Nanomaterials and their Properties
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Lecture - 19
Thermal Properties of Nanomaterials (I)

Students we are going to start lecture number 19 and this is in continuation of the last lecture that is on mechanical behavior of Nanomaterials. As I told you, mechanical behavior is a vast subject and we are only discussing a very small part of it regarding the Nano materials that is about the strength.

But you know there are other aspects like ductility toughness and even the motion of defects inside the Nanomaterials or even you have super-plus city, I mean there are other aspects also this is not possible to discuss all of them in one go. So, therefore, it is a part of the basic understanding of the subject we are taking only the strength.

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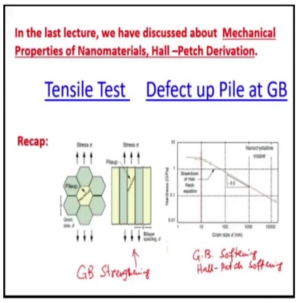

In the last lecture, we have discussed about Mechanical Properties of Nanomaterials, Hall –Petch Derivation.

Tensile Test Defect up Pile at GB

Recap:

GB Strengthening

G.B. Softening
Hall-Petch Softening

And what we did the last lecture is basically we talked about that only, we talked about the material properties which are decided by the application of the force or the stress. And finally, I showed you how to derive Hall Petch equation which it relates the grain size or the crystalline size with the strength of the material especially the yield strength of the material.

So, first let us have some recap ok, the first and foremost important thing is that in a polycrystalline nanostructure materials or multi layer materials the strength provided by the grain boundaries are mainly dictated by 2 things; one the generation of dislocations or the defects in the grain or the boundaries basically.

And then pile up of this dislocation defects and the boundaries, so that the grain boundaries can act as obstacle to the motion of dislocation. This can happen in a multi-layer structure also this is what shown here on this example. In a multi-layer structure where you have 2 different kinds of materials deposited on top of each other with certain wavelengths of this structure.

These dislocations will be generated one boundary can have difficulty in moving across the boundary and reach the other layer, because the materials are different the crystalline structure may be different and so on. Hence these boundaries can act as an obstacle to the motion of dislocations and this leads to what is known as a grain boundary strengthening ok and this we have discussed a lot this is what is known as grain boundary strengthening ok.

So, grain boundaries can be used as a mechanism or as a ploy to strengthen the material and that is why the nanostructure material comes into picture, where you can reduce the grain size drastically small enough to have a very high strength. And but you know as I have shown you at the end of the last lecture this does not seem to be happening for the grain size which are going down to below 5 nanometers or so.

And what you see is rather an opposite effect what is that? We do see a grain boundary is acting as a softening agent for the material. What does it mean? That means, if you reduce the grain size to a very small one grain boundary is no longer can be used as a strengthening agent, but material strength will go down and that is what is known as a Hall Petch softening or grain boundary softening or breakdown of grain boundary breakdown of the Hall Petch equation ok.

This is known as a grain boundary softening or Hall Petch softening because Hall Petch is the relationship, which dictates, how grain boundary a grain size relates the yield strength of the material hardness of the material. So, the basic model is basically known as the dislocation pile up model the grain boundaries dislocations generated from one grain boundary reaches the other grain boundary and gets piled up and that is leads to strength.

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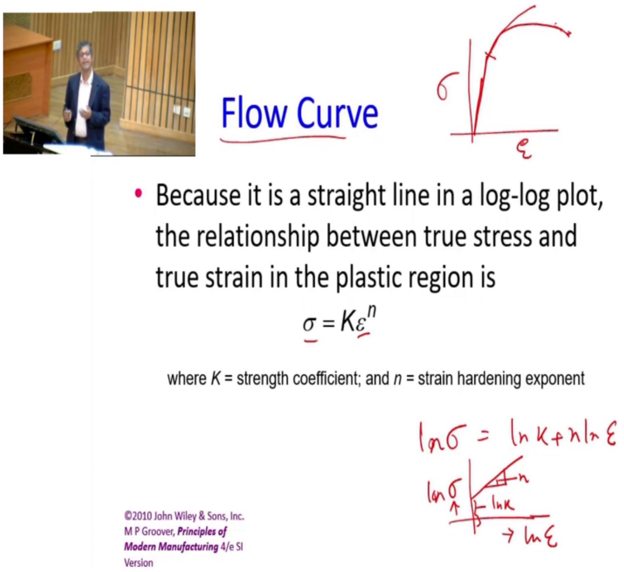

Flow Curve

- Because it is a straight line in a log-log plot, the relationship between true stress and true strain in the plastic region is

$$\sigma = K\varepsilon^n$$

where K = strength coefficient; and n = strain hardening exponent

$$\ln\sigma = \ln K + n\ln\varepsilon$$

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Well before we discuss we also discussed about we are mostly interested in plastic portion of the space the stress strain curve right. We are not interested in the elastic portion why? Because the yield strength is where which demarcates the plastic and the elastic portion of the stress strain curve.

So, therefore any kind of strengthening happening in the elastic portion is not we are not interested ok, we are most interested in the plastic region of this stress strain curve that is what is known as a flow curve and normally flow curve is given by the equation sigma equal to K epsilon to the power n. Where sigma is the true stress epsilon is true strain K is known as the strength coefficient and n is popularly known as strain hardening exponent ok.

So that means, this relationship basically governs the stress strain behavior in the plastic part of the flow curve or plastic part of the stress strain curve in a very very nice manner. The important parameters which are basically decided by the material is K and n and remember n is an exponent normally it is less than 1.

So therefore, it is a fraction ok and hence this relationship which is an relationship between sigma and epsilon is too much depend on these parameter n ok, because n value changing will leads to significant change in the flow curve.

So therefore, you must remember that we can always determine the value of n by simply taking a log on the both side that is what shown on this derivation I did it in the last to last lecture. And it is very clear the slope of the curve of log sigma was as log epsilon provides you the value of n and n is very basic material property.

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Hardness

Resistance to permanent indentation

- Good hardness generally means material is resistant to scratching and wear
- Most tooling used in manufacturing must be hard for scratch and wear resistance

Mohr

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Well most of the cases you may not be able to measure this tensile properties of material, because of the sample soil limitation because of the accessibility to the tensile testing machine. So, in those cases we use hardness as a parameter for any kind of obtainment of the mechanical properties mostly the strength right.

As you know hardness is nothing, but resistance to permanent indentation or deformation ok and it means that in resistance to scratching on the wear is related to hardness. Most tooling using manufacturing must be hard for scratch and wear resistance think of you are shaving blade it must be scratched and wear resistant, because you are using it to cut something which requires it to retain a sharp edge and if it is get blunt because of the scratch or wear then it does not serve the purpose.

So, there are many many such things which are used day to day life that needs to be that need to be you know hard and therefore hardness is used as a measure of strength a measure of scratch and wear resistance we can say.

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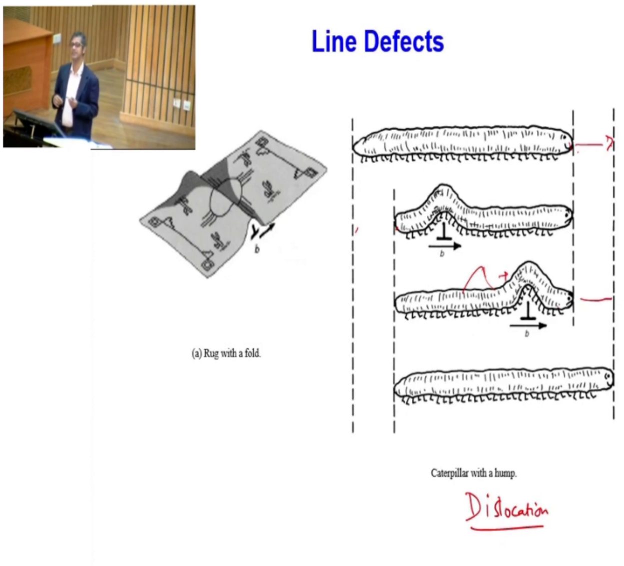

Line Defects

(a) Rug with a fold.

Caterpillar with a hump.

Dislocation

Well the this you know resistance to permanent deformation is related to the Line Defects or the defects of that movement of defects in the material and most important defects are the line defects ok. And line defects is nothing but the dislocation ok and you know dislocation can be viewed the motion of dislocation viewed as a rug in a with a fold.

Whenever you say carpet, if you have a rug and you give a light you know tapping on the on the carpet that rug moves slowly on the as with the fold right. And this is because the it is easy to move it over the carpet without much application of force. Something is true for caterpillar, caterpillar movement can be easily seen thought of same as like a dislocation moving in a material how it is done?

Well that is very simple caterpillar moves in a small part, it does not move the whole body like us when you walk we walk in a whole body right, but caterpillar moves on a small part of it and then that movement is transmitted from one part of the body to the other part of body.

So, the whole process leads to a finite displacement, as you can see from here to there the final displacement was possible simply by making a fold in his body in his body. So, that is something that is how the dislocation actually moves in a material and that is obvious because this motion requires very low much low energy than breaking the bond all together in the material fine.

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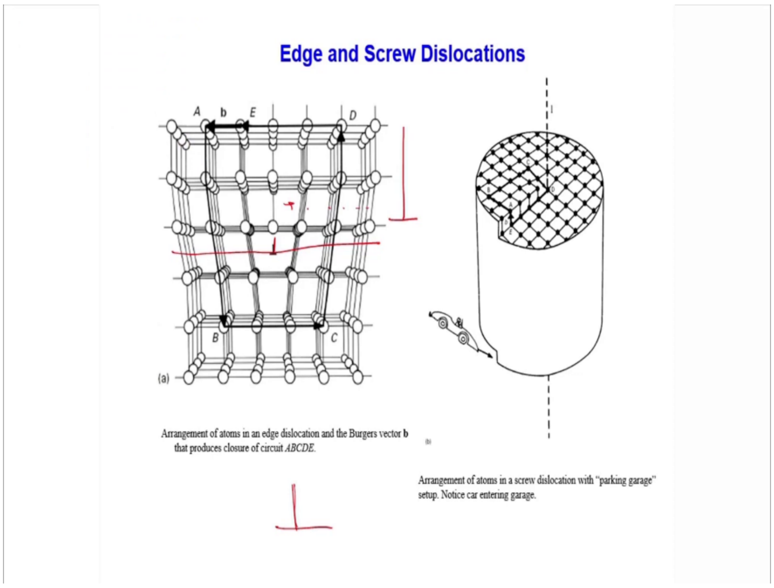

Edge and Screw Dislocations

Arrangement of atoms in an edge dislocation and the Burgers vector **b** that produces closure of circuit *ABCDE*.

