Advanced Materials and Processes

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Lecture – 26
Introduction to High Temperature Materials

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 start a new topic as introduction to high temperature materials. You may recall in the initial first week lectures, we have talked about high temperature and ultra-high temperature materials. And we have discussed a little bit about what are the application areas where we need materials for higher temperature applications.

Usually among 3 different type of materials a broad category of materials like metals and alloys polymer and ceramic, there is no doubt that ceramic need to be exploited with their properties at ultra-high temperature. Because no other class of material can survive above 2000 °C, only ceramics can survive. Ceramics means oxide, nitrides and so on. However, most of the metals and alloys has a melting temperature below 2000 °C, and therefore, they are mostly used below 2000 °C. However, composites means a metal matrix along with some other kind of ceramic fibber can be prepared for high temperature application. So, in this week and next week, we will discuss about those issues.

So, let us try to think that can we call any material as a high temperature material or do we need some characteristic, if those materials shows those characteristic, then only we can call them as a high temperature material, or we can use those material for higher temperature.

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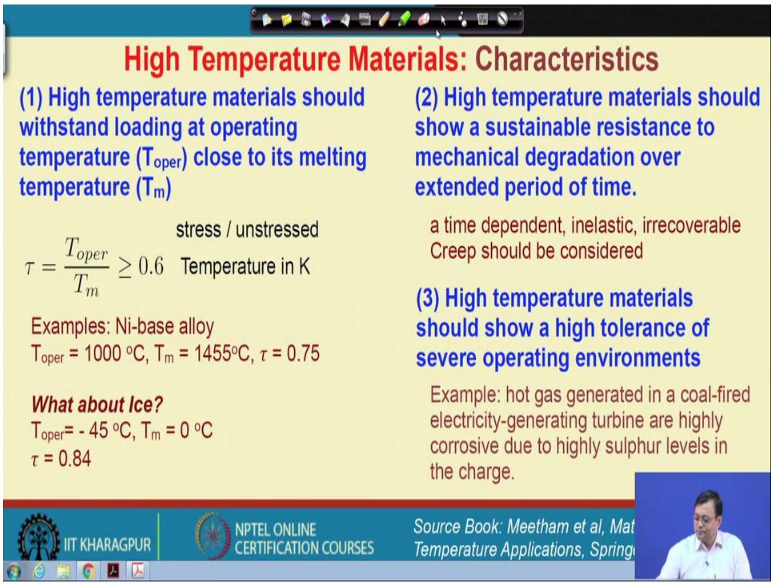

So, there are 3 very basic characteristic that a high temperature material should exhibit. The first one is that a high temperature material should withstand loading at operating temperature; means, the material may be exposed to high temperature with stress or without stress. However, the operating temperature means the temperature where it should be applied, it should be close to the melting temperature. And now we can simply make experiments, whether the material can be used at highest operating temperature, and then people came up with a parameter which is equal to $\frac{T_{oper}}{T_m}$. And if the ratio is greater than 0.6, here the temperature is expressed in Kelvin, please remember, in stressed condition or unstressed condition, depending on its application, we simply call this τ as a parameter to classify a material whether it can be used as high temperature.

Now, I simply give you a very first example of such material, we all know about nickel based superalloy. Now, here the operating temperature of nickel based superalloy is around 1000 °C, and melting temperature is around 1455 °C and there if we measure or estimate τ it has 0.75.

So, we can see these value are greater than 0.6, and we can immediately say yes this material can be used at high temperature. There is no doubt that we can classify this material into high temperature materials category. Now I can give you a very nice example, we may do not recall this material to be used, like ice. What you think about ice? Ice is basically a low temperature material; means, ice only exist at 0 °C, now the question comes whether ice can be used at as a construction material? Yes, because if you think about the polar region, there are some construction which are often called as igloo, you may recall we have read them in the childhood days.

The igloo is constructed by using ice. Where igloo is constructed the outside temperature is -45 °C, and inside igloo people try to survive in polar region, inside igloo in order to maintain a temperature around -7 to -8 °C. And so, ice is a construction material, but can we call it as a high temperature materials? Let us try to have a look.

