

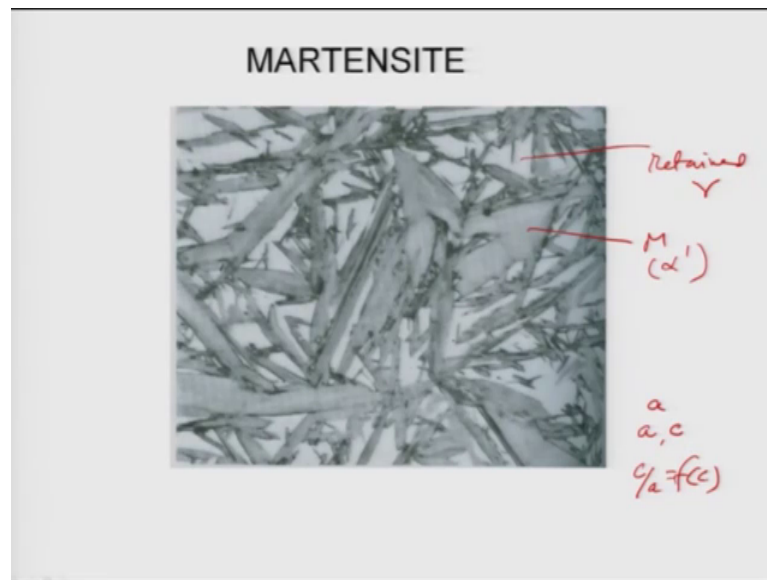
**Phase Transformation in Materials**  
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**Lecture - 42**  
**Martensite**

So, we will discuss in this lecture about martensites by the way a martensite is named after scientist Martens. He discovered this thing first time and that is why we call it martensites. As I told you that martensite forms when we quench austenite from high temperature. So, quenching can be done in water or you can do it in liquid nitrogen or one can do it in ice; depending on the quenching, the martensite fraction will be change in a microstructure.

First let us look at how it looks like, then we will discuss about details; remember martensite itself is a subject and it cannot be discussed in 1 lecture or 2 lectures; whatever the basic features from martensite if steel I am going to discuss; to be clear martensite is also observed in nonferrous alloys. So, it is a common feature in many of the microstructure. So, martensite is true in general; on the other hand pearlite and bainite is very specific to the steel. So, martensite is observed in nickel based super alloys, even some copper alloys; we use martensite transformation in nickel titanium alloys for the shape memory effects. So, therefore, martensite is not only present in steels, but in this discussion; we are discussing about martensites in stainless steels.

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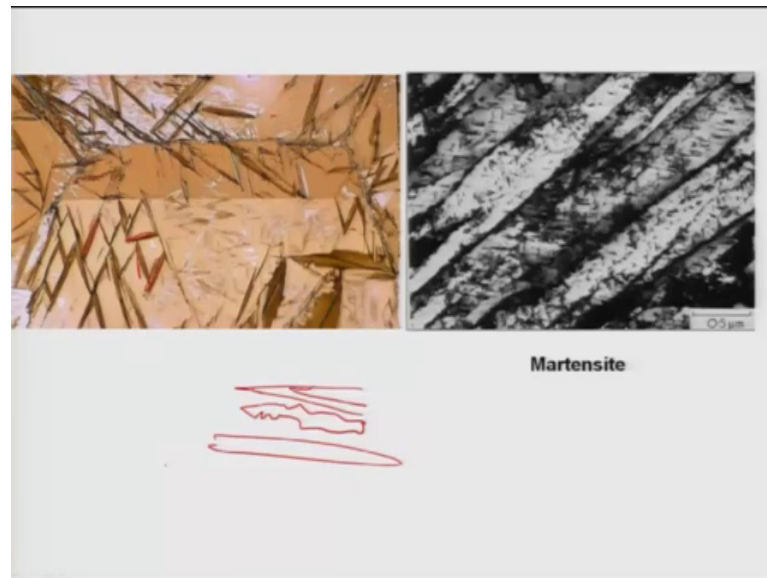
Martensites look like a plate or a lath in the microstructure as you see here this is a typical microstructure of martensites. So, these things; gray color plates they are actually martensites in between white things which you see here there is basically known as retained austenite written gamma. And these are actually martensite; many type books if they represent as an alpha prime to distinguish between alpha martensite is a distinct crystal structure is known as body centered tetragonal basically very low carbon concentration in steel they martensite tetragonality is very low.

