

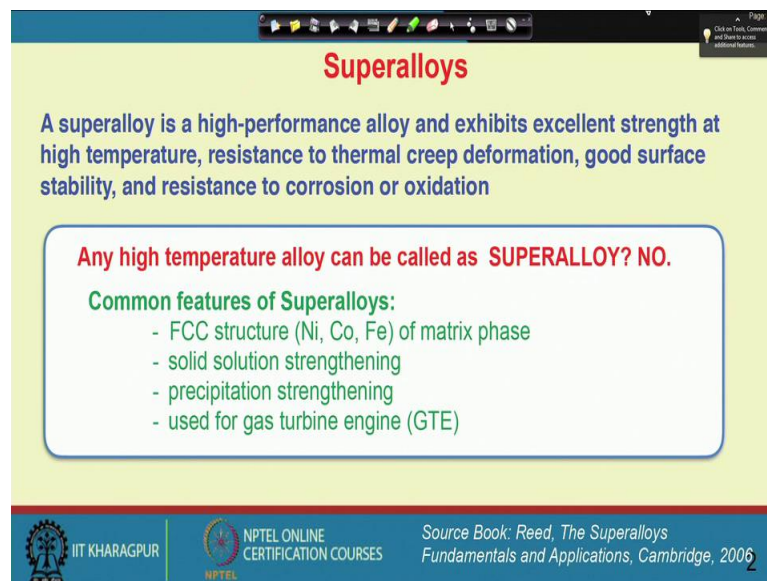
Advanced Materials and Processes
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Lecture - 31
Superalloys

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. This week we will start a new topic of discussion on Superalloys, it is basically a continuation of our earlier discussion on high temperature material.

However, in this is of discussion we will try to focus more on the superalloys. So superalloys are used for turbine engine or gas turbine engine, which is used for aeroplane or also some land base turbine for power plant application. However, when we call it as a superalloy, what we really mean? what is really superalloy termed as?

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Superalloys

A superalloy is a high-performance alloy and exhibits excellent strength at high temperature, resistance to thermal creep deformation, good surface stability, and resistance to corrosion or oxidation

Any high temperature alloy can be called as SUPERALLOY? NO.

Common features of Superalloys:

- FCC structure (Ni, Co, Fe) of matrix phase
- solid solution strengthening
- precipitation strengthening
- used for gas turbine engine (GTE)

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Usually, a superalloy is a high performance alloy; it is for sure that this material will be used for higher temperature at higher stress level for a longer time, so creep must be important. So, these high performance alloy should exhibit excellent strength level and at a very high temperature, means higher temperature the Carnot efficiency will increase.

However, so far we have discussed about high temperature steels composites, ceramics. However, these are metallic alloys and here high temperature means above 650 °C, which is beyond the high temperature steels or any other alloys.

Now, there should be significant resistance to the creep deformation means time dependent deformation. At the same time there should be a very good oxidation and corrosion resistance for the aggressive environment. And if you look at the very basic information that I just tell you, then you can always ask, Sir any of these high temperature materials so far you have discussed; like aluminides like high temperature, a martensitic steel.

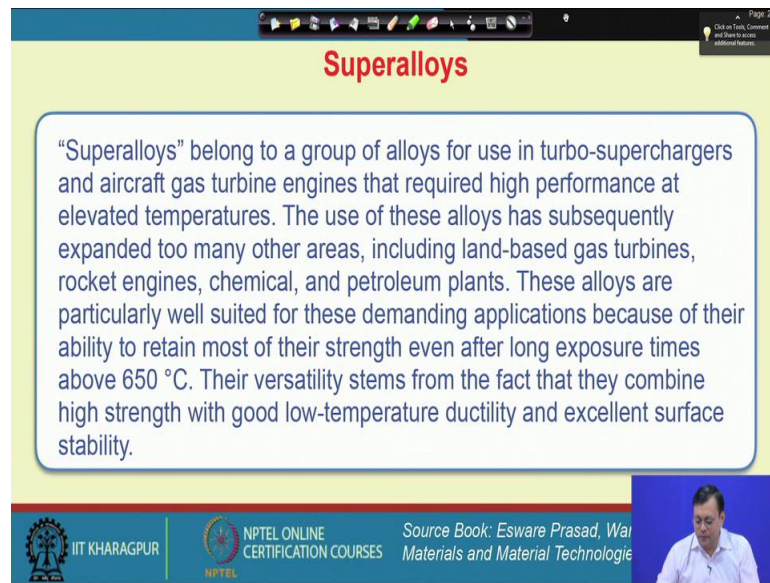
They have almost similar type of features or let us say the characteristic so, any high temperature alloy can be called as a superalloy? the answer is no. We cannot call any of the high temperature alloys as superalloy. So far, three different alloy system has been discovered as a superalloys and these alloy systems are nickel base, cobalt base and iron base. And the common features of all these alloys is that the matrix phase has a FCC crystal structure.