The ice has an operating temperature which is -45 °C and melting temperature of near 0 °C, it depends on how much salt concentration is there or not. But we can say it as 0 °C means 273 K Kelvin. If we take the ratio, then it will be 0.84. So, ice is also a high temperature material. Now you can ask sir, how it is possible? Yes, so, high temperature or low temperature, it simply depends on the application temperature. We cannot call all time that a material has to be used above 2000 °C, then only we will call it. So, it depends on the application temperature and its melting temperature. So, the ratio will tell us to classify a material or categorize a material whether it is a high temperature or not.

Now, the second important point or characteristic of a high temperature material, a high temperature material should show a sustainable resistance to the mechanical degradation over an extended period of time. Let us say, I put a stress on a material, and it is exposed to a higher temperature, or in some aggressive environment, and there the material is under use. So, with time the material will degrade.

So like, let us say a creep property means, which is the time dependent deformation, or let us say we call it as real time deformation; means, the even though the stress is well below yield point, yield point means basically the yield strength I am talking about. So, there should not be any deformation because the stress given to that material is below yield strength, but we will see that some time depend deformation will occur.

So, in that case, a time dependent inelastic and irrecoverable strain will appear which we call it as a creep, and that should be considered. So, how much degradation of the mechanical properties occur with time? And that should be one of the very important characteristic in order to classify a material as a high temperature material. And the third most important classification or characteristic that material should exhibit that it should have very high tolerance. Tolerance means, we are talking about let us say the defect tolerance, or any other engineering tolerance. So, under severe operating environment, like as an example let us say a hot gas is generated in a coal fired electricity generating turbine. That are highly corrosive in nature, and due to very high sulphur level is in the charge. So, the sulphur will produce some other kind of compound, and that are not at all protective like oxide and it will simply corrode the material.

So, let us say the sulphide compound are more stable than the oxide compound at a given temperature. And we need to look at whether the material can survive at such aggressive environment. So, this 3 important characteristic, once a material fulfil our criteria we call it as a high temperature material.

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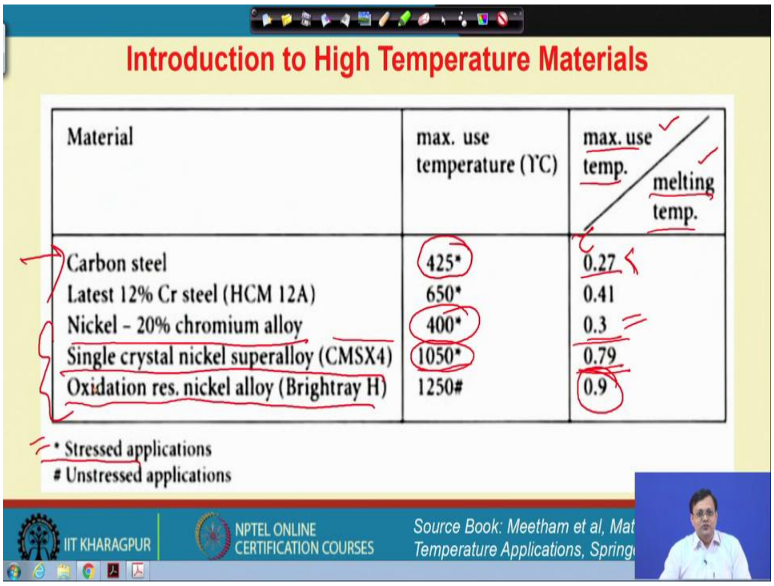

Now, let us have a look at some of the very common engineering material like carbon steel. In a carbon steel, it can be used at a temperature of let us say 425 °C under stressed condition, and if we simply make a ratio of the operating temperature or used temperature is the same thing by divided by the melting temperature which is basically the τ that I said then it is 0.27. Now next, come to nickel chromium alloy, that is the very earlier let us say something like a long time ago it was discovered, and a nickel chrome alloy used at 400 °C where the ratio is little bit higher than the carbon steel and let us say this is the 0.3, whereas if we think about a single crystal nickel superalloy which is CMX series, actually CMSX 4. And here we can see the operating temperature is 1050 °C under stressed condition, and the ratio is 0.79. It is a very good high temperature material. However, please remember that it should also satisfy other 2 criteria that I said that the time dependent deformation creep should be considered, and the second is the is the exposure to some aggressive environment, it should survive.

