Advanced Materials and Processes
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Lecture – 02
Introduction (Contd.)

Welcome to NPTEL, I am Jayanta Das from IIT Kharagpur, department of Metallurgical and Materials Engineering and, I will be teaching advanced materials and processes. So, today we will be mostly focusing the development of materials, chronological order of development and, how these advanced materials have been developed by several scientist and different companies.

In addition, the relative importance of this material compared to all other kind of engineering materials will be also discussed, at the same time we will try to look at what is the relevance of metastability in this aspect.

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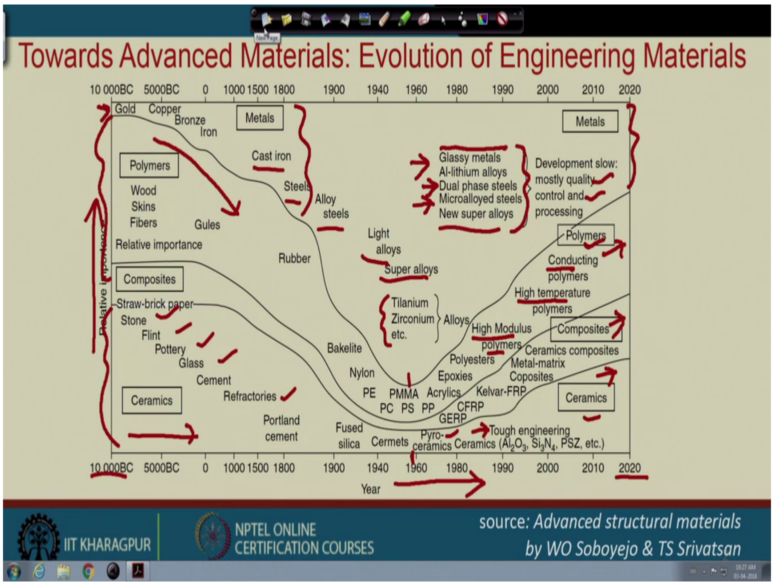

Now, here, if you kindly have a look this slide, towards advanced materials evolution of engineering materials. In the x axis, we have plotted year of development from 10000 BC to 2020 expected and in the y axis, we have the relative importance.

We will see during that period of 10000 BC, the ceramic was very much popular and, polymer was very much popular, except a very little part of part of a gold has been used.

Throughout the different years the stone, flint, pottery, glasses, cement, refractories, Portland cement has keep on developed and, the relative importance also has decreased during that period. Polymer has also decreased. Because importance of metal keep on increases. So, let us say the cast iron, steel, alloy steels has been keep on developing till let say something like 1960's; at this time, the zirconium titanium alloys has been also developed along with super alloys, light weight alloys.

But, after 1960's, if you kindly have a look, then again the relative importance of ceramic material has increased, polymer has also increased and composites also has increased. So, here high modulus polymers, let say transformation toughened zirconia, pyro ceramic, has been developed, including some high temperature polymers, conducting polymers.

But, instead of the plain carbon steel, or a mild steel, the advance steels like dual phase steel, got some preference and has been developed. Another example was micro alloyed steel. So, upon very minor addition of alloying elements in steel, how we can develop and, how we can increase the strength of the steel 3-4 times.

So, that was basically the idea, super alloy even though has been started to develop in 1940's, but very new super alloys here, new means the super alloys which can survive at much higher elevated temperature from let say 800 to 14000 degree centigrade.

At the same time even though glasses were very much popular in ceramic like oxide glasses, or polymer glasses, but metallic glasses has become in the market and, also the researchers try to develop.

So, here the development is slow, but the quality control processing, they has been more focused and the research has been done in that way. Even though the relative importance become a little bit less, compare to polymer ceramic and composites and therefore, we can try to understand that during this year 2010 and 20 a huge effort has been given towards these advanced alloys.

And interestingly most of these advanced alloys are metastable in nature. However, if we have a look, then we can see the importance of these material and, why one should focus on this.

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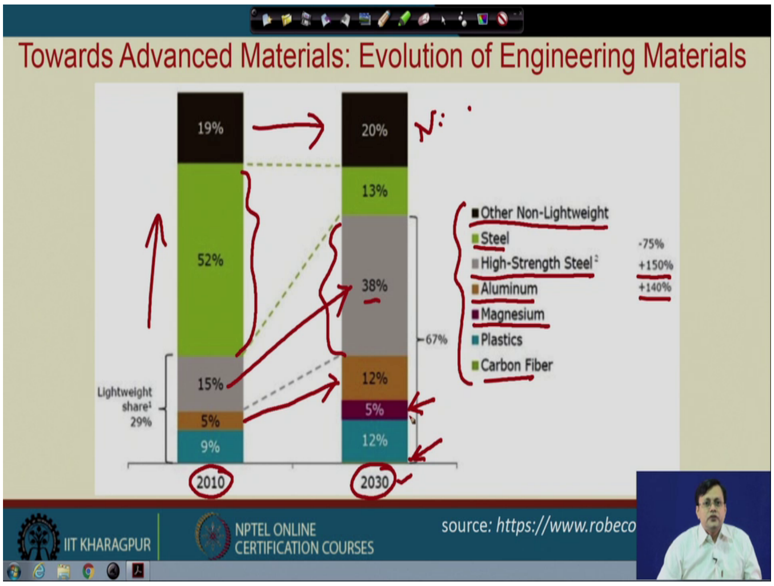