Arrangement of atoms in a screw dislocation with "parking garage" setup. Notice car entering garage.

So, dislocations can be edge or screw depending on how they are oriented in edge dislocation plane and the extra half plane, they are perpendicular to each other and the screw they are parallel to each other that we have been discussing a lot. And if you have problems understanding it we can always discuss during our discussion periods or we can even I can even refer some books, so that you can understand.

But as you some of you are not from the metallurgy or material science background you may need to work a little bit harder to understand this aspect and this is true for others also well.

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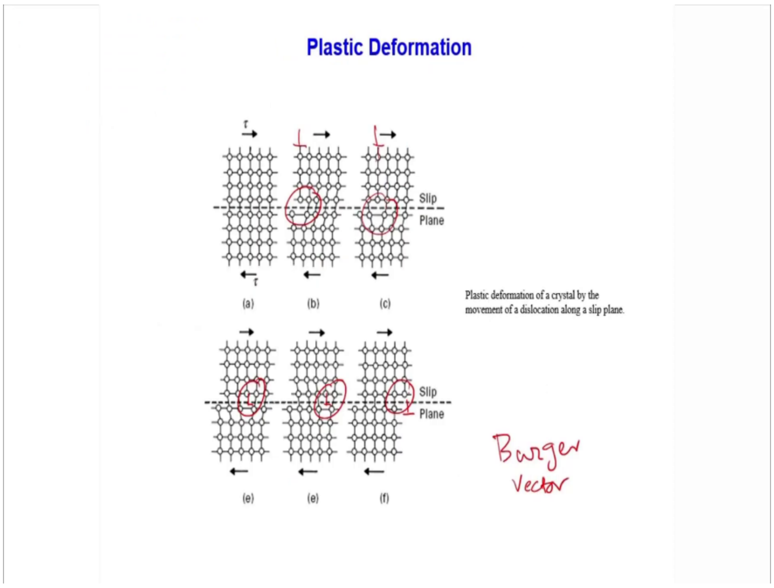

Plastic Deformation

Plastic deformation of a crystal by the movement of a dislocation along a slip plane.

Burger Vector

I know dislocation motion in the material happens by small you know segment that is basically done known as a burger vector and as the dislocation moves from one part of the crystal to the other part of the crystal it leads to a step on the surface and that is nothing but a slip step ok. And remember dislocation can move only on a slip plane it cannot move on any other plane. So therefore, these slip planes are basically the closest pack planes in a material in FCC so (1 1 1) plane.

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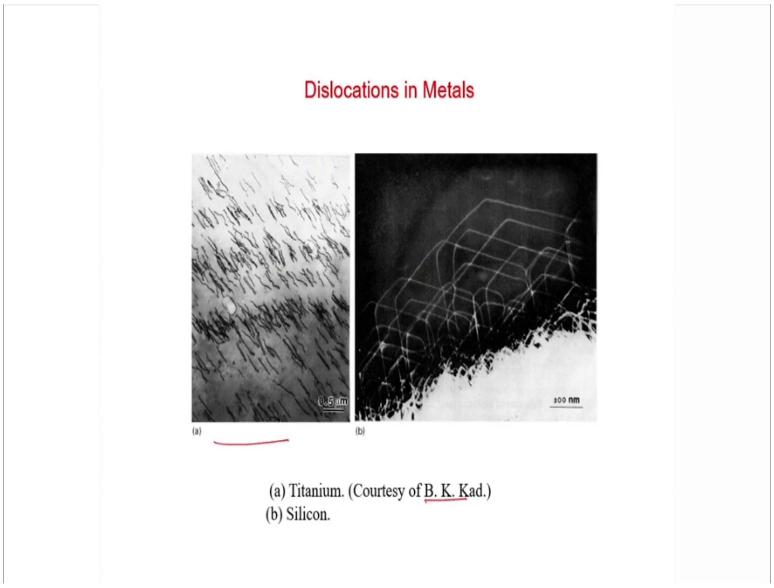

Dislocations in Metals

(a) Titanium. (Courtesy of B. K. Kad.)
(b) Silicon.

How do you see dislocations? You can be easily seen using (Refer Time: 10:46) electron microscope they are actually Nano scale objects, they looks like look like a line or a curve on the on the (Refer Time: 10:56) electron microscope and this is dislocations in titanium and silicon, you can also dislocation ceramics like aluminium oxide or titanium carbide and so they also look like a line or curve they are similar.

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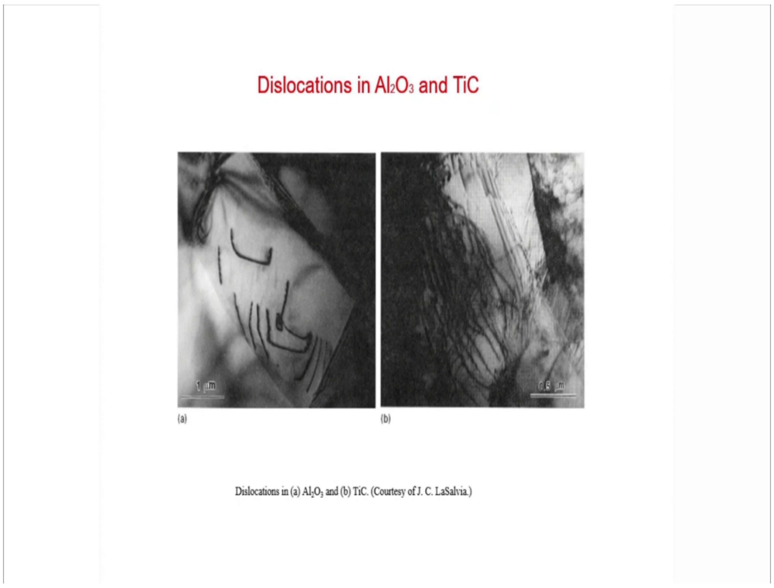

Dislocations in Al_2O_3 and TiC

Dislocations in (a) Al_2O_3 and (b) TiC. (Courtesy of J. C. LaSalvia.)

But remember the plasticity is because of the dislocation motion dislocation generation and motion only when these two things happens then only you can get some amount of plasticity, otherwise material breaks down like a brittle manner. Like you see a glass if you throw a stranded glass when shield or any glass it breaks down very easily.

So, that is there is no signature of plasticity at all in that kind of situations, but on the contrary most of the metals and many ceramics do. So, plastic deformations and that is why actually these aspects comes into picture Hall Petch equation Hall Petch equation will be valid for those materials only. If you cannot generate dislocations there will be no pile up there will be nothing like a Hall Petch.

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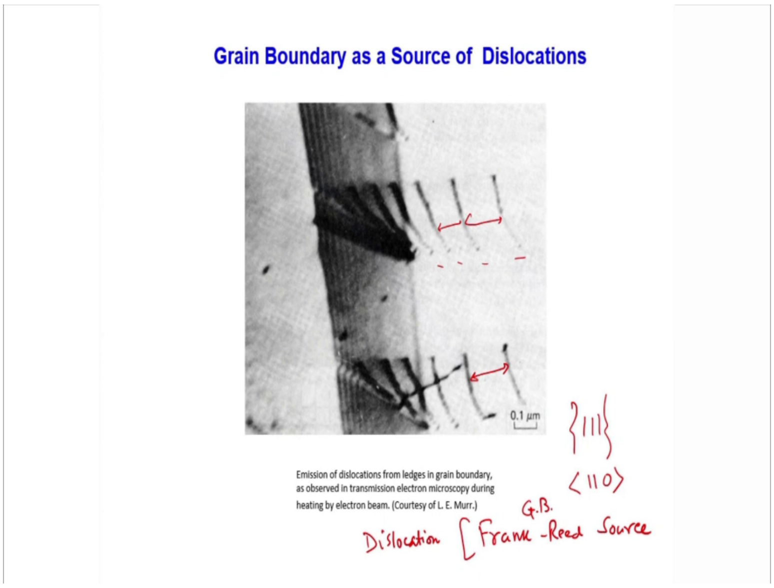

Grain Boundary as a Source of Dislocations

Emission of dislocations from ledges in grain boundary, as observed in transmission electron microscopy during heating by electron beam. (Courtesy of L. E. Murr.)

$\{111\}$

$\langle 110\rangle$

G.B.

Dislocation [Frank -Reed Source

Well, you know as I said dislocation can be generated from the grain boundaries, because grain boundaries we as we have discussed a lot in our previous lectures they have some kind of a lower order elements of the atoms or disorder arrangement of atom not perfectly disorder.

But it is kind of a disorder arrangement of atoms as compared to the grains and therefore they can actually acts as a source for dislocation generation or otherwise you can have a frank reed source that also possible inside a grain both are possible. So, grain boundaries can act as a source of dislocation or the frank reed source nonetheless, another dislocation generated they move through the crystal and then go away.

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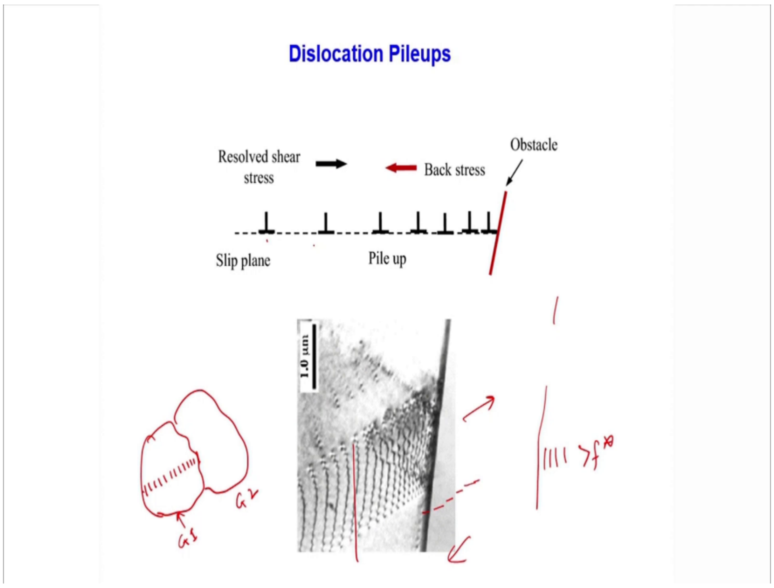

Dislocation Pileups

And once they go away then once they move inside the crystal; obviously, they are moving and sometime again they will also come in a contact or rather face to face contact with another grain boundary ok. So, very simple they have a grain like this and dislocation generated from this grain boundary, they just move you can see that and then reach this grain boundary and there they will find it is an obstacle present to cross over or to cut over and that is why they cannot move ok.

