

Nanomaterials and their Properties
Prof. Krishanu Biswas
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur

Lecture - 20
Thermal Properties of Nanomaterials (II)

(Refer Slide Time: 00:28)

In the last lecture, we have finished out discussion on Mechanical Properties of Nanomaterials, Hall –Petch Derivation. We started a new topic.

Tensile Test Defect up Pile at GB

Recap:

(b) **Amorphous SRD**

Students, we are going to continue our discussions on the Thermal Properties, and this is lecture number 20. We have 10 more lectures to go. But before we do that, let us me, let me say something more also. So, in the last lecture, what do we have finished? We finished the lecture on mechanical properties of nanomaterials, and most importantly we talked about Hall-Petch equation, the breakdown of Hall-Petch equation and other aspects related to it.

And followed that we start a new topic, that is on Thermal Properties of Nanomaterials. So, it in order to provide you some recap, let me just state you that you know Hall-Petch is basically originates from the grain boundary strengthening. Dislocations generated inside the grains are pile up at the boundaries, and this is the reason why grain boundaries can act as an obstacle to the pile up of dislocation.

So, Hall-Petch provides an very nice mathematical (Refer Time: 01:29) between the grain size and the yield strength. This is true only, not only for single phase materials, but also for multi-layers and even multi-phase materials also. But at the nanoscale, Hall-Petch equation

breaks down. For every nanomaterial Hall-Petch equation has been found to break down, all these basically every means metallic and ceramic, crystalline materials, Hall-Petch seems to break down at a grain size below a certain critical value and that value can range from 20 to 5 or 2 nanometers.

And this is something which is widely observed. The reason I have discussed about it, the pile up of dislocation is the main reason for grain boundary strengthening, if you reduce the grain size, the pile up will vanish and we will have a situation in which a grain can accommodate only one dislocation.

And hence, the pile up will not be present. And this will not lead to any further strengthening, rather it will lead to softening, ok. This is the region where grain boundaries can lead to softening. This is something which you we have discussed in the last class, right.

Now, this aspect also leads to us to another important concepts like, so fine; so, that means, if I decrease the grain size small and small and smaller, the strengthening due to grain boundaries it is not reflected. So, now question is that if I still decrease a grain size further down to about 2 or 1 nanometers, what will happen to material? Well, material will become completely amorphous. That is understandable, because grain boundaries are the regions of randomness, compared to the grains, right.

So, therefore, as you decrease the grain size further and further, the grain boundary area is increasing and because of drastic increase of grain boundary area, the region of disorder or disorder regions are also increasing and this leads to formation of amorphous structure. And this is the picture of an amorphous atomic structure, where random orientations of the elements of the atoms leading to total disorder has been depicted.

So, surprisingly this amorphous materials are very strong, much much stronger than even some of the nanomaterials. This mainly because an amorphous material the concept of dislocation can no longer be applied. Why? Because dislocation theory or dislocation aspects in the material relies on the arrangement of atoms in the crystalline lattice.

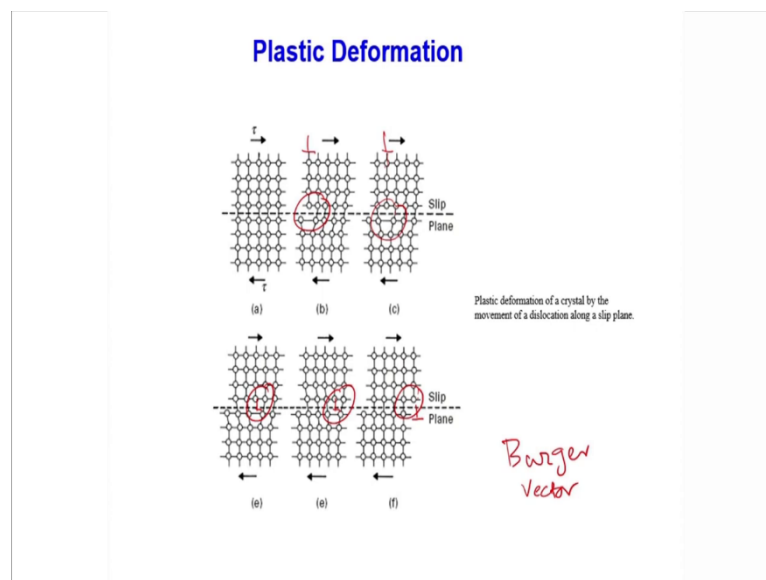
Look at the slip plane and the dislocation at this extra half plane. This whole concept is basically relies on the crystalline nature of the material. Say, amorphous where the atoms are

randomly arranged this concept cannot be applied. So, therefore, deformation we have amorphous material is different. Although, we are not going to discuss about it, but it happens because of the shear, or local shear of the atoms over each other.

Remember, amorphous thing does not have a long range order, but it also has short range order or what is known as SRO, right, SRO, Short Range Order. So, these short range order clusters can move over each other and that is how they can create, they can actually shear. And this localized shear is can only be accommodated in amorphous material. But nonetheless they have very high strength with a limited ductility and many cases almost 0 ductility.

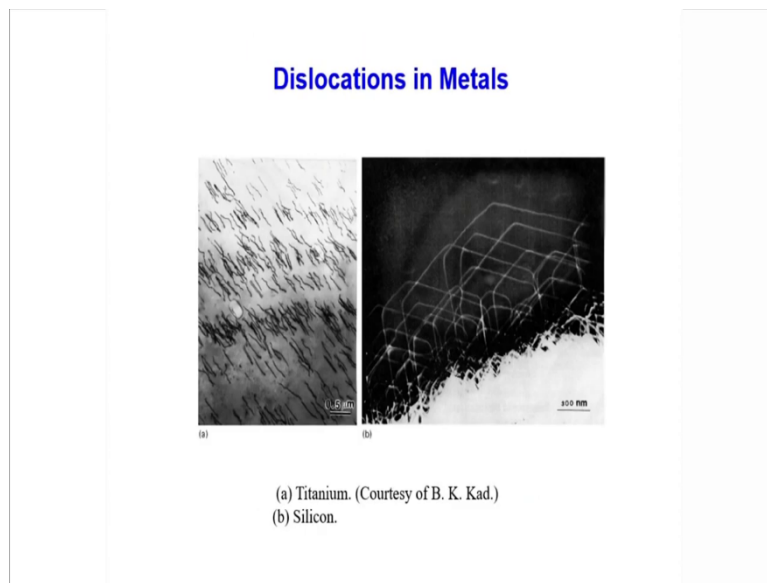
So, therefore, these materials cannot be used structurally because they have a very low damage tolerance, low ductility, so you cannot use them for structural application. You can use them for functional application or maybe something like a golf head or golf bat head actually, head of a golf bat, you can do that, but not for other things.

(Refer Slide Time: 06:23)



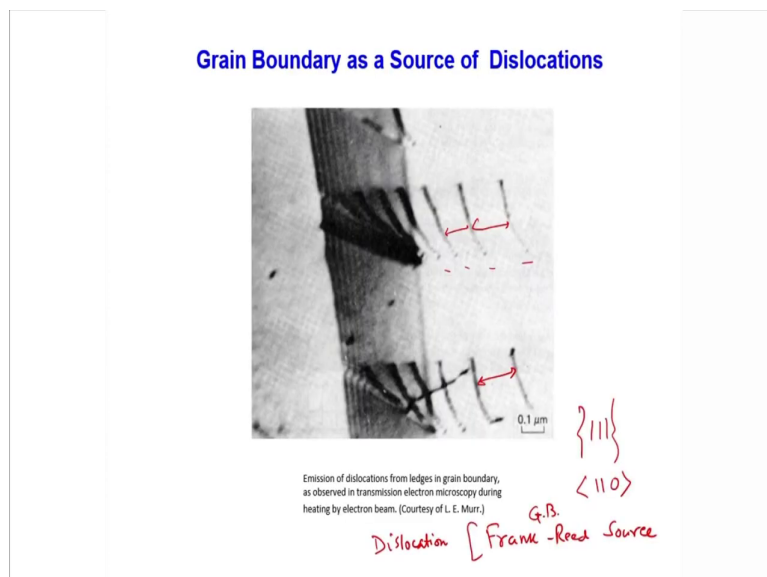
Well, as we said, so therefore, in nanocrystalline materials or normal material, plastic deformation which happens because of dislocation motion is kind of the predominantly observed. That is the mode of deformation in this materials as compared to the amorphous materials.