So now, there are some other interesting bright alloy oxidation resistance nickel alloy that has a τ value of something like 0.9. So, these are very good high temperature materials.

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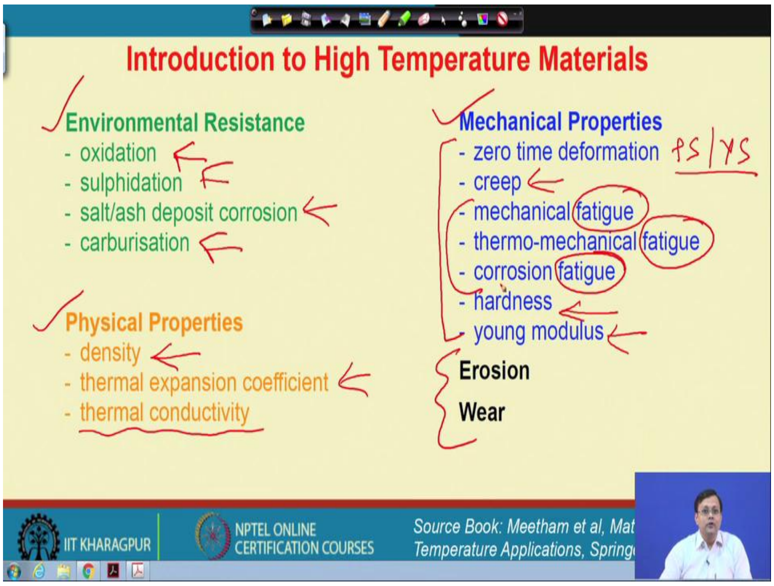

Now, interestingly if we look at the chronological order of development of materials, you can see that with time we completely and continuously developing materials for more higher temperature application, that is for sure; however, not only this characteristic, however, we should discuss a little bit more detail on those characteristic. Like, the first one I said that is one of the environmental resistance, mechanical properties like creep and a time dependent deformation, and some of the physical properties along with erosion and wear that is also another engineering aspect of choosing material for higher temperature. For environmental resistance, material should exhibit a good protection to the oxidation, sulphidation or let us say some set of deposit induced corrosion like salt or ash deposited corrosion, or let us say some sort of carburisation,. So, these four important environmental resistance the material should exhibit.

Now, in case of mechanical properties the zero-time deformation means proof stress at a higher temperature or yield strength, these are the same thing actually. Now a creep should be considered. Also there are a fatigue occurred in the material that fatigue could be due to stress fatigue means once we are loading and unloading, or maybe we are raising the temperature, we are decreasing the temperature. So, repetitive cyclic type of situation will occur. For any engineering component, and therefore, this fatigue behaviour in terms of mechanical or thermo and mechanical or let us say corrosion induced fatigue that should be considered, as well as the high temperature hardness and modulus should be considered.

Now, in case of physical properties, the density is very much important. Because density will tell you that how much weight the total structure has to carry, or some expansion related issues should be there. Let us say I have produced a protective scale; however, the scale has a different expansion coefficient than the base alloy. Then it will simply fall at higher temperature because of the mismatch of the thermal expansion coefficient, or let us say the thermal conductivity is also important. So, these are some of the mode in- depth properties that one should consider before choosing the material.

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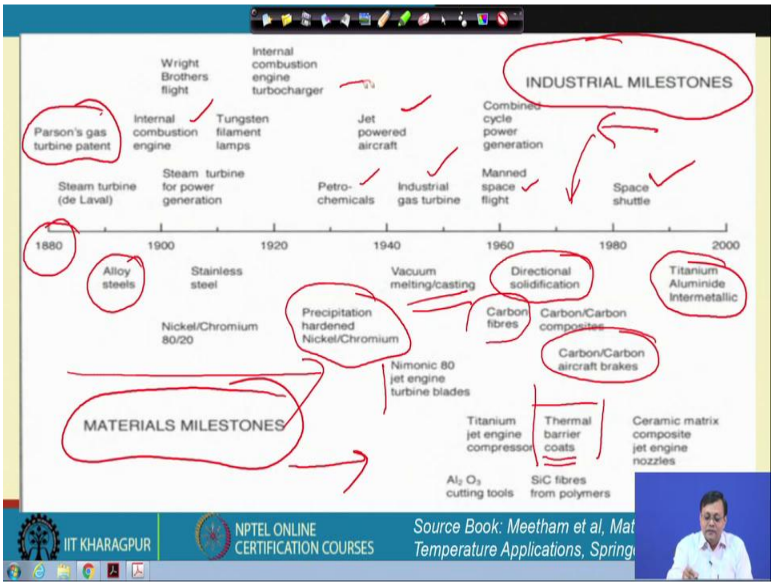

