Advanced Materials and Processes

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

Lecture – 30
Introduction to High Temperature Materials (Contd.)

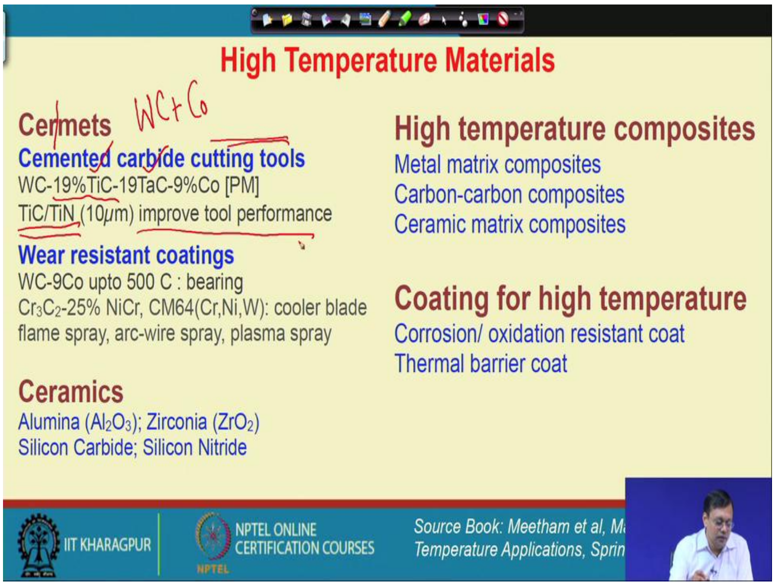
Welcome to NPTEL, myself Dr. Jayanta Das from department of Metallurgical and Materials Engineering, IIT Kharagpur. I will be teaching you Advanced Materials and Processes. Last couple of classes we were discussing about the high temperature materials and today you will continue the discussion along the direction.

Let us assume that we need to develop a tool material and the tool means a continuous friction rubbing between 2 surfaces with the workpiece. And here the most important engineering properties required at the red hardness. Red hardness means at a due to the rubbing or friction at very high temperature or thermal stresses are generated, and the material should survive in that cases.

Even though we can use some coolant, but there must be some temperature would be generated, and the wear and tear should be very high. In such a situation the tool material should be higher hardness than the workpiece then only the cutting action will occur right. So, these are also one class of high temperature materials, and today we will try to answer what are those material that can be exploited and has been exploited so far and the how the improvement has occurred.

On the other hand the engineering ceramics are very widely used as higher temperature or let us say the composite, where we have very high friction in the in the lightweight application areas like aircraft. Or may be in some cases the material, intrinsic properties we cannot change due to its application, and we can only apply some superficial coating on the surface or overlay coating on the surface and time to time we simply provide those coating during its working condition. So, these are the very different aspect of the high temperature material today we will discuss.

(Refer Slide Time: 02:56)



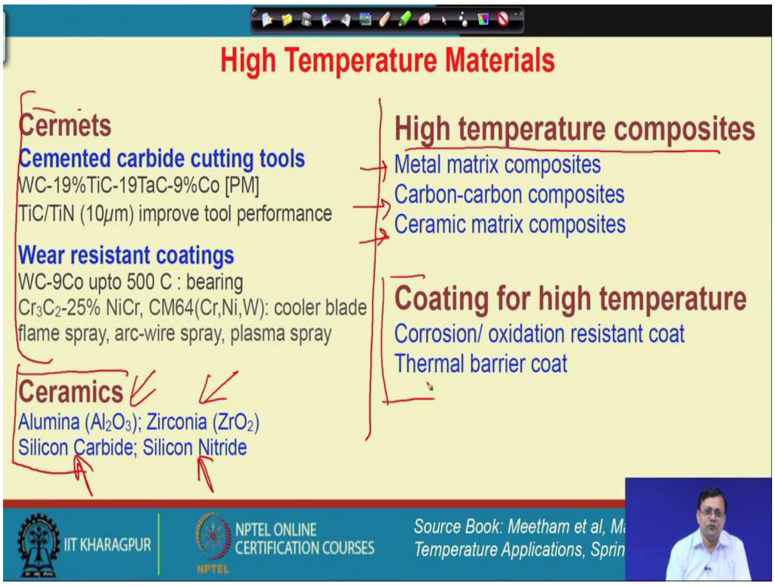
So, for tool material the very important cutting tool material are the cemented carbides, because carbide gives the very high strength and we have 5 to 10 % metal matrix that basically give advantage of a larger toughness; so, this name is itself is Cermet. So, the Cermet name came because of the ceramic and metal.