(Refer Slide Time: 06:42)



And dislocations are seen under TEM, I am showing this picture again and again with titanium silicon, this has been observed.

(Refer Slide Time: 06:51)

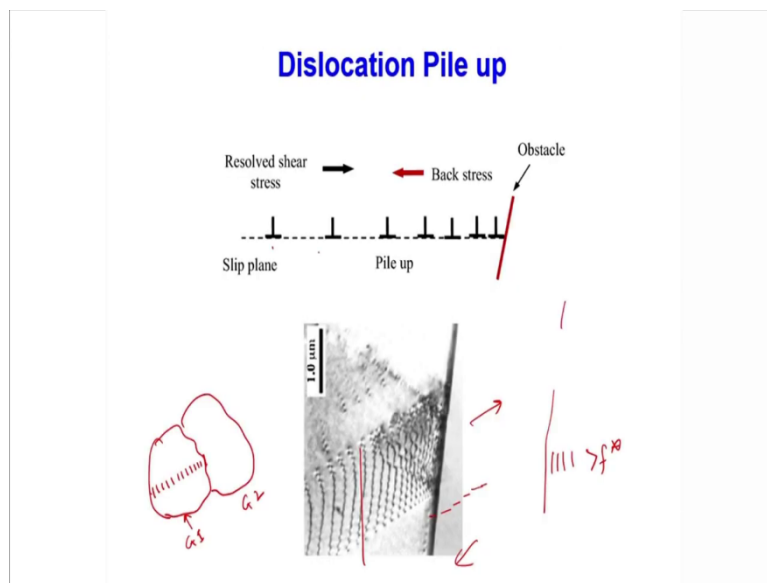


Similarly, it has been observed in ceramics also. And now, the basic reasons for grain boundaries strengthening is not only the grain boundaries acting as an obstacle, also grain

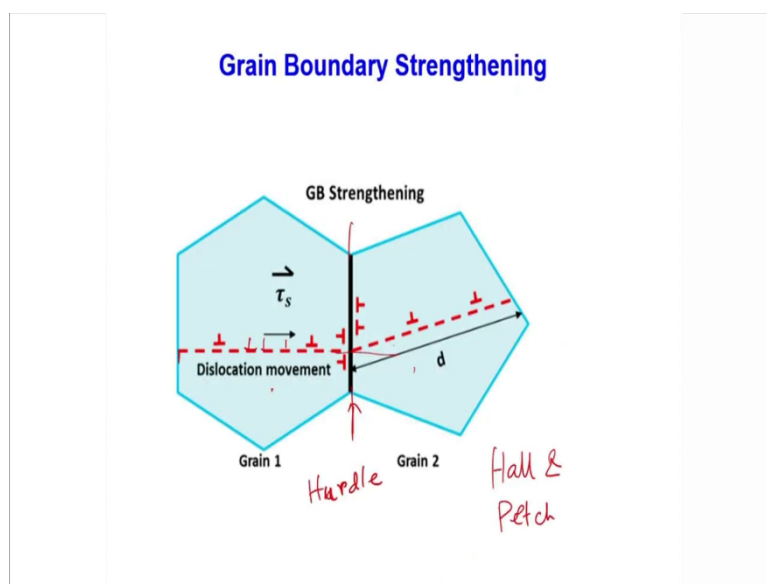
boundary can also act as a source of dislocation. Dislocations can be generate at the grain boundaries or maybe at the frank reed source.

Then they can move inside the grains, and that is how they can create a pileup. You can see that they have already pile up it started, 1, 2, 3, 4 pileup has started. So, one after another, just like a passenger standing in front of a railway ticket counter, same thing happens.

(Refer Slide Time: 07:28)



(Refer Slide Time: 07:34)



So, this pile up model which has been discussed for the couple of last 2-3 lectures is mainly the reason for Hall-Petch equation, correct.

(Refer Slide Time: 07:41)

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.

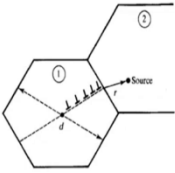


Figure 5.5
Microyielding in a grain (Grain 1) favorably oriented for slip may precede macroscopic yielding. Macroscopic flow requires dislocation activity in all grains (e.g., Grain 2), and this may be induced by the internal stress caused by the dislocation pileup at the boundary in Grain 1. This stress 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, central idea is dislocations are forced to pile up at the boundaries, either because there is a barrier crossing to crossover or because the source of dislocation must be activated in the next grain. This is something which is very important.

(Refer Slide Time: 07:57)

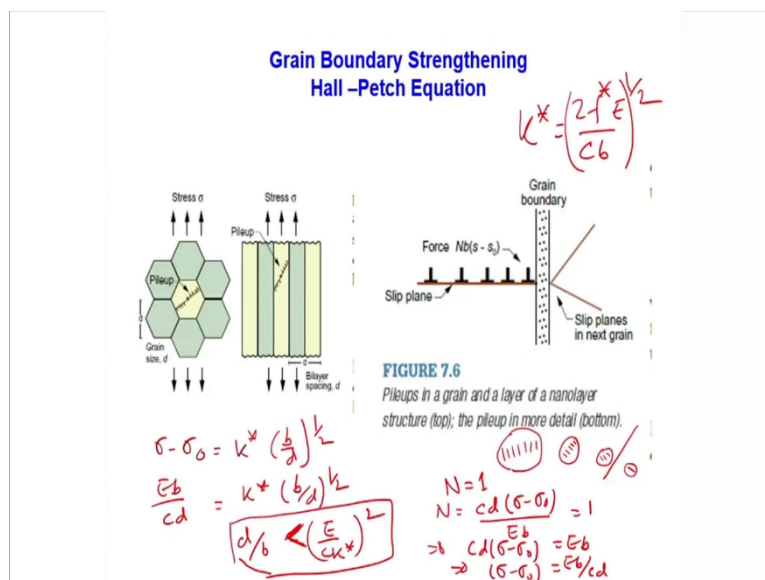
Grain Boundary Strengthening
Hall –Petch Equation

- 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.

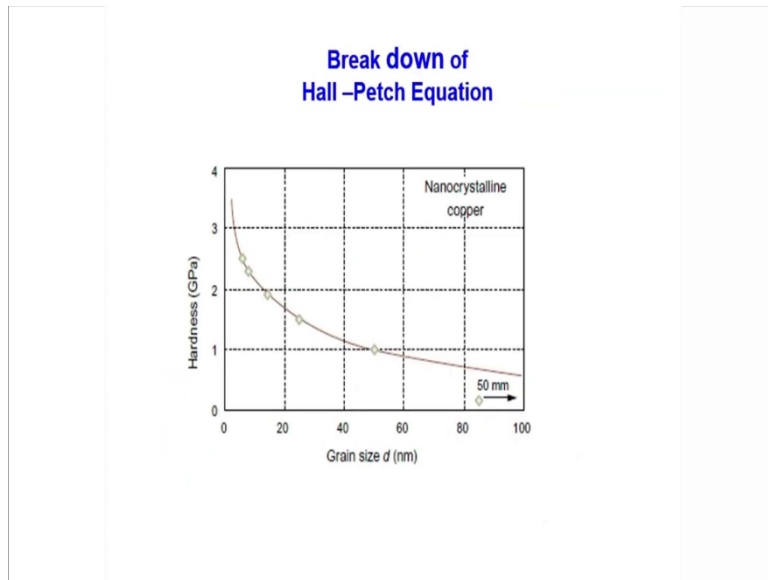
And so, classical explanation is very simple. The stress concentration in a given grain is required to initiate slip, initial slip in the neighboring grain and this leads to pile up that is shown in the last figure. The essence of the argument is that stress is higher as the number of dislocation increases.

