Advanced Materials and Processes
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Lecture - 24
Shape Memory Alloys: Case Studies and Applications (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 have discussed about the shape memory effect; and just in the last 2-3 classes we have elaborately discussed about various systems including ferrous alloy system and non-ferrous alloy system, which exhibit shape memory effect and pseudo-elasticity.

We have seen the role of phase diagram and addition of ternary alloying element in order to modulate and tune the martensitic start or austenite finish like the transformation temperature, which are very crucial in order to achieve a shape memory effect at a particular temperature range of our interest or for any kind of industrial or practical applications.

In those directions, we now need to discuss that how we can start from a pure element or a liquid melt and after processing, how we can achieve a final product, because we ultimately need to give a shape to the final object. And now you can easily imagine, let us take any of the shape memory alloy and deform it. And then what will happen, it will be anywhere heated; and after heating, you will see that the initial shape has been again recovered.

So, this shaping treatment does not fulfill our object of the final shape. So, there must be a temperature range where we will shape the material and then we will treat the alloy, so that after shaping, the memorizing effect or shape memory effect will be exhibited by the alloy. And this is a very, interesting thing, we call it as an elaboration like processing or steps of various processing in order to achieve the final product.

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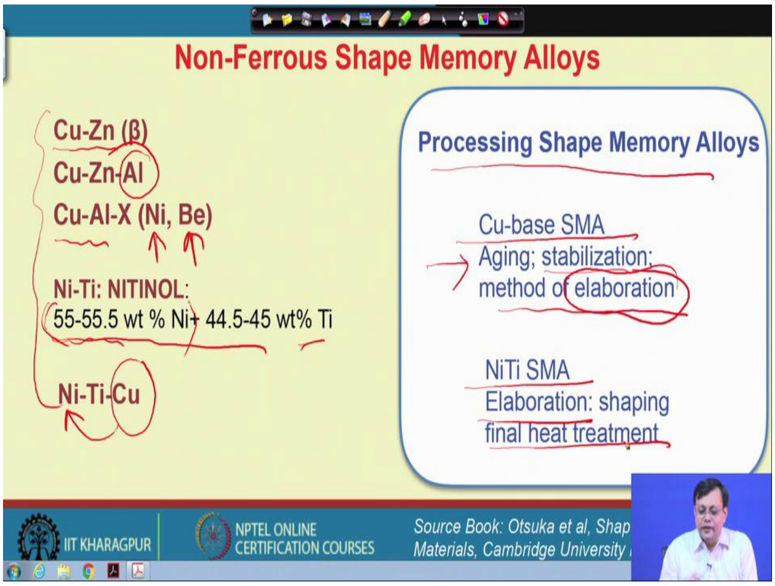

And today we will try to discuss, along this direction. And let us first try to look at what are those non-ferrous alloy we have discussed so far like a copper-zinc, where the β phase was important; and we purposely add aluminium. And here in case of copper-aluminium, we purposely add nickel or beryllium; beryllium was added very, small amount 0.4, 0.5; and nickel was added something like 4 %.

In case of NITINOL, the NITINOL is a nickel-titanium alloy, where near 50-50 composition, there is a particular composition range, where people mostly prefer somewhat like 50-50 all let us say plus minus 5. So, it is mostly like a nickel little bit nickel reach and a titanium depleted alloy or sometimes we basically replace nickel using copper. Usually we never go beyond let us say 25 %, so below 25 % from 7 to 8 to 10. And I have discussed all the things including the temperature and phase transformation sequence in this case of nickel-titanium, because the phase transformation sequence also interact with R phase formation.

Now, today we will talk about, basically this copper based shape memory alloy and nickel-titanium shape memory alloy, what is the effect of aging? Here, aging means if we allow little bit diffusion or little activation energy, then what are the effect on the shape memory effect or let us say the stabilization and method of processing or steps of various processing in order to achieve the final product, which is also called as an elaboration. And very similar elaboration technique in case of nickel-titanium alloy or let us say the final heat treatment why it is required.

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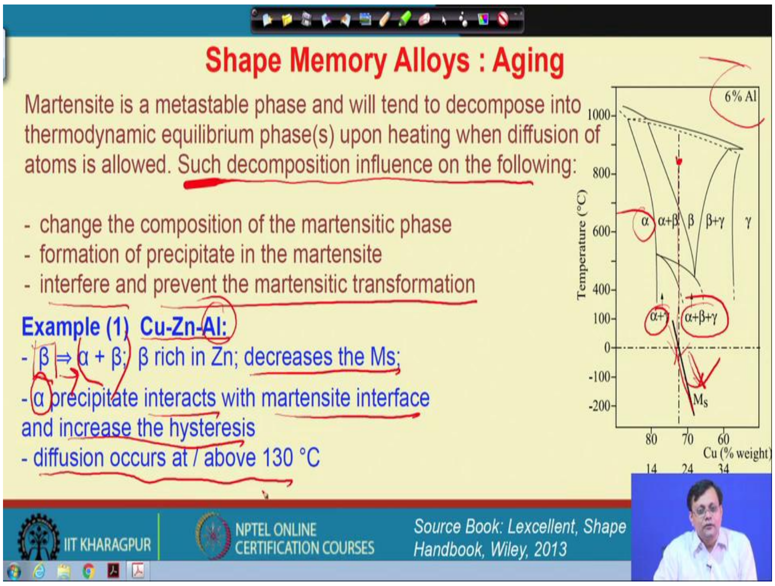

So, let us start with first the aging phenomena in case of a copper base or non-ferrous alloy. So, what we really mean by aging, martensite is a metastable phase, there is no doubt about it, because it is a diffusion-less phase transformation, martensitically transform product from the austenite phase. And it will always tend to decompose once into a thermodynamic equilibrium phase upon heating, once we have allowed some activation energy for diffusion to occur.