So, you remember you defined tetragons crystal structure by 2 lattice parameter a and c in cubic we have a lattice parameter a because in cube all the sides are of similar length and angle between each side is ninety degree in tetragonal structure the 2 sides have the same length, but one side is a higher length that is in a tetragon and angles between all the sides are 90 degree.

So, tetragonality is defined by ratio c by a c by a is basically a function of carbon content and the steel or martensite. So, when carbon concentration is very low the c by a ratio is very very small we sometimes we cannot distinguish between cubic a tetragonal structure of low carbon concentration steel in martensites. Therefore, we represent this as alpha prime because it is a derivative structure of alpha.

Now, martensites as you see here this is optical micro structure looks like a plates.

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And if you look at a much large you know much lower magnification microstructure what do you see here you see here these are actually all gamma grains and martensite forms like a plates you see the everywhere. In fact, they looks like this looks like some cases looks like such a kind of structure I am drawing one of them and some cases they looks like these; they are actually internally twinned they are twined in inside each of these martensites that is why they looks like a faulted.

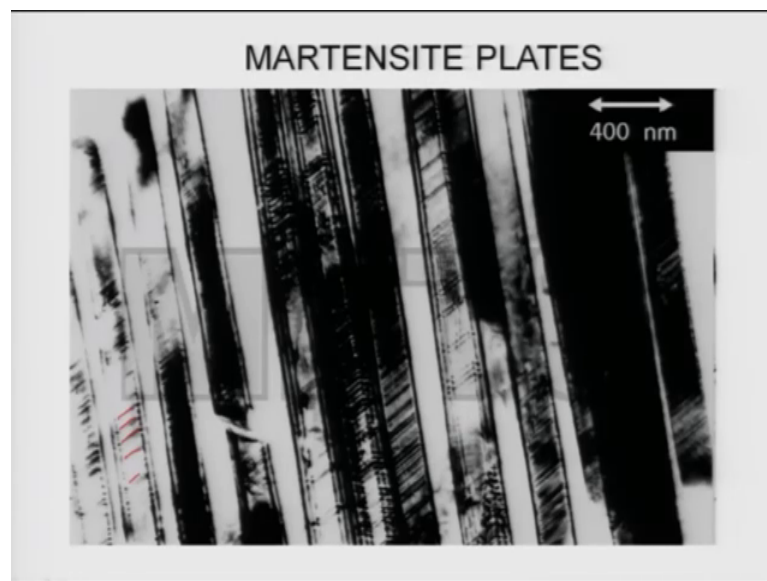
So, therefore, martensites basically forms what is known as a diffusion less transformation in which none of these PCs either carbon, iron or whatever present the steel undergoes any diffusion they goes a sapling basically by sheer force because it is quenched to water or some other things there is no time for any diffusion of the atoms to happen because diffusion requests time as you know. Therefore, we cannot actually have any choice other than you know transformation which is dictated by affiliation of shear forces. So, just to give an example; it just martensite is basically like this suppose you have a in a classroom you have chairs or kept in a particular manner and you if you ask the students to be just like behaves like atom they can go and sit and in a particular order suppose in a gamma iron.

Now, once you cool down to draw temperature very slowly these atoms can then change their positions and basically that is nothing but these students can change their positions and segregate. So, when they segregate they form Pearlite that is why carbon diffuses out

from the alpha and go to cementite, but if we do not get give them time, if do not give them time suppose if the students has to enter the class and sit very fast. So, are they will simply occupy the positions wherever it is available? So, that is nothing but it is just nothing but actually saying the atoms in a material to simply go to a seated positions and do not move exactly that is what happens in the martensite transformations.

