Advanced Materials and Processes
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Lecture – 21
Shape Memory Alloys: Case Studies and Applications

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 we have started this shape memory effect discussion with the classification of phase transformation. Because shape memory effect is directly linked with phase transformation and this phase transformation should be diffusionless martensitic transformation, because martensitic transformation is definitely a diffusionless.

However, not only martensitic transformation is the one criteria but the reversible transformation is also necessary; which means from austenite the martensite should form by the driving force during cooling. So, thermal cooling provides the driving force for martensitic transformation and once we get this martensite then this martensite should contain or accommodate the transformational strain from austenite to martensite by twinning and then this twin is expected to be two different types. Here type means basically we are talking about twin variant and this two different variant form during thermal cooling itself.

During deformation of this martensite at low temperature, one of this two in grows in expense to other, after that we get actually the strain means the plastic deformation which apparently looks like a permanent deformation, which is a generated due to the growth of the martensite twin variants and this strain could be further recovered during heating or increasing the temperature above austenite finish temperature.

So, this is the very general theory of the shape memory effect and now, we are more interested to discuss some specific case. We learn that austenite is a phase which transform into martensite through martensitic transformation and this austenite phase in case of Iron-Carbon system is FCC structured, we call it as γ austenite. However, this particular austenite phase in case of non-ferrous system may not be all time the FCC crystal structure.

Similarly, the martensite phase or martensitic phase not only necessarily has to be a body centered tetragonal which you already know from iron carbon martensite system. So, this could be some hexagonal closed back structure or any other face centered tetragonal structure or many other crystal structure. So, the way the phase transformation occurred will tell us that whether it is martensitic in nature or not and not like that this is a FCC phase, so, all FCC face should be austenite. So, we must clarify those things and today we must try to understand some of these aspects of case studies in different alloy system

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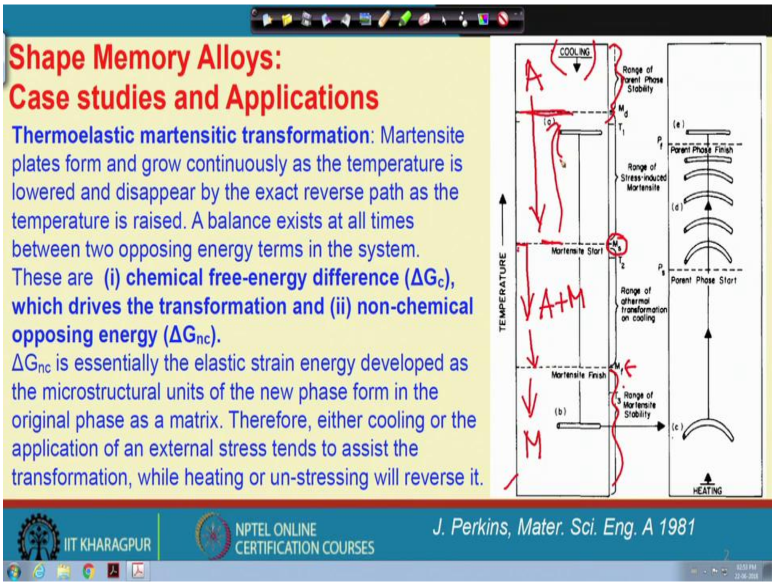

Now, I already told you that this martensitic transformation in case of a shape memory effect is expected to be thermoelastic in nature. Here thermo means thermal stress that gives the driving force as well as the elastic that part also contain another driving force for this transformation. In case of a thermoelastic martensitic transformation the martensite phase that basically form or nucleate in the austenite and they grow continuously as the temperature is decreased or lowered.

And, now how such thing really happen I must discuss this with a schematic diagram which is shown in the right hand side. You can see here in this first picture here, we are talking about actually the cooling from a higher temperature where the parent phase austenite, A stands for austenite here is stable and once we cool it down, the austenite will transform into martensite just below the martensite start temperature. The martensite start temperature is represented by M_s and so, we need some amount of the thermal driving force for that to initiate the transformation and as we decrease it continuously the martensite phase will continuously grow.

And, below when this temperature reaches to martensite finish temperature so, here all the austenite in the microstructure should be transformed into martensite and below this M_f temperature the whole microstructure will contain only martensite. So, here I have austenite plus martensite, which is why we show this is a temperature range where martensite is stable and this is the temperature range where austenite is stable.