So, a martensite will always try to decompose into a thermodynamically stable product at a given temperature; and such decomposition, you can have a look at simple the phase diagram and what can be the effect. Here, if you look at this β, which is the austenite phase transformed into the martensite phase. However, there are some competing phase, where β can be decomposed. You may recall, I told you that α phase is required, why α was required, because β is a very brittle phase. However, α is not required for martensitic phase transition; α is required for shaping the alloy, because β is a very brittle phase.

And, if the microstructure contain α + β, then we can shape the alloy easily. After shaping again we need to quench from the β phase field, then only we will get 100 % martensite and we can achieve the shape memory effect, which is the purpose.

And now if at all there is some aging phenomena this aging phenomena means, basically that martensite will try to decompose into the thermodynamically stable product. In that case, what will happen, the composition, if we allow diffusion, then the composition of the martensite phase will change. And you have already noticed if there is a compositional change, then immediately the M_s temperature will also vary. Like here, so here what will happen, if the β is rich with zinc, then immediately there will be fall of the M_s temperature.

Now, another phenomena is that precipitation will occur, if some thermodynamically stable phase appear, where they will appear they will appear in the martensite plates or near the interface or at the interface and they will interact with the interface. So, once they interact with the interface, it will prevent the martensitic transformation.

Now, let us say a particular case we can discuss about aging. Like an example, I can tell you it is like a copper-zinc with some amount of aluminum. Let us say here 6 or 4 at. % aluminium has been added or weight % aluminium has been added. In this case, you will see that β always tend to decompose to α plus β, and this β is rich in zinc, and it will basically decreases the M_s temperature Martensitic start temperature will decrease.

Now, if α precipitate, this α phase appear and interact at the martensite interface, it will simply increase the hysteresis, because it will retard the transformation or reverse transformation. And here the diffusion easily occur at or above 130 °C and that is the reason copper-zinc-aluminium system is not recommended for let us say high temperature shape memory effect.

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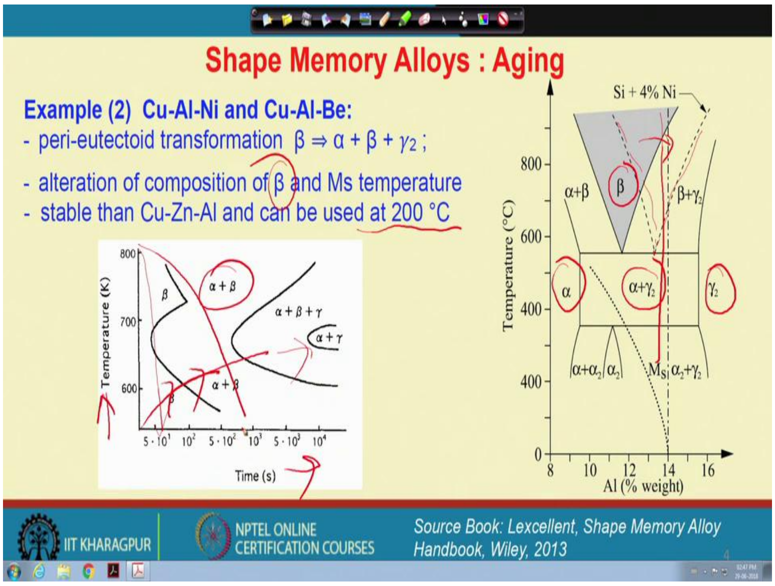

Now, let us take another example. The second example is that copper-aluminium-nickel or let us say copper-aluminium-beryllium. In that case, again the austenite phase is a β phase after adding nickel, this is the β phase field shifted you already know. And there is a eutectoid transformation here, in which basically β we will try to decompose into α plus γ_2. So, if we allow the martensite phase, little diffusion to occur of the atoms, then this martensite will finally transform into the thermodynamically stable product, because these γ_2 an α are the thermodynamically stable product.

Let us say I have chosen such a composition; so definitely due to this eutectoid transformation, it will decompose. And if such decomposition occur, then immediately there will be a change in the composition of the martensite and the M_s or β, and the M_s temperature will also change. Now, still compared to a copper-zinc system, this copper-zinc-aluminium system or beryllium system is quite good, and it can be used as a high temperature shape memory alloy at or above 200 °C because of the stability of the phases.

However, here this is also another interesting diagram of temperature versus time, where you can see that we can always cool down and get a martensite. However, a slower cooling or little bit diffusion, if we allow, you can start from here also then with time it can decompose into α, β or let us say α, β,γ. So, this is basically the understanding we really need how to get back or how to make this reversible transformation in such a way that no competing phase will appear in between a phase transformation sequence of martensite and austenite.

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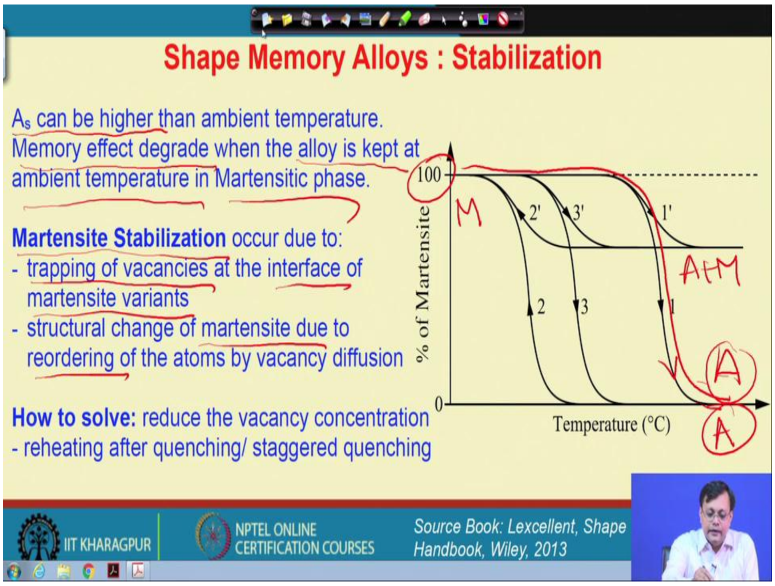

Now, the second phenomena after aging is basically the stabilization. What we really mean by a stabilization, here we are talking about actually the martensite stabilization means by some reason the martensite phase does not like to transform into austenite, and this is very interesting phenomena. So, usually austenite start temperature can be higher than the ambient temperature. In such a case, the memory effect actually degrade, when the alloy is kept at an ambient temperature in the martensitic phase. What will happen, we all know that vacancy play a major role on the martensitic transformation.