Here I show you another plot here, the percentage share is shown in the y axis, and x axis this is so, far different kind of materials which has been used, or under used. And in 2030, the predicted materials to be used, kindly have a look, here almost 52 percent of the steels has been used. And majority of them are let say low quality steels, mild steel, plain carbon steel, or some part of the alloys steel, tool steels, so on.

However, the market of high strength advance steel will increase. So, almost like from 15 to 38 percent and, this is expected by 2030. At the same time the aluminum alloys, or advanced high strength aluminum alloys should be developed and, which will almost cover and increase by 140 percent.

The high strength steel will increase 150 percent and therefore, if there is a basic need and general awareness among the engineers, to put effort and to develop this alloys. At the same time non-lightweight alloys will not change too much here, let say something like nickel alloys, titanium alloys, maybe there and some part.

Where the carbon fiber are very very less, we can see here. On the other hand, there is another big target of developing high strength, or advanced magnesium alloys, which is expected to cover almost 5 percent of the total materials market. And therefore, you can see that, we definitely need a very wide and general awareness on in this area.

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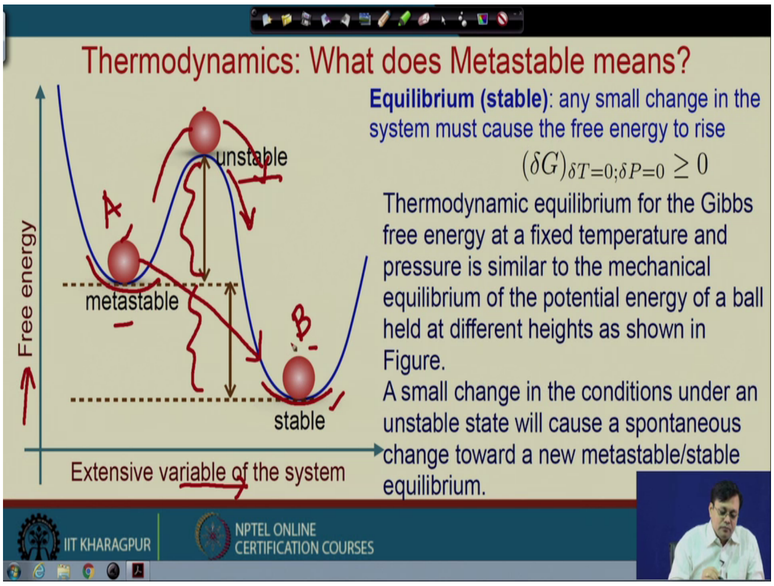

So, we first try to understand, that what is the metastability means, you may have heard about the terminology metastable, but we need to discuss and try to look at what does metastable means. Here, you show a free energy verses variables in the system plot.

We take a very simple example like a ball, which is kept in such a condition and, we can also keep the same ball under such a condition, definitely the energy is higher here, then here. So, there will be a net decrease of the energy, which is often called in terms of thermodynamics.

That there is a net decrease of the free energy; however, to go from this place to this place, we need some activation barrier and, the activation energy controls the kinetic of the process. So, from one state to another state let say state A to state B, if the state has to come from A to B, it helps to come through such a condition, which looks like an unstable condition.

So, if we keep the ball here, there are two probability, either the ball may come into this, B or it may go back to A.

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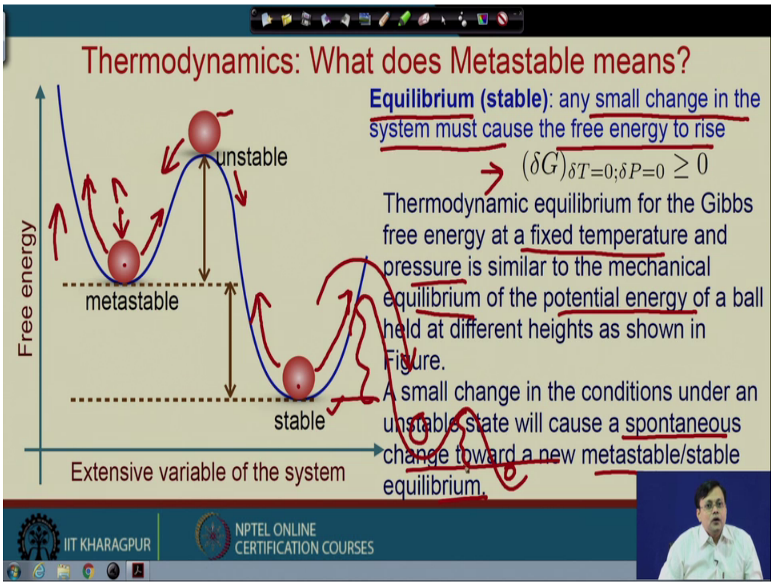

And therefore, the equilibrium, this terminology means, that any small change in the system must cause the free energy to rise. Lets say here also, if you considered position A. Here if we want to increase the position of the ball in any of the direction, then the free energy will rise the same condition is also valid here.