However, the driving force required for austenitic to martensite phase transformation could be a compensated by applying some stress where stress assist this austenite to martensite phase transformation. What does it mean, that if we apply stress then the M_s temperature will be raised that is what we learn from this Clausius-Clapeyron equation and diagram, t this M_s temperature can be increased here by the application of stress.

In such a situation,. we do not call really as a M_s, but rather we call it as M_d; it means that the initiation of martensite in austenite phase, initiation means nucleation and growth, by the application of stress that occur at a higher temperature level and that is why here and this is the range of stress induced martensitic transformation. So, we can apply both stress and thermal quenching to drive this transformation and to obtain shape memory effect in this particular case we can directly start with austenite and then below M_f we get actually the martensite.

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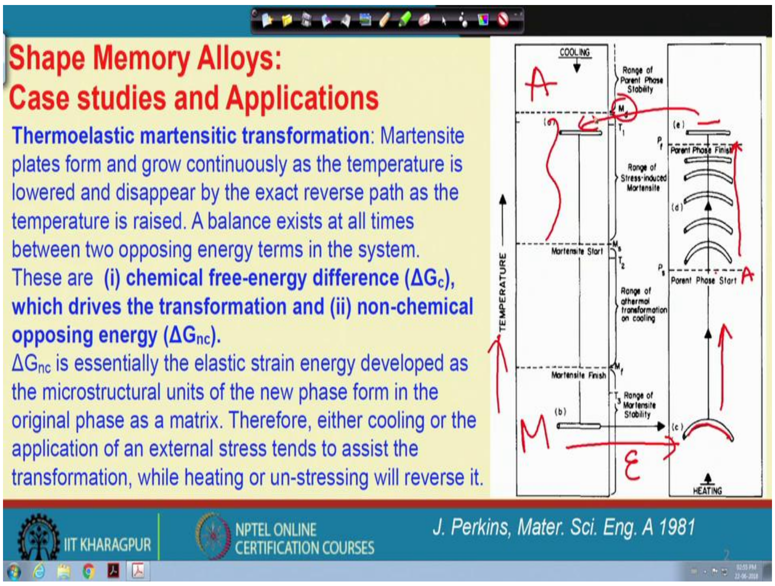

And, then this martensite we basically plastically deform it. So, that is why this straight bar is deformed or bended, and once we raise the temperature here this is the temperature axis actually, so, this parent phase means austenite starts forming and all the martensite will be transform into austenite and here we will get the original shape as it was.

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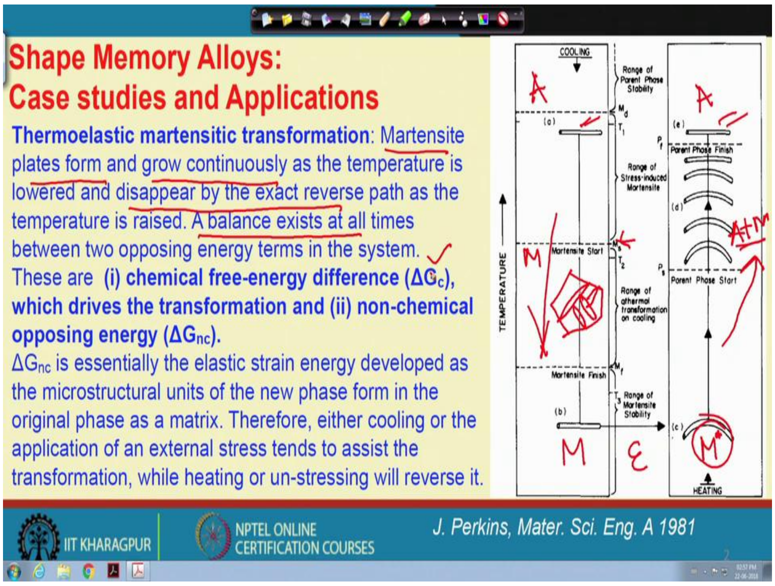

And therefore, here we have martensite we have strain and this is actually martensite which is deformed and here we have austenite plus some martensite and here we have all austenite which we have studied with and so, the initial shape remain as the same and this is the shape memory effect.