Each and every metals and alloy has a thermodynamically equilibrium concentration of vacancies. If you, raise that the temperature of metal then there will be equilibrium concentration of vacancy, and it will rise with the temperature. So, this martensite stabilization phenomena is linked due to the trapping of the vacancies at the interface of martensite variant, means, there are twin variants at the interface and vacancies get trapped.

Once, it is trapped the structural transformation will be retarded. So, the martensite will be there, these vacancies also may help in reordering in the martensite phase. And then, if there is a reordering phenomena, and then it will be difficult to go back into the austenite phase. I will try to explain you, which way we are talking about this particular stabilization phenomena. Let us say, I start with a martensite, I have 100 % martensite, I simply raise the temperature, and then it started transformation and goes to austenite phase. So, now I have austenite. So, here it is austenite plus martensite. So, after this I get 100 % austenite here.

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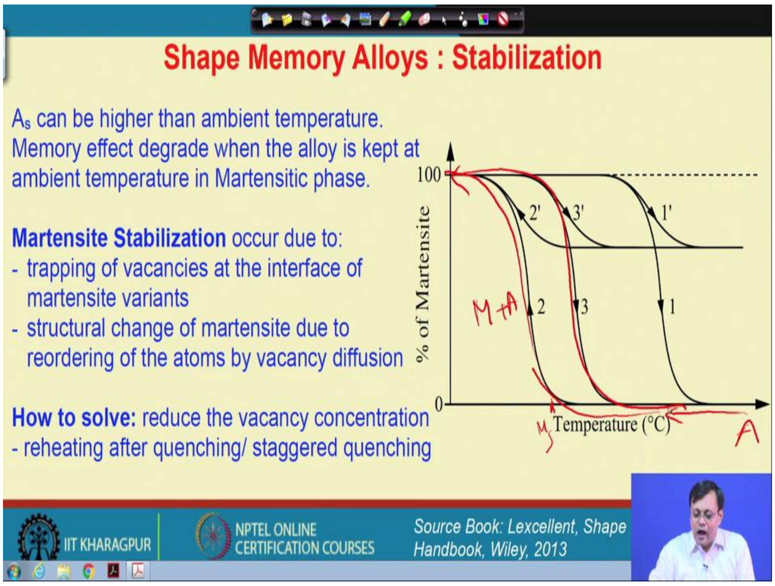

Now again I let say cool from the austenite, and then during cooling here at this temperature, martensite start temperature, the transformation begin, so I have martensite plus austenite in this region. And then all the austenite transform into martensite. Now, if we reheat it, so this is like a cycling, then in the third sequence, it will go in this way; there is little effect on that.

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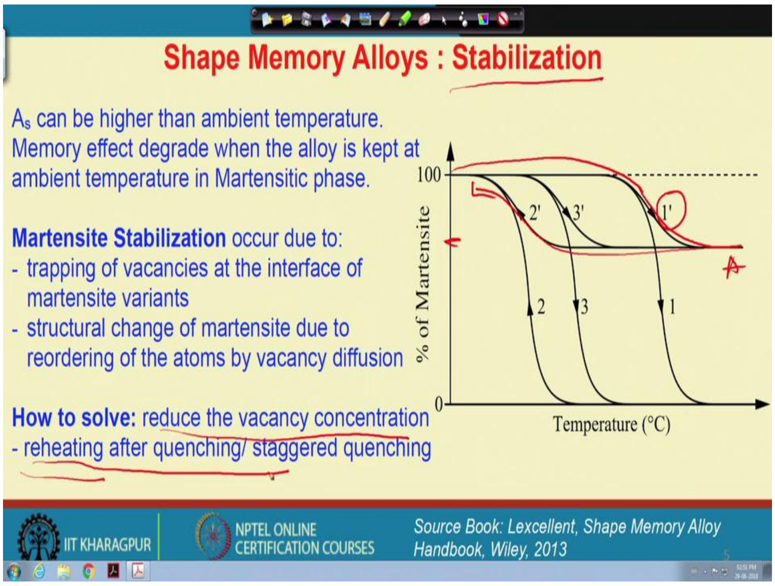

However, when stabilization occur then during heating, it will follow this 1'. So let us say something like 30 % of the martensite transform into austenite. And again, if I cool back, then it goes in this way. So, I will never get the highest recovery strain possible in a particular system due to this stabilization phenomena. And this stabilization phenomena is enhanced, due to the trapping of the vacancies which basically trapped at the interface or it helps in reordering in the martensite phase.

Now, how to solve it? Yes, there is a solution we simply reduce the vacancy concentration in the material. And how to reduce, we simply reheat after quenching or let us say staggered quenching and, if such a case occurred then all the vacancies goes away from the material and then we can achieve a higher percentage of shape recovery.