So that means, what dislocations can be piled up in a if there is a grain boundary in front of them. So, you must be thinking sir is telling one side dislocations generated from the grain boundary other side dislocations are getting pile up the grain boundaries ok. That is very simple see if you think of 2 grains like this fact that there are 2 grains the crystalline planes are not parallel to each other, that is why their orientations are different that is why they are called 2 grains right.

So, now if this is the slip plane on which dislocation is moving in this grain 1 ok; obviously, on the grain 2 the same plane will not parallel. So, same plane will likely to be unlikely to be parallel, but dislocation cannot easily move across from one grain to other grain, because of these aspects because dislocation as I said can only move on the slip planes.

Fact that the slip planes are not parallel from one grain to other grain they cannot cross over move am I clear. Therefore, that is what actually makes the grain boundaries as an obstacle and then dislocation gets piled up. So, as the dislocation get us piled up we have discussed a lot given analogy to the railway ticket counters right.

You could have seen that people standing in front of ticket counter buying tickets making a queue and they can this is something like a pileup of human standing in front of a ticket counter of a railway station ok. And that means, what then when that happens if there is a movement of the one of the human one of the persons actually standing in that queue to the back directions not in the front directions, there will be kind of a force acting on the person standing nearby.

And this will percolate and this will slowly go move forward or move actually from one to other and then there will be a back stress created ok. Some kind of force acting on that ok that is what you can clearly see and this is this back stress is basically creates strengthening.

So, back stress then you know makes the other dislocation coming over difficult, why because this dislocation which are which are actually following like this one this one they need to ha they need to cross higher amount of stress in addition to the stress required to move on the planes you plan right.

Because, the back stress is going to add up to these pores against the motion of the dislocations ok, so that is why actually grain boundaries acts as obstacle by providing this back stress right. So, it has a reserved shear stress which is making the dislocation to move on the slip plane right and back stress is stopping them or basically forcing them not to move on the dislocations.

And therefore they need to they need to you know cross over they need to not cross over and say they need to be pushed by additional forces which is equal to the back stress plus the reserved shear stress ok and that is leading to the strengthening of the material right. So, the extra force is extra strength that is how it can be correlated correct.

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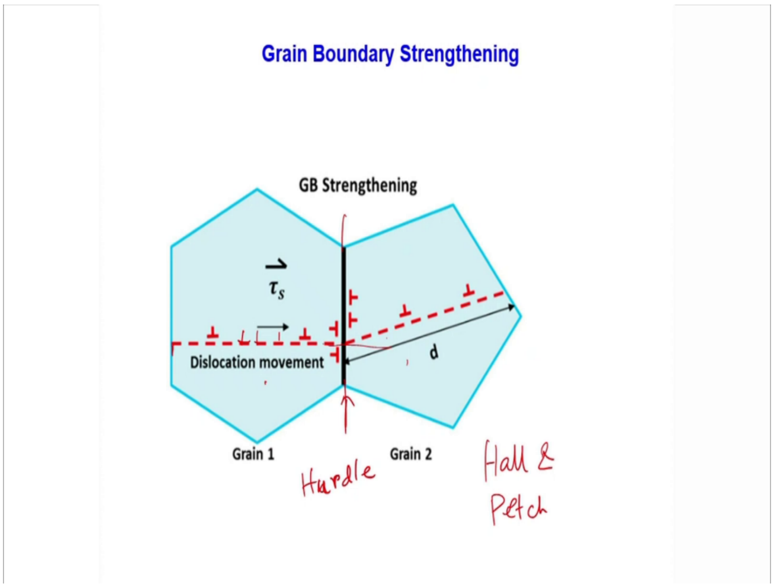

Grain Boundary Strengthening

Well, if I consider only the true grain model, which I discussed the last time, and as you said these are 2 grains in the first grain dislocations are moving on a slip plan. Because of the application of shear force tau S and that is nothing but critical reserve shear stress right, that is by tau S and these allows the dislocation to move on the slip plane and reach the grain boundary. Once the grain boundary reaches, the slip planes are not parallel to each other.

So therefore, this dislocation cannot simply move across a grain boundary and then move on the slip plane on the other side of the grain is not possible. And because of these aspects they started piling up, because they cannot go that is why they cannot pile up think of a bus in which the people want to go inside the bus ok, but the doors are closed right.

So, what will happen? There will be pile up in front of the doors, but as soon as the door is open all the passengers will go inside the bus the pileup is over. That is something like as soon as the slip planes are parallel dislocation can easily move from one grain to other grain right. So, that is very odd situation, which is very unlikely to happen in a normal grain structure materials, because grains have different orientations am I clear?

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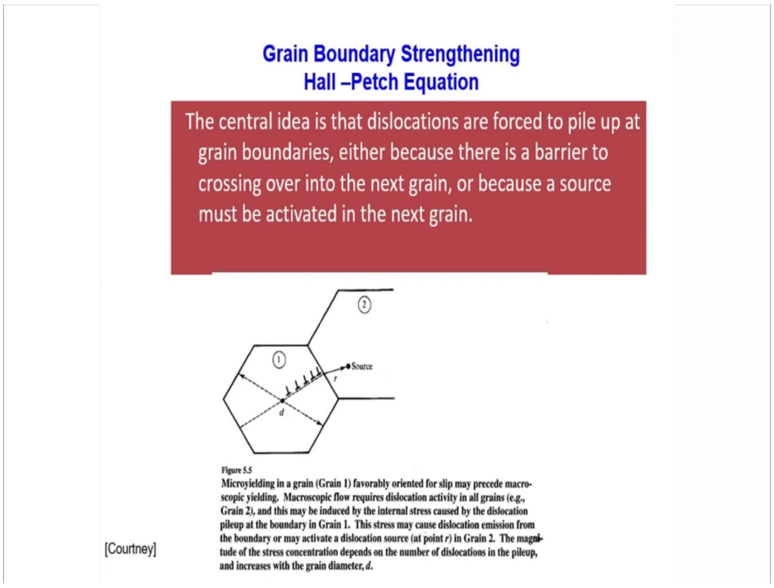

Grain Boundary Strengthening
Hall –Petch Equation

The central idea is that dislocations are forced to pile up at grain boundaries, either because there is a barrier to crossing over into the next grain, or because a source must be activated in the next grain.

Figure 5.5
Microyielding in a grain (Grain 1) favorably oriented for slip may precede macroscopic yielding. Macroscopic flow requires dislocation activity in all grains (e.g., Grain 2), and this may be induced by the internal stress caused by the dislocation pileup at the boundary in Grain 1. This stress may cause dislocation emission from the boundary or may activate a dislocation source (at point *r*) in Grain 2. The magnitude of the stress concentration depends on the number of dislocations in the pileup, and increases with the grain diameter, *d*.

[Courtney]

So, the central idea is that dislocation are forced to pile up at the grain boundaries, either because there is a barrier it to cross over into the next grain or because source must be activated in the grains. You understand that these are the 2 important things one can understand first is the barrier to crossover. What is the barrier to crossover? Barrier is nothing, but the slip planes are not parallel that is why or you needs to activate this you know source in the other grain ok whatever the slip plane is.

See FCC crystals most important slip planes is (1 1 1) because that is what is the closest pack plane am I right. But dislocation can also move on (1 0 0) or (1 1 0) planes also those planes require requires higher critical result shear stress am I clear? So, suppose this grain which only dislocation moving is the nicely oriented and dislocation moving on (1 1 1) plane, but on the other hand right there are grain 2 that is not the case right.

So, why do what a grain two probably the plane is (1 1 0)? So, in order to start the dislocation motion or dislocation rather movement processing of the grain, you need to create a source on (1 1 0) plane that is becomes more stress. The critically the obstacle says to move a dislocation on a (1 1 0) plane is much higher than (1 1 1) plane, because (1 1 0) plane is not the closest pack plane in FCC crystal am I clear?

So, these are the two important barriers or two important aspects will leads to the pileup of grain boundaries dislocation of the grain boundaries, that is something you should understand very well ok and that is the main reason the grain boundaries act as a strengthening agent correct.

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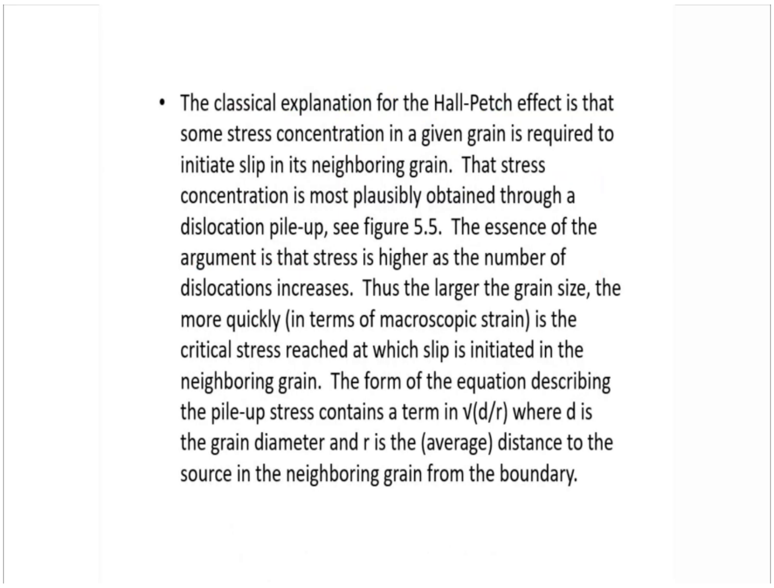

- The classical explanation for the Hall-Petch effect is that some stress concentration in a given grain is required to initiate slip in its neighboring grain. That stress concentration is most plausibly obtained through a dislocation pile-up, see figure 5.5. The essence of the argument is that stress is higher as the number of dislocations increases. Thus the larger the grain size, the more quickly (in terms of macroscopic strain) is the critical stress reached at which slip is initiated in the neighboring grain. The form of the equation describing the pile-up stress contains a term in $\sqrt{(d/r)}$ where d is the grain diameter and r is the (average) distance to the source in the neighboring grain from the boundary.

Well, you know classical explanation to Hall Petch effect is that some stress concentration a given grain is required to initiate the slip in the neighboring plane. I have listed it down taken from internet literature ok. So, you know this is what is the classical explanation for the Hall Petch effect, that you need some kind of stress concentration in a particular given grain to initiate the slip pass in the neighboring grain.

The stress concentration is most possibly obtained by dislocation pile up which is shown here in this picture 5.5 taken for the book of Courtney ok. The stress essence of the argument is that stress is higher as the number of dislocation increases, thus the larger the grain size more quickly is the critical stress is reached at which slip is initiated in the neighboring grain, that is obvious correct.