So, a very common Cermet you must have heard about tungsten carbide plus cobalt matrix; here cobalt matrix is in the range of 9 % to 15 % and these are mostly produced by powder metallurgy. But to improve the tool performance or red hardness, people have already explored some other carbides to incorporate in the microstructure including titanium carbide, tantalum carbide.

So, this provides a much higher hardness as a cutting tool material. However, to improve the tool performance further, we also provide some carbide or nitride coating of something like 10 µm to 20 µm on the tool surfaces and this improves the further properties in terms of let us say when the tool material comes in contact with some fluid, then it provide some further protection on the corrosion behaviour.

Now, there may be some other component which require some wear resistance coating. So, like bearing, there is a continuous friction and we need to provide some coating, these are wear resistant coating, we are talking about high temperature coating. So, this wear resistance coating, which lets say provide protection up to 500 °C, Here also we use Cermet as a coating.

(Refer Slide Time: 05:17)



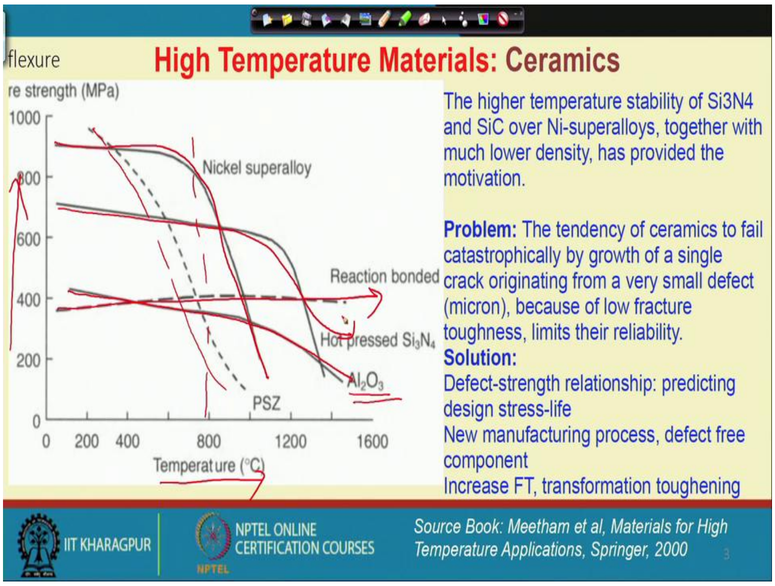
So, Cermet basically means that a tungsten carbide and cobalt and we provide those coating for the bearing and also there are some other coatings including chromium carbide, nickel chromium 25 % or let us say CM64, which contain chromium nickel and tungsten for cooler blade application and we usually adopt the technique of some flame spray. Or let us say arc wire spray or plasma spray, these are very common technique to provide those wear resistant coating on the surface of the material. So, these are the typical application areas of the Cermets, means ceramic metal combination, where metal is basically like a matrix which hold those ceramic particle together and provides a wear resistance properties.

Now, the engineering ceramics there are four common engineering ceramics often uses for various purposes including alumina, zirconia, silicon nitride and silicon carbide. So, these are also used as abrasive material and high temperature materials.

On the other hand, there are material where we need to improve certain properties within the working temperature range. People develop this composites, high temperature composite not for improving the range of the temperature of the application, but for improvement of the performance during that working temperature range.

So, there are metal matrix or ceramic matrix or let us say carbon-carbon matrix composites that are this 3 common high temperature composite has been developed, and today we will discuss this composites and the fourth category of this material are the coating for higher temperature like overlay or thermal barrier coating, where the intrinsic property of the material cannot be changed by adding some aluminium or chromium there may be some presence, but they are not sufficient to provide high temperature resistance.