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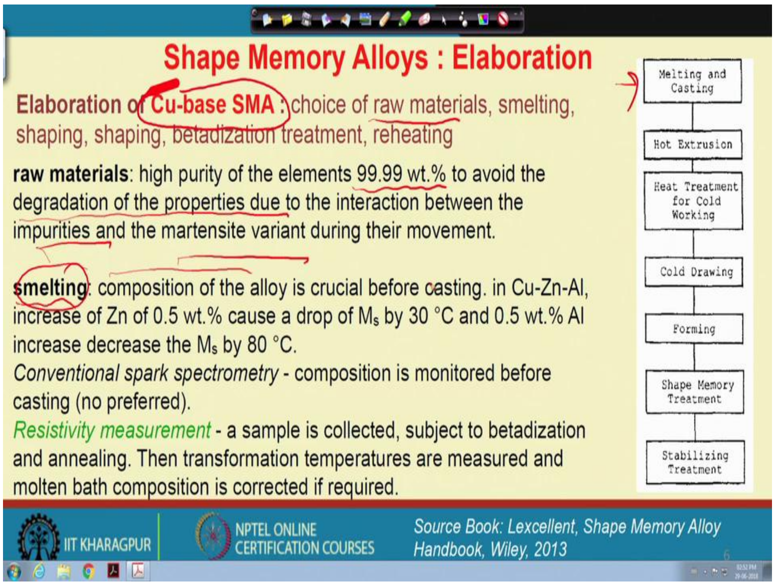

Now, the second part of today’s talk is on the elaboration, elaboration means to achieve a final product from the initial alloy, from the alloy making. In this particular case, let us say, if I take a copper base alloy copper base system, here in this particular case, the elaboration technique contain let us say the choice of the raw materials smelting, shaping and let us say the betadization treatment.

So, here we start let us say from the pure elements or let us say raw materials, and the raw material may contain some impurity element. And you know that impurity element always changes or altered the transformation temperatures. And therefore, it is recommended that we should start with a very pure quality of the elements in case of a shape memory effect.

In order to avoid the degradation of the properties, due to the interaction between the impurities and the martensite twin variant, during their movement, because those martensite variant has to move from one type of twin to another type of twin to finally to the austenite during heating.

Now, the second part is basically the smelting. So, the smelting is the process in case of copper base system we adopt during processing. So, here the composition of the alloy during this smelting before casting must be analyzed means, the composition is of the alloy is really what is desired, let us say copper-zinc. So, let us think about a copper-zinc, 38 % or 39 % zinc is there and aluminium is 4 or 5 %; whether the composition is really that, if the composition is not there, then definitely it has to be verified by some way.

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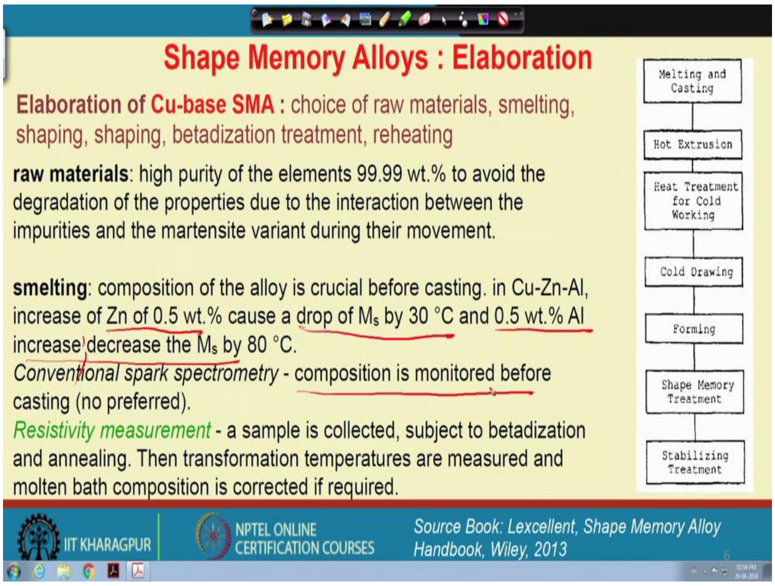

And like an example, I can tell you, if zinc content increases 0.5 %, there will be a drop of M_s by 30 °C, it is a huge. So, we cannot really predict what should be the exact M_s temperature, because there could be a processing sequence and large number of product could be produced, where all the expected temperature range will be completely changed due to 0.5 % of aluminium change. Very similar if it increases, then there will be a decrease of the M_s by 80 °C. However, the typical way of measurement of composition in an alloy is the composition, which is monitored by a conventional spark spectrometry.

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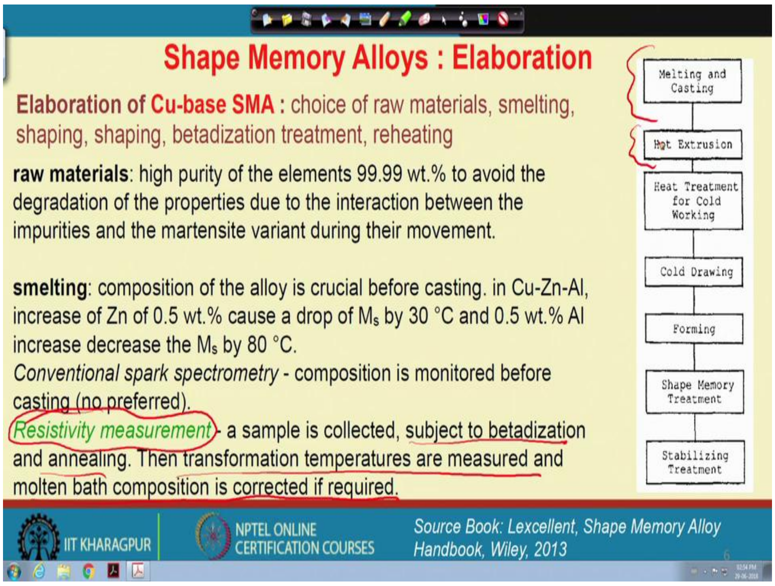

However, conventional spark spectrometry does not give you very accurate result. In that particular case, what we do, we simply collect a liquid alloy, and then we solidify it by casting which is subjected to betadization. I will come to betadization treatment what is the meaning of betadization and annealing.

And this transformation temperature is recorded in the molten bath composition and then it will be corrected. So, this temperature is recorded by the resistivity measurement. It gives us a perfect sequence of all this transformation temperature like M_s, M_f, austenite start, austenite finish. So, starting from a melting, hot extrusion this is a shaping operation which will discuss in the next slide.