However, just have a look at the chronological order of development, in terms of the material, and these are the material has developed with time and the industry by after developing those material they have implemented. So, they have implemented with time. So, starting from the parson’s gas turbine patent from 1880's actually, there are development of alloy steel to precipitation hardened nickel chromium, and the process development, for producing material under very high vacuum, or Nimonic jet turbaned turbine blades, and to a some carbon fibre, and further processed development like directional solidification.

Why directional solidification important I will come in a minute in the other classes. And then intermetallic alloys are also important, because intermetallic has a relatively higher melting temperature. So, we have developed in case of metals and alloys a lot, and along this direction, there are different thermal barrier coating has been developed in order to use material along with carbon-carbon composites, let us say breaks.

And on the other hand if you see the industry milestone, there are internal combustion engine has been developed, where you need material for a higher temperature, petrochemicals jet powered aircraft, and industrial gas turbine. Let us say, the manned space flight to space shuttle.

So, you see that as the material has been developed, then the application has been also chronologically improved with time.

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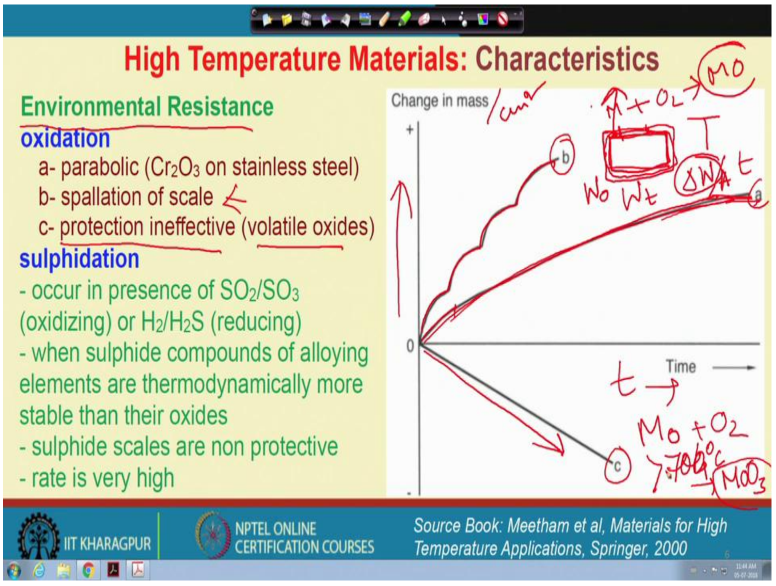

So now let us start with the important aspect or the characteristic that we are looking for into materials for their use at higher temperature.

So, the first one is the environmental resistance. First comes to our mind that a material because 20 % oxygen is available in the air. So, there must be oxidation at higher temperature. There is no doubt if we use any metals and if it is already oxide then there is no question, but we are mostly trying to understand the metals and alloys.

So, if you simply take a coupon, and expose it at higher temperature and a greater than room temperature and in an environment, in presence of oxygen, then metal will form with oxygen some metal oxide. And this metal oxide will first have a chance to appear on the surface. So, this is actually the metal oxide, now what we can do? We can start the initial weight of the sample, and after sometime we can measure the weight. We can see that difference in the weight that is ΔW over some period of time, with some period of time. So, here we plot a time in axis and this is ΔW. We can measure the net surface area, the total weight change divided by the surface area. So, this is change in the mass or per unit centimetre square of the surface area, which we can also do and we can plot to compare between different coupons of different materials.

And there are three different district plot can be observed which are written here as a b c. So, one type of weight change can be observed that is parabolic. You can see initially the weight has increased a lot and then almost it become stable.

Now, if we think about some other case, where the after some group of this oxide scale, which basically cracks and fall down. So, this appears like this kind of zigzag way. So, this is due to the spallation, where as the first one is a nature of a protective nature, because it becomes sluggish with time and then it is protecting.