(Refer Slide Time: 07:49)



And therefore, we need to provide some overlay coatings. Now, let us have a look at this plot and there are very interesting things we can notice where, X- axis is the temperature and Y- axis is the flexural strength. So, the workhorse material which we always compare is the nickel superalloy, where we have a range of something like 800 where the flexural strength is quite high.

However if you look at some of these alumina, which is a engineering ceramic, it has a lower strength or flexural strength than the nickel superalloys, but we can use for up to quiet higher temperature range or let say the zirconia, which we often use and or let us say the reaction bonded or hot pressed silicon nitride, they can be used for this application and the range of these reaction bonded or hot pressed silicon nitride or alumina, the range is much better than the nickel based superalloy.

So, ceramic has some better advantage except the toughness values actually. So, that is why the high temperature stability of this phases like silicon carbide or alumina and silicon nitride, they are getting more attention because of the stability of the phases together with a lower density and it has a motivated people, to make research and develop this material for this for this particular purpose.

However you may see that there are some other issues also told in this particular plot. Here is silicon nitride and this is a reaction bonded silicon nitride. The reaction bonded silicon nitride is basically this particular hot press are there and here the differently process material contain different type of defect why? Because due to the low toughness of ceramic material, there are defect present and you may recall initial lectures we have talked about that how much are the allowable defect in a ceramic, which is in the range of a micrometre means 1 to 10 μm.

Where 2 MPa√m or 10 MPa√m are the limit of the fracture toughness whereas in case of a metal or an alloy, we can allow up to 1 cm or may be higher than that. So, if there is a very tiny hole or pore present that is sufficient to fail the material catastrophically during its service. So, without much growth of a single crack during the operating range. So, very small defect of a micrometre size is sufficient to cause a brittle failure, due to low fracture toughness and basically limit the reliability of using the engineering ceramic for higher temperature also.

So, this is a very common problem of any of the ceramic material; however, there are 3 approaches people have tried to look at to find out the possible solutions. So, the first solution is that, let us think about some micromechanics based approach and try to correlate the defect and strength.

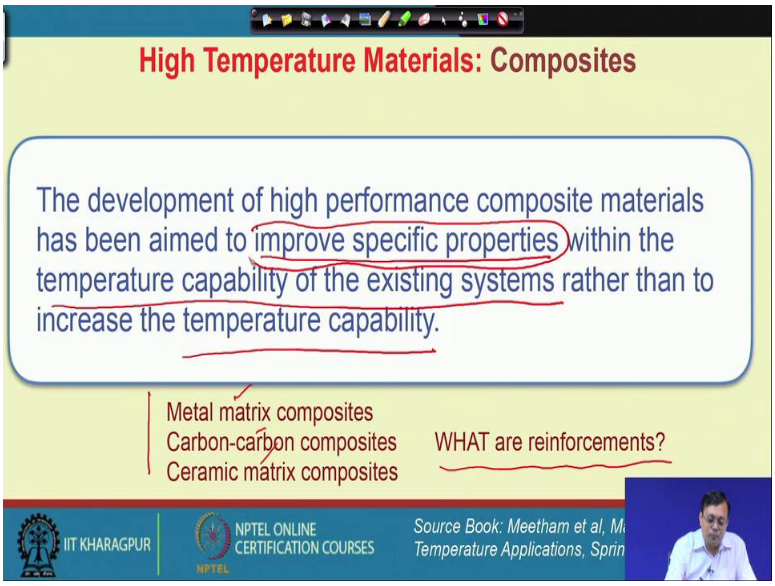
So, let us say I have a flexural strength, and how much strength is linked with how much is a defect size. And try to predict out of that a relationship between design stress and the life. So, this is a very nice example of using fracture mechanics concept and increasing to enhance or to predict the reliability; however, people has the second option that try to improve the manufacturing processes.

Means as I said the reaction bounded or hot pressing or try to make something like a defect free component even though it is not possible. Because for producing ceramic, if we go for powder metallurgy route, then a 99 % density to achieve is a remarkable achievement actually. So, this is a bottleneck of using any of the engineering ceramic, where the stress has to be applied in a ceramic.

However, there is other kind of or third approach that has been taken by the engineers that why do not we improve the fracture toughness. This is also one very nice example like alumina or zirconia, we can use some transformation toughening that you may have heard about. So, increase the fracture toughness by transformation toughening concept.

