**Advanced Materials and Processes**

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**Lecture – 20**
**Shape Memory Alloys (Contd)**

Welcome to NPEL; myself Dr. Jayanta Das from Department of Metallurgical and Materials Engineering. I will be teaching you Advanced Materials and Processes. Last couple of classes, we have discussed about classification of different types of phase transformation, martensitic transformation, effect of stress on martensitic transformation and shape memory effect. We have little bit learn about the very basic on the shape memory effect, how we can really achieve 100 % shape recovery of a material

Shape recovery means, that we deform a material plastically; however, by increasing the temperature of that material, we again get back the original shape and this shape memory effect involve martensitic transformation. Because we actually deform the material which is in the martensite microstructure or the structure and that martensite content type-I or type-II twin and one of the twin, will grow during loading in expense to the other type of twin and then only we can achieve some plastic strain. And then ultimately, we get a martensite only one type of twin that is the maximum plastic strain we can achieve at that condition and then if we warm it up, if we heat that martensite above austenite finish temperature, we will again get back the shape.

So, that was actually the understanding on the shape memory effect in metals and alloys. And today, we will again try to see the same effect, we will discuss today how one can achieve two way shape memory effect because. So, for whatever we have discussed that is a one way. Let us have a look and try to understand this matter.

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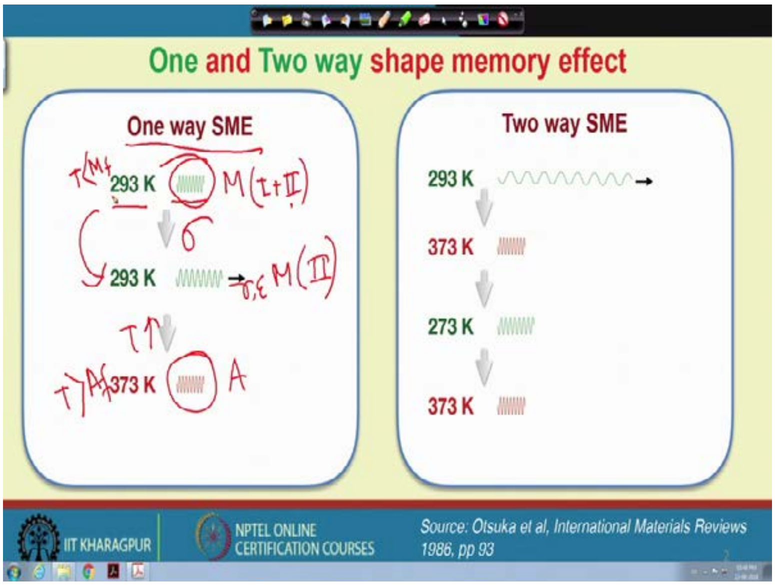


So, far, we have discussed one way shape memory effect; means let us say a martensitic spring is kept at 293 K, this temperature is well below the martensite finish temperature.

So, T is basically less than $M_f$ and here, I have martensite in the microstructure. So, let us say here, I write M which stands for martensite and I have actually type-I and type-II twin. And now, at the same temperature, I simply provide some stress or strain. What will happen? One type of twin will grow.

So, here I again have martensite; however, let us say I have only one type of twin, just for understanding at this movement. Now, I increase the temperature; I have provide some deformation. I increase the temperature above the austenite finish temperature, what will be the microstructure? The microstructure will content austenite.

And you will see, this is the shape which is same as this shape. And this effect is actually the shape memory effect and it is actually a one way shape memory effect. And now, if I think about straining or providing more stress to this martensite spring. Because I told you that stress required for twinning should be less in these materials and therefore, the twinning actually occurring and one type of twin is growing, is not it?; now I take this same material and straining it more.

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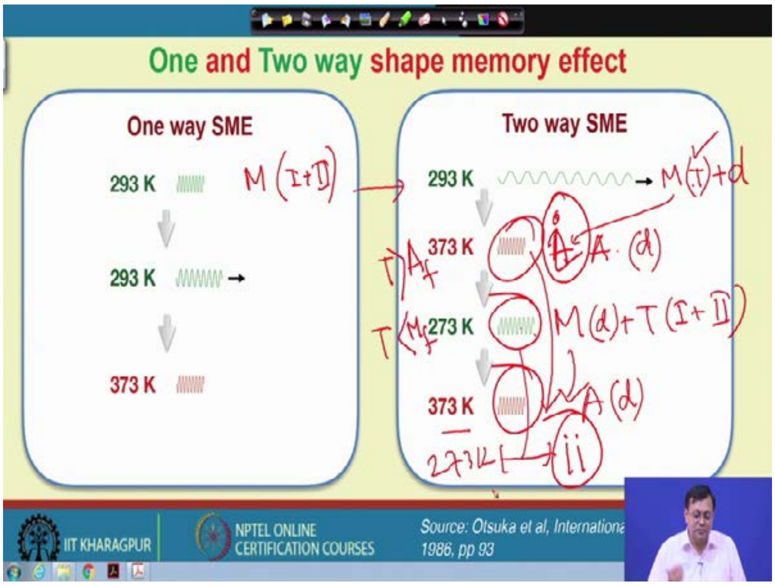