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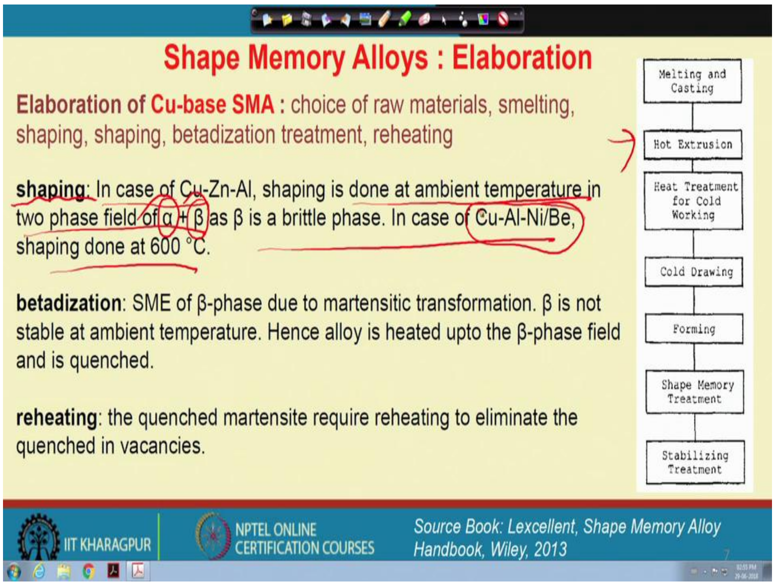

So, the second process is basically the shaping; so, shaping means that it could be a wire extrusion. So, particular shape what we want to achieve. In that case, shaping is done at a ambient temperature in two phase field. As I said that for shaping you need some malleability of the alloy; and β phase is a very brittle phase, and therefore we need the help of α phase. And in that case usually shaping is done at a temperature of 600 °C in case of copper-aluminium-nickel or beryllium system.

Now, once we shape it, then we again need a 100 % β phase. So, we again have to raise the temperature of the alloy, and this is called as the betadization means going to the β phase field.

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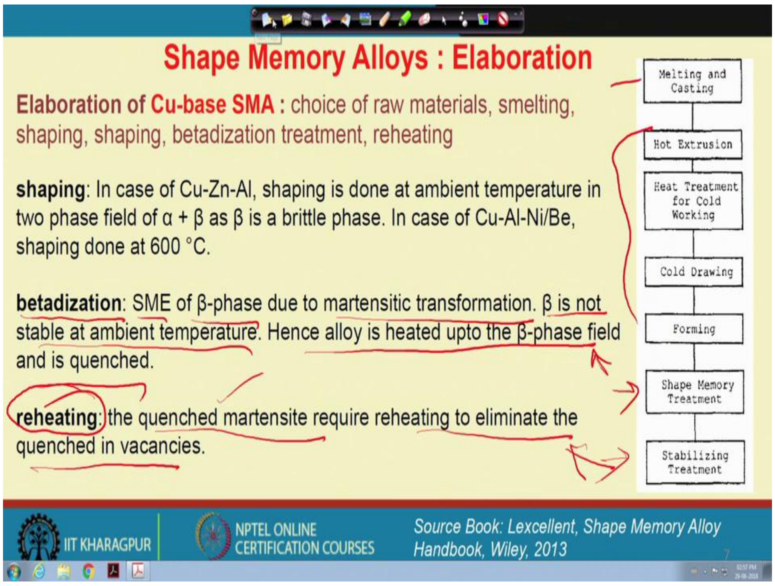

So, shape memory effect of the β phase field is due to the martensitic transformation; and β is not stable at ambient temperature. And therefore, we heat the alloy up to β phase field, and then it is quenched to get the martensite. And then in the martensite, during quenching, there is a lot of trapped in vacancies; and those vacancies has to be avoided, hence we go for some reheat treatment or reheating. In that case, we anneal the sample for some time; and this the quenched in vacancies are removed from the quenched martensite.

And this is basically, the treatment in order to avoid that stabilization phenomena. So, shape memory treatment is basically the betadization, and avoiding the defect is the stabilization. So, you can go for shaping and here is basically the melting and casting, so you can see the sequence that I have explained here.

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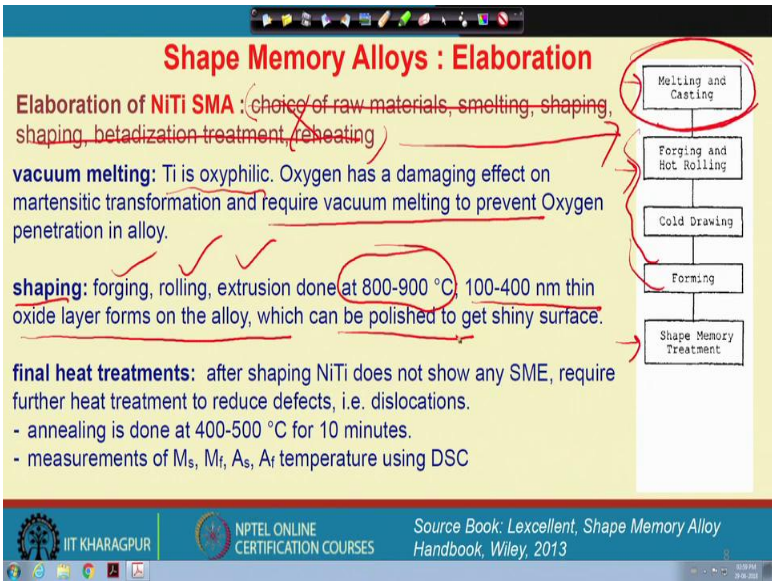

Now, let us discuss about another system very important non-ferrous shape memory alloy system. In that case, actually we will talk about nickel-titanium alloy. In case of nickel-titanium alloy, the choice of raw materials melting or shaping, betadization and reheating, are not at all required like in case of a copper-base shape memory alloy. So, these system we do not need at all.