The carbon atoms actually pushed along the c axis of these along the one of the axes of these cubic unit cells and that is why actually they become you know aligned along certain directions and tetragonality develops there is one of the important features from martensites that this is deputation layer transformations as I said the plates if you look at very carefully place actually internal twins you can see these are all twin peasants inside that every plate martensites as a twin structure.

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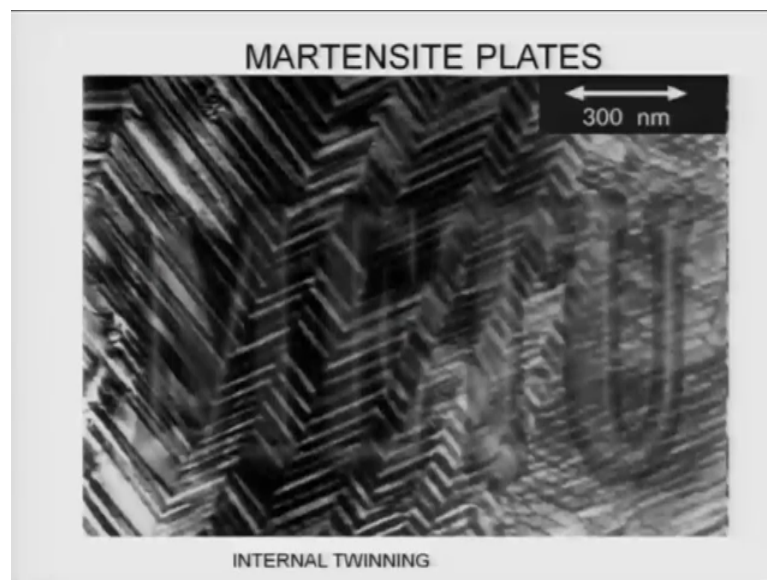


That is obvious because you are actually forming from a high temperature by quenching and these has to adjust its orientation we respect to the prier gamma grains. So, to do that it creates lot of defects inside and easiest defect to form is basically twin because that can take care of lot of strain because had higher the number of twins higher amount of strain can be accommodated. That means, what Martine transformation involves lot of strain plastic strain basically and this plastic strain can only be accommodated by either by dislocation motion are twins, but twins are better because twins can accommodate more strain as compared to the dislocation that is why all these martensites in a steel has

internally twin structures which is very normal in these martensites structure because these are distorted and this is internally twin structure therefore, they very hard they are extremely hard actually.

Martensite in the steel as the highest hardness if you look at Rockwell scale martensite is a hardness above sixty in c scale 60 to 65 is the hardness of martensite depending on the carbon concentrations on the other hand Pearlite and bennite is a hardness less than fifty. Therefore, there is a huge difference of hardnesses of martensite and the other phases is in the other PCs in these steel and this is the reason actually why they have this kind of structures. So, to give you an better idea you can see here the twins.

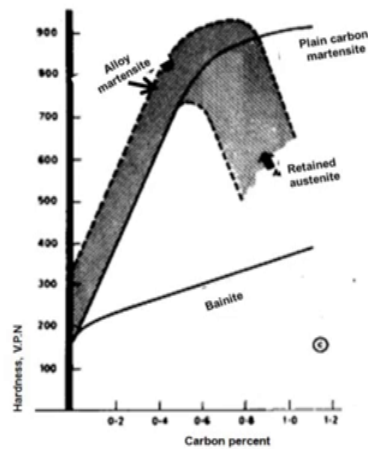
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You can see this is a twinning plane. And these are the twins very nicely you can see the twins.

So, twinning is easily observed internal twinning in the martensitic plates and this is the reason actually why martensites a hard.