In such a condition, I will have large plastic strain. In this condition, what we have? We have martensite, martensite means I type of twin and type-II twin here and if I strain too much, then let us say I have martensite with twin; however, this twin plus some dislocation will form because I have strained it too much,. And so, under such condition, if I heat it up, then I will have austenite. So, here temperature is greater than austenite finish.

So, let us say whatever twin we have, the twin will vanish during heating. But I will have some permanent deformation which is due to dislocation. And then, if I cool it below martensite finish temperature, here I have martensite with that dislocation plus that twin which is I and II type. And then, again if I heat again, I will get austenite. So, you see if I take this material, heat it up I get this original shape and if I cool it, then I will get this shape all time. So, this means again I cool it to 273 K, I will get the same dimension. So, here let us say I can remember the shape of let us say case 1 and I can also remember case 2; both are remembered by heating and cooling.

So, two way I can memorize the material shape and this is very interesting and we call it actually the two way shape memory effect, I will show you some of the real example of such effect.

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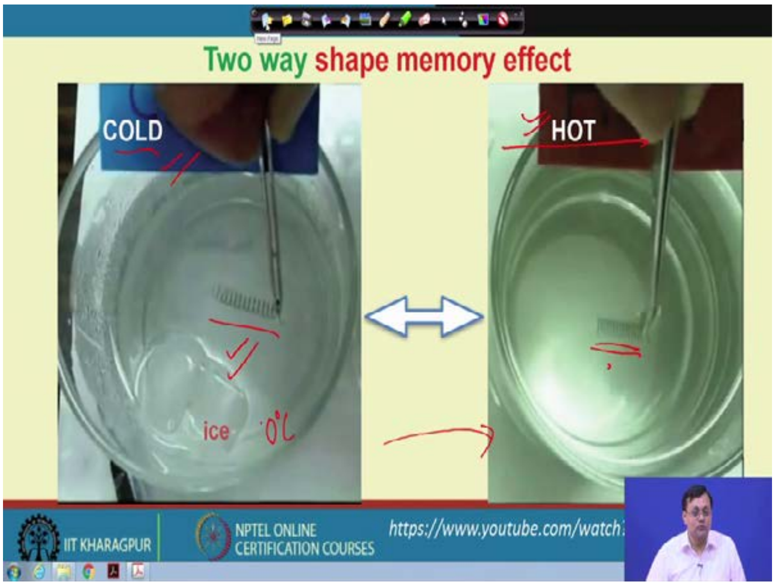


And I have just taken two images where a beaker is kept at an ice temperature around 0 °C.

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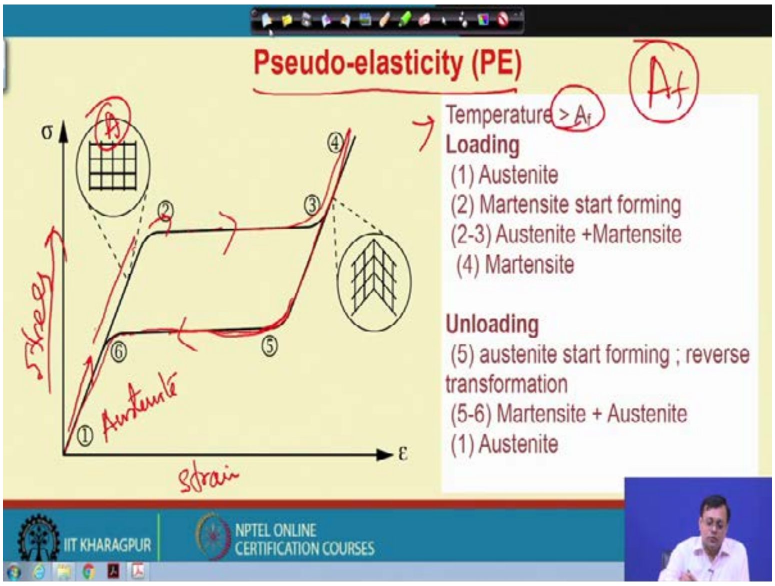