Now you can ask me that nickel is definitely FCC but, what about cobalt? it is hexagonal close packed HCP, iron it is BCC. We basically do alloying so, these hexagonal close pack no longer remain hexagonal close pack. And iron even though it has BCC, but we add sufficient amount of nickel in order to stabilize the iron nickel phase which has a gamma or FCC crystal structure.

So, all these alloys had a common feature that the matrix has a face centred cubic crystal structure. And engineers are not happy with only the matrix. Definitely it should be strengthened by further alloy addition and the feature is also observed that all these alloys are strengthened by solid solution strengthening means larger size atoms and the precipitation strengthening means some intermetallic that we purposely incorporate here that basically strengthen the alloy.

And all these superalloys the major application areas are gas turbine engine, which is called as GTE. So, at least now, we realise what are the superalloy means that; it has nickel based superalloys, cobalt base superalloys or it could be iron-nickel base superalloys. It has FCC matrix structure; it is strengthened by precipitation hardening and solid solution strengthening for the application in gas turbine engine.

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Superalloys

“Superalloys” belong to a group of alloys for use in turbo-superchargers and aircraft gas turbine engines that required high performance at elevated temperatures. The use of these alloys has subsequently expanded too many other areas, including land-based gas turbines, rocket engines, chemical, and petroleum plants. These alloys are particularly well suited for these demanding applications because of their ability to retain most of their strength even after long exposure times above 650 °C. Their versatility stems from the fact that they combine high strength with good low-temperature ductility and excellent surface stability.

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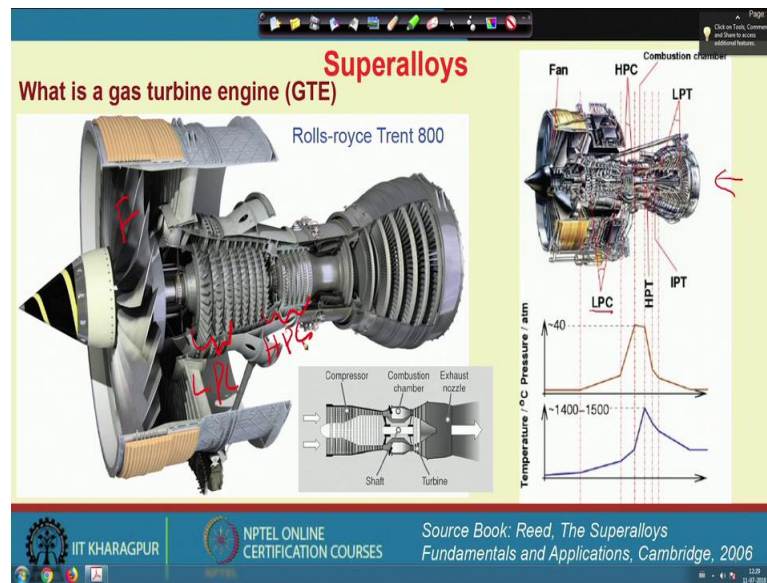
Very recently, one of the book that is very interesting and summarizes about the superalloys on aerospace material and materials technologies by springer. It says that super alloy belongs to a group of alloys, which use as a turbo superchargers and aircraft gas turbine engine. However, it requires very high performance as I said earlier at elevated temperature.

However, the use of these alloys day by day are expanding. So, that include many other areas like land base turbine for let us say for power generation, rocket engines, chemical petroleum plants. And these alloys are particularly well suited for an application demand in the area. Because the alloy can retain most of their high strength at a very high temperature for long duration of exposure above 650 °C.

where any other conventional alloys high temperature alloys fail. So, they have basically, a versatile feature for as a high temperature alloys, because they combine the high strength, very good ductility and excellent surface stability which can easily avoid any kind of oxidation or corrosion in aggressive environment.