So, you can have a look if I try to push the ball up, then the free energy will rise; however, this is a saddle point configuration, or system may go either any of this two ways. So, thermodynamic equilibrium for the Gibbs free energy at a fixed temperature and pressure is similar to this mechanical equilibrium, which I told here, as a potential energy of a ball held at different positions.

So, a very small change in the condition under an unstable state will cause a spontaneous change towards a new metastable or stable equilibrium, here this we define as a stable. However, there may be more or more such condition, where it will be more and more stable, but in every cases we need some activation energy.

And this activation energy will dictate the kinetic of the process. Let us try to understand the matter, in more in detail here, you see a 2-dimensional plot with free energy verses the variables.

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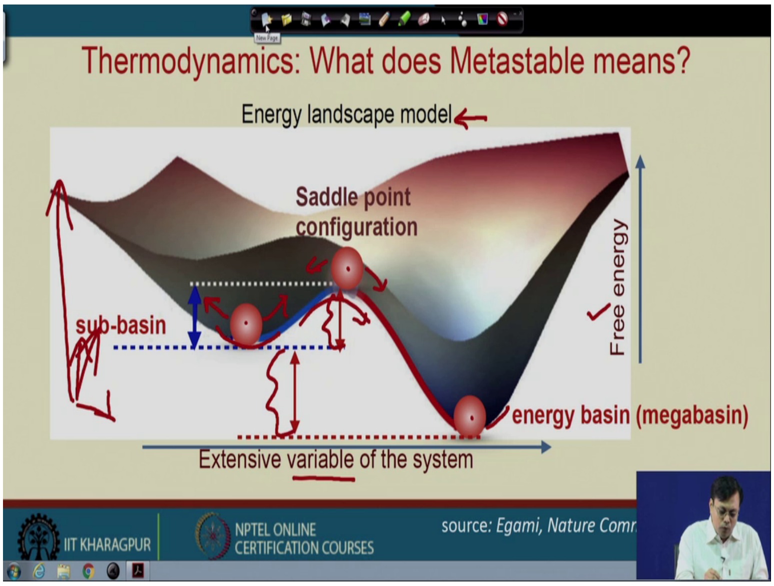

In this plot, the same plot; however, we try to show you in a three dimension, where we can think about let us say two different variables along with the free energy. So, extensive variable we have plotted here and, these are often called as sub basin or this is something like a mega-basin in a system.

So, this model has been adopted from a very well known model called energy landscape model and we again put this three different condition of a ball, where free energy will rise and this is called as a saddle point configuration. So, once the system has to pass to these saddle point configuration, we need a activation energy and, there will be net decrease of the free energy.

So, in this basin anyway, if we want to leave this ball there will be a net increase of the free energy of the system, this is from a very recent literature. However, we may also have a chance not only to go from this place to this way, but we can also push the system, to move from this way to the left, from right to left we can also go, but at that time the situation maybe little bit different, let us have a look. here.

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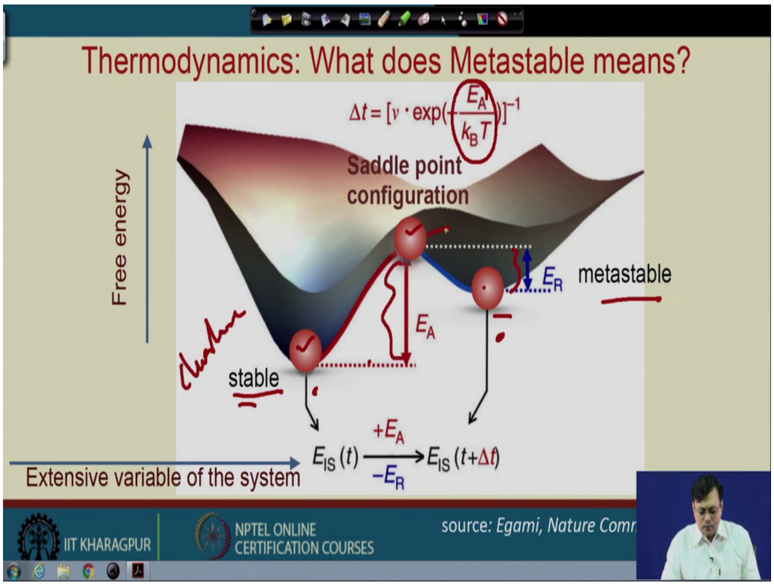

I just reverse the plot and liked to show you that from a stable configuration to a more metastable configuration we can also move. Here, we have shown in terms of the mechanical equilibrium of ball.