And here, let us say the temperature is somewhat very cold. So, that is why I write here as a cold and let us say somewhat close to 0 °C and I have taken one of these shape memory where after proper straining. What I call it is the after proper straining means, I have plastically deform a lot, so that I have introduced some dislocation into it. And so, at the low temperature, I basically have martensite with dislocation and then if I heat it up, then I get this shape actually.

So, I remember both the shape and the length of this spring in the hot condition or in the cold condition. So, this is something very much interesting in terms of material memorizing two different shape at two different temperature. And this could be used as various sensors. Now let us discuss another very important aspect that I told that is pseudo-elasticity. So, in case of a pseudo-elasticity, first thing we should remember that the temperature of the deformation, what we will discuss here is above austenite finish. A temperature of such material with austenite finish temperature above austenite finish; that means, that the microstructure contains only austenite.

So, the whole microstructure here is only the austenite. Now, I am plotting here the strain in the X-axis versus stress. If I apply some stress, then there will be a strain that will be generated in the material and here I still have that austenite lattice. And after this point, I see some strain where stress does not increase much apparently looks like a plastic strain is achieved. And we reach to 0.4 and then we unload it, after unloading, I can see that we have recovered the original shape.

Please remember that the temperature is above austenite finish. This is also another interesting phenomena which is very different than the shape memory effect. So, here now we need to talk about what are the micro structural constituents? During loading segment means, I am talking about this segment point A 1 here, I have all austenite.

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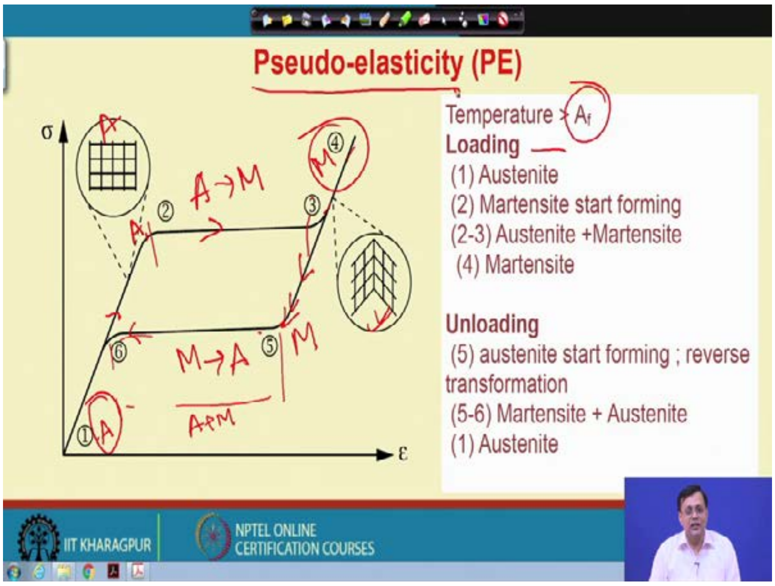


At point 2 here, I also have only austenite and this is a representative diagram of the austenite only.

Now, this austenite will be transformed into martensite by application of the stress. So, here austenite actually transform to martensite and therefore, we see such kind of deformation curve. Now, beyond point 3 here, all the austenite transform into martensite. So, here I have only martensite, which is why the schematic of martensite is drawn here or shown here.

Then again, I unload it and during unloading, since some activation energy is required to a transform back from martensite to austenite. So, here I still have martensite, here I have still martensite and during these region, martensite actually transform into austenite and then it comes back. So, I again get a hysteresis; the temperature as I said is above austenite finish temperature. And in these domain; I basically have austenite plus martensite and here also the same.

Where here I have full martensite and here, I have complete austenite in the microstructure. And this looks like an elastic like behaviour; even though in reality because we get back almost 100 % strain that has been given to the material and it appears to be like an elastic come back. And this is why such behaviour of the material is known as Pseudo-Elasticity, PE. And sure as a metallurgies; we must try to learn what are the transformation is involved.