So, this is a very general concept on the superalloys and we will understand the application of these alloys if we see that where it really used or what is the demand expected from this particular class of materials or alloys.

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So, in the left hand side, a gas turbine engine and one of the very famous gas turbine engine used in Boeing 777 is shown. The name of that engine is Trent 800 produced by Rolls Royce. Here at a very first glance it you may have seen by yourself during flying in any aircraft, but you may see that this is a structure which is very large and there are distinct few zones.

The first zone here; this part is basically the compressor. Where the air goes inside, it is compressed and then it is pushed into the combustion chamber. Inside the combustion chamber, we also inject fuel so once this fuel goes inside there is a combustion, expansion and power generation, it basically goes into the turbine section.

So, here is the use of this superalloy. Now it again the extra hot air that goes away from the exhaust and the maximum power is dragged from this combustion in this zone. So, this is the turbine section that I said this is the turbine section, this is the compressor and here is the combustion. So, these are the very distinct zone in a gas turbine engine.

Now the same engine I have schematically shown here, you can see this is a fan and after that there is a low pressure compressor in this domain. This is the LPC and after that there is a high pressure compressor, which further compress, from the moderate pressure the air is compressed. However, this fundamental is very similar if you look at any of the engine actually even for a car engine you need a compressor, to compress air that goes inside and combers and then there is a expansion that the power we use actually.

And after these high pressure compressor, this is the zone where the combustion occurred and after that the turbine basically used, where this is the turbine, where we have the again high pressure and we have low pressure and we have intermediate pressure.

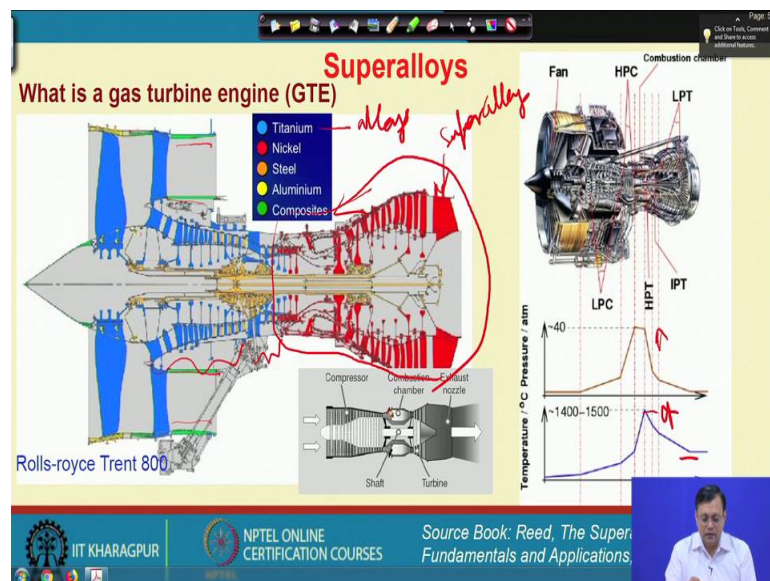
So, the interesting part is shown here with the pressure. So from inside this section the pressure actually goes higher and higher and also where fuel is injected; then the pressure goes almost like 40 atm. It is very high pressure and the temperature of combustion goes upto 1500 °C.

So, at a very high pressure, at very high temperature and then the turbine basically, creates or extract the power out of that, this is the major purpose of a gas turbine engine and you can understand that in this section where superalloys are used how much important component is made of the superalloys.

And now from the Carnot cycle we know that higher the pressure, higher the temperature as we make the combustion and the difference between these two will give more efficiency. So, if you see from a very series of different gas turbine engine that has been evolved with type. The temperature of combustion has increased a lot because of the high pressure and high temperature.

So, material should survive at such pressure and temperature and require a high creep resistance this is one of the very important criteria.

