said that the region of those earlier steel was lying here that was a class 3 type and here this is the austenitic steel with a very high strength. So, this has a very low domain and where these materials to be used. Yes, when we need to use a material for brake, then we need both higher temperature, high wear resistance. High wear resistance comes because of the higher strength, means hardness or red hardness is required. So, in that case actually so the jet engines or turbine disc where Discaloy, these are the common alloy that are used for those kind of application.

So, they are usually derived by precipitation hardening by Ni3TiAl type of precipitate. If you have a look at the very basic composition of Tinidur here we have nickel and chromium and we have basically titanium. So, titanium nickel and aluminium they basically from this precipitate which gives us a higher strength at an elevated temperature and also the Discalloy is you can have a look with a reduced chromium

But the same nickel content with a slightly higher molybdenum because people expect some precipitate of those molybdenum and so on along with those titanium aluminates. So, this is a very specifically designed with a very well composition range people used for engineers use for those higher temperature.

So, with this today we finish our discussion on the steels that are used for power plant or various high temperature application or let us say heating element. And in the next class we will discuss some more advanced alloys.

Thank you.