Now, the third type of curve where protection is ineffective. There could be a metal oxide which is volatile in nature. So, it is initially it is formed and then going away from the surface. So, the air is always or oxygen is always in contact with the sample surface, we cannot prevent oxidation in such a case.

So, type c curve is appeared due to the volatile oxide formation on the surface; one example if we take molybdenum, molybdenum is a metal with oxygen and greater than 700 °C, this molybdenum will form molybdenum molybdenum-trioxide. And this is volatile in nature. So, around 704 °C or above 704 °C, all the molybdenum trioxide will go away from the surface, and it become non protective in nature. So, this type of scenario may occur.

Now, the second type of environmental resistance that we should look for in a material is sulphidation, because of the presence of sulphur containing gases.

So, here this occur in presence of sulphur dioxide or sulphur trioxide ratio, which gives you the partial pressure ratio gives you whether it is mostly like a oxidising condition or maybe hydrogen and hydrogen disulphide type of scenario where the environment is reducing, in both way actually this sulphur containing compound may form. So, this sulphide compound of the alloying elements means, I have taken a material which contain some of the alloying element.

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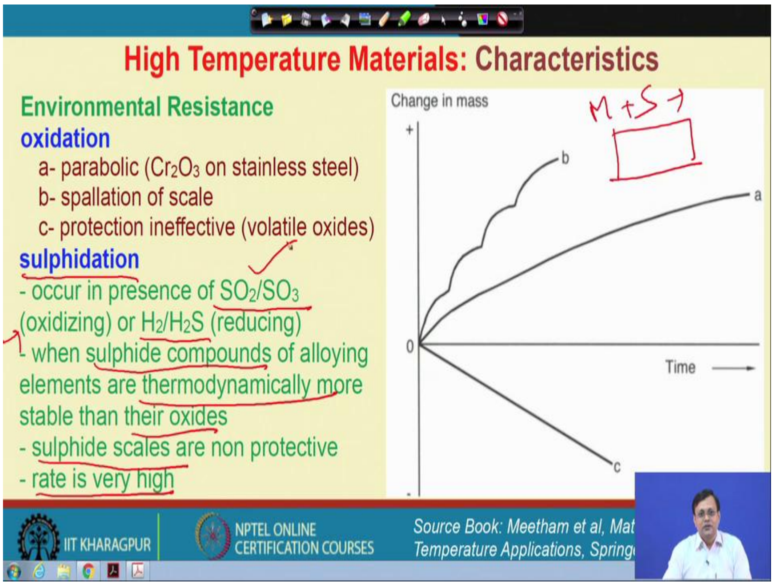

And they basically react with the sulphur. So, metal react with the sulphur to form sulphide compounds.

So, this sulphide compounds when it become thermodynamically more stable than the oxide then the chances of such formation become more prone. On the other hand, the sulphide scales are all time, it has been seen that they are non-protective in nature. And the rate of this sulphidation is very high. Oxidation occur in a relatively slower rate than the sulphidation.

So, the material where there is a chance in the environment presence of any kind of sulphur containing gases whether it could be oxidising or reducing, in both way the sulphidation is very much important aspect to consider.

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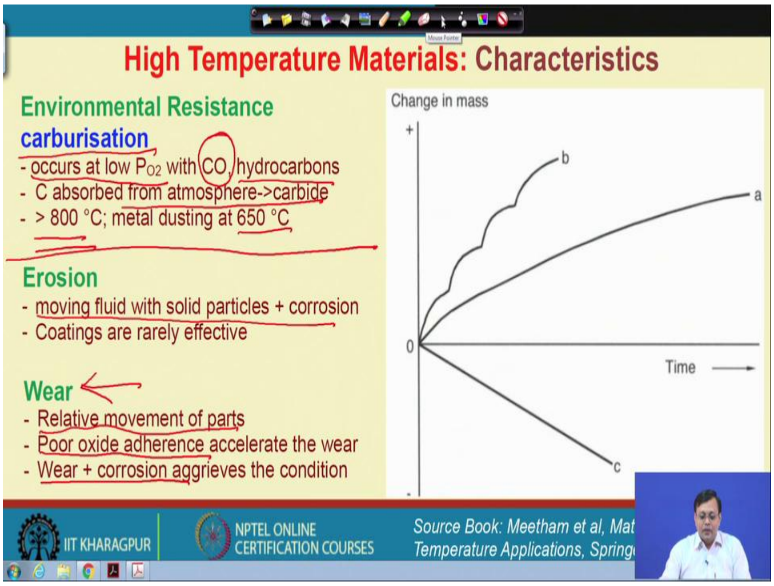