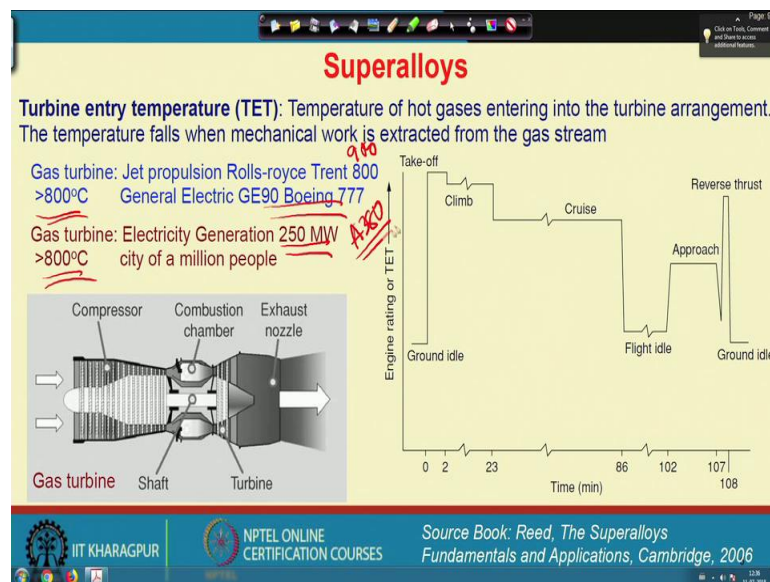
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Now I show you the same engine sectional view. Please have a look that the section the initial compressor section where there are fans and there are low pressure zone and there is high pressure zone. Here, mostly titanium based alloys are used and the red colour here, the superalloys are used. However, the high temperature steels are used here and aluminium is used in some of this region where there is very less effect of temperature actually. And for holding these structures mostly some of this composites are used.

So, this is a very general and very important information that the superalloys take care in a gas turbine engine, one of the most important part where power is extracted after combustion.

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So, let us have a look at that; here the important information is the turbine entry temperature. So, which means after the combustion here; in the turbine the temperature, which basically increases and enter into the turbine that is called as turbine entry temperature TET.

So, the performance depends on the turbine entry temperature and we can have a plot of this turbine entry temperature and try to look at about the various effect when a flight is just about to fly. So, here one of the important plot with time versus engine is shown, rating or turbine entry temperature, it is for sure in a ground ideal condition, we really do not need much power.

However, when the flight takes off then the turbine entry temperature goes to the highest level because, at that time the maximum power need to be generated. And it is a very important to know that majority of the failure in aircraft engine occur when the flight takes off or during the reverse thrust just before landing so, this is the two period. However, moderate power is required or expected from a turbine, when the flight is in cruise condition. So, after the take off, then power downs slightly because of the climbing and after that again there is a cruise and then the flight remain ideal for long time just before approaching to an airport.

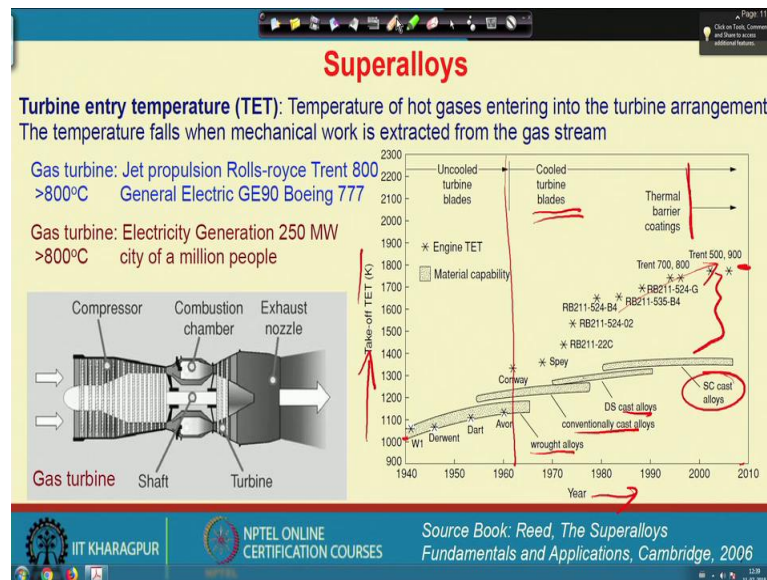
And then a reverse thrust is created and again it comes to a ground idle. So this is one of the very important part of any aircraft so that the maximum power can be extracted.