So, the treatment is very rather simple like melting casting, like forging or simply shaping operation, or forming operation and then we give for a shape memory treatment, this is something relatively easier. Why we need a vacuum, because titanium is very much prone to oxidation or oxyphilic. And presence of oxygen has damaging effect on the martensitic transformation. And therefore, we need a vacuum melting, so this melting phenomena has to be done in a very high vacuum where oxygen should not be present in an inert atmosphere and so on, in order to avoid oxygen penetration.

Now, in case of a shaping of the alloy, we can go for forging or we can go for rolling or we can go for let us say extrusion technique, we can do that at a 800 °C to 900 °C. Why, because we simply raise the temperature because shaping need some plasticity, and the plasticity can be achieved at higher temperature like hot deformation. And during the deformation temperature has been raised and oxygen will definitely react but not so extensively like in the liquid state. So, in that particular case means during shaping operation usually 100 nm to 400 nm thin oxide layer will form titanium dioxide layer will form on the top of this nickel-titanium alloy. Also there may be little nickel oxide also form. However, we can get rid of these oxide layer by simple metallographic polishing technique in order to get a very shiny appearance and so on like stainless steel.

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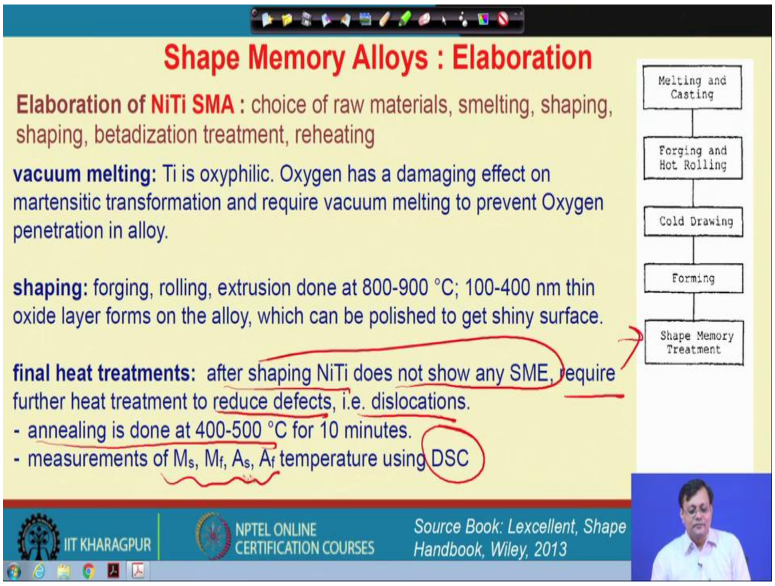

However, we need after shaping treatment, we need a final heat treatment. The final heat treatment is basically in order to achieve a good shape memory effect. How we do that, after shaping these nickel-titanium do not show any shape memory effect, but and that is why we need a heat treatment in order to reduce the defect. In case of nickel-titanium, I have talked about this that dislocation is very harmful or any other defect is always harmful, then we cannot get 100 % shape recovery. And therefore, we can simply get rid of dislocation by annealing at a temperature of 400 to 500 °C.

Then we collect the sample and we simply go for differential scanning calorimeter in order to measure whether all these transformation temperatures are as per our requirement. So, these are basically the different elaboration technique that we need to think about in case of this non-ferrous alloy. However, in case of titanium nickel, you know that R phase is one of the competing phase and that has some effect on the shape memory effect.

If you look at since, I talked about the DSC of the shape memory alloy in this a DSC trace, if we start with a martensite phase, if we heat the alloy then we will get such kind of peak. And this peak correspond to let say austenite start and austenite finish. So, here it start, here it finish. And if I cool it down, then this is here, where martensite start to form, and here all the martensite will finish, means here, I have complete martensite, and here I have complete austenite, this is the way. And in between this temperature range, there will be martensite plus austenite.

So, this is a very typical austenite martensite transformation sequence. And on the other hand, if we take a nickel-titanium, and if R phase is promoted to form by little addition of aluminium and iron, I have discussed earlier, then you will see a little different DSC trace.

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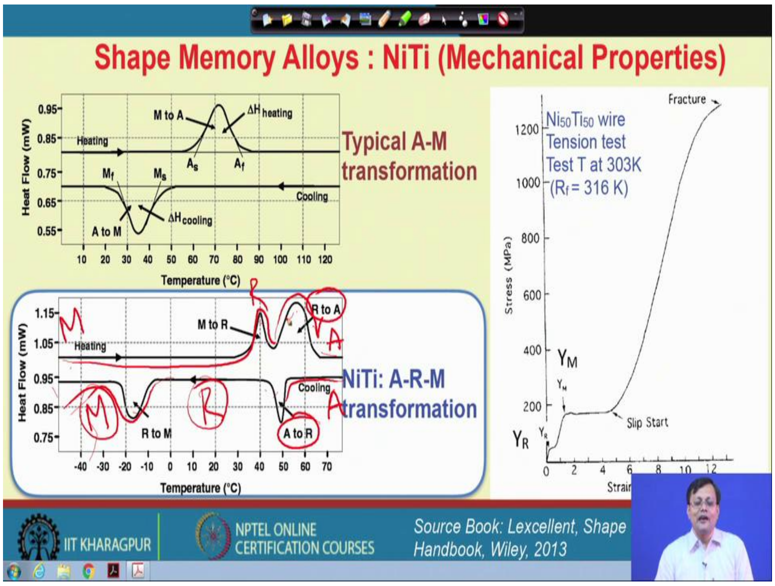

Here, please have a look I start with a martensite. And this martensite actually transform into R phase first, and then this R actually transform into austenite. And then here I have 100 % austenite. Now, if I again start with f austenite, R will transform from austenite, and then here I have complete R phase, and these R again transform into martensite phase.