So, this is a very nice examples or the possible solutions or these 3 solutions we can do with the any of the engineering ceramics, but in some cases, we have to use the ceramic otherwise the material cannot survive as a common alloys.

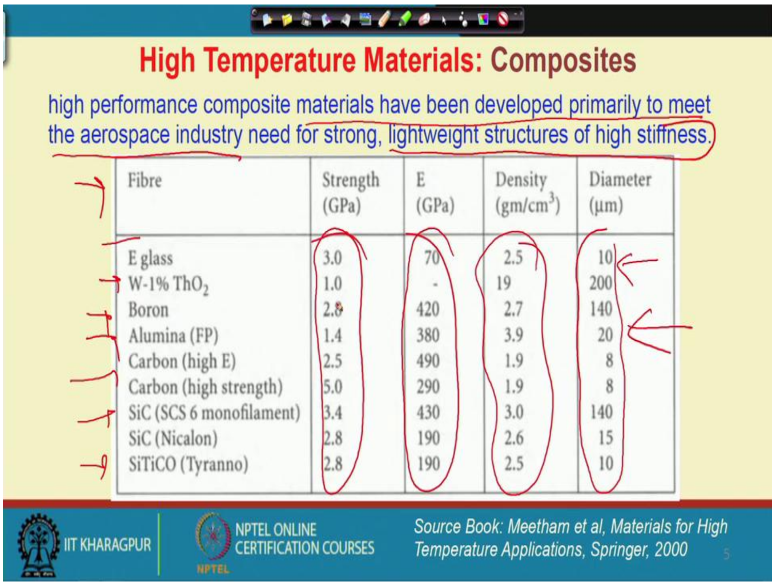
(Refer Slide Time: 13:38)



Now, if we think about composites, composites are developed not to enhance the limit of the temperature. So, the development of these high performance composite material is aimed to improve some specific properties, within the temperature capability of the existing system rather than the temperature capability. So, this is very important aspect when we really need to develop a composite.

So, the composites as I said are the metal matrix or carbon or ceramic matrix composites, but when we talk about composite we talk about the matrix here, but what are the reinforcement we are going to use. And why we need to use the second phase in a composite to improve a specific properties, what kind of properties we really mean about this.

(Refer Slide Time: 14:50)



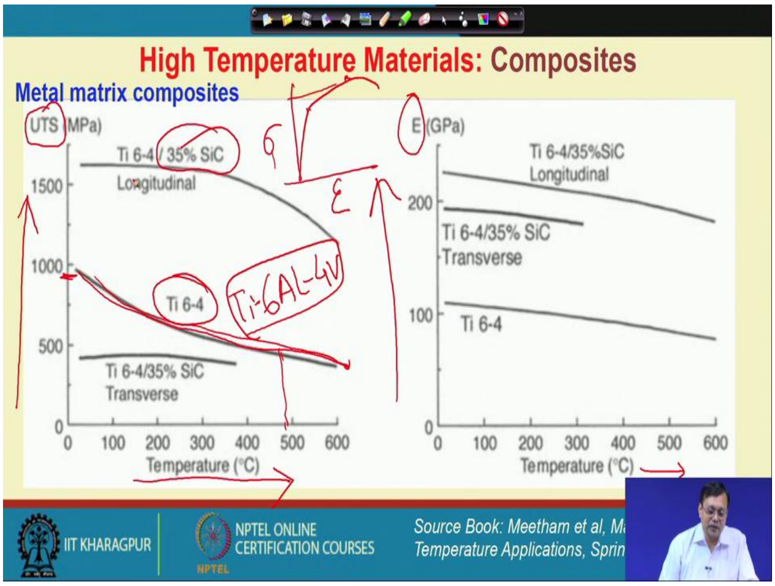
So, here for the composite, let us have a look at these different fibres that we can employ. So, the basic purpose of using this composite is aimed for developing primarily to meet the requirement of the aerospace industry, for very strong lightweight structure with very high stiffness.