The form of the equations described in pile up is contain a term root d or root d by r rather, where the d is the grain diameter r is the distance to the source in the neighboring grain from the boundary ok. Fine forget about r but it is basically proportional to root d 1 by d actually like this formation of equation ok, the pile up stress is basically proportional to root d that is very clear right.

So, larger the grain size more quickly in terms of macroscopic strain the critical stress reached at which slip is initiated to the next ok. What does it mean? That means, if the grain is bigger, you need less stress to start the dislocation activity in next strain.

As the grain becomes smaller you need more stress to start the dislocation next to the next grain, that is how actually this can happen. Or other way as the grain size becomes smaller you have more grain boundary areas, so more obstacles to the resolution motions and that also can provide to strengthening.

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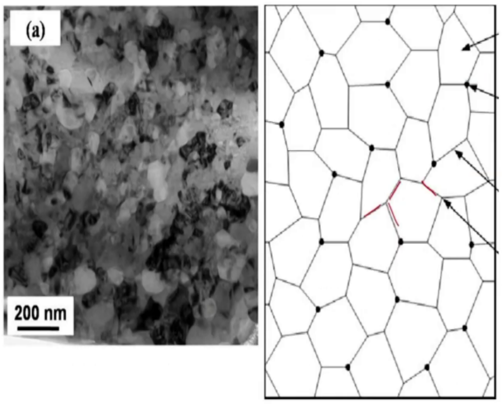
Grain Boundary Strengthening



So, you can understand that there are 2 aspects of that and this is what I showed you in a in a bulk nano section material have so many large number of grains, small size nanostructure grains under the very large grain boundaries. So, therefore dislocation find more difficulties in moving from one grain to other grain.

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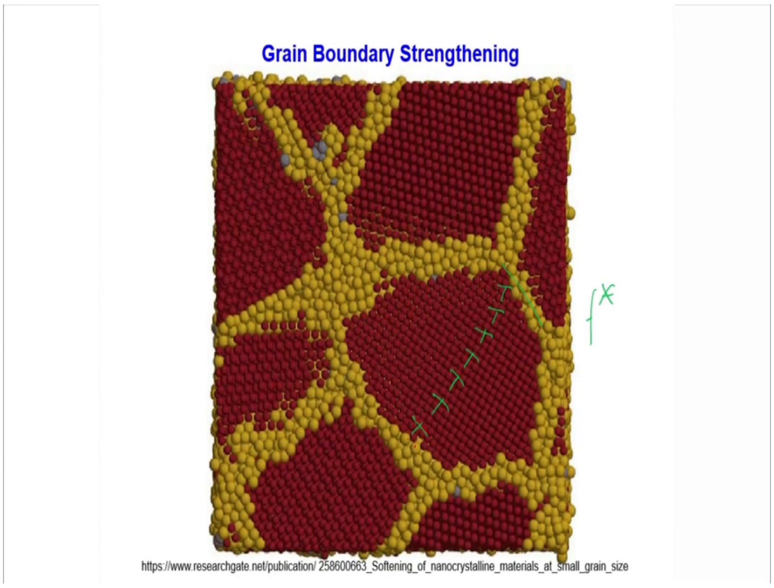

Grain Boundary Strengthening

https://www.researchgate.net/publication/ 258600663_Softening_of_nanocrystalline_materials_at_small_grain_size

This is again shown here also I am not going back into this.

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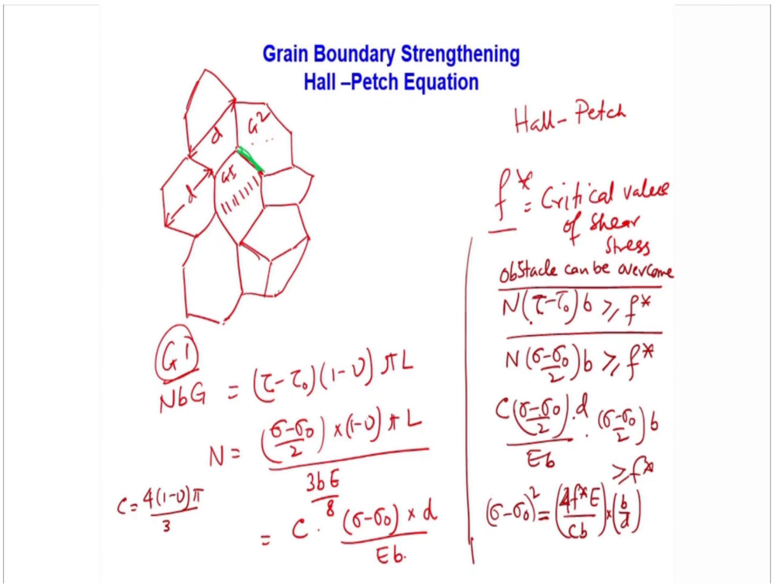

Grain Boundary Strengthening
Hall –Petch Equation

Hall- Petch

f^* = Critical value of shear stress

obstacle can be overcome

$N(\tau-\tau_0)b \geq f^*$

$N\left(\frac{\sigma-\sigma_0}{2}\right)b \geq f^*$

$C\frac{\left(\frac{\sigma-\sigma_0}{2}\right)\cdot d}{Eb}\cdot\left(\frac{\sigma-\sigma_0}{2}\right)b \geq f^*$

$(\sigma-\sigma_0)^2 = \left(\frac{4f^*E}{Cb}\right)\times\left(\frac{b}{d}\right)$

G1

$NbG = (\tau-\tau_0)(1-\nu)\pi L$

$N = \frac{\left(\frac{\sigma-\sigma_0}{2}\right)\times(1-\nu)\pi L}{\frac{3bE}{8}}$

$= C\cdot\frac{(\sigma-\sigma_0)\times d}{Eb}$

$C = \frac{4(1-\nu)\pi}{3}$

$$NbG = (\tau - \tau_0)(1- \vartheta)\pi L$$

$$Where \quad G=\frac{3E}{8}$$

$$N = \frac{\left(\frac{(\sigma - \sigma_{0})}{2}\right)(1-\vartheta)\pi L}{\frac{3bE}{8}} \qquad \text{where } c = \frac{4(1-\vartheta)\pi}{3}$$

$$N = c\frac{\left(\sigma - \sigma_{0}\right)*d}{Eb}$$

f^{*} =Critical value of shear stress

Obstacle can be overcome,

$$N(\tau - \tau_{0})b \geq f^{*}$$

$$N\frac{(\sigma - \sigma_{0})}{2}b \geq f^{*}$$

$$\frac{C\frac{(\sigma - \sigma_{0})}{2}*d}{Eb}\left(\frac{(\sigma - \sigma_{0})}{2}\right)b \geq f^{*}$$

$$(\sigma - \sigma_{0})^{2} = \left(\frac{4f^{*}E}{cb}\right)*\left(\frac{b}{d}\right)$$

Well, so, then I discussed about these Hall Petch equation which I not go back again, only to tell you that the way you can think mathematically is this that grain boundary accessing as a barrier to dislocation motion. So, therefore we can think about the barrier has a certain strength and that strength can be a star that is the critical strength required to be crossed over.

Now, obstacle can be overcome only when number of dislocation multiplied by the burger vector that is the total you know displacement into the critical reserved shear stress. That is this not critical stress that is the shear stress are required for these process the tau minus tau 0 greater than this obstacle value obstacle ok.

Now, N can also be related with the with these things by you know the size of the grain and many other things like Poisson ratio vector I have already discussed all the shear modulus z.

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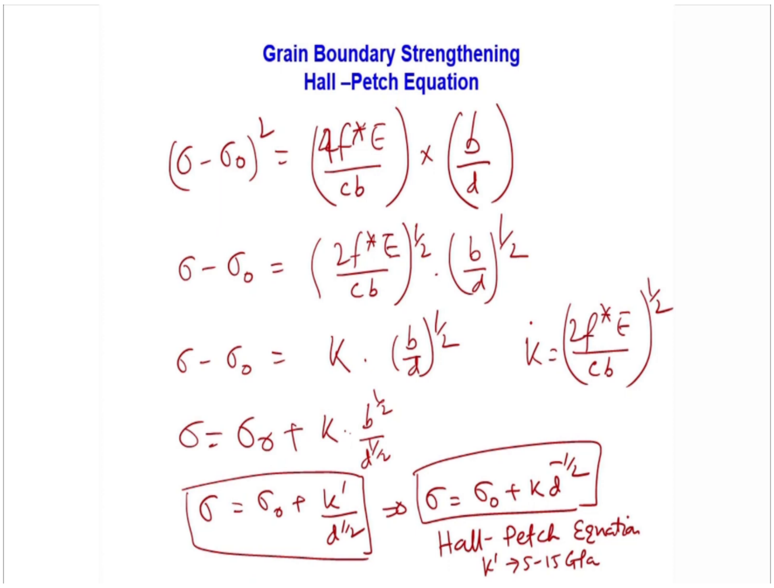

Grain Boundary Strengthening
Hall –Petch Equation

$$(\sigma - \sigma_0)^2 = \left(\frac{4f^*E}{cb}\right) \times \left(\frac{b}{d}\right)$$

$$\sigma - \sigma_0 = \left(\frac{2f^*E}{cb}\right)^{1/2} . \left(\frac{b}{d}\right)^{1/2}$$

$$\sigma - \sigma_0 = K . \left(\frac{b}{d}\right)^{1/2} \qquad K = \left(\frac{2f^*E}{cb}\right)^{1/2}$$

$$\sigma = \sigma_0 + K . \frac{b^{1/2}}{d^{1/2}}$$

$$\boxed{\sigma = \sigma_0 + \frac{k'}{d^{1/2}}} \Rightarrow \boxed{\sigma = \sigma_0 + k d^{-1/2}}$$

Hall- Petch Equation
$k' \rightarrow$ 5-15 GPa

$$(\sigma - \sigma_0)^2 = \left(\frac{4f^*E}{cb}\right)*\left(\frac{b}{d}\right)$$

$$(\sigma - \sigma_0) = \left[\left(\frac{4f^*E}{cb}\right)^{\frac{1}{2}}\right]*\left(\frac{b}{d}\right)^{\frac{1}{2}}$$

$$(\sigma - \sigma_0) = K.\left(\frac{b}{d}\right)^{\frac{1}{2}} \qquad K = \left(\frac{2f^*E}{cb}\right)^{\frac{1}{2}}$$

$$\sigma = \sigma_0 + \frac{K'}{(d)^{\frac{1}{2}}}$$

$$\sigma = \sigma_0 + Kd^{-\frac{1}{2}}$$ Hall-Petch equation

K'=5-15 GPa

And then we can do a mathematically analysis found out that you know the $\sigma = \sigma_0 + \frac{K'}{(d)^{\frac{1}{2}}}$ and that is the classical Hall Petch equations. And in which case try the strength coefficients which can have value within 5 to 15 G pa and sigma 0 is the constant value the sigma is as the yield strength.