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Again I am showing you here a plot is may not look. So, good between hardness and the carbon concentration this is the this is the hardness of bennites; it increases as a function of carbon, but not more than 300 in a picas hardness (Refer Time: 08:26); martensite hardness you can see it is very height; incase of carbon can reach up to 900 actually and so, therefore, it is about 0.6 is what is the weight personal carbon at which the martensite hardness is maximum after that martensites had may decreases that mainly because amount of retained austenite increases.

So, first of all; why do you have written austenite in the microstructure; let us also discuss that part whether that is very important because that dictates the I know total hardness of these martensites aim of martensite actually forming from high temperature by quenching therefore, they form by a shear deformation process and when they form because under cooling is very large your quenching gamma phase from 950 to room temperature. So, quenching see that higher under coolings of their top 7 to 800 or even sometimes higher than that degree cells Kelvin such a large amount of under cooling what will happen because it is less them under cooling. So, diving force for transformation is very large and because it has been quenching to such a fast way and diffusion cannot happen. So, diffusion is also not possible.

So, therefore, martensite plate started forming in a peculiar manner or actually it happens in a bust just like this picture I showed you it happens like a bust you see here they said

the grains of the gamma and so, martensite plates have form like a bust among martensites plates nucleate and grow very very fast. So, it is very difficult to distinguish between growth and nucleation and growth, but they actually form like a bust. And because they form and they are twins; they having lot of defects structure there these free energy which is available for is blust under cooling is taken away taken away by these deform structure by internal stewing structure all the free energy you will be taken, I remember; these strain energy is basically positive term in the free energy expression.

So, total free energy has a volume free energy plus ten energy plus they suppress energy right. So, because of these 2 the free energy which is volume free energy which is available to the system to do the work bulk up is taken away by the strain energy. So, therefore, when you started transforming large number martensite forms in the microstructure if all the free energy available chemical free energy available to the system is eaten away by the surface energy as well as the strain energy there will be no free energy available for the transformation and that is why actually up some it austenite retain in the microstructure.

So, it is never possible to produce Harris percent martensite you can always get about 90 to 95 percent martensite into the microstructure some on the retain austenite will retain, but remember the retain austenite is very bad as per my chemical properties concerned why because the interface between martensite retain austenite is very very strained and the cracks normally originated when you apply force on these steels from these pieces and then it can lead to catastrophic failures that is one the biggest problem in the martensitic steels.

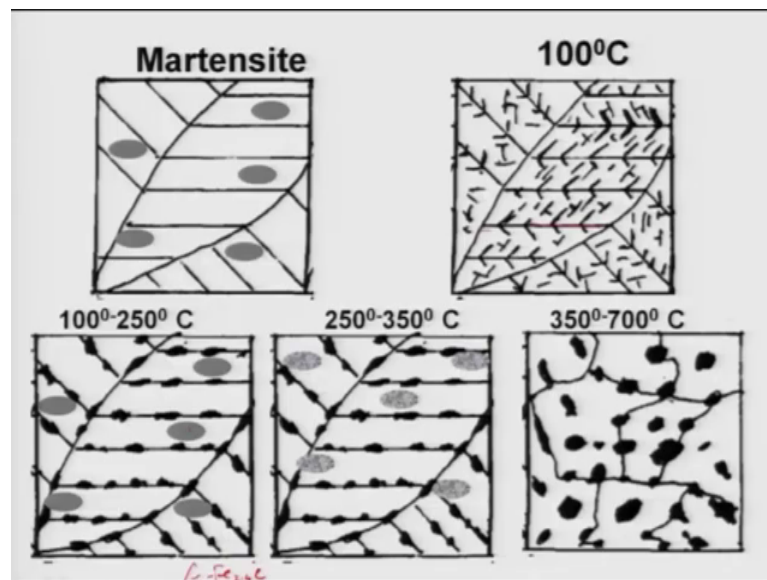
So, that is one part and this is what is shown that you can see here martensites internally twined structure martensites plates or came internally twined structure martensites plates are seen; now the reason; actually it has a different hardness in as a function; carbon concentration because the carbon is a PCs which actually gets supplied from one position to other position from FCC position to the edge corners in the bcc in the BCD structure and because it is basically going in that way; that means, they are actually getting supplied and that is why actually that the amount depending on the carbon concentration in presents there is say optimum value of the hardness when it is increases happening is no longer can be done effectively.