Because let us say, if I have a material and that material we continuously used for higher temperature, if we increase the temperature then the Young's modulus decreases and that has nothing to do with the overlay protection, like alumina or chromia we can have we can have always a better oxidation resistance, but it cannot improve the stiffness. So, stiffness is one of the very important aspect for any aerospace application or many other engineering application, and there we need the fibre to enhance the stiffness.

So, like E glass, tungsten, thorium, boron, alumina, carbon, silicon carbide SiTiCO these has a very high strength of 3 GPa to 5 GPa range. So, it is 5 times higher or 10 times higher than any metals and alloys whereas, the Young's modulus is almost 2 to 5 times higher than any conventional metal matrix, and the density is also quite low and we use this material as a common fibre having a diameter of few micrometre.

So, this is very important that as the diameter could be smaller and smaller, the stress will be continuous in the matrix even though we use some short fibres. So, the stress continuity can be improved by using smaller diameter fibres into a metal matrix, and that will maintain the stiffness at much higher temperature.

(Refer Slide Time: 17:21)



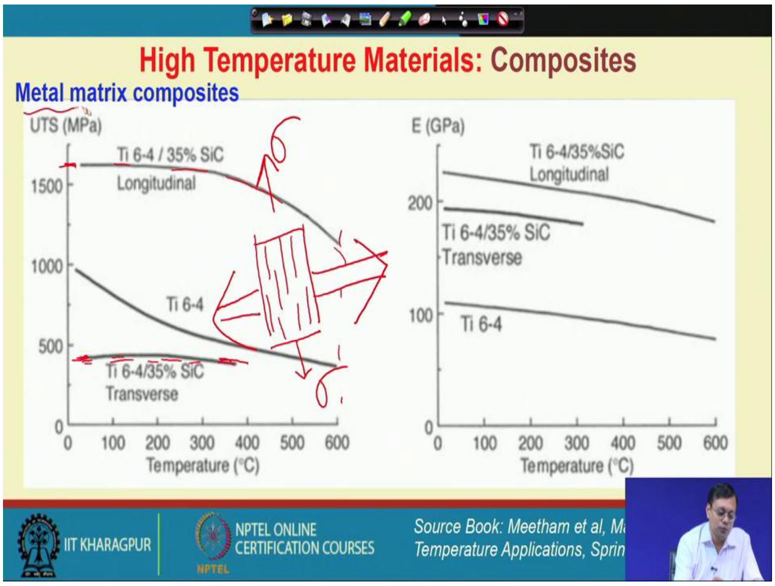
And that is basically the purpose of using metal matrix composites and let us see the example these metal matrix composite used for higher temperature.

So, here I show you one plot with temperature versus ultimate tensile strength of the material. So, if you look at any of the stress strain diagram. So, here is the yielding and then we go to the ultimate strength, here is the yield strength or proof stress, this is stress versus strain plot. And here I show you the Young's modulus which is E with the temperature.

Now, let us assume that I have an alloy which is titanium 6-4; you may have heard about titanium 6-4 it is basically titanium, aluminium, and vanadium alloy where there is 6 wt. % aluminium and 4 wt. % vanadium is present in short form we often call as Ti 6-4. So, this is the matrix and if you take this only matrix, then you will see that from the ultimate strength that basically decreases with increase of the temperature, when we go let us say something like 400 °C to 500 °C.

Now, if we apply some silicon carbide fibres into it let us say something like 30 %, and measure the ultimate tensile strength along the longitudinal direction, a longitudinal direction means we are talking about that this is a composite and these are the fibres.

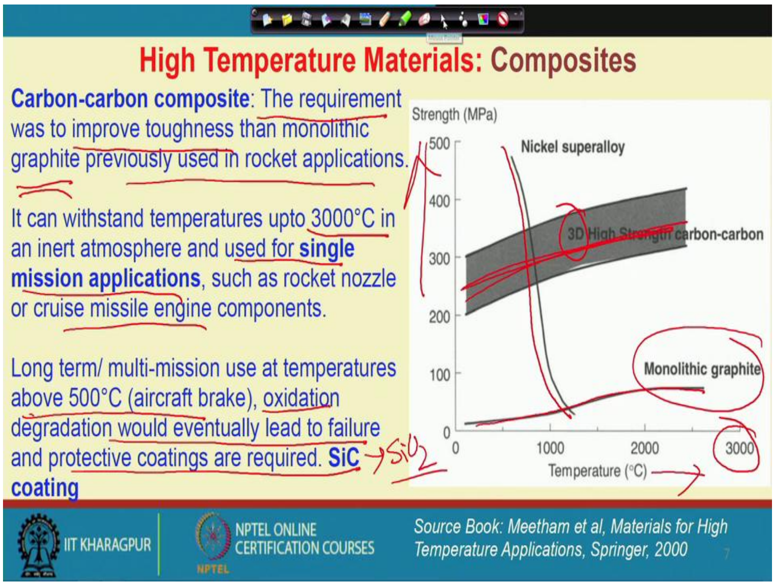
(Refer Slide Time: 19:01)