So, strains will be much higher as a pile up number of dislocation pile up increases, right. So, as this size goes down, number of dislocation inside the grain goes down, and at a particular grain size, you have only one dislocations can be accommodate inside the grain and Hall-Petch concepts or Hall-Petch mechanism breaks down.

(Refer Slide Time: 08:35)



(Refer Slide Time: 08:40)



(Refer Slide Time: 08:40)

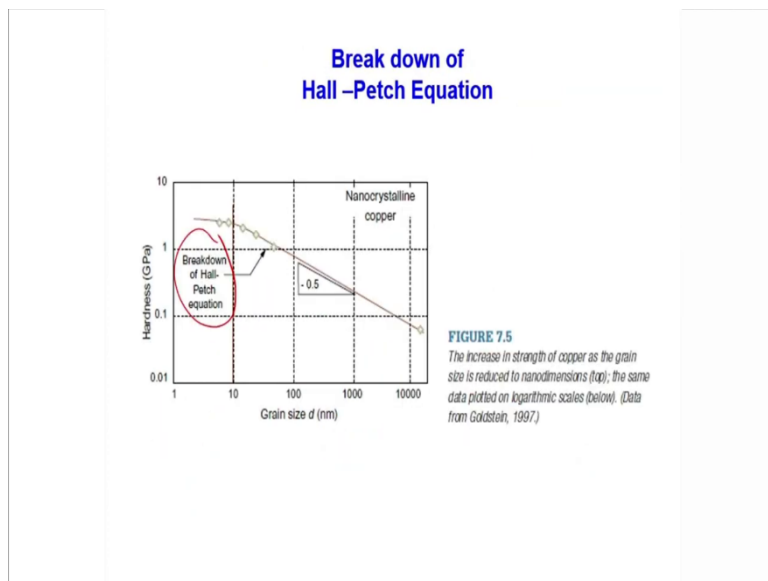
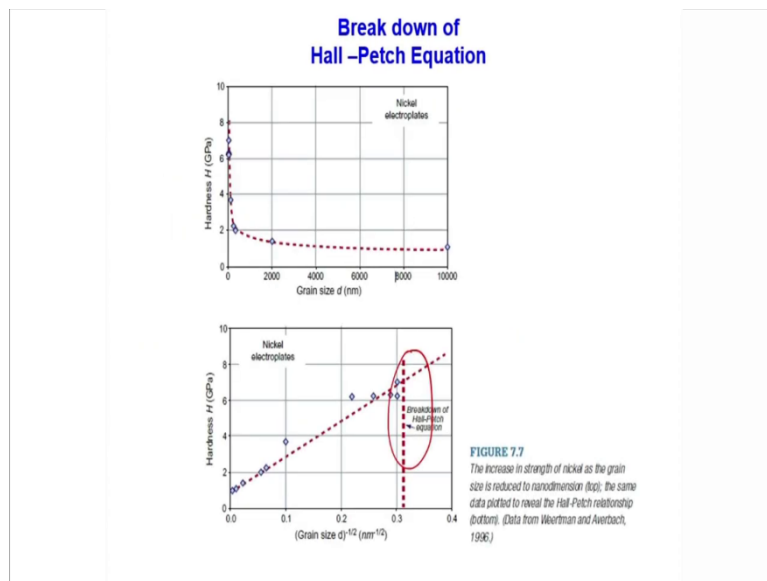


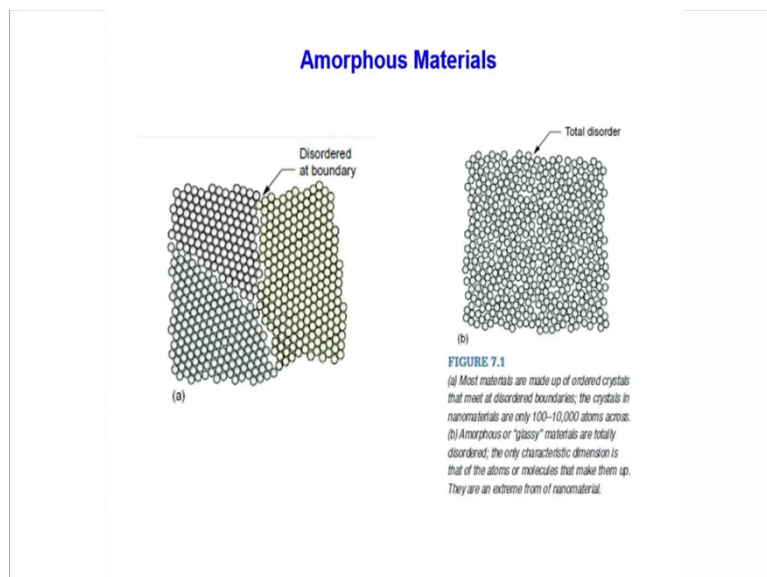
FIGURE 7.5
The increase in strength of copper as the grain size is reduced to nanodimensions (top); the same data plotted on logarithmic scales (below). (Data from Goldstein, 1997.)

(Refer Slide Time: 08:45)



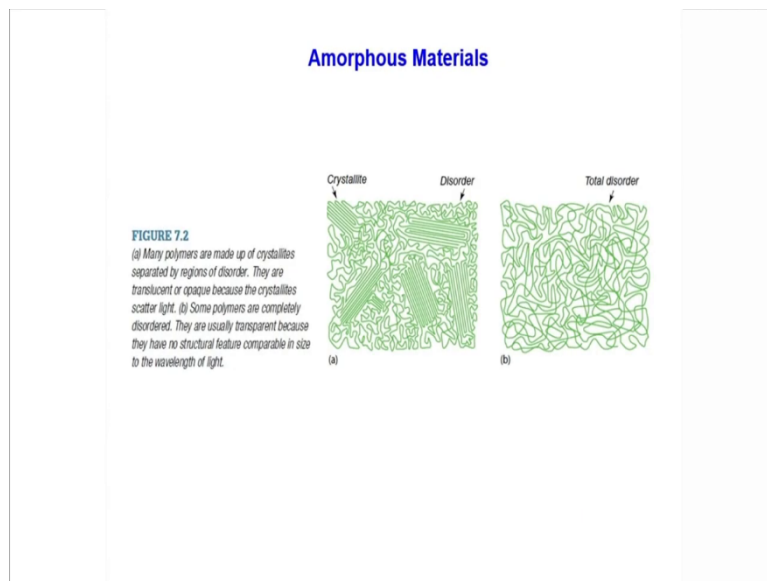
That is what we discussed a lot. And this is the mathematical derivations. I will not go back into it, ok.

(Refer Slide Time: 08:49)



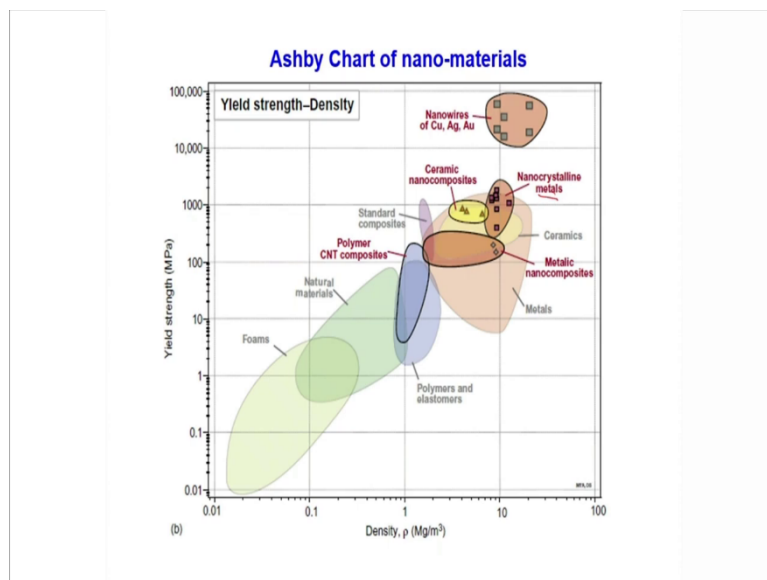
These are the some of the things which I have shown you how the Hall-Petch breaks down in copper and nickel or maybe in case of multi-layers also.