So, here I have austenite; here I have R phase; here I have martensite phase. So, you can see that there is a transformation sequence that is little different. And simply it will have effect on the mechanical properties, how the R phase will effect on the mechanical properties?.

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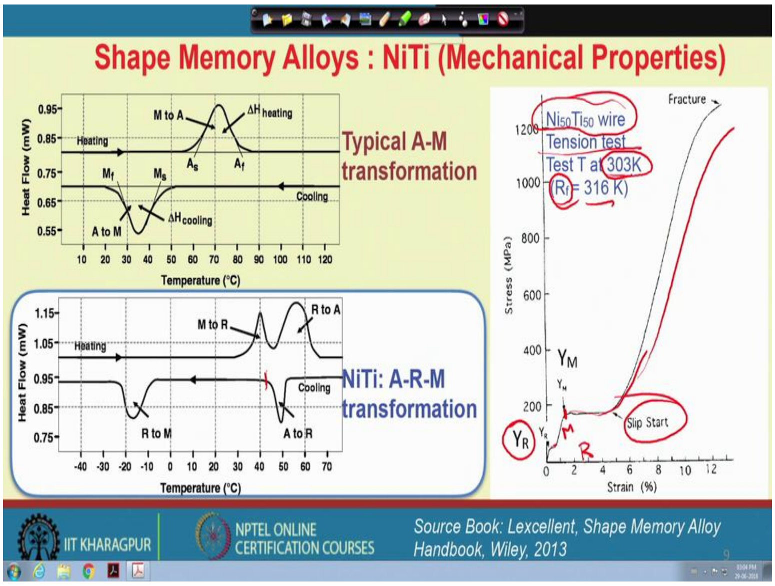

I can take such a nickel-titanium wire and, if there is R phase, then you will see a difference in the tension test curve. So, this tension test is done at 303 K, and let us say the R_f is 316. So, here basically R_f is the 316 K let us assume at this moment. So, I have taken a sample with a complete R phase. So, I am starting with R phase only. So, once the deformation begin, then I will get a yield point, here. Here is the yield point and which is stands for Y_R, then I have martensite here and this is the yielding of martensite. So, I have consecutive two yielding phenomena.

And after that, slip will start. So, till now it was only twin base deformation in the martensite. But, I now started basically incorporating some dislocation. And therefore, you try to think during shaping operation to, if dislocation are present too much in the alloy, we must get rid of this dislocation, so that these austenite martensite reversible transformation should not be retarded by anyway.

Now, this is a very different aspect of shape memory alloy, where we need to think about what is the effect of thermal cycle, means, we already know about the transformation sequence, we know about the stress sequence means at austenite phase field, if I have given some stress, and if pseudo-elasticity exist then after unloading all the martensite transform into austenite.

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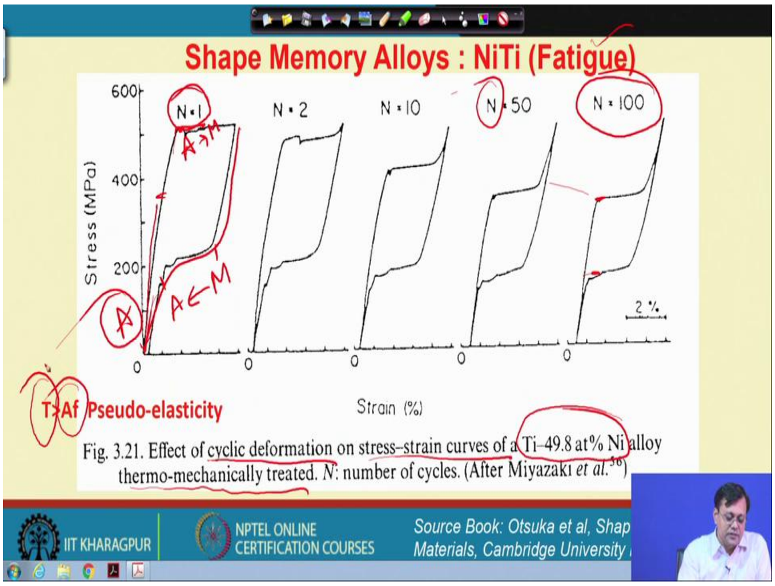

How the curve basically looks like means that. I start with austenite and here, the austenite started transforming into martensite. If I unload it, then again it goes back, because here martensite will transform into austenite.

So, here I get 100 % austenite, and the whole strain is recovered, this is a typical pseudo elastic effect. However, if I keep on doing the same thing on a particular sample, the material will not show similar behaviour means let us say this is a cycle number 1, I keep on increasing the cycle and then let us say this is cycle number 100. In that case, you will see that all the transformation stresses will be changed. And this is a stress induced or deformation induced fatigue in the shape memory effect.

So, this is a cyclic deformation what we are talking about, because loading and unloading is a cyclic deformation,cyclic stress-strain curve of titanium around 49.8 at. % of nickel alloy, which are thermo-mechanically treated. N stands for the number of the cycles. So, here temperature of deformation is above temperature of the austenite finish temperature means I have 100 % austenite phase at the initial microstructure. And here I have martensite and again that martensite starts transforming in this region and so martensite transform into austenite,

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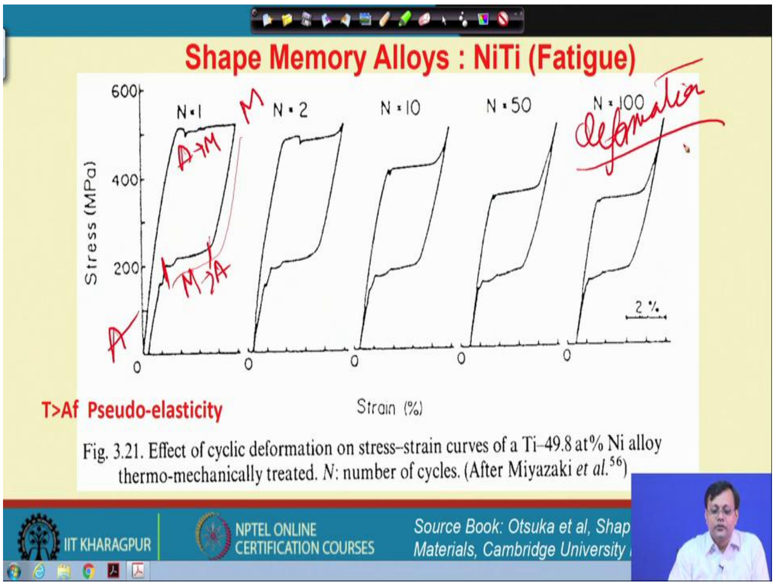

And here austenite transform into martensite the same thing is here, so, this is a very interesting phenomena. However, this is a deformation induced or cyclic deformation induced fatigue on the shape memory effect on the pseudo-elasticity.