Aligned along particular direction and we apply some stress in order to measure the strength of the composites. So, we will get such a high temperature, and then we can have a good ultimate tensile strength over up to 600 °C. Now if we apply stress along this direction, which is the transverse direction, then we will automatically get a lower strength value, which also does not change significantly with the temperature range. So, using of a let us say aligned fibre composite or let us say random fibre composite are also not a bad idea to use or develop this composites.

Now, let us have a look at the change of the Young's modulus with the temperature. So, here this is a typical let us say 100 or 105 Giga Pascal is the is the Young's modulus of titanium 6-4, and there is a slight decrease with the temperature, where the stiffness can be improved and we get much reliable stiffness values at much higher temperature. So using this composites always a beneficial for higher temperature application.

(Refer Slide Time: 20:41)



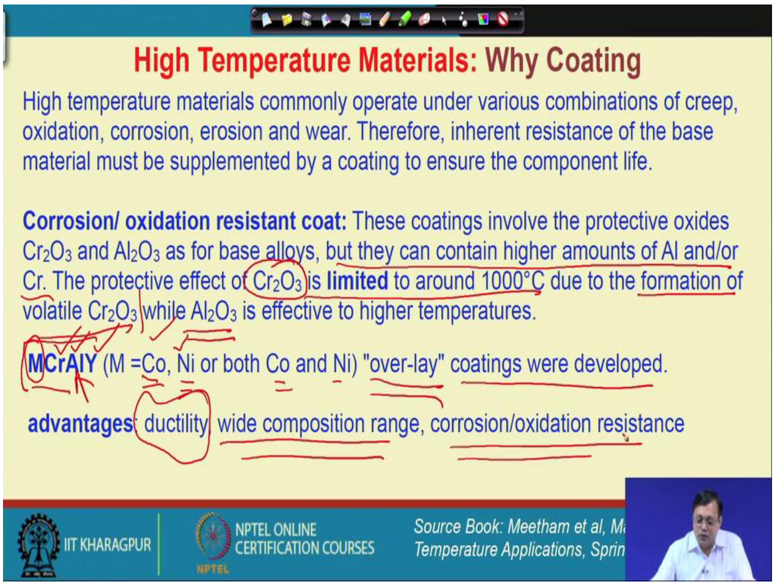
Now, the other composites are like the carbon-carbon composites; and you may recall that carbon-carbon composites could survive at much higher temperature than the any metal matrix composite because carbon itself is a high temperature material, but carbon appear as a graphite, where graphite oxidises into carbon dioxide and leaves the material.

And therefore, we need to think about of giving some protection mechanism to avoid high temperature oxidation, because the high temperature strength retention of carbon fibre is remarkable. How to see that? Please have to look at this diagram with temperature versus strength. Where around 1000 °C, the nickel based superalloy basically falls like this and monolithic graphite has such strength level. Where if we produce 3 dimensional high strength carbon-carbon composite, they has a very wide range and this could be used for aerospace industries and not only can be used they are used, and improved toughness can be achieved for any kind of rocket application.

So, that basic requirement for developing carbon-carbon composite is to improve the toughness of the monolithic graphite, which is quite less and previously used for the rocket application. So, this carbon-carbon composites can easily withstand up to 3000 °C in an inert atmosphere. Inert atmosphere means in absence of oxygen, where carbon has no chance to form carbon dioxide; however, these can be used for single mission application. So, like rocket nozzle or let us say some of the missile engine components and this can be used.