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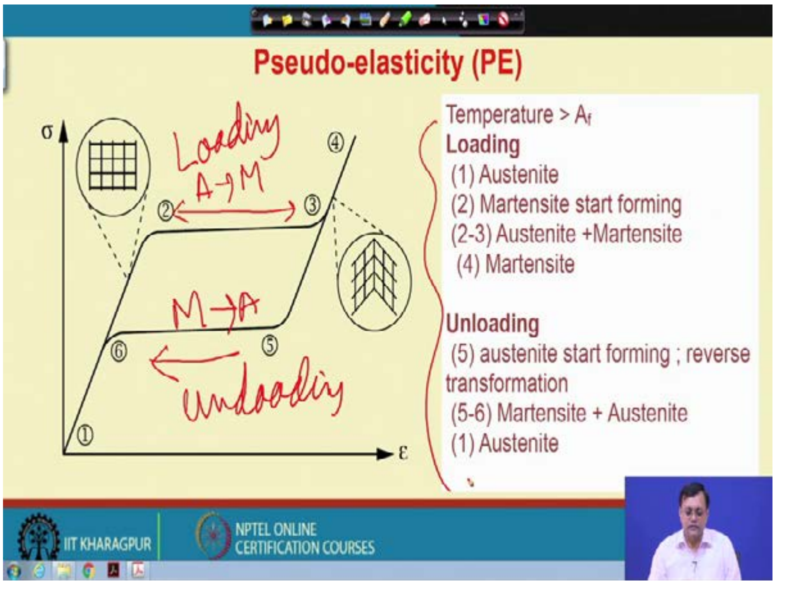


And we have already looked at that from 2 to 3 in between these what austenite transform to martensite and here during unloading cycle, this is the loading cycle and this is the unloading cycle.

Here, martensite transform into austenite and this is the reason of this Pseudo-Elasticity.

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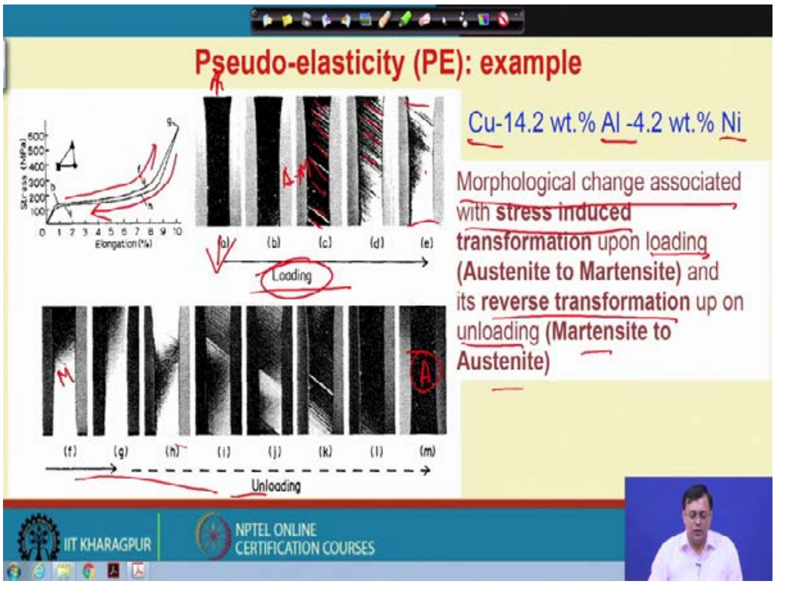


Now, I show you one of the example of pseudo elastic behaviour in case of a copper-aluminium-nickel alloy where we have made some tension test on such sample. During loading, you see some of this lines that represent actually that martensite is forming from austenite to martensite is forming in the loading cycle. That I have explained in the last slide and then, this complete material full of basically martensite only and then it was proceeded with some unloading cycle during which it basically comes back to austenite. So, you can see, these kind of marking again vanishes.

So, this is a morphological change which is associated with a stress induced transformation during loading, this is the loading cycle where you see martensite is forming. Just by looking at the over macro and micro structure and the reverse transformation is again happening due to unloading cycle that involved from martensite to austenite. And this is the typical stress strain curve even though here hysteresis is less ah, but it shows such kind of pseudo elastic like; pseudo elastic behaviour.