But this could be a cluster, here a cluster means, I am talking about atomic clusters like HCP hexagonal close packed cluster, or FCC cluster or body centered cubby cluster ok. And from let say, one crystal structure, the system can move to another crystal structure ok, it has to pass to some equilibrium. So, from a stable material we can also develop some metastable material, if we provide some activation energy.

And this definitely the activation energy appears like a Arrhenius type of equation, even though there is a net increase, but we can consider such a situation, where there will be little decrease of the energy from a saddle point configuration. So, this is very much important understanding one should need for developing the metastable alloys. Because, here metastability means a micro structure, may be a crystal structure may be a phase and all could be a metastable.

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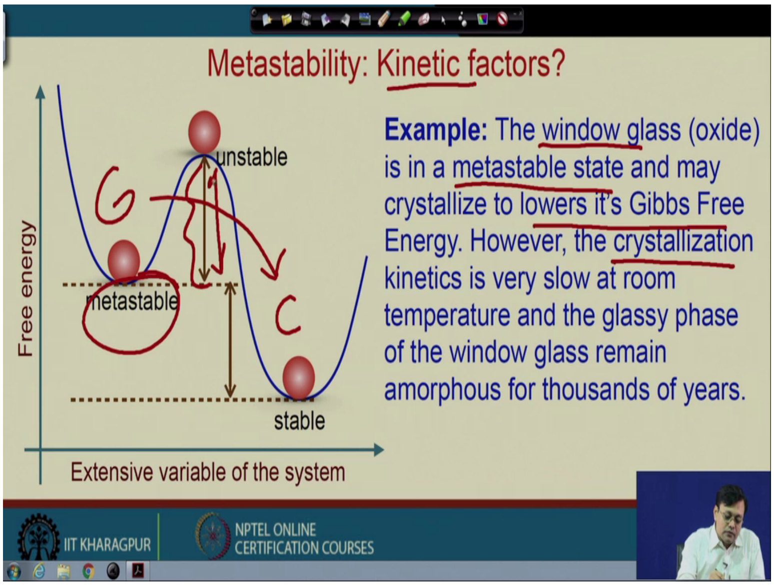

Now, let us look at what is the importance of the kinetics in this process. Since, I said the kinetics, if we can restrict, then we can hold this metastability of a system. As an example, we all know about window glasses, these are oxide glasses like silicon dioxide with some of the additives people add to make some colour. And that is also under metastable state; however, a glass always try to crystallize if some activation energy is given. So, here we are talking about a glass and here this is a crystal.

So, from a glass to crystal, we can we can we can change the state. So, which will also lower the Gibbs free energy; however, the crystallization kinetics here that is governed by this activation energy. And the crystallization kinetics can be very very slow at room temperature and, that is why all these glasses in big temples, or mosque or anywhere you will see that.

The window glasses are stable for 1000 of years. because, we control the kinetics of the process and, restrict the kinetics so, that the glass remain in the glassy phase, for 100's and 1000 of years and this is the importance of developing all these advanced alloys.

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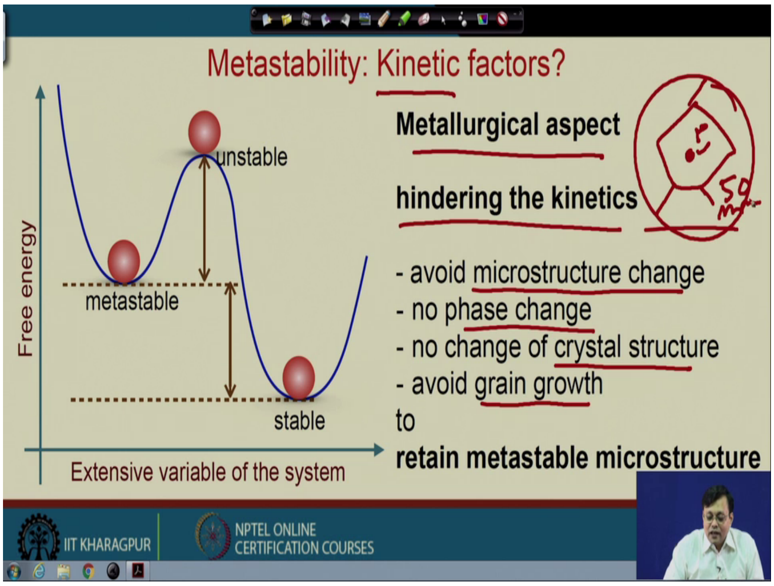

And since we are metallurgists, we try to look at the metallurgical aspect in this kinetic and to control the kinetics of this process. As I said that the hindering of the kinetics is very much important and, how we can hinder the kinetics like, the micro structural change, it means as an example I may have grain of let say some 50 nm.