And, now let us again come back what we are talking about a thermoelastic nature of the martensite. So, the martensite plate we will form and grow continuously. So, we are talking in this temperature range, we are talking about where the martensite which has nucleated just below M_s temperature, they should continuously grow. So, if I think about austenite grain and this martensite which form and continuously grow in this way it should cover the whole microstructure, which is what we are talking about.

Now, it should disappear exactly in the reverse path as temperature is raised, which means that we have martensite which has been deformed; however, it should simply disappear by the application of thermal or temperature. So, there should be a balance at all times between two opposing energy terms in the system. So, one is the chemical free energy difference which means ΔG_c it is basically the difference between the free energy of the martensite and austenite, that is we are talking about which drives the transformation and there is a non chemical opposing energy that is why we used this term nc.

Ah. So, there are two of this term, one is basically the elastic strain energy, another one is the free energy difference which is a chemical free energy difference and there should be a balance in this whole process and this $\Delta G_{nc,}$ nc is essentially the elastic strain energy that develop as the microstructural unit of the new phase, new phase here is the martensite that form in the in the parent phase as a matrix. And therefore, either cooling or the application of external stress tend to assist the transformation while heating or unstressing will again reverse the transformation.

So, in order to obtain a shape memory effect this thermoelastic nature of the martensite is very much important and now, we can always ask what we mean by a non thermoelastic martensite. Actually the basic feature of a thermoelastic a martensite is that it forms and grow continuously with decrease of the temperature, but in case of a non thermoelastic martensite basically there is a growth burst occur, burst mean all of a sudden the martensite form and it without showing a very typical nucleation and growth type of features. So, very burst kind of formation of martensite is a very usual nature or common feature of a non thermoelastic nature of the martensite.

But, in some shape memory alloy systems, it has been observed that non thermoelastic martensite could play also a vital role and which gives some percentage of the shape recovery.

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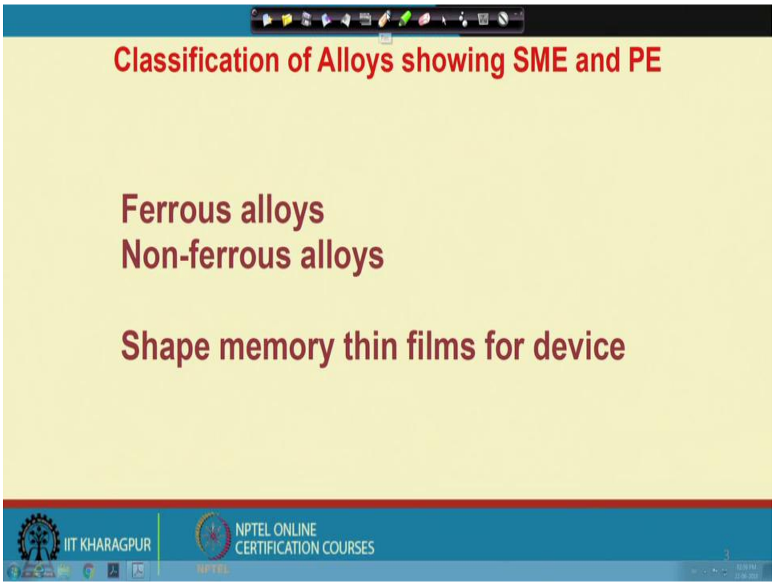

So, we like to classify all these different alloys that shows the shape memory effect and its pseudo elasticity. So, when we are talking about alloys, it is basically the bulk alloys; like in iron containing alloy in case of steel, also you know that we call it as a ferrous alloy and there are many non-ferrous alloy. In case of shape memory alloys, we also classify very similar way like ferrous or non-ferrous alloy.

However, these are the bulk alloys and there are also some other processing technique where people deposit some of these elements which makes this shape memory effect after alloying and let us say nickel and titanium are co-deposited on a substrate and such a thin film of few micrometer, they are used for making devices and we call those thin film as shape memory thin film for devices, those we will discuss later on.

But, in case of a ferrous alloy and nonferrous alloy, these are very much important and so, we need to talk a little bit in detail and try to look at what are the common features and how the shape memory effect is developed. However, in general it has been observed that ferrous alloys are very less because as I told you that at twinning is a less prone to form in case of ferrous alloys and a large amount of dislocations are also associated However, there are always some example where people observed such kind of shape memory effect.