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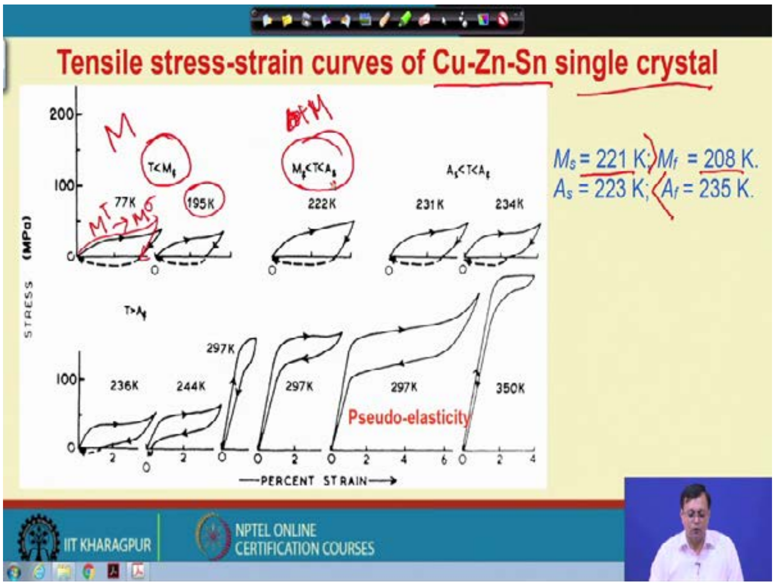


Now, let us consider one of such very interesting tensile stress strain curve of a copper-zinc-tin single crystal which is also well known as a shape memory alloy. And this is the single crystal, please consider the martensite start temperature is 221 K and martensite finish is 208 K which is lower than $M_S$ as expected and austenite start is basically 223 K and austenite finish is 235 K.

So, as expected, so here the temperature is less than $M_f$, means basically the microstructure contains only martensite. Now, if we deform that martensite, then martensite contains type-I and type-II twin and if we release the stress, then again some elastic recovery will occurred. However, this particular strain involve martensite that form during cooling and that transform into martensite during deformation.

Means, let us say one type of twin grows in expense to other or rearrangement of the twin variants. And then, let us say at 195 K also, we can see the similar type of plot. Now, if the temperature is in between $M_f$ and $A_S$; what are the microstructure constituent? The constituent is only the martensite here.

Since austenite does not form at all, so we only have martensite here. This deformation curve is very much similar; now, let us go back and try to look at what will happen if the temperature is lying in the range of austenite start and austenite finish, means it is a mixture of martensite plus austenite.

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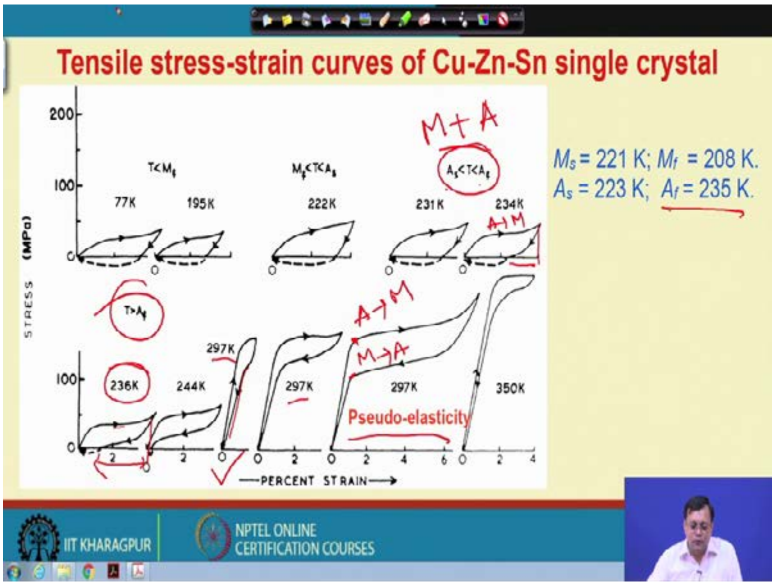


In that case actually, we see that the recovery has increased. This means, some part of the austenite must have transformed to martensite during deformation itself. Now, we increase the temperature further to 236 K, which is above austenite finish. So, here we see that the recovery of that strain has increased and if we keep on increasing, we can see from here itself, 297 K we can get back the 100 % strain.

That is the typical pseudo-elastic like behaviour; so, here basically, the understanding is required even though the temperature has reached to such austenite finish temperature; still, we are not getting actually 100 % shape recovery and we need to understand this and we need some measurement to do. So, what we can do at different temperature, we see these case and strain curve and then we measure what was the minimum stress required for austenite to martensite transformation or martensite to austenite transformation. That may give us that how stress is linked with the transformation temperature.