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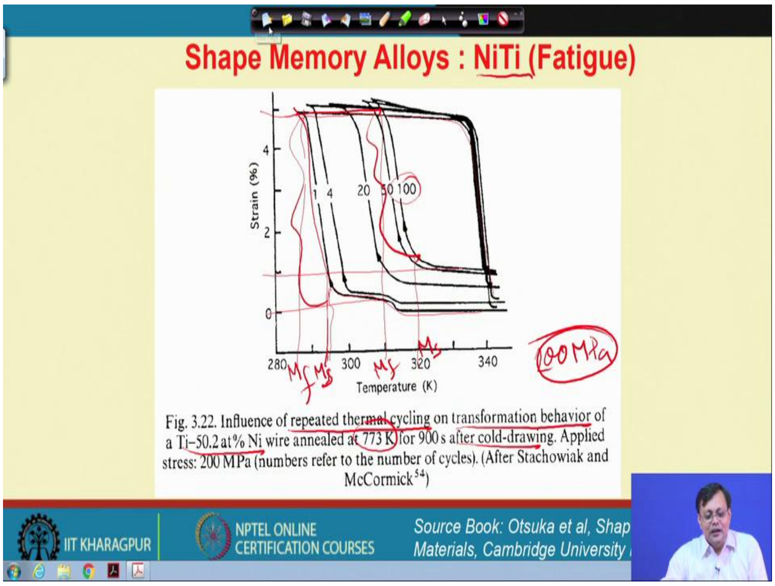

Now, similar effect we can see in case of a thermal fatigue, means, if I keep on increasing and decreasing the temperature what will be the effect, this is very interesting phenomena. Please have a look here, this is a repetitive thermal cycling on the transformation temperature and behaviour of a titanium-nickel alloy, which has been annealed at 773

Kelvin after cold drawing. Here at a constant stress level at 200 MPa, we are looking at how is the temperature cycle.

So, the first cycle you see here that it goes here and then we cool it down. So, the transformation temperatures are here. So, here is the transformation temperature. Now, after some repetitive cycle at 100, you see the transformation temperature means here it is M_s, and here it is M_f, this is the M_s temperature, here this is the M_s, and here is the M_f. And you see the magnitude of the strain recovery has also changed. At the initial stage, I had a larger strain recovery; whereas, later stage there is a less strain recovery. So, the effect of a thermal cycle also changes the memory effect in case of a nickel-titanium alloy.

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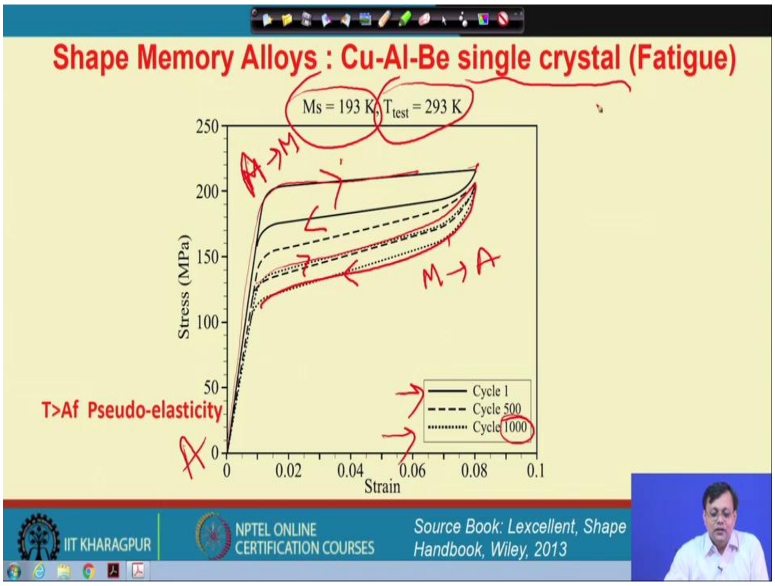

A very similar behaviour also observed in case of other shape memory non-ferrous alloy. I should show you another example like copper-aluminium-beryllium. So, here the test temperature is 293 K almost close to our room temperature, and the M_s temperature is well below. So, now we are talking about actually pseudo-elasticity. Here this is a cycle 1. So, here I have started with austenite, austenite transform into martensite, and here the two phase exist, and here almost it finish and once we unload the sample it comes back. So, this is unloading and this is loading this is a cycle 1.

Now, let us have a look at the cycle 1000. Here this is a cycle. So, here is the loading here is unloading sequence. So, here basically martensite transform into austenite. So, this is a single crystal that has been tested. And you can have a look that the thermal fatigue or thermal cycle has an effect on the on the pseudo-elasticity effect.

So, so far we have discussed this shape memory effect and the effect of various defect, and how to take care or precautions must be taken during processing itself, where does the process sequence of nickel-titanium is different than the copper, so it depends on the system to system. And we must be avoid various difficulties during shaping operation, during heat treatment to achieve the highest possible shape memory effect or pseudo-elasticity effect in the different alloy system.

So, in the next class, we will continue with different application areas we will go into deeper side in the next class.

Thank you.