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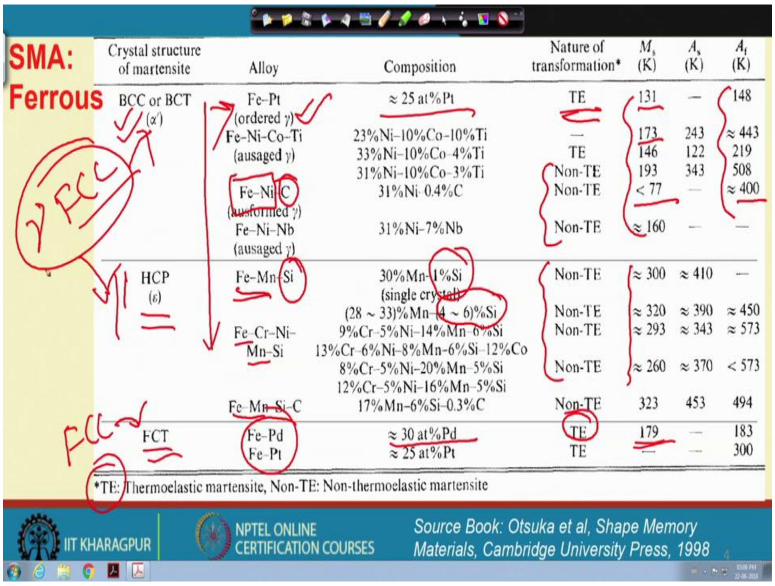

So, here I show you a summary of all the ferrous shape memory alloys so far has been discovered and different system. So, very interesting system is the iron-platinum system. It's an ordered austenite phase and people observed such a shape memory effect where the composition range is somewhat like at 25 % platinum. The nature of this transformation is a thermoelastic in nature.

So, here TE stands for thermoelastic martensite where there are also some example of non thermoelastic martensite and in this particular case, this phase which is the martensite has a BCT or body centered tetragonal structure and we know that this tetragonality basically develop if very little amount of carbon is somewhat present.

So, iron-nickel system is also very much well known for showing some shape memory behavior, even though the extent is not very large. And, the interesting part here that the M_s temperatures are quite a low let us say 131 K or 173 K or below 77 K.

So, these are the behavior people have observed at a very low temperature whereas, the austenite finish temperature, it has been observed something like 400 K and another very important aspect of these ferrous shape memory alloys that they required very particular training. Training means several time you cool and heat the alloy and give some sort of thermal cycle as well as stress in order to get the recovery of the plastic strain. So, that was the very common feature of most of the ferrous shape memory alloys.

Now, in case of iron manganese system this is also another very interesting system where martensite is here called as ε because they have a hexagonal close packed structure, but in all these cases the austenite is the γ, which is the FCC phase. So, the shape memory effect is generated which is the property of the of a phase itself, an even though we talk about alloy and so on, but the plastic strain accommodation of the strain all these things appear because of a phase where austenite is a FCC phase and which transform into BCC or body centered tetragonal or let us say it can be transform into hexagonal closed packed martensite structure.

So, here silicon is also important to add, we will discuss later on even though the silicon is a somewhat like 1 % or a maximum up to 4 to 6 % large effect has been observed. In this particular cases people have observed that these are also non thermoelastic martensite that form, even though the M_s temperature is little bit near the room temperature in all these cases, where this is a typical iron-manganese system where some of the substitution of the other alloying element is also present.

The third system where a martensite has a structure of face center tetragonal means from FCC austenite it transform into FCT and here also let us say 30 % Palladium is involved in this alloy and here these are thermoelastic in nature and also the temperature is rather low. However, day by day people have discovered some more but you see very common nature of all these alloy series that the phase should transform from γ FCC phase which is a face centered cubic structure in to either body centered tetragonal or body centered cubic or hexagonal closed packed or face centered tetragonal.