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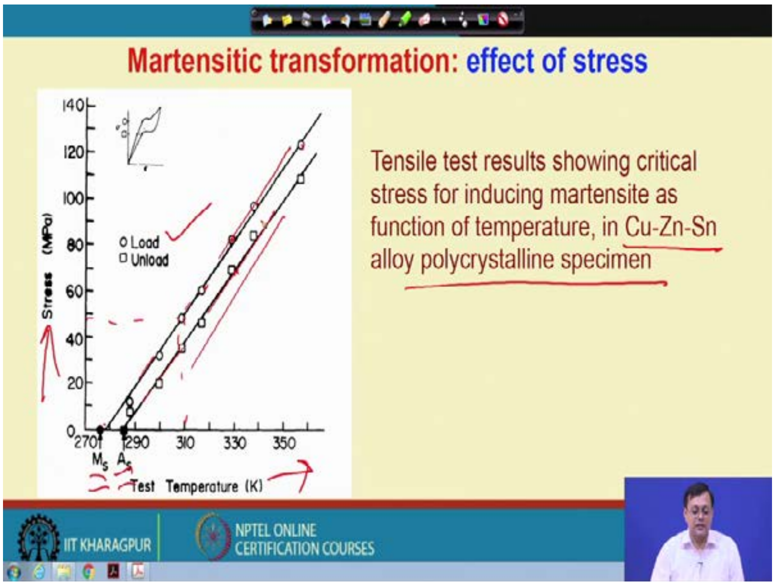


And therefore, people have tried to draw the diagram and develop several diagrams of some of these as example; I show you which a copper-zinc-tin polycrystalline sample is.

Here, you can see that the stress and the test temperature and here this is the stress at this particular temperature, let us say 310, this was the stress during loading cycle and this was during unloading cycle. In unloading cycle, means actually that was the stress required for austenite and martensite transformation. So, in the loading and unloading cycle, we got the locus of these or the variation of the $M_S$ and $A_S$ temperature with the stress and temperature.

So, this is the way we see that there is an increase of the temperature that simply means the transformation temperature increases with the application of the stress. And this means that the stress assist the transformation which means there is increase of the martensite start temperature. That has been discussed in an earlier classes and we can have a look again on that aspect.

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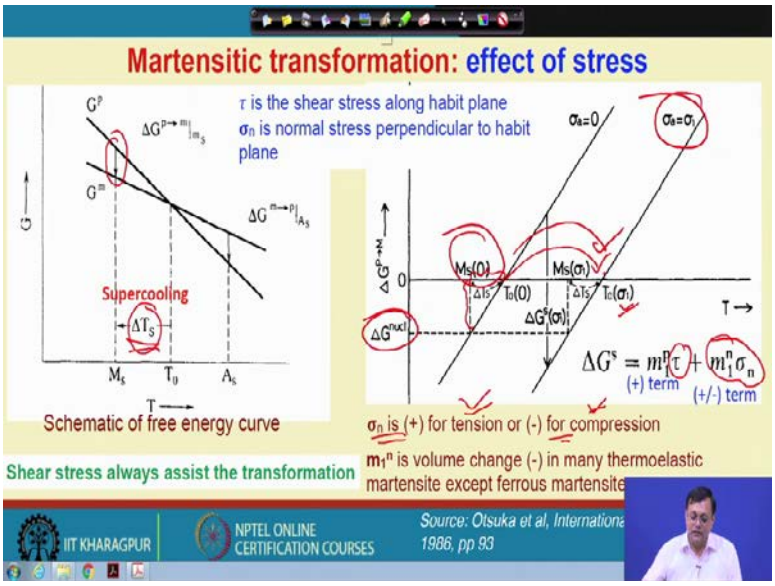


Because I had told you that, we need some excess super cooling in order to form a martensite. And this particular $G_m$ or the ΔG for nucleation of the martensite require some supercooling.

And this $G_s$ required these amount of super-cooling. And we can simply introduce some stress, then temperature will be shifted to higher side. And this gives us the magnitude whether it is in the positive side or negative side, it depends on whether it is in tension or in compression. Even though the shear stress always assist the transformation; however, the normal stress may affect which become positive, which may oppose or which may in favour of the transformation.

So, we can directly see here that martensite start temperature will increase by the application of the stress. This is the understanding we have in our earlier discussion. And now, we can develop a plot based on that which I will give us the overall picture and how is that? Here, I show you that how the $M_S$ temperature changes with the stress?