So, you can see yield strength is directly proportional to $(d)^{\frac{-1}{2}}$ or it is inversely proportional to $1/(d)^{\frac{1}{2}}$ whatever you can take evaluate it.

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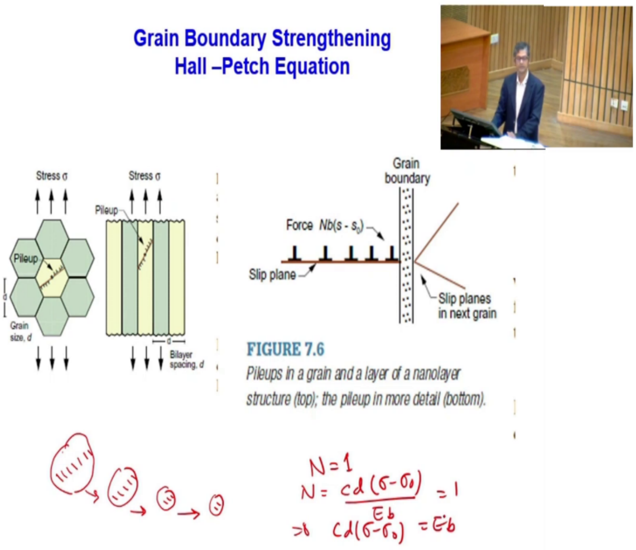

Grain Boundary Strengthening
Hall –Petch Equation

FIGURE 7.6
Pileups in a grain and a layer of a nanolayer structure (top); the pileup in more detail (bottom).

$N=1$

$N=\frac{cd(\sigma-\sigma_0)}{Eb}=1$

$\Rightarrow cd(\sigma-\sigma_0)=Eb$

And this is what is the thing which I discussed in the beginning of the lecture and telling you again and again, so that you do not forget.

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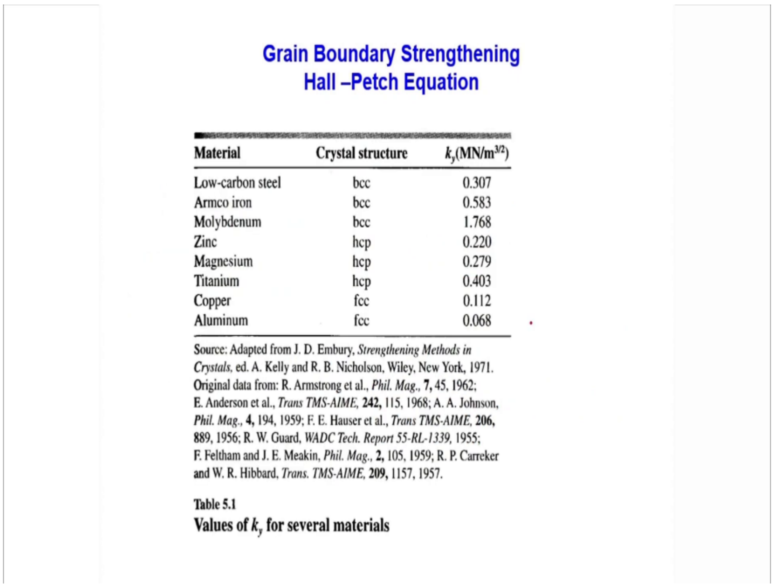

Grain Boundary Strengthening
Hall –Petch Equation

Material	Crystal structure	k_y(MN/m$^{3/2}$)
Low-carbon steel	bcc	0.307
Armco iron	bcc	0.583
Molybdenum	bcc	1.768
Zinc	hcp	0.220
Magnesium	hcp	0.279
Titanium	hcp	0.403
Copper	fcc	0.112
Aluminum	fcc	0.068

Source: Adapted from J. D. Embury, *Strengthening Methods in Crystals,* ed. A. Kelly and R. B. Nicholson, Wiley, New York, 1971. Original data from: R. Armstrong et al., *Phil. Mag.,* **7,** 45, 1962; E. Anderson et al., *Trans TMS-AIME,* **242,** 115, 1968; A. A. Johnson, *Phil. Mag.,* **4,** 194, 1959; F. E. Hauser et al., *Trans TMS-AIME,* **206,** 889, 1956; R. W. Guard, *WADC Tech. Report 55-RL-1339,* 1955; F. Feltham and J. E. Meakin, *Phil. Mag.,* **2,** 105, 1959; R. P. Carreker and W. R. Hibbard, *Trans. TMS-AIME,* **209,** 1157, 1957.

Table 5.1
Values of k_y for several materials

Well, K has values in GPa or milli or the GPa N or newton/mm^2 ok. That is what it is this is taken from the book of J.D Embury strengthening methods in crystals and many others al Kelly and Johnson or maybe some other papers also written here as you can see BCC HCP metals has very high values of k.

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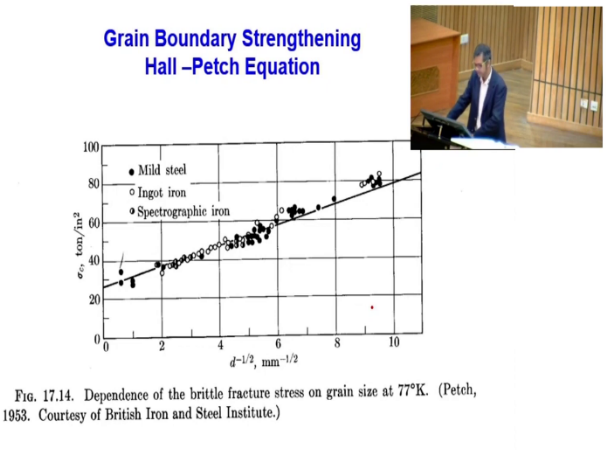

Grain Boundary Strengthening
Hall –Petch Equation

Fig. 17.14. Dependence of the brittle fracture stress on grain size at 77°K. (Petch, 1953. Courtesy of British Iron and Steel Institute.)

W ell one can this is taken from Petch equation 1953 page original paper and I clearly see the dependence of brittle fracture stress on the grain side at 77 kelvin and you can clearly see that the for the mild steel inverter and the spectroscopic iron all of them fall on one line and sigma versus d to the power minus half. That also tells us that this equation is very nicely very nicely can describe the whole behavior of the grain size dependence on the strength.

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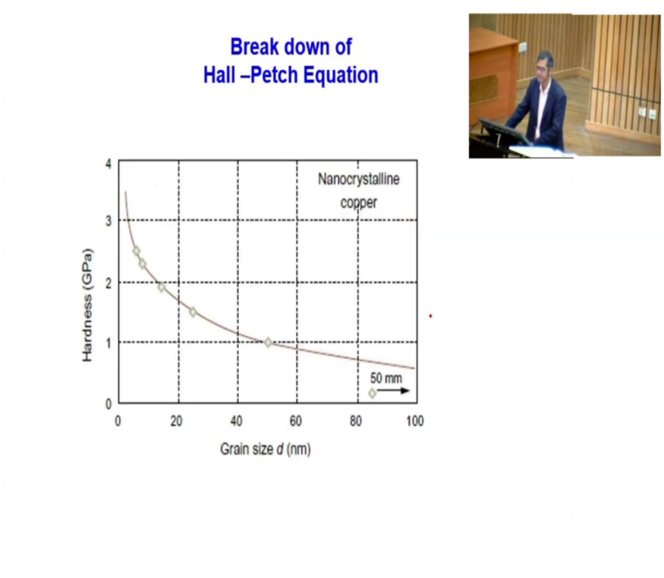

Break down of
Hall –Petch Equation

Well, but then in those days there was no concept of grain nano crystalline grains like 1953 like although they are there, but people did not know about it ok. And so once you have could prepare the materials with nano crystalline grains, then start measuring it and people have seen or many researchers have seen the strength can increase sometimes 3 to 4 or so on ok.

You can clearly see that one becomes 3 or 4 see it becomes triple or even 4 times ok not order mentioned, but times actually so therefore from 50 nanometers to about 10 nanometers I have a drastic increase of the hardness that is possible for this is nano crystalline copper same thing has been observed for nano crystalline.

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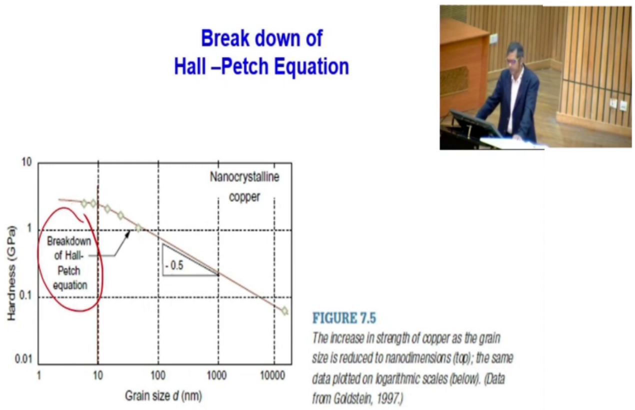

Break down of
Hall –Petch Equation

FIGURE 7.5
The increase in strength of copper as the grain size is reduced to nanodimensions (top); the same data plotted on logarithmic scales (below). (Data from Goldstein, 1997.)

But ok once you increase decrease a grain size further as you can clearly see that below a certain grain size of 10 nanometer or so the strength started going down or rather than remaining constant it does not increase much and that is why the breakdown of the Hall Petch equation happens this is what is it is the Hall Petch equation started breaking down.

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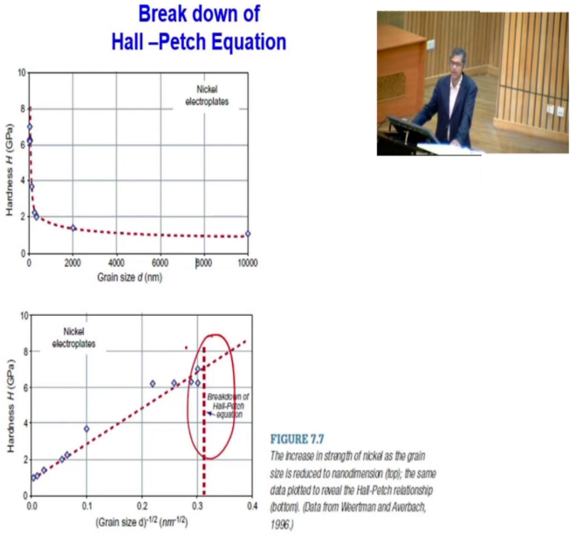

Break down of
Hall –Petch Equation

FIGURE 7.7
The increase in strength of nickel as the grain size is reduced to nanodimension (top); the same data plotted to reveal the Hall-Petch relationship (bottom). (Data from Weertman and Averbach, 1996.)