But if we have to reuse that component means re-entry vehicles, when it goes out of the surface atmosphere again it enters into the atmosphere, and multiple times we have to use we have to think about a multi mission purpose at temperature higher than 500 °C; as an example aircraft brake. Because since it is carbon, it has a very low density and it is very lightweight and we use as a brake and the oxidation degradation; we can eventually lead to the failure and protective coatings like silicon carbides coating can be given. So, if we use silicon carbide, silicon will produce silicon dioxide, and this gives us a protection to the composites, and this is one of the very nice example of very high strength carbon based composites.

(Refer Slide Time: 23:50)



Now the other kind of a high temperature materials as I said are the coating. You can always ask that we can improve the inherent corrosion resistance or oxidation resistance of the material, but a high temperature material for various combination of creep, oxidation, corrosion, erosion wear, and all these properties are very mandatory properties for choosing a high temperature material. And therefore, necessarily, let us say for improving the inherent resistance to the base material, sometimes maybe complimented by using some coating in order to ensure the life.

A material may have a very good creep resistance, but it may not have a high corrosion resistance at higher temperature, and then we have to go for developing some coating or may be due to continuous friction the coating has damaged. And during that particular time we have to re-apply the coating so that we ensure the service and elongate it and that is basically the purpose of developing coating. And we have already seen that those aluminide we can deposit on some of the material, and we can also exploit those properties.

So, this corrosion resistance or oxidation resistance coating is one type, and this coating basically involve a protective oxide like chromia or alumina as for the base alloy. However, they can contain a higher amount of aluminium or chromium. You can think about that alloy that contain very high amount of chromium or aluminium and what is the need for coating. Let us say the chromium has a problem that I said that the chromium is protective only up to 1000 °C. The formation of volatile, chromium oxide is the major problem of chromia forming elements and where alumina is the only substitute at higher temperature.

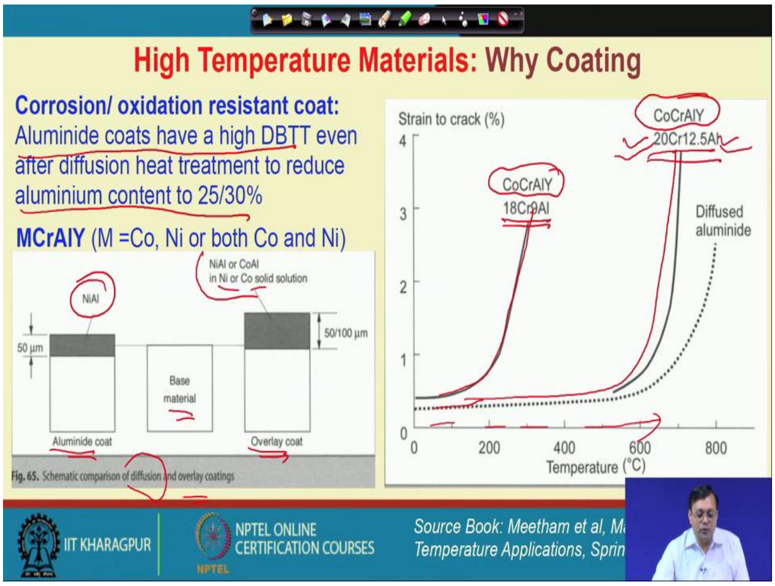
So, I can take an engineering component, which has already chromium and aluminium inside the material and I want to improve the service life. So, we simply coat it using aluminium or we give some aluminium simple on the surface not alumina, and aluminium form aluminium oxide during high temperature exposure to produce the coating itself. So, both way we can basically produce coating.

So, therefore, the recent or the one of the very important coating that has been developed is MCrAlY. So, here M stands for cobalt, nickel or nickel and cobalt both. Here M, along with chromium, aluminium and yttrium. So, yttrium has a purpose that you already know that it basically has a mechanical keying effect and peg or locking effect that improve the spallation property which means the scale will be very much sticky with the surface of the component.

Whereas, the aluminium will form an alumina at higher temperature and chromia forms from chromium. So, the principle behind developing this chromium containing compositions is very much simple. And overlay coatings are developed with that. The advantage is basically the ductility, because of addition of cobalt and nickel which provides an inherent plasticity of the scale.