And, there are some 2 to 3 nanometer precipitate inside ok. And if I have to keep this microstructure in these way, then we should simply avoid the grain growth, also the precipitate, there will be no change in their crystal structure, the phase should not change.

And then only we can retain, such kind of very very fine microstructure of 50 nanometer. And this is the importance of the metallurgical aspect to control the kinetics. And in this way we can develop newer and newer alloys to the system.

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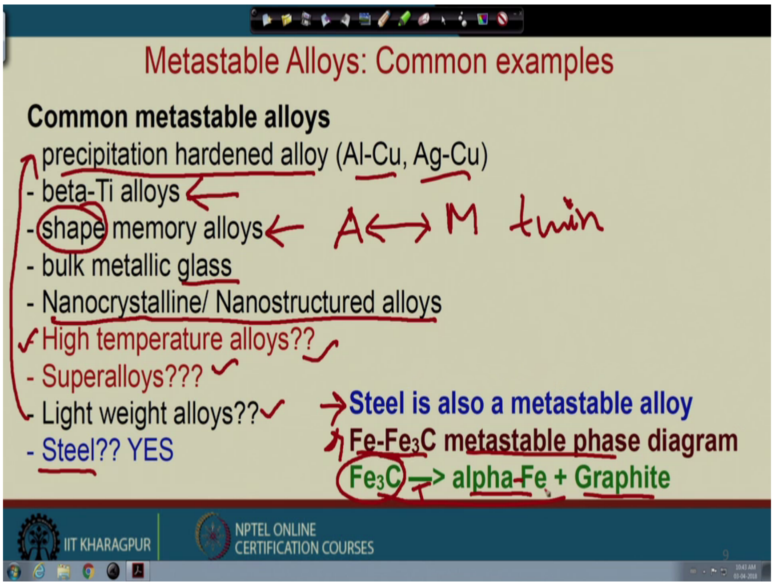

However, I should first talk about some of the very common examples of metastable alloys. As I said the precipitation hardened alloys are also metastable alloys because, the precipitate alloys tend to grow and, reduce the strength, or if under certain thermodynamic condition temperature let say here precipitate dissolve.

So, we need to retain those precipitate in aluminium, copper alloys, or silver copper alloys so that we can retain their properties, mechanical properties. β-Titanium alloys is also very famous, as a metastable alloys because, α to β phase transition is important to retain all these properties of such lightweight alloys, which is often used as a aircraft and high temperature also.

The shape memory alloys are also a very common metastable alloys. because, here austenite to martensite, this phase transition is very much important, along with twinning is important to get the shape memory behavior in alloy system, definitely glassy phase is metastable.

So, far I have already discussed, retaining the nano size grains in nanocrystalline, or nanostructured alloys, they are metastable alloys. Also high temperature, there are several metallurgical tricks we use. So, that the precipitate should not grow, at even at elevated temperature above 1000°, then only we can we can develop such high temperature alloys.

Same as superalloys, superalloys is also one type of high temperature alloys. Lightweight alloys which is also a common example of some precipitation hardened alloys and, also cast aluminium alloys. Now, what about steel? Yes, steel is also a metastable alloys. So, in case of steel we all know that the α-iron, Fe_3C is a metastable phase diagram ok. This Fe- Fe_3C diagram is a metastable phase diagram because, they are we have iron carbide.

And if you increase the temperature and anneal this sample, then all time this α-Fe and graphite will evolve. So, iron carbide will simply decompose into two phases that is alpha iron and, graphite. graphite is more stable. So, steel is also a metastable.

So, if we develop advance steels, we can call them as advanced metastable alloys. Now, let us have a look at some of the historical events, in metastable alloys.

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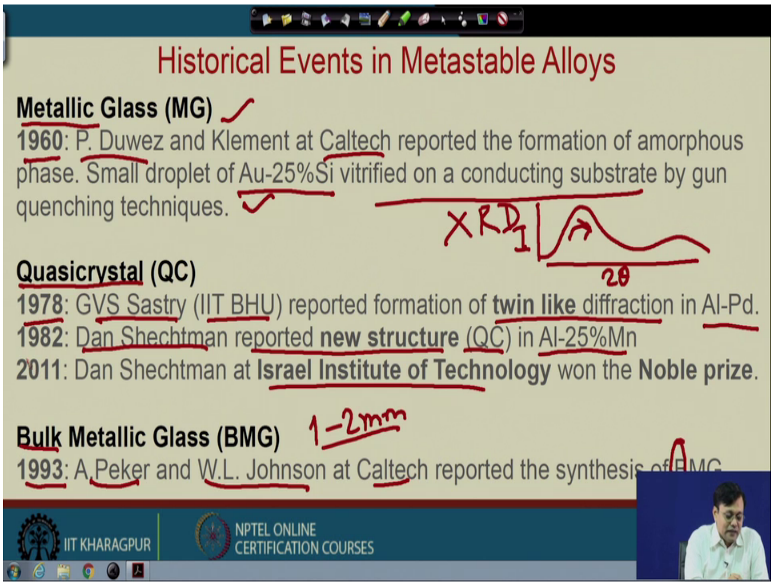

Simply metallic glasses here, we use the terminology metallic because the bonding itself is metallic and professor Pol Duwez he was a professor of Caltech and Klement of one of his postdoc was a studying at the time gold silicon alloys and, vitrified on a conducting substrate. And did some X-ray diffraction studies ok. And this show such kind of halo pattern, that I told in the last class ok. So, this is 2 theta versus intensity plot.