So, therefore, strain buildup is also low hardness drops. Secondly, as a carbon content increases the driving force available is also eaten up mostly by the retained austenite concentration is more or less fraction is more in the microstructure retained energy is sufficient enough to really allow retained austenite present in the microstructure a large volume fraction and retained austenite is very high in a soft face; so, there for hardness drops of.

As I said the martensites is actually not; does not actually lead to good physical mechanical properties as far as the combination of strength and ductility and toughness is concerned martensites is hard. So, therefore, it can give you very high strength, but exactly it is poor. Therefore, all this martensite is tempered martensites basically kind of structure formed by aging at different temperatures and this is done in different ways remember martensites can be tempered at different temperatures depending on the temperature of the tempering martensites can have different product.

So, as you know very low temperature tempering treatments at about hundred degree centigrade temperature can lead to reorganization of these defect structures in the martensitic plates.

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And what is the meaning of that the meaning of these the dislocation our twins will arranged nicely in the microstructure as you see here twins the arranging like these and these are the dislocations presents in the microstructure and they actually arranged in



such a way that their energy gets reduced that is what is known as a reorganization of the defect structures that happens at lower temperature.

But this will not reduce the; this will not lead to improvement of the ductility; this will lead to no relaxation of the stress because there are lot of stresses inside it because of these defect structure; this can be reduced a little bit by or reorganizing them properly; now second is this if we heat a little higher from 100 to 250 Celsius temperature, it can lead to new failures formation and this new failures can be epsilon carbides what is known as Fe<sub>2.4</sub>C that is what happens in the Saudi's temperatures this epsilon carbide precipitates basically what is happen martensites is basically a supersaturated solid solution of carbon in iron having a BCT structure.

So, therefore, this excess carbon is present has to come out somehow to start to basically maintain their equilibrium or Pearite is metastable equilibrium in the micro in the system. So, one of the one of the ways to do that is to form a carbide which is non stoichiometric like a Fe<sub>2.4</sub>C; this is known as epsilon carbide in their literature compared to Fe<sub>3</sub>C. So, these carbides will always forms on the defect structures that is what you see here; if these locations can be actually a twins can be nucleation points for these carbides. So, these carbides will similarly nucleates along these along these defects and grow that is the way carbon can be taken over taken away.

Now, if you heat further from 250 to 350; is those temperatures some other carbide forms like Fe<sub>2.6</sub>C when some carbides can be formed and these carbides looks like a different morphology in the microstructure. So, by simply precipitating different carbides the carbon concentrations which are present super statutory carbon present in these grains can be taken care of that is what happens. So, slowly the grains of martensites will become lean in carbon.