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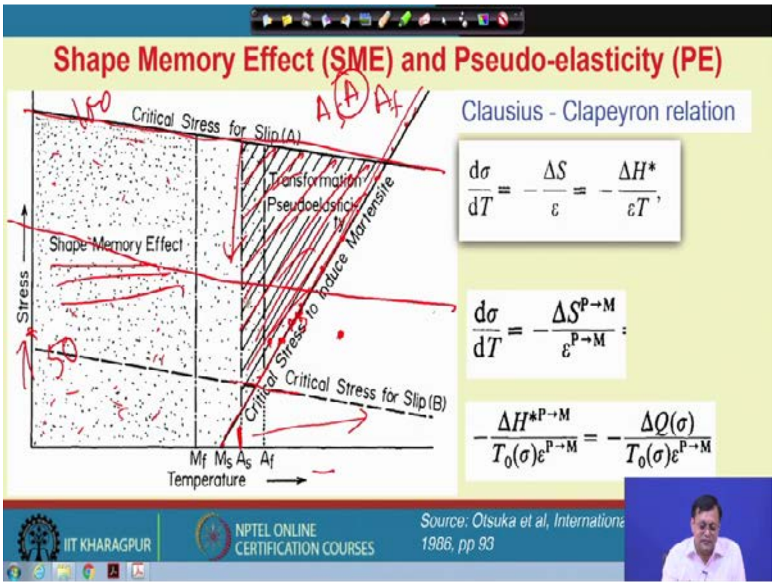


If we increase stress, then martensite start temperature will increase. Please have a look at this particular diagram and this particular aspect because there are lot of thing to discuss here. And if that is the condition mean stress increases the martensitic start temperature increases and the shape memory effect means deformation should be given to achieve shape memory effect should be lower than the $M_S$.

So, it is very clear that we will get the shape memory effect below this temperature. On the other hand, there is another criteria that we discuss. That was the critical stress required for slip should be much higher than the twinning stress. So, I will have the critical stress for slip which is higher. So, below that stress twinning will occur because the material should exhibit twinning with those different twin variants and I will get shape memory effect below that stress level.

So, I have a zone of this shape memory in this. And now, this is under stress. Now, the pseudo-elastic effect will occur only when the temperature is above austenite finish or some part of the Pseudo-elasticity can be observed where the temperature is above $A_S$. $A_S$ means, austenite start temperature. In between austenite start and austenite finish temperature, I have austenite. So, some part of Pseudo-elasticity can be observed.

So, from here, this temperature to the higher temperature, I will get the Pseudo-elasticity, but I will never get Pseudo-elasticity here because martensite has to form. Martensite will form only below $M_S$ temperature, martensite will form. So, here it is not possible, here it is possible. Here it is possible because this is a temperature which is below $M_S$ and this is the locus of the $M_S$ temperature.

So, this is the $M_S$ temperature. So, here martensite will form from austenite during application of the stress. So, I will get a zone of the pseudo-elasticity in this. So, I will get shape memory effect which is here; now, if the critical stress for slip decreases means, let us say that 100 MPa stress has been given, which is just sufficient to introduce dislocation.

So, this means if I apply 50 MPa, I will get twin, is not it? But, if I go above 100 MPa then I will get dislocation and if that critical stress of 100 goes down, then let us say come back to 50 MPa, then above if I give 100 MPa stress, I will get dislocation. So, let us say here it is 50 MPa and here it is 100. So, here in this particular case, then slowly the pseudo elastic region will vanish.

So, let us say this is the critical stress for slip; then I will get pseudo-elasticity only in this domain. Let us say this is a new critical stress for slip for a material. So, I will get pseudo-elasticity only in this region; however, I will get shape memory in this region. Let us say in such away, I keep on changing critical slip stress, due to some sort of change of the composition or some processing condition, if the slip stress decreases then, I may reach here. So, in that particular condition, I will only get shape memory effect, but there will be no pseudo-elasticity. And for such a situation, shape memory effect will be achieved, but there will be no pseudo-elasticity in the material.

It simplifies, that there could be material that we have produce that we will show only shape memory effect, but no pseudo-elasticity. However, it is expected that if the stress is higher, then we will get both the effect. So, to get pseudo-elasticity, we need a critical stress for slip must be higher and higher. Now, regarding this particular line we have learnt such from thermodynamic studies that Clausius - Clapeyron equation was very much important. What does it said? It said $\frac{d\sigma}{dT} = \frac{\Delta S}{\varepsilon}$that d sigma by d T is equal to entropy change by the strain. And here, something is very much interesting and correlated with this shape memory effect actually because here we are applying stress and the transformation temperature is changing.