Now for a gas turbine application there are two example; that I show you where the jet propulsion the temperature here is much higher than $800\text{ }^{\circ}\text{C}$, gas turbine very similar like for a city of a million of people; the power consumption can be given by let us say 250 milliwatt gas turbine engine for electricity generation.

They have very similar kind of features or maybe the Trent Rolls Royce 800 engine that is used for Boeing 777 aircraft. So, there are many different versions of this engine and the higher version means basically the turbine entry temperature increases and the more power is extracted. So, Trent 900 is used for air bus A 380, you may have heard about the largest passenger carrier aircraft.

So, the temperature basically falls when the mechanical work is extracted from a gas stream. What it means that when the gas stream just enters into the turbine, here there is a turbine in the end part of this turbine section so temperature basically again falls here. So, temperature goes up here and then again it falls, so once we extract these mechanical work actually from the gas stream and the temperature automatically falls down.

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So, with this information we like to see that from a very first time, when these gas turbine has been or about to develop; how these turbine entry temperature or take-off temperature has changed or expected.

So, there is a very interesting plot is shown here with the year and the turbine entry temperature in Kelvin. So, from 1940's, the turbine entry temperature was somewhat like 1000 K and today we are somewhat in the range of 1800 K. So, almost like two times. Along this time, so many superalloys has been developed in terms of not only alloy composition, but the processing condition like wrought or cast or directionally solidified and the latest one was the single crystal.

And initially up to 1960 or 1965 mostly the uncooled turbine blades were used, but these days the performance has been increased by introducing some cooling system. However, as the temperature is going higher, I mean that TET turbine entry temperature going higher, the use of thermal barrier coating is getting more popular.

so that; we can increase the application temperature and go to a higher side without making much failure. So, this is the purpose of; using some thermal barrier coating along on a superalloys actually.

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Superalloys

Land based Industrial Gas Turbine

Year of introduction	1967	1972	1979 ^a	1990 ^a	1998 ^b
Turbine inlet temperature (°C)	900	1010	1120	1260	1425
Pressure ratio	10.5	11	14	14.5	19–23
Exhaust temperature (°C)	427	482	530	582	593
Cooled turbine rows	R1 vane	R1, R2 vane, R1 blade	R1, R2 vane, R1, R2 blade	R1, R2, R3 vane, R1, R2, R3 blade	R1, R2, R3 vane, R1, R2, R3 blade
Power rating, MW	50–60	60–80	70–105	165–240	165–280
Efficiency, simple cycle (%)	29	31	34	36	39
Efficiency, combined cycle (%)	43	46	49	53	58

Note: ^a Corresponds approximately to GE 7F, 7A/9F, Westinghouse 501F/701F and Siemens V84.3/94.3 turbines.
^b Corresponds approximately to GE 7H/9H, Westinghouse 501G/701G, Siemens V84.3A/94.3A and ABB GT24/26 turbines.

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So, again from this very earlier time, the turbine entry temperature as I said was in the range of an 800 °C to 900 °C around 1965.

And there the power rating was somewhat in the range of 50-60 and on today let us say the typical power consumption of a million of a people in a city, required something like greater than 250. And along this time; along this time the inlet temperature has raised from 900 to around 1425 °C or around 1500 °C on today.

The important information here that not only we have increase the temperature or turbine entry temperature in order to increase the power, but the Carnot efficiency like a single cycle or a combined cycle efficiency has increased from 29 % or 30 % to 60 %. So, this is one of the very great achievement so far and still people demand to apply those kind of superalloys for much higher temperature.

So, the cooled turbine rows are here used in a R1 vane and now it is there are many blades and vane which are cooled and at the same time even though the turbine entry temperature has raised, however, the exhaust temperature because, the difference gives us the how much power we extract and the this has not increased too much so, the exhaust temperature is in the range of 593 °C.

So, if you look at that the GE, Westinghouse and or Siemens these are some of the very important companies produces this, so all of these ratings and power they are almost known.