Now, let us talk about another category of environmental resistance that a material should exhibit. That is called carburization. Here we can always think about that may be a steel containing carbon that is why carbonization, no it is not like that. It depends on the partial pressure of oxygen with the carbon monoxide presence in the atmosphere. So, if carbon monoxide present or any hydrocarbon is present, then carbon could also be observed on the surface and form some carbides. And that is the material should exhibit some sort of protection.

So, the first chance is that it occur at a low partial pressure of oxygen, and in presence of carbon monoxide or let us say hydrocarbon. On the other hand, the carbon as an elemental form may be present in the atmosphere of material could form carbide. Usually, this carbon containing carburisation process has been observed at greater than 800 °C, where carbides are mostly stable. However, it may also aggrieve in presence of some other compounds which we call it as a metal dusting. So, the metal carbide will form on the surface and this metal dusting also aggrieves the situation.

So, these are so far as environmental resistance. Now at the other important aspects of the characteristic that a material has that is the erosion. Here we are talking about erosions means removal of material from it is surface, how it can occur?

Let us say we have expose a material to higher temperature; however, there may be a fluid is flowing. So, the moving fluid may also contain some solid particle, which is continuously heating the surface of the material. And then also there may be a presence of some corrosion in nature, because there is a fluid. So, this erosion may occur at that time. And you can think about, yes we can put some painting or let us say some coating, on the material, that can survive, no it really does not, because the coating are very thin and under that kind of physical rubbing action or, let us say erosion, it will hardly prevent. And once the coating goes away then corrosion aggrieve the situation.

So, erosion of the material means hardness of the material at the surface is also important, and we will come into detail later on.

Now, another aspect is the wear. Here we are talking about wear means, there are component which may be moveable. So, the relative friction between 2 different parts of a component could cause wear. So, this is due to a relative movement of the parts, and a poor oxide adherence may occur, because two part is let us assume that it is under some oxygen environment, or maybe in air. So, oxide scale has formed, now there is some rubbing between the 2 parts. What will happen, the oxide scale will go away from the surface. So, it will again further get oxidized. So, these are so many consideration people has to consider.

Now, the other part is basically the wear and corrosion that may also aggrieve the condition. So, wear and a corrosion both if together, then we will see a larger effective wear in that case.

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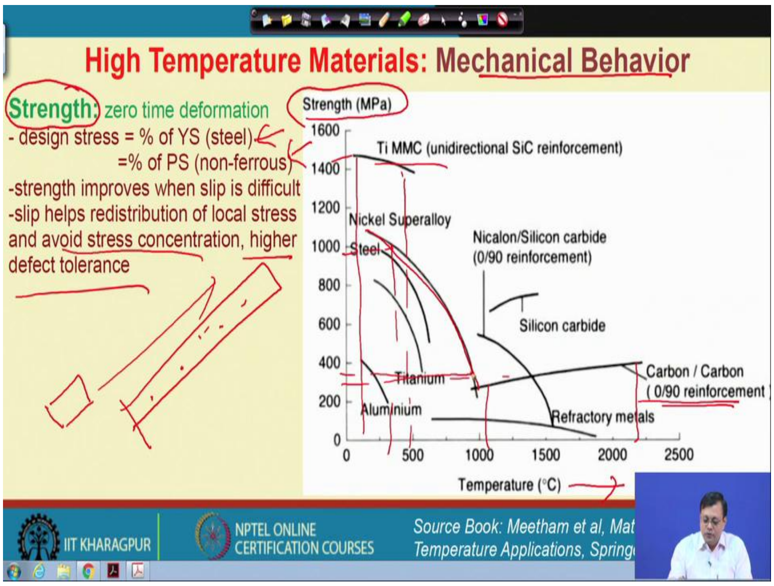

Now, the other aspects are the mechanical behaviour of materials. In that case, definitely we must first think about the strength. So, here this is the strength we are talking about like a zero-time deformation strength, means we are talking about yield strength. So, let us say at a given temperature we do not allow any creep, immediately we load the sample and we get the yield strength of the material. Usually in case of steel we call it as a yield strength for non ferrous we can call it as a proof stress that is 0.2 %.