So, you must be thinking why does it happen then we will discuss about that. Same thing happens for nano crystalline nickel and you can clearly see here also its shown very nicely in the ground of Hall Petch equation ok and there also I am showing you for multilayers.

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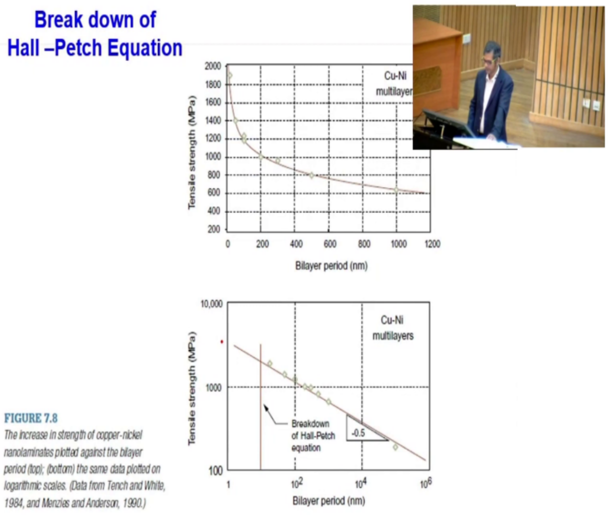

Break down of
Hall –Petch Equation

FIGURE 7.8
The increase in strength of copper-nickel nanolaminates plotted against the bilayer period (top); (bottom) the same data plotted on logarithmic scales. (Data from Tench and White, 1984, and Menzies and Anderson, 1990.)

So, how does it Hall Petch equation breaks down ok that is very simple to understand. And is as you see you know I will go back to this picture and explain ok, remember this picture yes. As you see in this picture as the grain size decreases only fewer number of dislocations can be packed in the pileup right.

So, I draw last time also I am drawing again if I reduce a grain size. So, here you can have many dislocation can pile up. But there it is getting reduced reduce further right. So, what you see? From here to there then to there the fewer number of dislocations can be packed in the pileup right.

So, (Refer Time: 27:19) lower is you know; obviously, then lower is the magnifying effect if you have more pile up more is the back stress lower is the pile up, lower is the back stress right. So therefore, applied stress should also be required to be less to cross the obstacle and there comes a point that N which I derived in the last class N become 1, so no pile up is possible right.

So, now you know that $N = c\frac{(\sigma-\sigma_0)*d}{Eb}$ =1. So, I can easily write ok $c(\sigma - \sigma_0) * d$= E b right that is one aspect second thing $(\sigma - \sigma_0)=\frac{Eb}{cd}$ this ok let me erase this part and do it for you. Second thing is this that we know that Hall Petch equation right. What is the Hall Petch equation, we know ok we know very easily that in case of Hall Petch equation what do I know.

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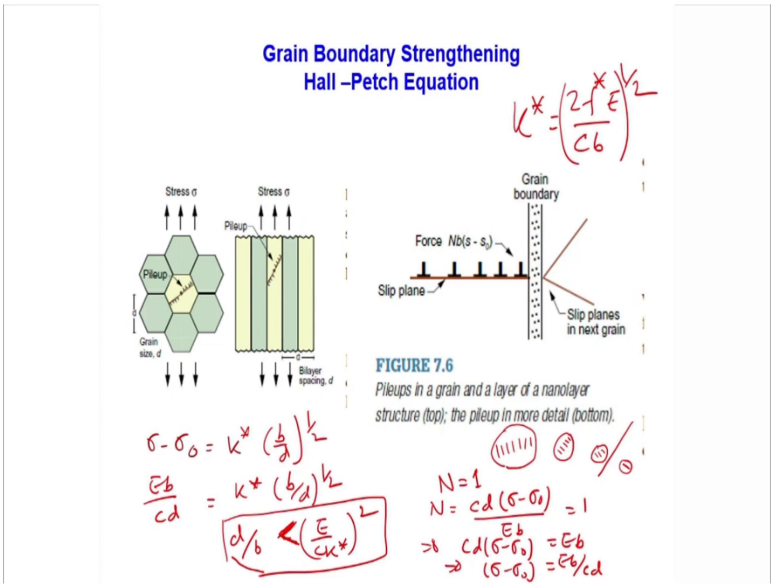

Grain Boundary Strengthening
Hall –Petch Equation

$K^* = \left(\frac{2f^* E}{cb}\right)^{1/2}$

FIGURE 7.6
Pileups in a grain and a layer of a nanolayer structure (top); the pileup in more detail (bottom).

$\sigma - \sigma_0 = K^* \left(\frac{b}{d}\right)^{1/2}$

$\frac{Eb}{cd} = K^* (b/d)^{1/2}$

$\boxed{d/b < \left(\frac{E}{cK^*}\right)^2}$

$N=1$

$N = \frac{cd(\sigma-\sigma_0)}{Eb} = 1$

$\Rightarrow cd(\sigma-\sigma_0) = Eb$

$\Rightarrow (\sigma-\sigma_0) = Eb/cd$

$$K^* = \left(\frac{2f^* E}{cb}\right)^{\frac{1}{2}}$$

$$N=1$$

$$N=\frac{cd(\sigma-\sigma_0)}{Eb}=1$$

$$cd(\sigma - \sigma_0)= Eb$$

$$(\sigma - \sigma_0)=\frac{Eb}{cd}$$

$$(\sigma - \sigma_0) = K^* \left(\frac{b}{d}\right)^{\frac{1}{2}}$$

$$\frac{Eb}{cd} = K^{*}\left(\frac{b}{d}\right)^{\frac{1}{2}}$$

$$\frac{d}{b} < \left(\frac{E}{CK^{*}}\right)^{2}$$

We know $(\sigma - \sigma_0) = K^{*}\left(\frac{b}{d}\right)^{\frac{1}{2}}$ right. So, let us put down this sigma minus sigma 0 value here right. So, E, b, c, d remember d is the grain size c is a constant E is the elastic modulus and b is the burger vector right. So, if you do the maths properly what do you get you can clearly see $\frac{Eb}{cd} = K^{*}\left(\frac{b}{d}\right)^{\frac{1}{2}}$ or $\frac{d}{b} < \left(\frac{E}{CK^{*}}\right)^{2}$ right.

So therefore, this equation will break down when this will be applied, it tells you that d which is the grain size divided by the burger vector must be less than or $\frac{d}{b} < \left(\frac{E}{CK^{*}}\right)^{2}$ you know right. And you know the value of K^{*} what is the value of K^{*} ok? Can be written here $K^{*} = \left(\frac{2f^{*}E}{cb}\right)^{\frac{1}{2}}$.

So, the K^{*} is dependent on obstacle strength elastic modulus and the burger vector, constant c is obviously fixed for a particular material right. So, that is it so that means you know when this condition is satisfied the Hall Petch equation will breaks down. That is very simple way of thinking is that if you have only one dislocation inside the grain there is no pile up.

So, there is no grain boundary strengthening, but there is no pile up there is no black back stress there is no grain boundary strengthening. That is why the Hall Petch equation breaks down below a certain grain size am I clear? That is very something which is you should always remember this is the reason actually Hall Petch equation breaks down ok. So, from big grain very big grain ok let me just redraw this picture I think I have done it pretty big ok.

Let me redraw it again like this you have many dislocation pile up gradually decreasing, there is only one dislocation possible to be accommodated and that is why this breakdown a Hall

Petch happens and that is why this equation d$\frac{d}{b} < (\frac{E}{CK^*})^2$ and you must remember this aspect ok.

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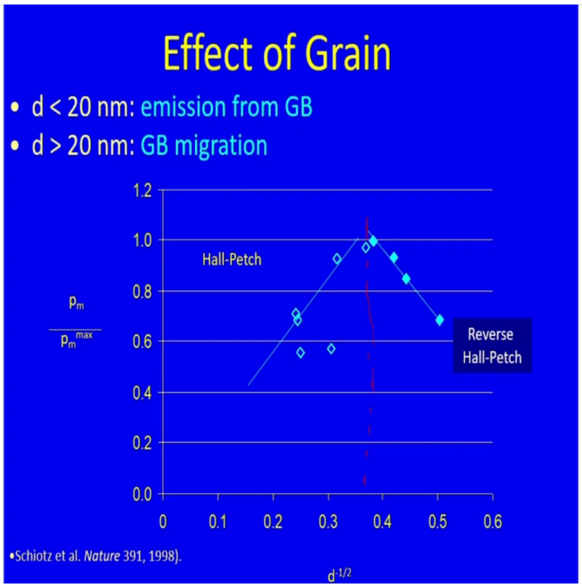

Effect of Grain

- d < 20 nm: emission from GB
- d > 20 nm: GB migration

•Schiotz et al. *Nature* 391, 1998).

So, that is something which you have probably understood I do not know this is taken from a paper in nature 1998, you can clearly see this is basically hardness and you know for grain size more than 20 nanometer less than 20 nanometer. For I think gold and you can clearly see the Hall Petch and the Hall Petch inverse both are possible. Hall Petch obviously means tells you that strength is increasing as the d to the power half minus half is increasing right.

But then you reach a critical here you can see there is a critical point below the strength is further decreasing and this happens below 20 nanometers ok. And they say it is basically grain bound is to migrate but no basically the mechanism is same what I discussed just now below 20 nanometers you can no longer accommodate more than 1 dislocation. So, pile up is no longer possible and that is how they get this effect breaks down.

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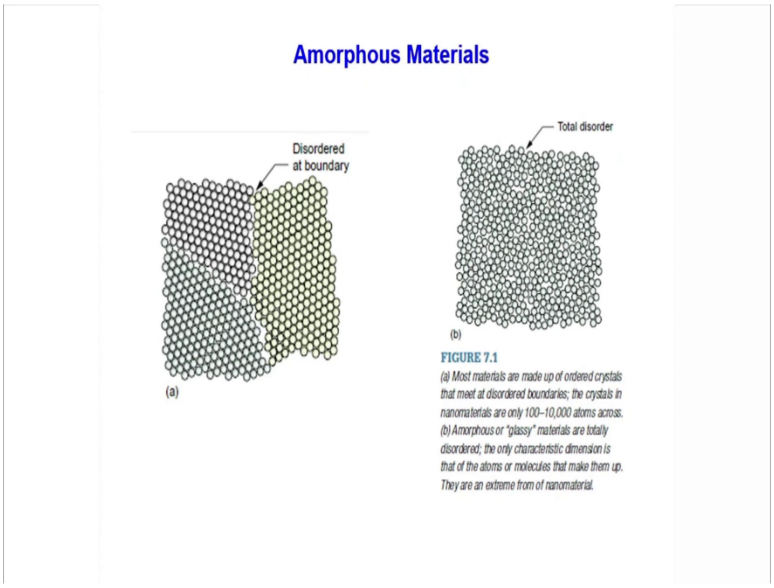

Amorphous Materials

FIGURE 7.1
(a) Most materials are made up of ordered crystals that meet at disordered boundaries; the crystals in nanomaterials are only 100–10,000 atoms across. (b) Amorphous or "glassy" materials are totally disordered; the only characteristic dimension is that of the atoms or molecules that make them up. They are an extreme from of nanomaterial.