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Superalloys
Larson-Miller approach for ranking of creep performance

Creep strain rate $\dot{\epsilon}_{ss} = A\sigma^n \exp\left\{-\frac{Q}{RT}\right\}$
 at steady state: balance between creep hardening, dislocation multiplication and softening, dislocation annihilation recovery

Monkman-Grant relation
 time to rupture $t_r \times \dot{\epsilon}_{ss} = B$ creep strain, constant

$t_r \exp\left\{-\frac{Q}{RT}\right\} = C$
 C, D constants

$\log_{10} t_r - 0.4343 \frac{Q}{RT} = D$

$T[E + \log_{10} t_r] = P$
 E = Larson-Miller Constant
 P = Larson-Miller Parameter

Graph: Activation energy for self-diffusion (kJ/mol) vs. Activation energy for high-temperature creep (kJ/mol). Materials plotted include W, Al₂O₃, Nb, UO₂, MgO, γ-Fe, α-Fe, β-Co, δ-Fe, Ni, AgBr, NaCl, Cu, Pt, Au, Mg, Zn, Pb, Al, In, Sn, β-Ti, Cd, α-Ti.

So, the direction of research along the superalloy is well established. Now, since I said that a long exposure, long duration, higher efficiency, means COP efficiency or performance is demanded out of the superalloys. The engineering or science consideration in terms of creep has to be established well and we must need to develop some framework where different type of high temperature materials can be accessed.

And for that, getting a better creep performance, one important aspect is the diffusion. Because, as we increase the temperature the diffusion become higher that is already known to you and the creep strain rate has to be linked with the diffusion.

So, very basic Arrhenius type of equation is shown here:

$$\dot{\epsilon}_{ss} = A\sigma^n \exp\left\{-\frac{Q}{RT}\right\}$$

that is the creep strain rate = $\dot{\epsilon}_{ss}$, here A is a constant and Q is basically the activation energy R and T.

So, when we reached to a steady state strain rate it basically signified that there could be a creep hardening and dislocation multiplication that counteract with the softening and dislocation annihilation process in the recovery. So, the steady state can be reached only when this two process is in equilibrium and so the creep hardening and dislocation multiplication is a stress driven phenomena, whereas the softening and annihilation recovery required the diffusion.

And therefore, we can think about the Monkman-Grant relation that is a very important relation that said about that a component how much time requires for a rupture. So, 'tr' is the time required for rupture and there is a strain rate that can be measured, it has been observed that:

$$t_r \times \dot{\epsilon} = B, \text{ where } B \text{ is a constant.}$$

So, if you considered a rate multiplied by time rate itself is basically creep rate and that basically means 'that the creep. So, it is the creep strain that we are talking about and creep strain for a particular duration of exposure is known to us right. So, we can see many different superalloys or high temperature alloys and try to link with this equation. Let us derive a little bit more and put this creep strain rate here and replace it here and so, what

$$\text{we get: } t_r \exp\left\{-\frac{Q}{RT}\right\} = C$$

and if we take a logarithmic scale then we get:

$$\log_{10} t_r - 0.4343 \frac{Q}{RT} = D$$

The meaning of C and D are the same. One is in the log scale another is the normal one so they are basically the constant.

Again at the end of this, we get:

$$T[E + \log_{10} t_r] = P$$

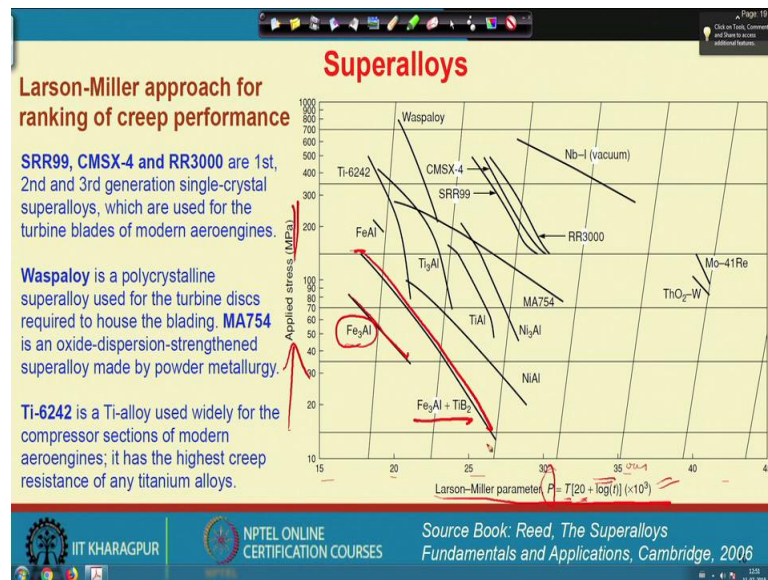
This one will give us a new parameter which is called as a Larson Miller parameter. It means that the temperature we multiply with the log of 'tr' because, here you see if we multiply here with temperature then it will vanish and we will get a constant here which is equal to here and we get the Larson Miller parameter.