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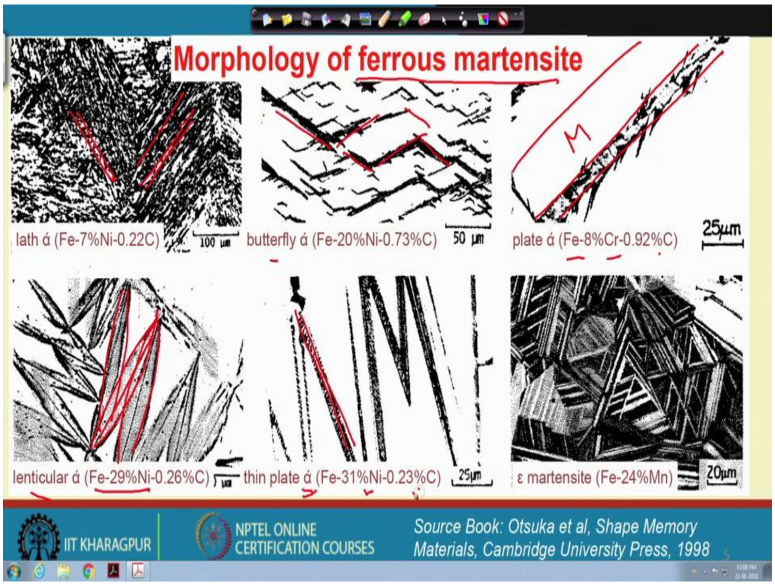

Now, we must look at the nature of the morphology of the common ferrous martensite microstructure. So, here I show you some of the common feature that I discussed earlier also that there are four major types of martensite has been observed even though those are not shape memory alloys let us say a conventional martensitic transformation.

So, those are lath or let us say butterfly or lenticular or plate type of morphology and here I show you the same four major types of martensite phase that form here in case of ferrous martensite and those are well known let us say some of the feature you can see here these are the lath type.

So, a lath is a very common feature of the martensite and here it just looks like a butterfly type of shape and ah now, the plate type of martensite is also common in case of this iron-chromium alloy where martensite forms in this shapes; where a lenticular is also a another feature which is a very common feature in iron-nickel system. So, iron-nickel system is also well known for such shape memory behavior and this is a typical lenticular morphology of iron nickel martensite. So, it looks like a disc or some section of a disc actually.

Now, very thin plate of α' which also form in case of a high nickel content alloy with a very low carbon percentage. Now, usually it has been observed that if you increase some carbon concentration or otherwise the morphology of the martensite depends on the transformation temperature; means if M_s temperature goes higher, then lath morphology will change to thin plate type morphology. So, very similarly a plate like morphology or here has been observed in case of ε-martensite which has a hexagonal close packed structure that form in iron-manganese system.

So, iron-manganese is also well known of a shape memory behaviour as a ferrous martensite and here usually people add some amount of silicon. So, ε-martensite is also very much common to show such kind of a plate like features.

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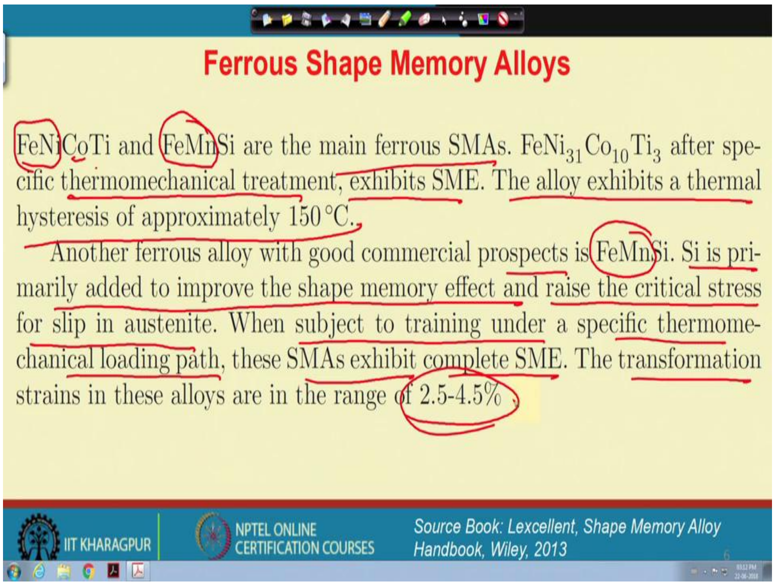

And, all these different morphology of martensite involve this martensitic transformation from austenite and incorporate some defect. So, that they can exhibit or recover the strain or the shape strain, a very general statement about the shape memory alloys. One can recall that this iron-nickel system with cobalt and titanium addition or iron-manganese system these are the very two common system or the most important system in a ferrous martensite in a ferrous shape memory alloys.

where the specific thermo-mechanical treatment must be given only then the alloy will exhibit the shape memory effect. Here we are talking about heating and cooling and giving some deformation at a given temperature and that is why we are calling it as a thermo-mechanical treatment or let us say proper training to the shape memory alloy. So, this alloy exhibit a thermal hysteresis of approximately 150 °C means M_s and austenite finish temperature that hysteresis is somewhat like 150 °C.