Well now it brings us to a very interesting thing ok. What is that? So that means, what if you keep on decreasing the grain size you have seen the strength is not increasing right that is a point below which the strength decreases.

Now, if you still further decrease a grain size. What will happen what will happen have you ever thought about it or not? Suppose that crystal size shrinks further until it becomes atomic dimensions. What does it mean? And it will become 1 nanometer size or so this is the question some of you already been asking me.

So, if I decrease the crystalline size further 5 10 5 2 and 1 nanometer correct. So, material now will be completely disorder ok. What does it mean? So, this is a nano crystalline suction right in which you have order arrangements of the grain atoms in the grains and disorder arrangement of atom in the boundaries. So, we have discussed a lot right.

Now, if you decrease the grain size too much smaller atomic dimensions the grain boundary area will be very large and all the structure will be completely disorder. And you know many amorphous materials are there glass window glass is amorphous material ok. Ordinary glass what you call correct even your metallic ceramic other ceramic materials which are glass polymer materials are also glass are present correct.

Among them are the polycarbonate acrylic or pixy glass or polystyrene which is used as a one of the material for dress materials, the burger vector by dislocations in cannot be defined even in amorphous material right.

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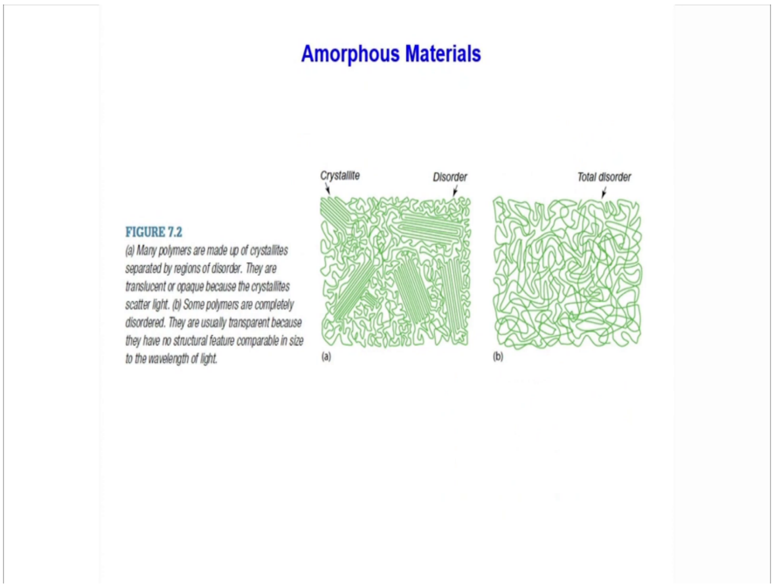

Amorphous Materials

FIGURE 7.2
(a) Many polymers are made up of crystallites separated by regions of disorder. They are translucent or opaque because the crystallites scatter light. (b) Some polymers are completely disordered. They are usually transparent because they have no structural feature comparable in size to the wavelength of light.

So, let us think of polymers ok you know polymers can be partially disorder or disorder and you know many polymers are there in a small crystal regions within in the disorder matrix or you can also have polymers which completely disorder. So, this thing the concept which I am talking about it is also valid in those kind of things also.

Now you know when dislocations cannot be thought about it because dislocations are only at the constant dislocation is all a valid for odd arrangements of atoms. Because you are thinking of the slip plane extra plane movement of these dislocations, that is only possible when you have a completely odd arrangements of atoms in a disorder arrangement of atom like amorphous structure you cannot think about dislocation ok.

Dislocation concept will no longer is valid. So, in such a situations material has extreme high strength you cannot believe it strength can go even further, if it if you decrease the grain size and make it amorphous it can reach even 5, 6 times of the normal material and people have seen it. But that increase of strength come at the cost of ductility, ductility and the fracture toughness reduces substantially if you are increasing the strength by this way.

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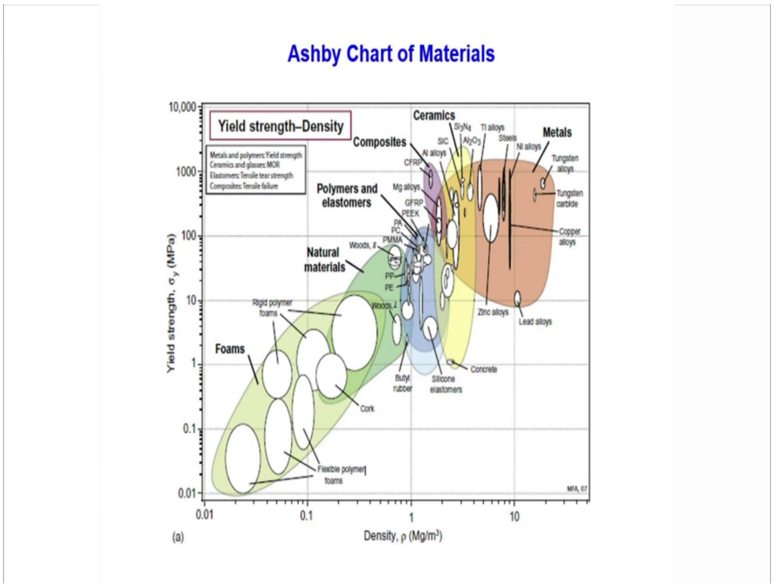
Ashby Chart of Materials

So, ask me Michael Ashby whose book is this has given some charts ok, you know here is one of those there are many charts actually given in this book. And there is a book by him I told you the design of material mechanical design of materials you know she talked about different kind of charts to segregate the materials depending on the type of properties you are looking at.

One of the properties which is important yield strength versus density and you can clearly see most of the polymers will be on the left side because they have lower strength lower density right. And then comes the natural materials then you have metal ceramics allows us components. So, metals as well as high density compared to ceramics and polymers, so that will be they will be on the metal also has high strength correct.

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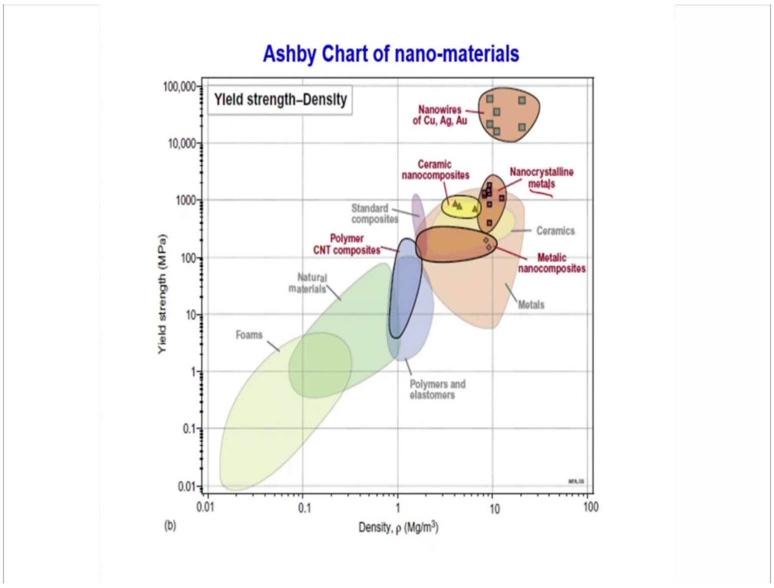

Ashby Chart of nano-materials

Now, what happened to nanostructure materials that is what happens. If you make the same plot for different nanostructure materials like here, you can see these are the nanowires of gold silver and copper and then you have nano crystalline metals here you can see here then you have ceramics nano composites even CNT composites.

So, you can clearly see still the nanowires yields over the others nanowires can have yield strength of the order of 10000 ampere that is 10 G pa ok that is very classical. Well why it is so that is we have separate discussions, but we thought of an nanowires even if you think of normal nano crystalline materials you can look at the yield strength of 1 G pa. Normally steel stainless is about 200 ampere or 250 ampere or maybe 300 correct.

So, we are talking about 1 G pa 4 times higher than that that is something which is very very significantly high. So, you can also have ceramic nano composites having such a kind of high strength with the density of about 10 or so correct. So that means, why by making nano crystalline materials you can increase the strength further amorphous ones will be much higher they will be close to this nanowires two times or even much higher something like about 10 to 15 G pa ok.

Many of these materials have such a kind of highest yield strength unless I know about metallic glasses which can go up to 5 to 6 G pa yield strength that is pretty large. But then you have very limited ductility it fails miserably on the other hand these nano crystalline metals may not fail miserably they will have certain amount of ductility which can be used ok. So, that is something which you must remember, so this winds up our discussions on the mechanical wear on material.

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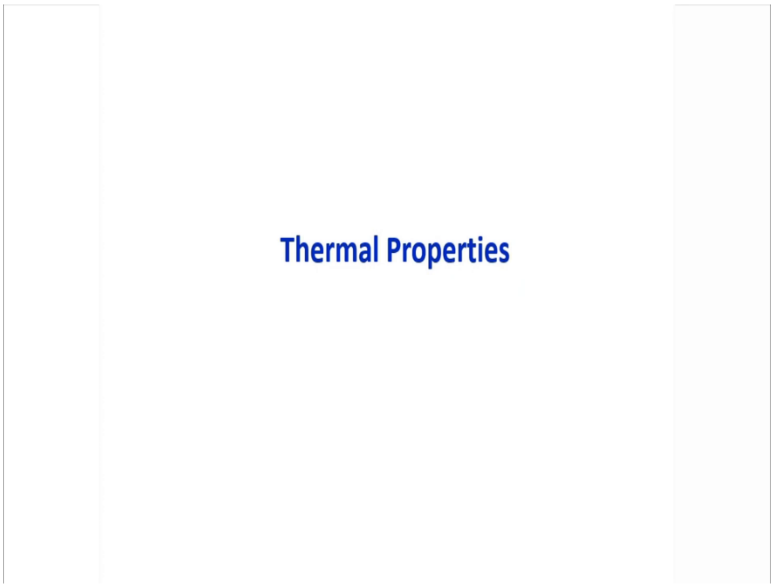

Thermal Properties

So, we are going to start a new chapter a new topics that are not chapter that is on the thermal properties ok. You know what do you mean by thermal properties? Mechanical properties you understand you apply force how the material behaves thermal property is obviously. If you increase the temperature decrease temperature how the material behave that is something which is very important.