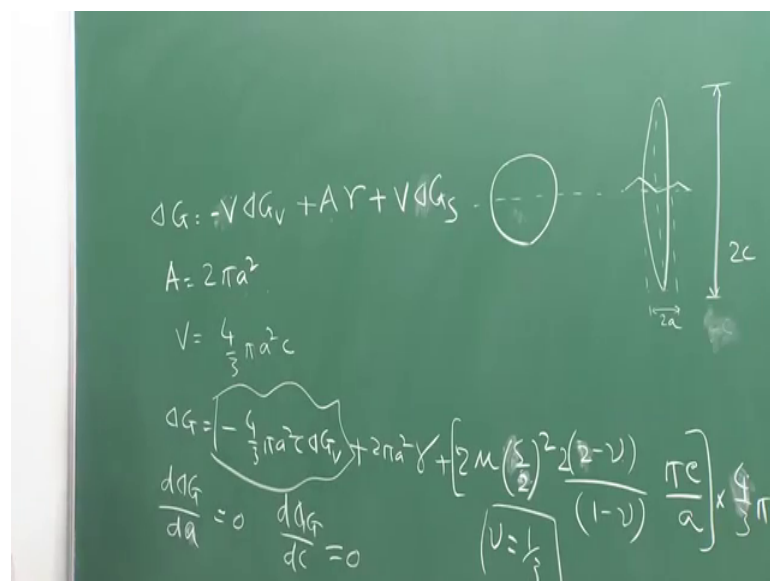
Now, as you heat very high temperatures something like very close to these eutectoid transformation temperature something like about 650 to 700 d cells temperature; these carbides will starts forming becoming Fe<sub>3</sub>C or basically they will become cementite and not only the cementite carbides will be looks like a spherical because at a high temperature. They can actually you know form nice distorted sphere structures and they can form along the boundaries or inside these defect structures also which are present steel in the microstructure. And because Fe<sub>3</sub>C will come out remaining grains will

become alpha. So, complete carbon partitioning happens from the grains of martensite 2 Fe 3C and slowly a Fe 2.4C; Fe 2.46C will transform to Fe 3C.

So, finally, we will have a microstructure with the coarse Fe 3C near spherical structure along with the alpha grains same like a pearlite or bennite same kind of failures. So, as you see here final trade is almost remained same whether it is you start with a gamma to pearlite gamma to bennite or gamma to they martensite and then hit it does not matter whichever paths we take phase mixture will become similar at the end, but morphologically they are distinctly different. Therefore, depending on our requirements in the actual mechanical physical properties, this heat treatment temperatures in time can be controlled for the martensites martensite can be tempered at different temperature different timescale based on the requirements from the from the user the strength level backtactly level toughness level as well as any other physical properties which are required by the customer this is a typical you know heat treatment cycle normally is done.

So, let us now discuss about a bit about nucleation of martensites as I said you that nucleation is very important in marten transformations. So, we will again do the 2 dimensional one.

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Let us assume that this is a undistorted austenitic cell. So, therefore, there is no distortions and I should know the martensites actually looks like a lens supparate

elliptical structure we can actually do the twinning like this way to show that so; that means, what the distortion of these 2 these is accompanied by a twin and this means that the twinning leads to lot of defects inside the martensites see if this has to be a crystallographically important feature. That means, the nucleation must process must take care the distortion process distortion things.

So, as you know the total free energy system if with difference basically can be because of the we can write down like this; this is  $V \Delta G_b$  that indicate the chemical free energy part plus  $A \gamma$  is the area and  $\gamma$  is the interfacial energy that is always present in a nucleation process; we have seen that is right because this is the available energy the system that is volumetric term this is the area term.

Now, because of the distortion, we need to add one more term and that is the strain energy term that is also basically related to volume. So, I can write down volume multiplied by the strain energy that is strain energy, it reflects in terms of a  $\Delta G$  Vs. So, now, if I assume that this ellipse has a major axis up  $2C$ ; this is the length so; that means,  $C$ ; the is major axis and  $a$  is that minor axis as you know  $a$  is the minor axis. So, this is  $2a$  and this length is  $2c$ ; see, if I assume that then we can actually get these values volume and the area very easily that is what I have done. So, I will write down that  $a$  is basically equal to  $\frac{2}{3} \pi a^2 c$  that is possible to calculate area of the ellipse and volume will be equal to volume is basically equal to  $\frac{4}{3} \pi a^2 c$  that is also understandable, but the difference will come in the in the strain energy term.

So, let us write down that  $\Delta G$  is basically nothing but minus  $\frac{4}{3} \pi f^2 c \Delta G$  plus  $2 \pi a^2 \gamma$ ;  $\gamma$  is the interfacial energy between austenite mortensite and strain energy term; it has to determine very nicely this will be equal to  $2 \nu \nu$  is the CR modulus;  $V$  is the no; this is  $S$  by  $2$  whole square I have to check; now what is  $S$  and  $2 - \nu$  is the Poisson ratio  $1 - \nu$  that is to  $2$  here and multiplied by  $\pi c$  by  $a$  and this again this is the strain energy term actual total multiplied by volume correct that is what is the thing; this  $S$  is basically shear strain; shear actually particular shear that is the reason that is the main factor which leads to this kind of a clutch were this twinning.