So, there the strength should improve when slip is difficult, there is no doubt. However, one should consider that strength also help in redistribution of the stress. Let us assume I have developed a high temperature material, which helps to form in a particular geometry. Then if slip does occur, then there will be a homogenous deformation at a given temperature. And then the material will deform. In such a case what will happen. We can avoid the stress concentration. Because material is deforming, let us says this is the initial shape of the material, and after deformation it is elongated in length. And it has homogenously elongated and we can avoid the stress concentration.

Now, if we avoid stress concentration during plastic deformation, or let say any kind of forming operation, then the defect will be less in the sample. Because the higher defect tolerance we can allow in the material. Now let us have a look at some of the material, and it is zero-time strength, means basically zero-time deformation or yield strength of the material. And here titanium MMC could be used at higher temperature, and this is let us say the usable temperature range. Whereas if we think about carbon-carbon composite the strength may be low, but we can go let us say up to 2000 °C.

Now, in case of nickel based superalloy if we apply higher stress level, we have to apply lower temperature. And for higher temperature, we have to use lower stress. So, this is a very interesting plot of different kind of ceramic, different alloys or let say composites, or let say these are also some of the composite micro structure.

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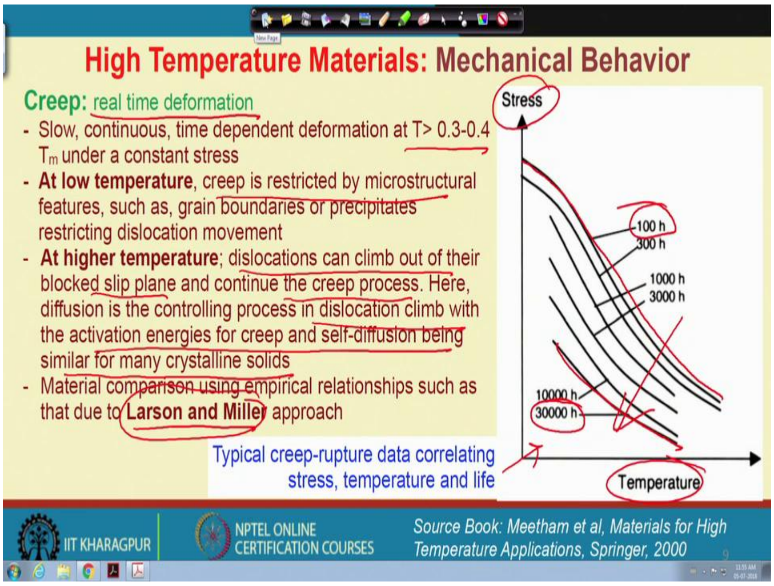

So, the strength is a very important criteria. Now in case of mechanical behaviour, the second important criteria is the time dependent deformation. Like, I said about time independent deformation means the normal strength, and here this is the real time deformation, which is called as a creep. So, creep is usually a slow process which is continuous and time dependent, and a temperature is somewhat around 0.3 to 0.4 T_m. However, at lower temperature creep is restricted by some micro structural features, such as let us say the grain boundaries or precipitate which restrict the dislocation movement. However, at higher temperature, the dislocation can climb out of their blocked slip plane and continue the creep process. So, here the diffusion is the controlling process and dislocation climb with an activation energies for creep and self-diffusion becomes similar in many crystalline solid.

So, for that particular purpose, we can think about let say an approach that is called Larson miller approach, and we will try to see later on how to classify material using this Larson miller approach. I show you here one of the important plot with temperature versus stress for a particular extent of time, let us say, for 100 hour, we can use material at higher temperature and higher stress, whereas if we need larger exposure time then we need to go for a lower stress level. So, the higher the time of exposure of a material due to the creep, we simply need to go for lower stress and lower temperature level. This is the important learning out of this.