(Refer Slide Time: 08:59)



Then, we discuss something about amorphous materials, as you decrease the grain size smaller and smaller, grain boundary increases and the material becomes completely random amorphous. This is also observed in polymers.

(Refer Slide Time: 09:02)



And so, therefore, if you make kind of strain versus density plot or strain versus ductility plot, you can do many. Some of them are there in the books also, I am not discussing all of them. You can put all the metals in nanocrystalline form very nicely.

(Refer Slide Time: 09:16)



Thermal Properties

- ① Melting temperature of NMs
- ② Thermal transport

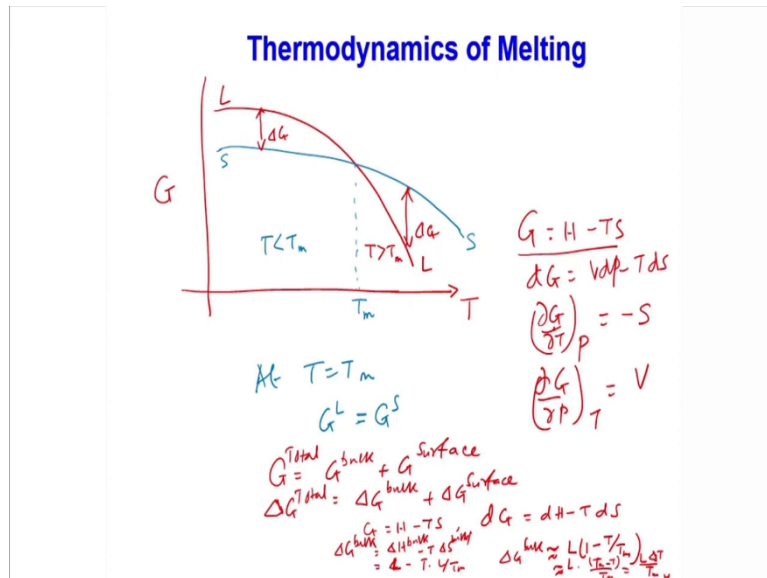
So, far so good. We are going to start a nano thermal properties. We have already started some part of in the last lecture, ok, but thermal properties I like to reiterate something here. Thermal properties means what? Thermal properties means if you apply heat, how the changes happen, right. That is what it is. So, on the most important characteristics of the material is the melting temperature, ok.

So, therefore, first thing we will discuss is the melting temperature of nanomaterial, right. That is the 1st thing we will discuss, but that is something which is very fundamental, right. And this is very important also. 2nd thing we will discuss is the transport, thermal transport. And thermal transport means how heat is transported. And this happens because of phonons or electrons, correct.

So, we will discuss about that also. But we will discuss this aspect, melting temperature in today's lecture. Please remember that. So, we are focusing on these two particular things. Well, there are many other things also possible, but we are not going to discuss all of them

because from time constraint and because of the you know some fundamental concepts may be required for you to understand, that is why.

(Refer Slide Time: 10:55)



$$G = H - TS$$

$$dG = VdP - TdS$$

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

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

At $T = T_m$,

$$G^L = G^S$$

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

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

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

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

$$dH - T_m dS = 0$$

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

So, we started with that how what is thermodynamics description of melting of a bulk material. As you know, the basic concept is the free energy. At the melting temperature free energy of solid and liquid must be equal. That is the fundamental concept. And below the melting temperature solid is more stable above liquid is more stable. So, therefore, relative disposition of these two free energy curves dictates how the free energy can be used to describe the melting phenomena in a bulk material. And you know free energy means Gibbs free. Gibbs free energy, it can be given as $G = H - TS$.

(Refer Slide Time: 11:50)

Thermodynamics of Melting

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

$\Delta G \propto \Delta T$
 $\propto (T - T_m)$ L, T_m are constant for materials.

$$\Delta G_{total} = \Delta G_{bulk} + \Delta G_{surface}$$

$$\Delta G_{bulk} = \frac{L(T - T_m)}{T_m}$$

$$\Delta G = \frac{L}{T_m} (T - T_m) \approx \frac{L}{T_m} \Delta T$$

$\Delta G \propto \Delta T \propto (T - T_m)$ Where L, T_m are material constant

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

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

And by doing a simple calculation, I showed you that Gibbs free energy difference $\Delta G = \frac{L}{T_m} (T - T_m) \cong \frac{L}{T_m} \Delta T$, where ΔT is always considered as the super cooling, right. How much lower the melting temperature you can do the melting? Ok.

So, this is how we can actually, one can actually derive the delta G of melting while melting the phase the amount of free energy because of melting. So, as you can clearly see, this difference is, or $\Delta G \propto \Delta T \propto (T - T_m)$. Why? Because latent heat and T_m are constant for a particular material.

Remember, we are discussing about bulk. We are not discussing about for a particular material we are not discussing about nano. So, this is something which is very very important for you to understand. This derivation is there any thermodynamics books we can do. But what happens when you have nanomaterials, right that is something which you should know very well.

So, as you know, so, therefore, for nanomaterials we have written already many times, $\Delta G^{total} \propto \Delta T$ can be written as $\Delta G^{total} = \Delta G^{bulk} + \Delta G^{surface}$, right because nanomaterials have a high surface-to-volume ratio. And therefore, ΔG^{bulk} as we have written above then can be written as $\Delta G^{bulk} = L \left(\frac{T_m - T}{T_m} \right)$, correct.

(Refer Slide Time: 13:51)

Thermodynamics of Melting

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

$\Delta G \propto \Delta T$
 $\propto (T_m - T)$ L, T_m are constant for materials.


$$\Delta G_{total} = \Delta G_{bulk} + \Delta G_{surface}$$

$$\Delta G_{bulk} = \left[\frac{L(T_m - T)}{T_m} \right] \cdot V_l$$

$$\Delta G_{surface} = \gamma \Delta A \quad \Delta A = \text{change in area}$$

$$\Delta G_{total} = \frac{L(T_m - T)}{T_m} V_l + A_l \gamma_l + A_{sl} \gamma_{sl} - A_s \gamma_s$$

$$\frac{\partial \Delta G_{total}}{\partial t} = 0$$



$$\Delta G = \frac{L}{T_m} (T_m - T) \approx \frac{L}{T_m} \Delta T$$

$\Delta G \propto \Delta T \propto (T_m - T)$ Where L, T_m are material constant

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

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

$$\Delta G^{surface} = \gamma \Delta A \quad (\Delta A - \text{change in the area})$$

$$\Delta G^{total} = L \left(\frac{T_m - T}{T_m} \right) \cdot V_l + A_l \gamma_l + A_{sl} \gamma_{sl} - A_s \gamma_s$$

$$\frac{\partial \Delta G_{total}}{\partial T} = 0$$

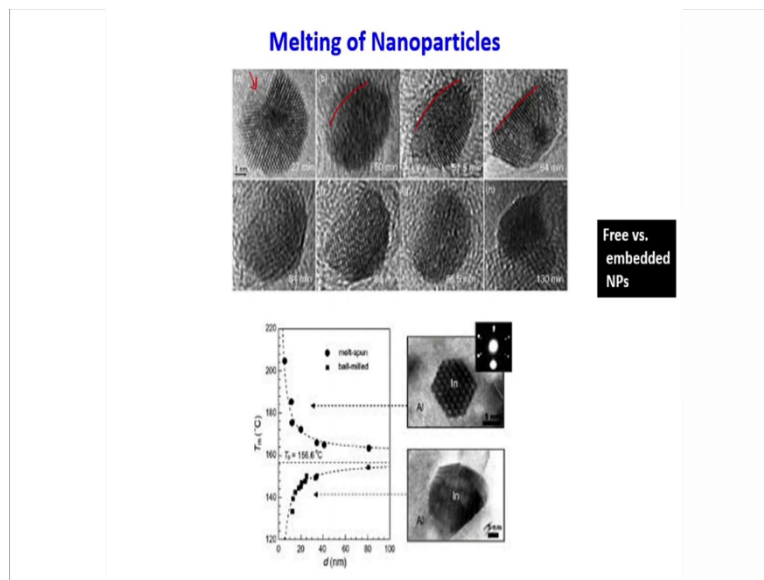
So, it is $(T_m - T)$ multiply a volume because this is the volume free energy. So, you find total free energy; you have to multiply the volume of the liquid, correct. This part is the free energy change because of the transformation from solid to liquid, per unit volume.