So, S is critical to H by T. So, we can rewrite this equation in that term. So, here this is the transformational strain involve with P stands for the parent austenite to martensite, the entropy change. And so, this particular equation tells us how the transformation temperature will change with the application of the stress. And this is the activation energy with the stress and $T_0$ is the transformational temperature change due to the application of the stress. So, Clausius - Clapeyron equation actually interpret the locus of this line. So, we see that this is a very important diagram for understanding the shape memory effect in materials.

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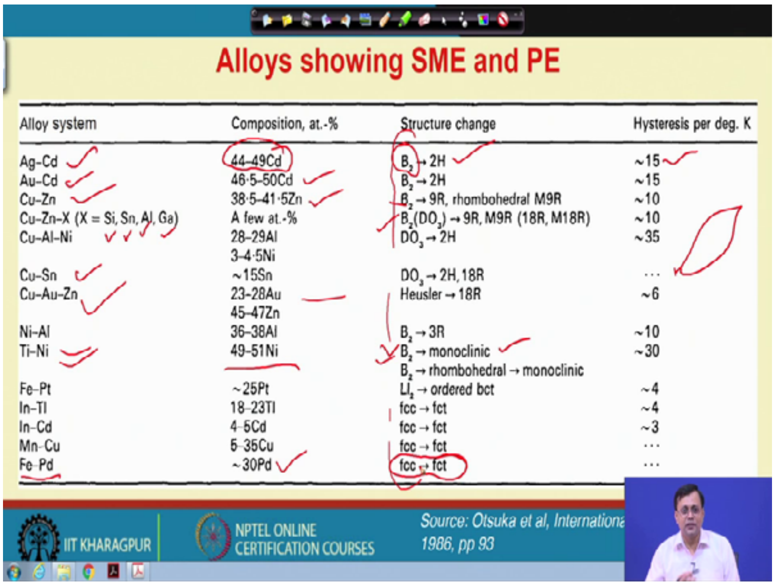


Now, there are many different material so, far that show or alloys that show these shape memory effect.

Just have a look at those alloy system. So, here , this is  silver-cadmium system, the composition is around 50-50 and there is a structural change from a ordered BCC which is the B2 structure to 2 H, H stands for basically hexagonal system. And here, this is the transformation hysteresis which is represented like this and this is per Kelvin, this is per degree Kelvin, how much is the change and let us say this is a gold-cadmium system, similar 50-50 composite; copper-zinc also have something in between where there is some ordered these are the transformation from B 2 to R rhombohedral type of structure, copper-zinc and X, X stands for silicon, tin, aluminium, gallium.

So, you see is there are so many alloys has been discovered and the reason was just to tune and modulate the transformation temperatures and the hysteresis loop. So, so there are various types of transformation that are involved in that and characteristics also changes.

So, with that tuning with change the transformation temperature, so that, we can bring down the $M_s$ temperature or goes up.

So, copper-tin system and copper-gold-zinc system, such kind of thing happen in the next classes, we will also discuss some of these example and we will do some case studies about the crystallographic changes and how this transformation occur; nickel-titanium is also very good example and which is already under used for very long time where a B2-type of structure transform into a monoclinic type of structure. And in case of let us say iron-palladium, here this is something like 30 palladium where FCC transform into face centered tetragonal.

So, you can see that austenite does not necessarily means that it has to be only FCC like in case of steel, we only have learnt about face centered cubic structure and body centered tetragonal structure. But in here, we have learnt that there are so many different type of crystallographic structure of austenite is possible and it depends on various systems and the structure means crystal structure of martensite is also different in different system.

So, the transformation itself says whether it is martensitic or not. It depends on how the transformation does occur. So, so far, we almost a covered a very important aspect of phase transformation that are associated with the shape memory effect and shape memory effect and pseudo-elasticity which we discussed today and not only one way shape memory is possible; however, we can produce material which memorizes the two way shape means, the initial one and the final one both.

If we just change some experimental parameter like temperature, I have shown you one example of such hot and cold; so, there we can memorizes the shape. So, in that particular case, for two way shape memory behavior dislocation plays a very major role. Whereas, in case of a 100 % shape memory effect, we need only the twin variant of two different types and this twin variant, will play a major role, where one of the twin grows in expense to the other during the application of the stress.

So, in the next classes, we will be discussing a little bit more into detail of this effect in different-different system.

Thank you.