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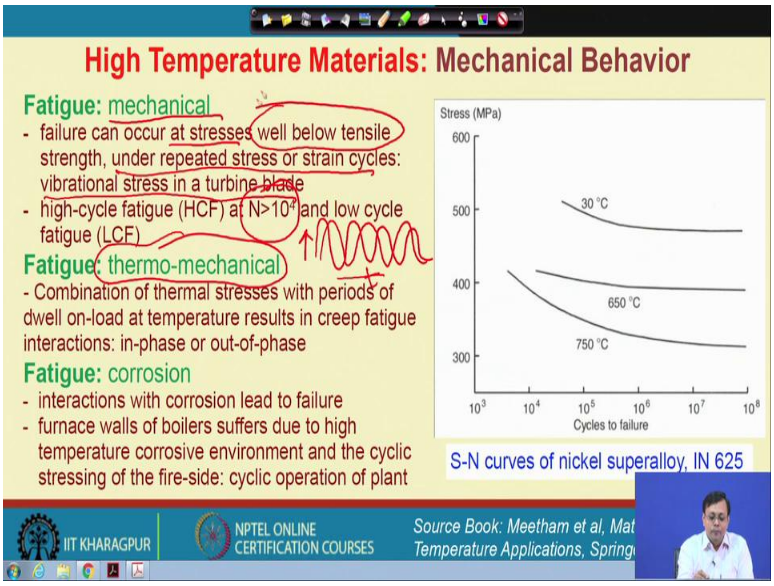

However, we can also think about the fatigue behaviour of materials because fatigue is important aspect of another mechanical properties. So, this fatigue could be mechanical fatigue, means the failure can occur at a stress well below the tensile strength level. And under repetitive cycle or repetitive stress or strain cycle like a vibrational stresses that occur in a turbine blade. The situation may be very different.

Usually the fatigue are of two different types. One is called as high cycle fatigue and low cycle fatigue. The high cycle fatigue, the number of cycle is greater than 10^4 or low cycle fatigue is less than 10^4.

Now, let say here we talk about only the stress cycle or strain cycle. This is with time and here is the amplitude of the stress. It may also occur that I may increase the temperature and decrease the temperature. So, there could be a fluctuation of the temperature, and we call it as a thermo mechanical fatigue. Means: a combination of thermal stress which could be in phase with the load or out of phase with the load.

Now, the third category of the fatigue behaviour is the corrosion fatigue; means, a fatigue under aggressive environment due to the interaction of corrosion which will lead to the failure.

A furnace wall will have in a boiler that suffer let us say high temperature, which is also under a fatigue condition, due to the cyclic operation of the planet. So, this is like a corrosion fatigue, and you can see this is let us say the cycles to failure where below 10^4 , we call it as a low cycle this is basically low cycle fatigue and this is high cycle fatigue.

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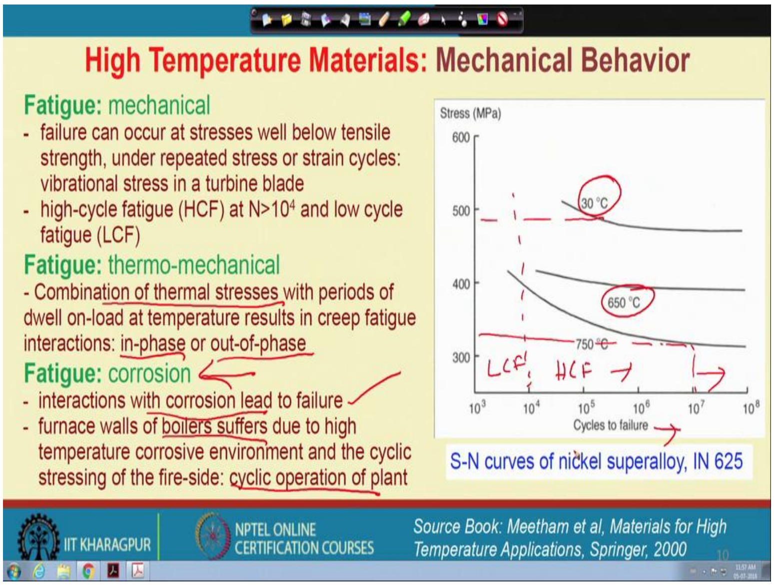

And here let say you can see that a lower temperature we can use a higher stress, higher as at higher temperature we have to go for low stress in order to ensure that the material will survive at higher cycle.

With this, today we finish our discussion. And we will continue this discussion in the next class.

Thank you.