So, if you want to know what is the total free energy change, you need to multiply by volume of liquid. So, therefore, L is a latent heat, T_m is the melting temperature of the bulk material, and T is the melting point of the, basically, T is any temperature. And as this book it has been written as the melting temperature of extended system that when me when surface effects are there. So, that is something which we can easily, we have derived in the last class and we can use it.

What about $\Delta G^{surface}$? $\Delta G^{surface}$ is equal to what? That is equal to you know that that is $\Delta G^{surface} = \gamma \Delta A$, right. γ is the specific surface energy and (ΔA - change in the area), right. That is something which is basically (ΔA is nothing but change in area, right).

So, evidently, at the melting temperature, something must be happening and that you should know, then only you can calculate delta A. So, that means, to know the change of A you all must know how melting happens for a nanoparticle, right? Then only can we come back to it and then calculate it.

(Refer Slide Time: 16:08)



So, let us see that how it happens. So, these are the few experimental things, ok. Just look at the structures. This is a nanoparticle; something like about say dimension is about 10 nanometers or so. And it has been heated up. Because of heating it started melting, from here you can see. How do it has melting happen? Well, liquid has an amorphous structure;

obviously, you can see all this thing under the transmission electron microscope. You cannot see these particles things happening in other microscopes.

So, you have something happening at the surface here. The contrast which is mainly because of the crystallinity of the material is lost. And that is why you can see there is a amorphous like picture, that is a random arrangement of atoms. And slowly the liquid, the things start melting down, slowly the things will start melting down, you can see here and this part is slowly decreasing, this molten, molten, ok or finally, everything is molten after 130 minutes or so.

So, that means, liquid layer forms on the surface that is part is clear, ok. And then it grows inside. That is understandable. Because melting requires formation of the liquid. Liquid cannot form inside the particle. It can form there are some peculiar cases, but in general liquid can only form on the surface of the particle, because surface acts as a nucleating agent for the liquid, right.

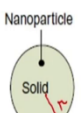
So, this is something which is very very widely observed in many particles. Even you can look at this particle which is indium, ok and once you start heating up it will melt nicely, ok. So, I will show you some pictures later, but you know very clear that the melting happens in a surface kind of things, surface starts melting first.

(Refer Slide Time: 18:15)

How does melting occur?

$A_s \gamma_s$

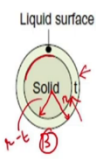
Nanoparticle



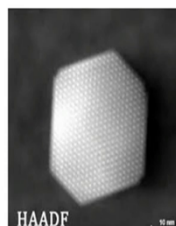
Solid

$A_L \gamma_L + A_{SL} \gamma_{SL}$

Liquid surface



Solid



HAADF

10 nm

FIGURE 7.13
Upon formation of a liquid layer on the nanoparticle's surface, an interface between the liquid layer and the solid core develops.

$$\Delta G = \gamma \Delta A$$

$$= [A_L \gamma_L + A_{SL} \gamma_{SL} - A_s \gamma_s]$$

So, the model which people normally use is like this. This is in there from Ashby's book, Michael Ashby, and let us assume a solid particle of something like a radius of r , correct radius of r . And so, this particle started melting down. So, when it started melting down it formed a thin layer of liquid in the surface. You might be thinking in the picture liquid was forming from one side, but remember the T_m you see only the position of the image. You do not see the whole solid particle.

So, whether liquid has formed all throughout the surface or not, it cannot be completely confirmed. But we can always assume the liquid will likely to form in this surface evenly on the particle. So, suppose this liquid forms and because this liquid is formed. So, this is r and this thing becomes $(r-t)$, am I right.

So, now we can do something. We can very easily understand. And this is the some kind of particles on which if liquid forms you cannot apply use basically assume spherical assumptions. You have to know the particular shape and calculate it. So, my idea is to show that the actual life is more complicated than whatever you do to understand things. But nonetheless to keep it simple and nice, let us assume the particle is spherical.

Let us not assume the particle has facets and then we have to calculate area of the facets, and other complication comes into picture which facets will melt first or not. This I assume is spherical particle with radius of r . When it start melting, it forms a liquid layer on the surface of this particle, and liquid layers of specific thickness t , ok.

So, now; obviously, $\Delta G = \gamma\Delta A$, right. So, this can be expanded. Then what? A_l l , ok. What is A_l l ? Ok. A_l is the area of the liquid which is formed, and the inter surface energy of the liquid. See, the difference is this. Compared to configuration A, to if you compare them what is the difference, in the configuration A you have only A_s s because this is a complete solid. So, γ is the surface energy of the solid.

And if you know the area of the solid then you know what is the total surface energy. But here you have A_l l . Why? Because liquid has formed on the surface. Liquid has formed a surface of the solid and it discover the solid. So, therefore, the new surface which just formed

is a liquid, plus you have formed a surface A_{sl} , right. This is the surface, within solid and liquid.

So, the formation of liquid leads to two kinds of surface formation, one liquid with the atmosphere; another one is liquid with the particle. And each of these surface area, surfaces has different surface energies. So, that is why if I have to consider gamma and ΔA properly, so I should write down $(A_{sl} - A_s)$ this is the difference, correct. This is the main difference between these two situations.

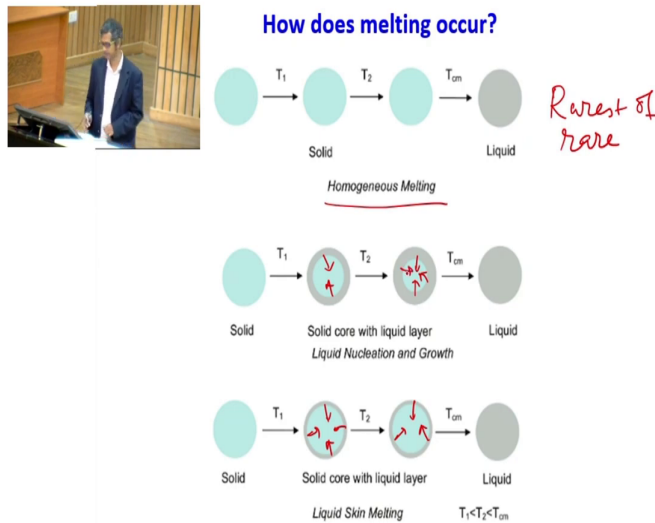
That part should be clear, ok. Am I very clear? If you are not understanding properly, you can always ask me question later on when the discussion happens. So, this is something which is very difficult even in nucleation of solid also. Those of you who studied metallurgy they know that for hydrogen and nucleation of solids from the liquid we use such a kind of expression or so.

So, A_l is this surface energy, surface energy means surface energy of the liquid. A_{sl} is this surface energy and this one is this surface energy. So, new configuration minus the old configuration, that is what gives you the change of the ΔG .