So, why we really need to consider this Larson Miller constant? We will discuss it in a minute, but let us have a look at what is the link between the diffusion and creep. So, you may have a look at this plot earlier that says the activation energy for creep and activation energy for self-diffusion. If we take different elements or compounds and simply measure their activation energy of self-diffusion and for creep, then you will see that they are lying on a line.

It is useful designing an alloy, we really do not need to go for high temperature creep activation energy measurements, if we only know the self-diffusion coefficient or activation energy for self-diffusion, then automatically we can guess that whether niobium has a higher activation energy required for creep or an indium required for a high activation energy for creep.

Because they all lie in a single line. So, by considering all these aspects we can plot this particular Larson Miller parameter to rank the creep performance of various types of high temperature materials or alloys.

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Let us have a look at that plot, here a plot is shown in terms of applied stress which is in a mega Pascal unit and here these are the Larson Miller parameter that is P, which is equals to temperature into a constant and logarithmic of time to rupture. And here is some constant is given so that we can represent in different numbers, because number have quite a high value.

. We have discussed widely about the aluminides, we know about iron aluminide, nickel aluminide, titanium aluminide. Titanium aluminide has a very low density, very good for performance. So, iron aluminide has the highest strength, but if you put in a Larson-Miller approach to rank the creep performance then we see that Fe_3Al is lying here.

Now, we have also discussed that we can add some further alloying elements or other; other compounds so that a composite can be made which will have a better performance. So, here this is Fe_3Al with titanium diboride, which is also a high temperature material so that has a quiet wider range of applied stress with the Larson Miller parameter.

So, you see this Larson Miller parameter takes care of creep, the diffusion, the time to rupture and everything almost. On the other hand, the 50-50 iron aluminides have a relatable lower range whereas at higher ranges, you can see for a nickel aluminium. Now in case of other aluminide like the lightweight Ti_3Al or TiAl they have a better performance compared to iron aluminides.

It is for sure, now we can also have a zone where thorium dispersed tungsten which is used for many of the filaments and very high temperature application is almost lying here or let us say the niobium if we take under vacuum; where there is almost no oxygen at all, the Larson Miller parameter and the application of the stress is quite high.

However, we can think about the competitive alloys with the superalloys, so one of the alloy that is used for those compressors at the entry of any turbine, where we often use titanium 6242. So, this is one of the best alloy among all the titanium alloys with creep performance. So, this alloy shows that we can apply or use this alloys to a much higher stress range and relatively good Larson Miller parameter.

Whereas, the Waspaloy was a very ancient superalloy the very beginning the Waspaloy has started and this is actually a polycrystalline superalloys. And you have seen the polycrystalline superalloys was used with a turbine entry temperature in the range of 800-900 °C around 1960's. And during the years, many different generations of superalloy has been developed from a polycrystalline alloys to a directionally solidified alloys, to a single crystal alloys.

So, here we basically get the series of SRR99 which is the first generation single crystal, then the second generation single crystal CMX series and RR3000. So, from 1960's the

superalloys reach from Waspaloy to the single crystal blades here so we have increased the Larson Miller parameter and let us say the stress range lying almost in the same scale.

Now as I said that MA754 here is basically an oxide dispersion strengthened superalloy that is usually made by some powder metallurgy technique and that has also given a better performance. However, the stress range is little bit lower than the Waspaloy and the single crystal blades. And as I said that the modern aero engine requires titanium 6242 alloys which are used in the compressor section.

So, today we have discussed all the very basic fundamental aspects of the superalloys. We have also discussed how the gas turbine engine are developed and its different section, the demand of the material at different sections along with their performance. And the performance of these alloys could be easily classified using Larson Miller approach for the creep performance where the diffusivity of the material is important. In the next class we will continue our discussion along this direction.

Thank you.