And they saw the disappearance of crystalline peak and, at that time people were clueless that even in case of metallic system, one can obtain a glassy phase. So, that was almost the initial discovery of metallic glasses, in 1960's ok. And after long period in 1993

Atakan Peker, who was a PhD scholar of professor W.L. Johnson at Caltech, they have reported the first synthesis of bulk glasses here. The bulk this terminology or this bulk it basically means in any dimension 1 to let say 2 mm in different different books, they defining different way. So, it is something like 1 to 2 mm in any dimension and we call them as bulk metallic glasses so, larger dimension.

Another big historical event was the quasicrystals that, we discussed in the last class where there is only rotational symmetry exist, but there is no translational symmetry in the lattice. So, in India, during 1978 professor GVS Sastry, who is still a professor at IIT Banaras Hindu university, he was studying aluminum palladium alloys and, he find that twin like diffraction, but at the time it was not told that it was a it was a quasicrystalline structure.

But very similar alloy in aluminium magnesium Dan Shechtman from Israel institute of technology and, he basically reported the first new structure, as quasicrystalline structure in 1982. And we are very very glad as a material scientist that, he won the Nobel Prize in 2011, this a because of the discovery of the quasicrystal. So, this is bigger and bigger let say news, in case of all this material scientist.

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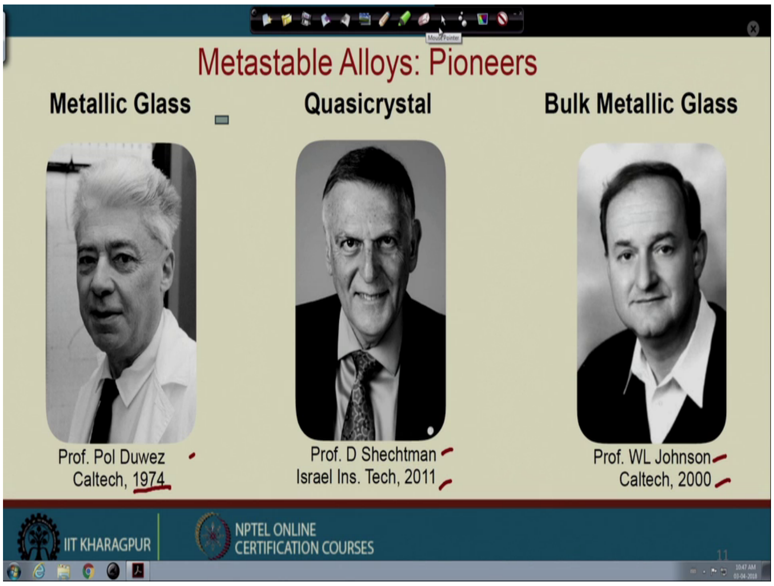

And I show you here the people who have the pioneered this field, in case of metallic glasses and, this is professor Pol Duwez, this is the picture taken in 1974, professor Don Shechtman from Isreal institute of technology, in 2011, and professor Johnson from

Caltech in 2000. And they almost pioneered these metastable alloy field actually, contributed more and more there are many many scientist who has also contributed and develop the field so far.

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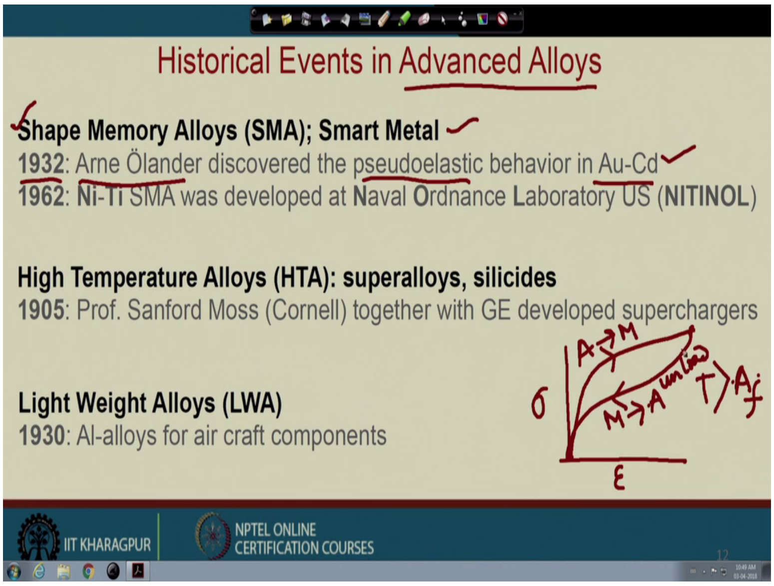

Also there are many other advanced alloys, which is under the development like, shape memory alloys as I said this is a smart metal, or let say because it can remember it shape, initial shape. So, if we change some of the thermodynamic condition like temperature, pressure and so on, then the material regain its old shape.