So, now, I can go back. So, therefore, $\Delta G^{total} = L \left(\frac{T_m - T}{T_m} \right) \cdot V_l + A_l V_l + A_{sl} V_{sl} - A_s V_s$ that is what we did. This is the total free energy of the system. Now, if you want to know the equilibrium between these because of melting, then you should make sure the ΔG as a function of the thickness must be 0 because you are creating a liquid layer on a solid. This liquid layer on the solid is the thickness of that is a variable.

So, at any temperature how much will be this thickness that is will depends upon the equilibrium between the solid and the liquid. So, that is why if we apply this minimization principle of the ΔG with respect to thickness t, this is the thickness t, ok, then you can get a relationship between melting temperature and something, right. That is what you have understood.

(Refer Slide Time: 24:42)



Now, I go back, ok. So, this is again to show you how the melting actually happens. You see as this is called homogeneous melting which is very rare, rarest of rare, rarely has been observed or you can say it is never observed. This is something heterogeneous nucleation of liquid and growth. This is something which happens very regularly, ok.

You can see solid liquid layer and liquid layer growth and melts, ok. Or you can also have liquid skin melting; that means, you have a very thin layer formation, a thin layer slowly grows, and whatever situation this liquid layer grows inside every time and melts. This is the model which is widely used in the literature. And this is acceptable. That is what we did, ok. Again, I am showing you this aspects.

(Refer Slide Time: 25:36)

Thermodynamic Model

$$\Delta G^{total} = \frac{L(T_m - T)}{T_m} \cdot V_L + A_L \gamma_L + A_{SL} \gamma_{SL} - A_S \gamma_S$$

$$\Delta G^{total} = \frac{L(T_m - T)}{T_m} \cdot \left(\frac{4}{3} \pi r^3 + 4\pi r^2 \gamma_L + 4\pi r(r-t) \gamma_{SL} - 4\pi r^2 \gamma_S \right)$$

$$\frac{\Delta G^{total}}{4\pi} = \frac{L(T_m - T)}{T_m} \cdot \left(\frac{r^3}{3} + r^2 \gamma_L + (r-t) \gamma_{SL} - r^2 \gamma_S \right)$$

$$\Delta G^{total} = L \left(\frac{T_m - T}{T_m} \right) \cdot V_l + A_l \gamma_l + A_{sl} \gamma_{sl} - A_s \gamma_s$$

$$\Delta G^{total} = L \left(\frac{T_m - T}{T_m} \right) \cdot \frac{4}{3} \pi r^3 + 4\pi r^2 \gamma_l + 4\pi (r - t)^2 \gamma_{sl} - 4\pi r^2 \gamma_s$$

$$\frac{\Delta G^{total}}{4\pi} = L \left(\frac{T_m - T}{T_m} \right) \frac{r^3}{3} + r^2 \gamma_l + (r - t)^2 \gamma_{sl} - r^2 \gamma_s$$

So, now, so I will write down again the whole thing. $\Delta G^{total} = L \left(\frac{T_m - T}{T_m} \right) \cdot V_l + (A_l \gamma_l + A_{sl} \gamma_{sl} - A_s \gamma_s)$. Am I clear. So, now, how do you calculate A_l , A_{sl} and A_s ? How do you calculate that?

(Refer Slide Time: 26:09)



How does melting occur?

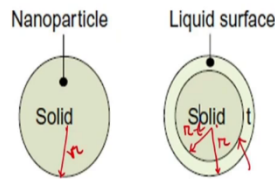


FIGURE 7.13

Upon formation of a liquid layer on the nanoparticle's surface, an interface between the liquid layer and the solid core develops.

$$A_s = 4\pi r^2$$

$$A_l = 4\pi r^2$$

$$A_{sl} = 4\pi (r-t)^2$$

$$V_l = \frac{4}{3}\pi r^3 - \frac{4}{3}\pi (r-t)^3$$

$$= \frac{4}{3}\pi r^3 - \frac{4}{3}\pi (r^3 - 3r^2t + 3rt^2 - t^3)$$

$$= \frac{4}{3}\pi (3r^2t - 3rt^2 + t^3)$$

$$V_l = \frac{4}{3}\pi r^3 - \frac{4}{3}\pi (r - t)^3 = \frac{4}{3}\pi r^3 - \frac{4}{3}\pi (r^3 - 3r^2t + 3rt^2 - t^3) = 4\pi (r^2t - t^2r)$$

Higher power term of r^3 and t^3 cubic power term is ignored

$$A_s = 4\pi r^2, A_l = 4\pi r^2, A_{sl} = 4\pi (r - t)^2$$

Let us do that, ok. Again, so, this is the advantage of using. So, $A_s = 4\pi r^2$, surface area of this particle, right. What about A_l here? Again, this is r and this is r minus t . So, A_l is what? $A_l = 4\pi r^2$, right because it is a liquid. Liquid has a radius of r . So, what about A_{sl} ? A_{sl} is this surface area. So, that is nothing but $A_{sl} = 4\pi(r - t)^2$. Am I clear? Correct. So, A_l and A_s are same, A_{sl} is different, correct.

So, what you do? You plug in all the values and this remains constant $L\left(\frac{T_m - T}{T_m}\right) \cdot V_l$. And what is the volume of the liquid? Volume of this liquid is what? Do not know, right. Obviously, you should know it. Volume of the liquid is in the annulus place. No, that is not the volume we are considering. Volume when the whole thing is molten, then only the whole transformation is complete.

So, therefore, that volume is $\frac{4}{3}\pi r^3$, ok. So, we can write down that;

$$\Delta G^{total} = L\left(\frac{T_m - T}{T_m}\right) \cdot \frac{4}{3}\pi r^3 + 4\pi r_l^2 \gamma_l + 4\pi(r - t)^2 \gamma_{sl} - 4\pi r^2 \gamma_s. \text{ Am I clear.}$$

So, now what do you do? Ok. I think we are making here mistake, that is very clear. They are not considering this liquid. So, I am sorry. I should have I have made a wrong assumptions. So, this should be this liquid, liquid layer, which is nothing but; so, if you see this is a difference between the volume four-third pi r cube minus four-third pi r minus t cube, right. So, that is become, that you can easily calculate, ok.

So, $V_l = \frac{4}{3}\pi r^3 - \frac{4}{3}\pi(r - t)^3 = \frac{4}{3}\pi r^3 - \frac{4}{3}\pi(r^3 - 3r^2t + 3rt^2 - t^3) = 4\pi(r^2t - t^2r)$. So, let us correct it.

(Refer Slide Time: 30:49)



Thermodynamic Model

$$\Delta G^{total} = \frac{L(T_m - T)}{T_m} \cdot V_L + A_L \gamma_L + A_{sl} \gamma_{sl} - A_S \gamma_S$$

$$\Delta G^{total} = \frac{L(T_m - T)}{T_m} \cdot V_L + 4\pi r^2 \gamma_L + 4\pi(r-t) \gamma_{sl} - 4\pi r^2 \gamma_S$$

$$\frac{\Delta G^{total}}{4\pi} = \frac{L(T_m - T)}{T_m} \cdot V_L + r^2 \gamma_L + (r-t) \gamma_{sl} - r^2 \gamma_S$$

$$\frac{\Delta G^{total}}{4\pi} = \frac{L(T_m - T)}{T_m} \cdot 4\pi(r^2 t - t^2 r) + r^2(\gamma_L - \gamma_S) + (r-t) \gamma_{sl}$$

$$\frac{\partial(\frac{\Delta G^{total}}{4\pi})}{\partial t} \text{ At limit } t \rightarrow 0, \frac{L(T_m - T)}{T_m} = \frac{2\gamma_{sl}}{r-t}$$

$$\Delta G^{total} = L \left(\frac{T_m - T}{T_m} \right) \cdot V_L + A_L \gamma_L + A_{sl} \gamma_{sl} - A_S \gamma_S$$

$$\Delta G^{total} = L \left(\frac{T_m - T}{T_m} \right) \cdot \frac{4}{3} \pi r^3 + 4\pi r^2 \gamma_L + 4\pi(r-t)^2 \gamma_{sl} - 4\pi r^2 \gamma_S$$

$$\frac{\Delta G^{total}}{4\pi} = L \left(\frac{T_m - T}{T_m} \right) \frac{r^3}{3} + r^2 \gamma_L + (r-t)^2 \gamma_{sl} - r^2 \gamma_S$$

$$\frac{\Delta G^{total}}{4\pi} = L \left(\frac{T_m - T}{T_m} \right) 4\pi(r^2 t - t^2 r) + r^2(\gamma_L - \gamma_S) + (r-t)^2 \gamma_{sl}$$

$$\frac{\partial \frac{\Delta G^{total}}{4\pi}}{\partial t} = L \left(\frac{T_m - T}{T_m} \right) 4\pi(r^2 - 2rt) + (2t - 2r) \gamma_{sl}$$

$$\text{At } \frac{\partial \frac{\Delta G^{total}}{4\pi}}{\partial t} = 0$$

$$L \left(\frac{T_m - T}{T_m} \right) = \left(\frac{2\gamma_{sl}}{r-t} \right)$$

We will write it here and next step we are going to write it $\Delta G^{total} = L \left(\frac{T_m - T}{T_m} \right) 4\pi(r^2 t - t^2 r)$