So, as you know there are various kinds of thermal properties which are important in the material ok and as this book they start with melting temperature and then go to thermal transports and many aspects of that mostly these two. And in the book of whole earth there will be some aspects of thermal conductivity and other things are discussed.

So, we are going to discuss or limit our discussion to these aspects, because as I said this course is of 1 semester long. So, if I start discussing about one subject for long, then what will happen? I will miss out some other things which many of you may not like it ok. So, when you talk about thermal properties the most important thing you talk about the melting temperature material right.

Why it is important? Because application temperature must be lower than the melting temperature material anytime you are thinking of using a material right that is something which is always will be true am I clear.

If you want to use it in the arrow engine which burns a fuel at about 1200 degree Celsius temperature the application temperature or the melting temperature of the material must be higher than that, otherwise the material will melt down and then everything will be gone. So now, question is this if I decrease the grain size of material what happens to melting temperature and does it increase or decrease.

This is the question which we are going to answer right. So, in the bulk system surface to volume ratio is small, the curvature of surface is negligible we have seen that. So, therefore, for a solid in the bulk form surfaces effects are always neglected you never consider. On the other hand in case of nano scale solid following the surface to volume ratio is very large and therefore you can no longer ignore the aspects of these surfaces ok.

In addition for the 0 D and 1 D nanomaterial's the curvature is also an important aspects, you have a strong effects of curvature on the material behavior right. So, consequently nanomaterial's the melting temperature is size dependent correct you understand that. So, nano material melting temperature will be very much size, you know size dependent why? By the way you know how does the melting temperature dictated well this is dictated by the equilibrium correct.

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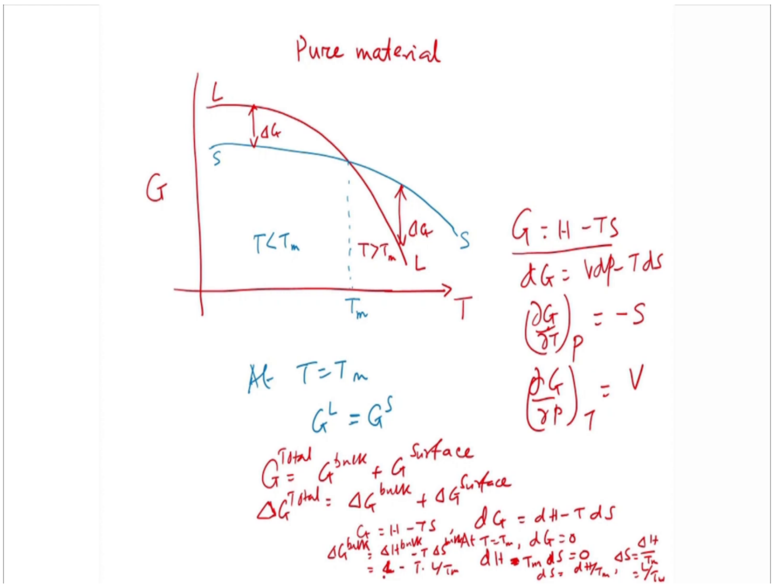

$$G = H - TS$$

$$dG = VdP - TdS$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

$$G^{total} = G^{bulk} + G^{surface}$$

$$\Delta G^{total} = \Delta G^{bulk} + \Delta G^{surface}$$

$$\Delta G^{bulk} = \Delta H^{bulk} - T\Delta S^{bulk}$$

$$\text{At } T = T_m,\ dG = 0$$

$$\Delta G^{bulk} = L - T\frac{L}{T_m}$$

$$dH - T_m dS = 0$$

$$dS = \frac{dH}{T_m}, \quad \Delta S = \frac{\Delta H}{T_m} = \frac{L}{T_m}$$

So, if I you know for a pure metal suppose if I plot G or the free energy versus sub temperature or any pure material ok, like you can talk about pure water, pure iron or may pure titanium, pure polyethylene ok a single component. So, you know that G versus x curve G versus temperature curves will have ok you know that right $G = H - TS$

If you do $dG = VdP - TdS$ right.

So, $(\frac{\partial G}{\partial T})_P$ = -S is constant pressure is watched it will be entropy right and

$(\frac{\partial G}{\partial P})_T$ = at constant temperature equally volume correct.

So that means what? That means, very simply that the slope of this curve G versus T will be negative because entropy is always positive S, S is the entropy is always positive it cannot be negative right. So, because there is a negative sign it has to be negative slope. So, that is why most of the cases they go down like this ok let me just draw it properly and show you this is very important concept which you know very well.

So, therefore, suppose this is the free energy for the liquid phase of the pure material, let us say suppose this is free energy for water liquid water. So, what will happen to the free energy of this solid ice let me just draw using a different color; obviously, below the melting temperature free energy side will to be lower above the melting temperature free energy side will be higher and let us suppose this is solid.

And therefore, you can see here this if this is the crossover point this is the crossover point that is why the free energy of the 2 phases are equal. This must be melting temperature, because at the melting temperature at $T=T_{m,}$ G^{liquid} = G^{solid} phase, then only they will coexist otherwise why they will coexist at 0 degree Celsius temperature both ice and water exist.

So, this is the most important fact, but below this that means, this is $T < T_m$ below this you can see the $G^L > G^S$ you can see that know. So, this kind of curves tells you relative disposition of the free energy curves and that is tells you relative stability of the free energies and on this side ok this is $T < T_m$, $G^L < G^S$ correct am I clear?

So therefore, in a bulk material this is what happens, because in the bulk material free energy is given by this we do not consider any surface energy effects, because surfaces are neglected. However, as you know for a nano crystal material sorry for a nano crystalline material $G^{total} = G^{bulk} + G^{surface}$ right this must be the case you cannot no longer ignore.

So, then you know delta G total change, change is very important right change is this. So, this is the change here correct or this is the change here change mean difference difference from one to other, but what is change. So, $\Delta G^{total} = \Delta G^{bulk} + \Delta G^{surface}$ right. So, what is ΔG^{bulk}? You know that you do not know well that is ok, if you do not know there is no problem ΔG^{bulk} can be easily calculated ok.

Let me just tell you delta G is from this equation ok alright let us start from the beginning. So, $G = H - TS$ ok and then $dG = VdP - TdS$ at constant temperature correct. Now at the melting temperature at $T = T_m$ both have similar free energies solid and liquid are same actually, so therefore $dG = 0$.

So therefore, $dH - T_m dS = 0$ right. So, what I can write? I can write down that $dS = \frac{dH}{T_m}$ or $\Delta S = \frac{\Delta H}{T_m}$ and what is ΔH? ΔH is nothing but latent heat for the melting. You can get ΔS is as T_m, now I can write down then $\Delta G^{bulk} = \Delta H^{bulk} - T\Delta S^{bulk}$ right.

So, this I know this is equal to $\Delta G^{bulk} = L - T\frac{L}{T_m}$ right. So, I can then get an value of this what will be the thing ok, let me just erase this part I hope you have taken down.

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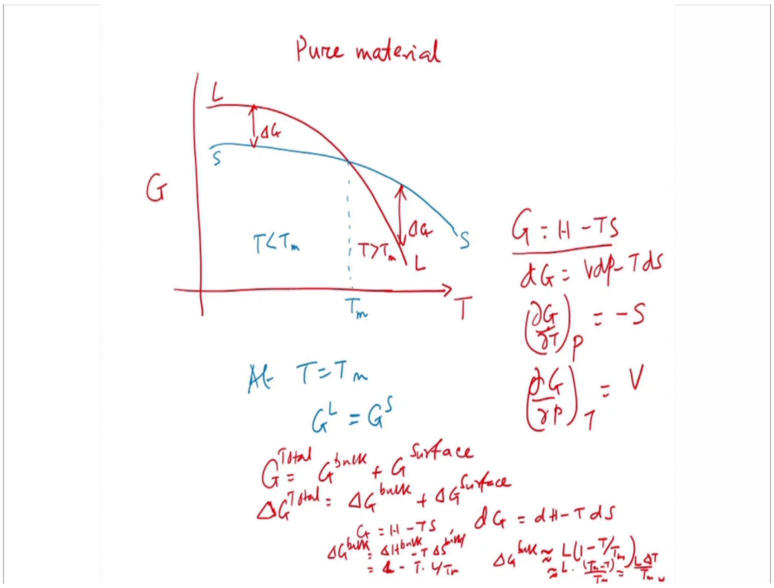

$G = H - TS$

$dG = Vdp - Tds$

$\left(\frac{\partial G}{\partial T}\right)_P = -S$

$\left(\frac{\partial G}{\partial P}\right)_T = V$

At $T = T_m$

$G^L = G^S$

$G^{Total} = G^{bulk} + G^{Surface}$

$\Delta G^{Total} = \Delta G^{bulk} + \Delta G^{Surface}$

$G = H - TS$, $dG = dH - TdS$

$\Delta G^{bulk} = \Delta H^{bulk} - T\Delta S^{bulk} = L - T \cdot L/T_m$

$\Delta G^{bulk} \approx L(1 - T/T_m) \approx L \cdot \frac{(T_m - T)}{T_m} = \frac{L\Delta T}{T_m}$

$$G = H - TS$$

$$dG = VdP - TdS$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

$$G^{total} = G^{bulk} + G^{surface}$$

$$\Delta G^{total} = \Delta G^{bulk} + \Delta G^{surface}$$

$$\Delta G^{bulk} = \Delta H^{bulk} - T\Delta S^{bulk}$$

$$\text{At } T = T_m, \quad dG = 0$$

$$\Delta G^{bulk} = L - T\frac{L}{T_m} = L\left(1 - \frac{T}{T_m}\right)$$

$$dH - T_m dS = 0$$

$$dS = \frac{dH}{T_m}, \quad \Delta S = \frac{\Delta H}{T_m} = \frac{L}{T_m}$$

So, $\Delta G^{bulk} = L - T\frac{L}{T_m} = L(1 - \frac{T}{T_m})$ where T is the undercooling. So, you can see this is actually an approximation this is not exactly true that is ok, that approximation is good enough. So, that is means I know what is, $\Delta G^{bulk}$and you all know what is $G^{surface}$.

I will stop here we will come back from this expression in the next class ok, from these aspects how when pure materials we can correlate the change of melting temperature or melting temperature function of size we will come back to it.

Thank you.