So, Arne Olander which is a Swedish scientist in 1932, he first discover a pseudoelastic like behavior in gold-cadmium system and, this was a really big achievement. So, pseudoelastic here means actually that if we take a stress versus strength plot of such material, then the material shows such kind of deformation ok. At temperature which is greater than austenite finish temperature ok.

Austenite finish temperature means, it is all in austenite ok, austenite is a phase which transform into martensite and then if we unload it, we saw that the same material comes back. And this is somewhat a very large importance, in this particular aspect that, it looks like a plastic deformation, but it is not plastic it looks like a elastic because, we can get this back.

Because, here martensite transform to austenite and, here austenite transform to martensite. So, during deformation austenite transform into martensite and the martensite transform into austenite during unloading cycle, this is unloading ok. So, this is also a great achievement in this particular case.

Now, another big discovery in this direction was 1962 from naval ordnance laboratory from US and, they develop the nickel, titanium shape memory alloys, which is known as nitinol. And this nitinol is a very commonly used for several application like heart surgery, very small antenna and robotics and, these are also a category of smart materials or functional alloys.

From 1905 the high temperature alloys keep on developing because of the turbine engine and professor Moss at Cornell, they along with general electric, they have developed this superchargers, which is also a part of this development of super alloys. A very common lightweight alloys are aluminium alloys, which is used for air craft component. So, that has started almost development in 1930.

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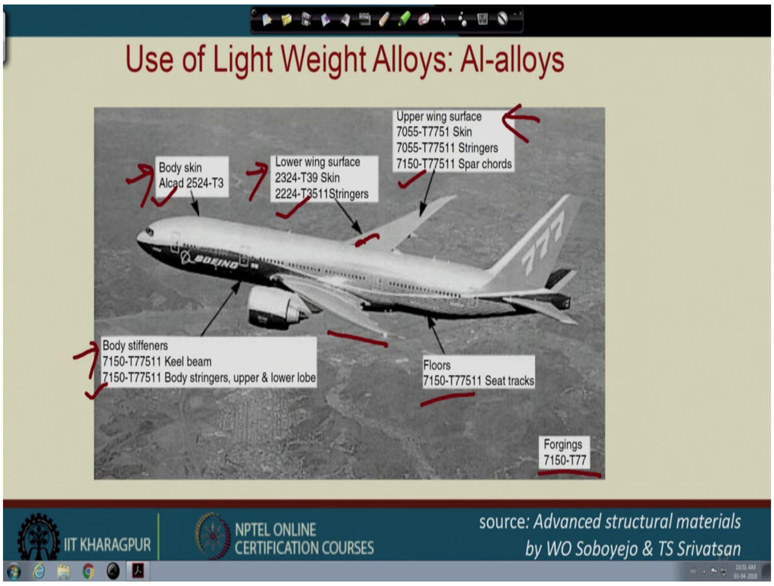

If you have a look to any this air craft and, and Boeing let say this is a Boeing-777 and so, you can see that starting from the body stiffener to body skin, to lower wing of the surface. Here the upper wing of the surface and floor and, forgings all are these are all titanium alloys, aluminium alloys.

So, all of them are very very important as a lightweight because, if we have to design such an aircraft, then we need very very lightweight and very high strength. And so, these are developed because of the demand, during those periods and also still those materials are under development.

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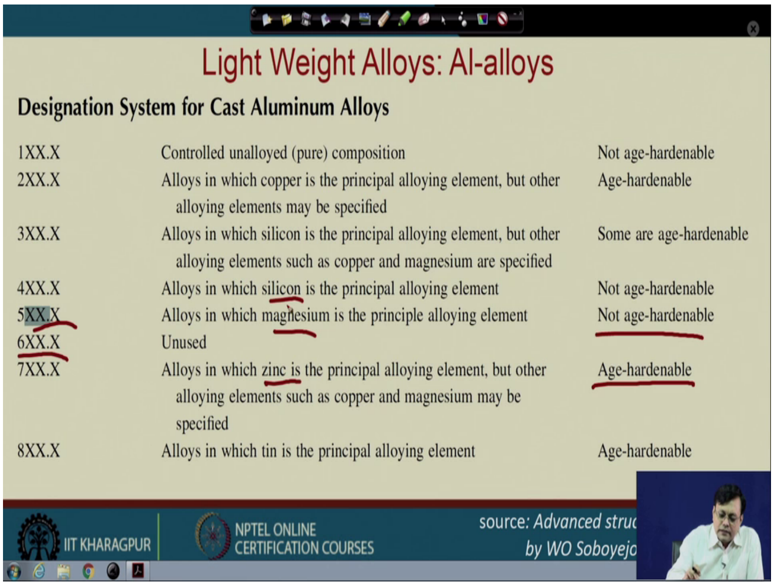

So, I show you these 5000 series, 6000 series and so on, there are some of these alloys are non-age hardenable and some of the alloys are age hardenable alloys, where zinc, magnesium, silicon are added as per the purpose.