$+ r^2(\gamma_L - \gamma_S) + (r-t)^2 \gamma_{sl}$.

So, now if you this is what is $\frac{\Delta G^{total}}{4\pi} = L\left(\frac{T_m - T}{T_m}\right) \frac{r^3}{3} + r_l^2 \gamma_l + (r - t)^2 \gamma_{sl} - r^2 \gamma_s$, correct.

$$\frac{\Delta G^{total}}{4\pi} = L\left(\frac{T_m - T}{T_m}\right) 4\pi(r^2 t - t^2 r) + r^2(\gamma_l - \gamma_s) + (r - t)^2 \gamma_{sl}$$

$$\frac{\partial \frac{\Delta G^{total}}{4\pi}}{\partial t} = L\left(\frac{T_m - T}{T_m}\right) 4\pi(r^2 - 2rt) + (2t - 2r) \gamma_{sl}$$

$$\text{At } \frac{\partial \frac{\Delta G^{total}}{4\pi}}{\partial t} = 0$$

So, you can write down these aspects very easily. So, when at the limit, at limit t goes to 0, you will find this relationship valid. That is $L\left(\frac{T_m - T}{T_m}\right) = \left(\frac{2\gamma_{sl}}{r-t}\right)$. You will find that both the cases you are getting r minus t, correct, both the cases, ok. Let me do it before I derive it. So, let me erase it up. You guys may be thinking bad. So, let us do that.

(Refer Slide Time: 33:15)

Thermodynamic Model

$$\Delta G^{total} = \frac{L(T_m - T)}{T_m} \cdot V_L + A_L \gamma_L + A_{SL} \gamma_{SL} - A_S \gamma_S$$

$$\Delta G^{total} = \frac{L(T_m - T)}{T_m} \cdot V_L + 4\pi r^2 \gamma_L + 4\pi(r-t)^2 \gamma_{SL} - 4\pi r^2 \gamma_S$$

$$\frac{\Delta G^{total}}{4\pi} = \frac{L(T_m - T)}{T_m} \cdot V_L + r^2 \gamma_L + (r-t)^2 \gamma_{SL} - r^2 \gamma_S$$

Assignment

$$\frac{\Delta G^{total}}{4\pi} = \frac{L(T_m - T)}{T_m} \cdot 4\pi(r^2 t - t^2 r) + r^2(\gamma_L - \gamma_S) + (r-t)^2 \gamma_{SL}$$

$$\frac{\partial (\frac{\Delta G^{total}}{4\pi})}{\partial t} = \frac{L(T_m - T)}{T_m} \cdot 4\pi(r^2 - 2rt) + (2t - 2r) \gamma_{SL}$$

$$= \frac{L(T_m - T)}{T_m} \cdot 4\pi r(r-t) + 2(r-t) \gamma_{SL}$$

So, what you can do? You can write down this expression in a nice manner, $L\left(\frac{T_m - T}{T_m}\right) 4\pi(r^2 - 2rt) + (2t - 2r) \gamma_{sl}$, right. So, this is something which is the actual expression.

(Refer Slide Time: 33:48)



Thermodynamic Model

$$\left(\frac{\partial G}{\partial t}\right)_{k \rightarrow 0} = 0$$

$$\frac{L(T_m - T)}{T_m} = \frac{2\gamma_{sl}}{r-t}$$

$$t \rightarrow 0$$

$$\frac{L(T_m - T)}{T_m} = \frac{2\gamma_{sl}}{r}$$

$$T_m^{Nano} = T = T_m \left(1 - \frac{2\gamma_{sl}}{L_0 r}\right)$$

$$L\left(\frac{T_m - T}{T_m}\right) = \left(\frac{2\gamma_{sl}}{r-t}\right)$$

$$t \rightarrow 0$$

$$L\left(\frac{T_m - T}{T_m}\right) = \left(\frac{2\gamma_{sl}}{r}\right)$$

$$T_m^{Nano} = T = T_m \left[1 - \left(\frac{2\gamma_{sl}}{L_0 r}\right)\right]$$

So, as you decrease the particle size, the effect of r becomes stronger; this factor increases substantially because γ_{sl} for a particular system is constant and L_0 for the particular system is constant.

So, once you do this analysis properly; that means, once you assume $\text{At } \frac{\partial \Delta G^{total}}{\partial t} = 0$. Then,

what you get? You will get this expression. $L\left(\frac{T_m - T}{T_m}\right) = \left(\frac{2\gamma_{sl}}{r-t}\right)$ ok.

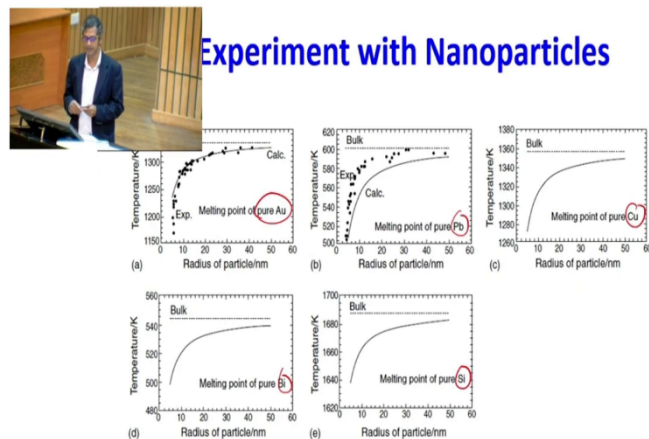
So, if you assume $\rightarrow 0$, then it becomes $L\left(\frac{T_m - T}{T_m}\right) = \left(\frac{2\gamma_{sl}}{r}\right)$, ok. We are making T as $T_m^{Nano} = T = T_m \left[1 - \left(\frac{2\gamma_{sl}}{L_0 r}\right)\right]$. So, this is the relationship which can be easily obtained by using this model.

So, therefore, melting temperature of any nano particle is given by this expression. So, it is getting reduced by a factor $\frac{2\gamma_{sl}}{L_0 r}$. So, as you decrease the particle size, the effect of r becomes stronger, this factor increases substantially because you know γ_{sl} for a particular system is constant and L_0 for the particular system is constant.

So, therefore, the factor which is playing a role is the melting r or radius of the particle, some part of this we discussed already in some lectures before, but this is the thermodynamic model which can be increased. So, as you clearly see this $\frac{2\gamma_{sl}}{r}$, this term is associated with increase in the internal pressure, resulting from the increase in the curvature of the particle.

That is we have seen. This term, ok, $\frac{2\gamma_{sl}}{r}$ is associated with increase of the pressure because of increase in the curvature of the particle decreasing particle size. So, variables like γ_{sl} , L_0 , r are all positive quantity. This means that upper melting temperature of a spherical particle decrease with the decrease in the particle size.