Now, another ferrous alloy with a good commercial prospect is basically this iron-manganese system where the silicon is primarily added to improve the shape memory effect and it raises the critical stress for slip in the austenite because as I said that to cause a slip in the martensite to cause a slip and it will simply destroy the shape memory behavior. So, we need to add about some other alloying element. So that the twining can form and when it subject to proper training under specific thermo-mechanical loading path these shape memory effect or alloys exhibit a complete recovery of the strain.

However, the transformational strain is only in the range of 2.5 to 4.5 %. So, they are not so high that a large amount of strain can be given in the martensite state, so that you can recover a large amount of strain. So, that is not possible and that is not the nature of the shape memory alloys in ferrous alloy system.

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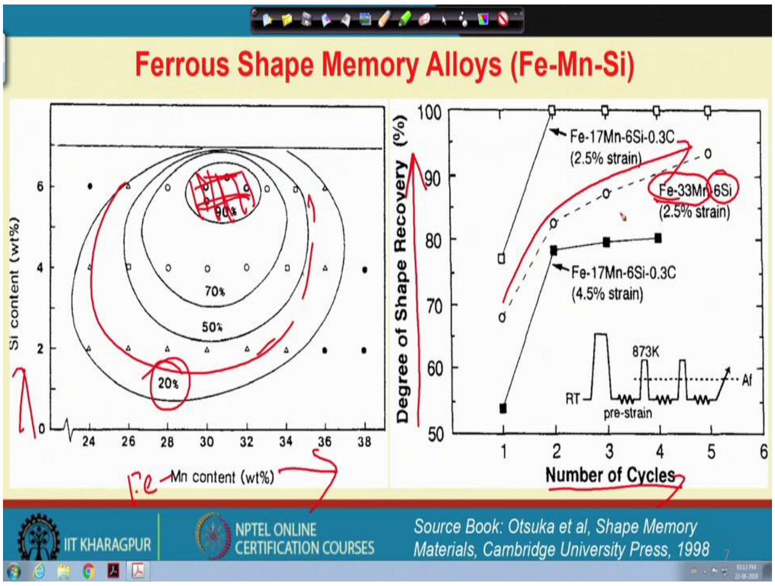

Now, since I said that alloying elements are important in case of this iron-manganese system I am talking about actually iron-manganese here. So, this is the manganese content and this is the silicon content and people have observed that 20 % of the strain can be recovered not a total 20 % strain so, the strain given in the martensite and out of that strain or let us say out of 2 out of 3 % of the total 20 % of the strain will be recovered in this composition range, where 90 % can be recovered in this. So, there is always some percent let behind. So, it is not a fully recoverable strain can be given.

However, if you increase this number of cycle means the training or let us say the thermo-mechanical treatment then the degree of the shape recovery will improve. So, let us say here iron and manganese system with some amount of silicon it has been observed that there is some increase of the recovery strain. So, this is also an important information that in case of a ferrous martensite or ferrous shape memory alloys a thermo mechanical treatment is required in order to obtain a good shape strain.

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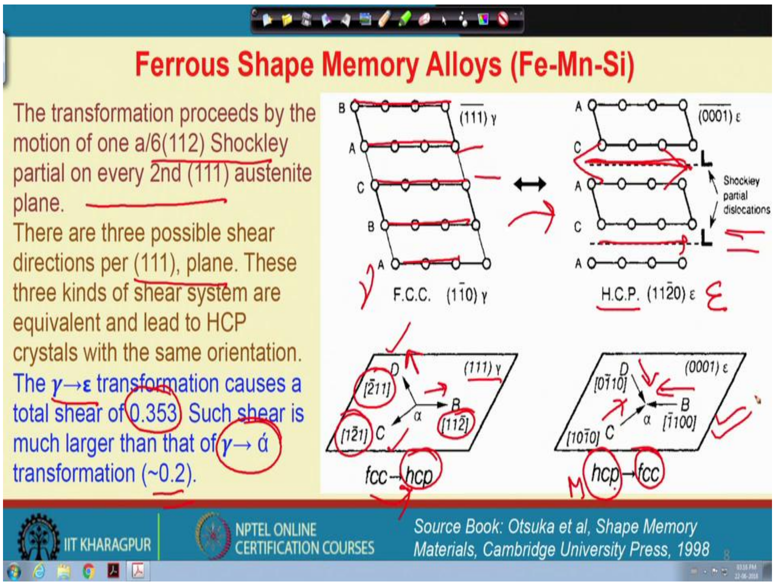