So, during stress application the coating itself will not be cracked on the surface. That is very important criteria. And we can produce wide composition range and wide composition range will give us wide range of engineering properties, and it has a very good corrosion oxidation resistance.

(Refer Slide Time: 28:32)

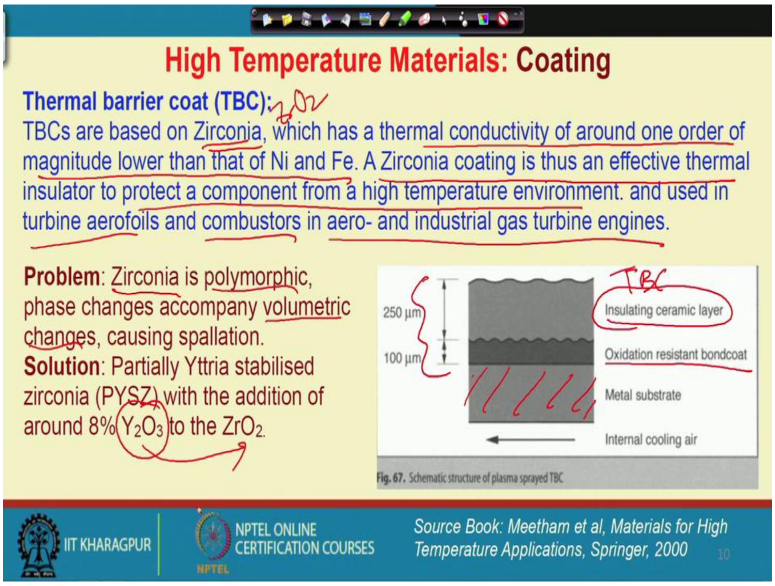


So, let us see one of the example of such corrosion resistance coat, where you can see here the amount of chromium aluminium has been changed in this particular coating that I just told you. And with the operating temperature, by changing the composition, this is the strain that require cracking. So, it improves. So, we can use or change the composition for a better service life.

So, this aluminide coat like nickel aluminide which we can use as a coating and a cobalt aluminide, where inside nickel or cobalt solution on a base material, we can use as a overlay coat or aluminide coat or this is like a diffusion coat or overlay coating we can employ, where the aluminium content reduces to only20 to 30 %, even after diffusion heat treatment.

So, initially we start with a composition and then we allow some heat treatment and basically allow some diffusion bonding. So, that the coating will have a very good inherent strength at the interface, and we can use that coating at high temperature. So, this is basically the purpose of this overlay coating.

(Refer Slide Time: 30:05)



Now there are another two type of coating; one is oxidation resistance coating and another is thermal barrier coat. Thermal barrier coat basically contains zirconia; zirconia is zirconium dioxide, which has a thermal conductivity, which is one order magnitude lower than any of the nickel and iron.

So, this coating not only protect from corrosion and oxidation, but protect from extremely high temperature; let us say 3000 °C temperature. We give a thermal barrier which provides the heat to go inside the material. And here the zirconium coating is a very effective thermal barrier or insulator that protect component from a very high temperature environment and let us say for a turbine, aerofoil or let us say some of the combustor in an industrial or gas turbine, we can provide these coating. So, let us see here I have a metal substrate.

So, we give first an oxidation resistance bondcoat like this M cobalt nickel yttrium, and then on the top of it we can give some insulating thermal barrier coat and both coating can improve the reliability of the life.

So, there is only one problem with this thermal barrier coat like zirconia, that it is polymorphic, which means it has different changes in the crystal structure from tetragonal to other and that basically causes a volumetric changes and calls spallation of the zirconium. And here again the solution is to use the partially stabilized zirconia by adding some yttrium oxide into it.

So, yttrium oxide improve the toughness as well as the solution of the spallation can be achieved.

So, with this we almost discussed all the different high temperature materials available, and the recent trend as an advanced material so far besides the nickel based superalloy; starting from the aluminide to a steel based composition where heavily alloyed steel used for power plant boiler, 9Cr1Mo steels to a coating. These are very important aspect of any of these high temperature material to be used and next week we will start discussing on the superalloy and the workhorse material.

Thank you.