Now, one can actually do every analysis this is my total free energy. So, this  $v$  can be again written as  $\frac{4}{3} \pi a^2 c$ . So, you can actually take this expression and do

$d \Delta G$  by  $d a$  equal to 0 and  $d \Delta G$  by  $d c$  equal to 0; you have to understand there are 2 parameter sets not no longer sphere it is basically a ellipse. Therefore, you have a  $c$  and because you have 2 parameters the minimization requires differential differentiation respect to both of them to go to 0.

So, once you do that then you will see that  $c^*$  which is nothing but a critical value critical value of  $c$  that will be equal to again same as same as a star the same as  $r^*$ .

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$$c^* = \frac{2\gamma}{\Delta G_v}$$

$$a^* = \frac{16 \gamma \mu \left(\frac{S}{2}\right)^2}{(\Delta G_v)^2}$$

$$\Delta G^* = \frac{512 \gamma^3}{3} \left(\frac{S}{2}\right)^4 \mu^2 \pi \text{ J/nucleus}$$

Actually we have seen, but  $f$  star will be a complex it you thinks little bit different a star is basically to  $16 \gamma \mu$ ; we always assume  $\mu$ ; this  $\mu$  is basically one third in metal always assume that is basically one third remember that; you can replace that also.

So, that is actually a star equal to; no that is not a (Refer Time: 23:59) star equal to  $\mu \gamma$  this is  $S$  by 2 whole square divided by  $\pi$  no  $\pi$  is not there till the  $G_v$  square yes its correct and  $\Delta G$  star is a much more different distinct thing that is a very important for us 5 and 12 by 3  $\gamma$ ; obviously, remember this is not 16 by 3; this is 5 and 12 by 3 by  $\Delta G_v$  to the power 4 naught square and  $S$  by 2 4 multiplied by  $\mu$  square  $\pi$  and this is equal to joule per nucleus.

So, what is important for you for you to important is to know this expression basically this expression tells you; obviously, this expression tells you  $\Delta G$  star is a strong function of  $\gamma$ , but it is a much stronger function of  $\Delta G_v$  and  $S$  the shear

strength and the shear modulus these things what is important. So, as you see here these values just increase  $\Delta G^*$  height increases.

So, that is why nucleation is difficult because every transformation from austenite to martensite requires up to shear strain requires shear and that is what makes this nucleation very difficult and that is why actually nucleation in martensites takes a lot of energy and this is one thing second important part is that this free energy if you look at this is total free energy both for nucleation and growth and as growth is very fast we have only considered this as a homogeneous nucleation. Here we have not considered heterogeneous part it can happen anywhere in the inside these grains are there is no preference shear; preference shear thinks about the grain boundaries being a nucleation site for martensites, but if this is my free energy available to me chemically because of quenching this is used to create interface to take care of strain.

Now, interface is fine you are forming a new phase interface will be there, but here the interface energy will not be very high why because there is a distinct crystallographical relationship between martensite and austenite, but important thing which will be high here is this part the strain energy part and this is substantially higher as compared to thus the surface energy parts, and because it is higher this actually takes a lot of chemical free energy available to the system and that makes these transformations incomplete even if you quench liquid nitrogen temperatures

And this is the reason austenite is retained in the microstructure austenite can never be fully transformed to martensites, because of this strain energy this energy takes away a lot of part of the chemical free energy and that is also evident when you calculate nucleation barrier. So, these are the things you should remember, because these are not taught in the normal lectures or normal textbooks is there in the book and you should look at it in detail manner. So, that it helps you to understand the transformation better way.