Now, the transformation from austenite which is a FCC structure to a hexagonal closed pack ε-martensite, the transformation usually proceed by the motion of a Shockley partial and every a second of the (111) austenite plane. So, this is the (111) austenite plane and here let us say one of the partial Shockley partial should pass, so that the transformational strain can be accommodated. So, usually this Shockley partial that <112> type of Shockley partial, three of such Shockley partial are available here is shown as a vector that is B, D and C from FCC to HCP transformation on (111) austenite plane.

However, these three possible shear direction on these (111) plane, there are three different kind of shear system is equivalent that lead to this formation of this HCP phase. However, this austenite to martensite transformation causes a total shear of 0.35, this is a quite large strain actually and this is a much higher then let us say iron-carbon system you know about α' a martensite where there is a transformation strain of only 0.2. So, this is a quite large amount of transformational strains are involved whereas, when we need to get back these recovery of the strain given to the sample this HCP should transform into FCC austenite. HCP is the martensitic phase.

However, one should remember that this partial dislocation where it went in a particular direction it should come back. So, there should be a reverse movement of these partial dislocation then only the shape recovery will occur. So, that I summarize in a minute.

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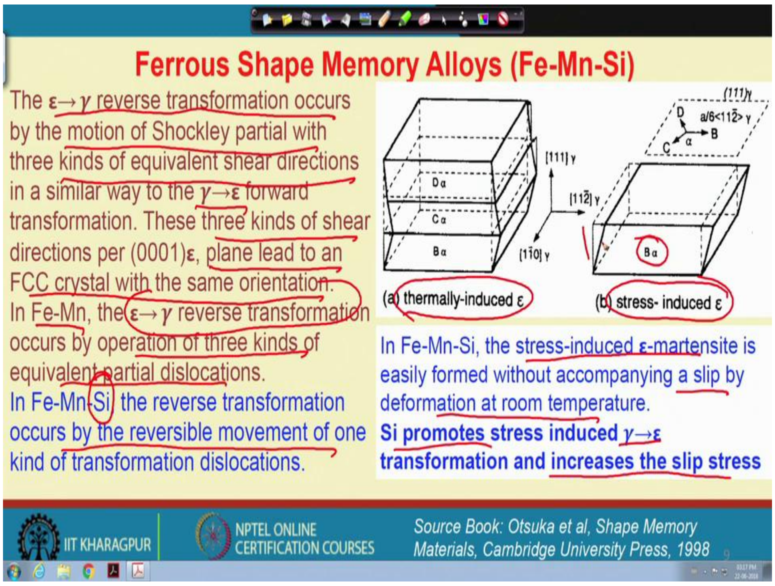

So, like here the ferrous shape memory alloys let us say here the reverse transformation occur by the motion of this Shockley partial with three kinds of equivalent shear direction from a γ→ε. However, these three kind of shear that I show in the earlier slide actually that plane lead to a FCC crystal with the same orientation and unfortunately in case of iron-manganese system this reverse transformation that occur by all this three equivalent partial dislocation whereas, if you add silicon into it then only one type of dislocation they actually involved in this reversible transformation.

So, the stress induced ε-martensite is easily formed by accompanying a slip by the deformation at room temperature and here we actually add silicon in order to promote the stress induced transformation and increase the slip stress. So, that was basically the purpose and you can see here the schematically I have shown you a thermally induced ε-martensite and stress induced ε-martensite.

So, here this is the austenite which is shown as a dotted line and this is a particular B type of direction where partials has moved and this is the B actually and this is a martensite where these are B, C and D three different types of stacking of the thermally induced ε martensite.

So, today we briefly discussed about the ferrous ah shape memory alloys and the next class we will be starting with some non-ferrous system and we will continue this discussion.

Thank you.