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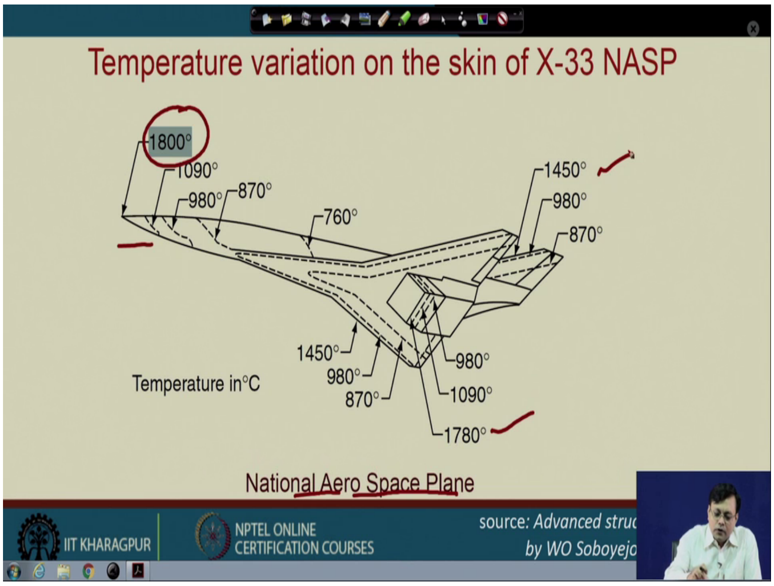

So, at the same time, the high temperature alloys are also developed because of such kind of demand. And you can have a look, that the temperature here is something like 1800 at the nose of a of a space plane, national aerospace plane like, 1780°C temperature and, 1450 °C temperature.

And, we need to develop this alloys and therefore, people need to develop the high temperature alloys.

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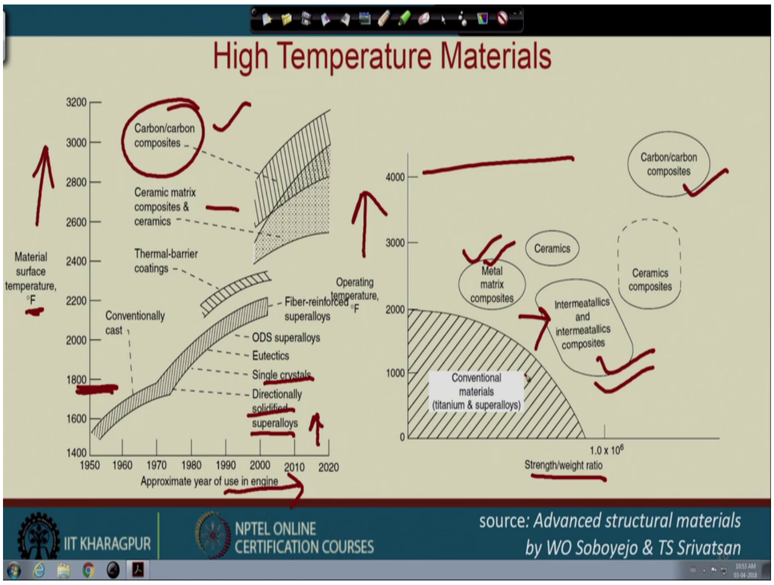

So, like here I show you some of the example, with the materials surface temperature with the approximate year of the use of the aero-engines. So, like here you can see the 2010, or 2020 the mostly develop materials are the ceramic, ceramic matrix composite, even though the single crystals and directional solidified super alloys has been developed. But there temperature is relatively lower, then the carbon carbon composite and there therefore, all the space craft the outer surface is made out of carbon carbon composites.

Here also I show you a plot with strength to weight ratio and, this carbon carbon composites become more and more popular due to higher operating temperature and so, on. And we are mostly concentrated on the metallic system and, therefore, we are in the development of metal matrix composites and, intermetallics with functional properties and higher temperature.

And therefore, today you can see that we have discussed about a brief overview of all the materials that has been developed so far and what is the need of their development. At the same time by 2030, what are the different type of metastable, or advanced or functional alloys, we need to develop is discuss today.

And thank you very much for your kind attention.