(Refer Slide Time: 36:12)



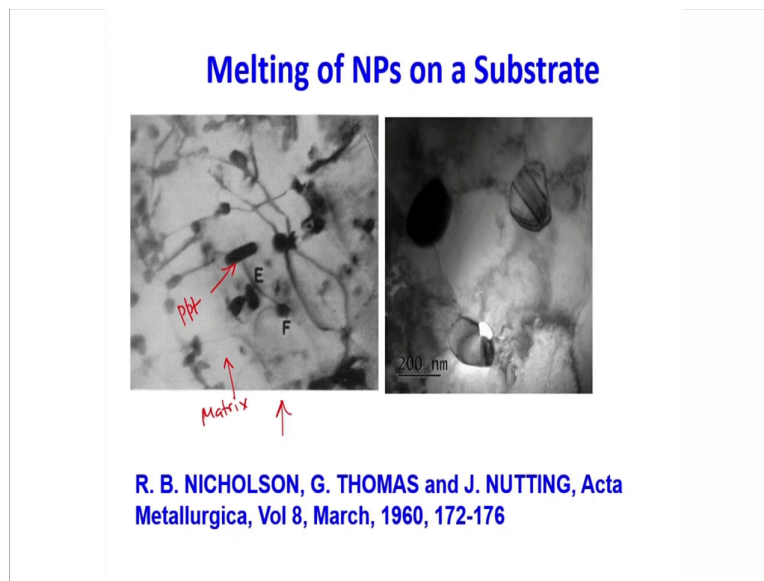
And I will show you some of these you know experimental results. But this is for the gold, pure gold. See, this is the bulk melting temperature, ok 900 something, and then as you decrease the particle size this is how the trend follows. So, about 40 nanometers so, decrease is not much, but it goes down to 10 or 5 nanometers decreases substantial, almost like a 200 degree Celsius, ok. Almost 150-200 degree Celsius decrease.

This is true for lead, this is true for copper, bismuth and silicon. Obviously, there is no experimentation experimental results are put up only, for the copper bismuth and silicon, but trends should be same. And that is what is observed in real picture. So, that means, the experimentations validates this model which I just now discussed.

So, nanoparticles will lead to decrease in the melting temperature. That is what is very clear. And these results also show that. Remember, these discussions are mostly for free nanoparticles, nanoparticles which has nothing on the surface, ok. I know I am making a big statement here because all this material nanoparticle may have oxide on the surface.

That is fine. But we are talking about nanoparticle coated with something embedded in some matrix, that is a completely different situation. So, I hope you have understood this model. And this calculation I would like you to do yourself and confirm. So, whenever we come back, we will discuss further.

(Refer Slide Time: 37:45)



Well. So, you know that is why we are going to change, and next 10 minutes or so, we are going to discuss something different. So, that is discussion was mainly for the nanoparticles which are free, which are not embedded, which are not coated. But I have shown you some pictures earlier, and in fact, express the left-hand side picture you see this is the left-hand side picture. And in this picture, you can see nano particles are dispersed in a matrix, ok. This is the matrix, right.

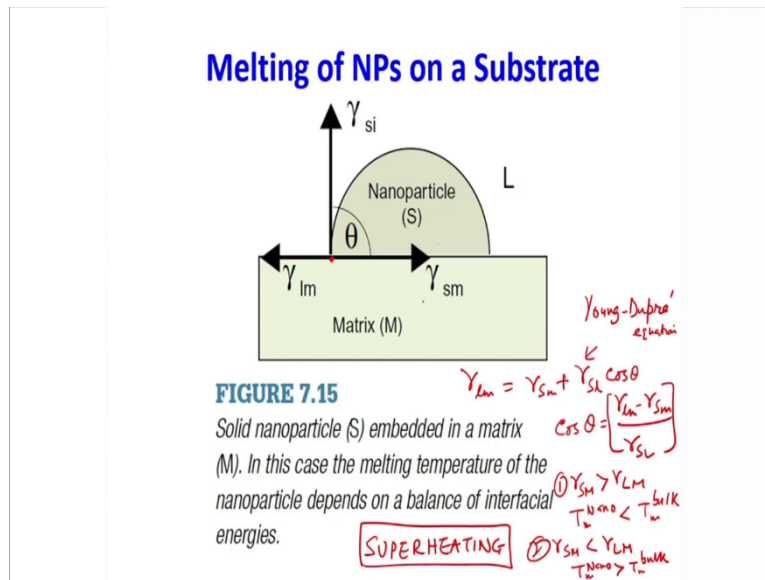
And here this is taken from Nicholson and Thomas, and nutting this is basically aluminum matrix. And this is the precipitates. So, that means, what? Here the precipitates are embedded in a matrix. So, what will happen, this kind of particles? Will they follow the same model? Obviously, not because here the particles are embedded in a matrix. So, their behavior will depends upon the matrix particle interface.

Remember, in the earlier model here, what is the model is using. When you see a free particle liquid is pointing on the surface. So, here the particle is not free. They are embedded. So, how the liquid will form? Between the particle in the matrix, that is why we will dictate how the melting will happen. So, let us talk a little bit about that.

Will this nanoparticle melt, as usual below the melting temperature of the bulk or not? Well, to answer this question, we need to consider the fact that surface of the nanoparticle is in

contact with the matrix instead of a being exposed to the surrounding atmosphere, like in the earlier case. Surface of the nanoparticle is covered or in contact with the matrix. Therefore, the interfacial area and interfacial energy per unit area, γ_{sl} which we have used must be energetically balanced by Young's theorem.

(Refer Slide Time: 39:43)



Young-Dupre equation

$$\gamma_{lm} = \gamma_{sm} + \gamma_{sl} \cos \theta$$

$$\cos \theta = \frac{(\gamma_{lm} - \gamma_{sm})}{\gamma_{sl}}$$

$$(1) \text{ If } (\gamma_{sm} > \gamma_{lm}) \rightarrow T_m^{nano} < T_m^{bulk}$$

$$(2) \text{ If } (\gamma_{sm} < \gamma_{lm}) \rightarrow T_m^{nano} > T_m^{bulk} \rightarrow \text{superheating}$$

What is that? What is that Young's theorem? This is what it is. So, if you have a particle sitting on a substrate, and there will be contact angle between the particle and the substrate. And this is where the surface energies are balanced. This is the point here. You see this is again taken from book of Michael Ashby and others. And you can write down very easily γ_{lm} is equal to; γ_{sm} equal to what? You can balance that. Cannot do that? You should be able to

do that. $\gamma_{lm} = \gamma_{sm} + \gamma_{sl} \cos \theta$, right. So, we can write down $\cos \theta$ which is the contact angle $\cos \theta = \left[\frac{(\gamma_{lm} - \gamma_{sm})}{\gamma_{sl}} \right]$.

This is what is known as this top equation is known as Young-Dupre equation, ok. This is again Thomas-Young, same guy who discovered double slit experiment of diffraction, ok. So, this is something which is very clear. So, that means, what? The γ_{sl} is now replaced must be energetically balanced by the other two surface energies. Remember, nanoparticle is embedded in a matrix, right. That is what we showed. Nanoparticle is embedded in a matrix.

So, therefore, matrix nanoparticle energies must come into picture. And that we must not forget to include, correct. So, therefore, γ_{lm} ; here γ_{lm} is what? γ_{lm} is the liquid matrix interfacial energy when it is molten, and γ_{sm} is the solid matrix interfacial energy per unit area, and theta is the what is known as the d wetting angle.

By arranging the equation, and if we assume theta to be 90 degree, that is what is shown here it can be shown here, there very easily when theta is 90 degrees when gamma sm is greater than gamma lm, melting temperature of nanoparticles should be melting temperature of nanoparticle should be less than the melting temperature of the bulk, correct. $\cos \theta$ when theta is 90 degree, $\cos \theta$ is what? 0. $\cos 90$ is 0.

So, therefore, the sign will depends upon $(\gamma_{sm} \text{ and } \gamma_{lm})$ correct. The energy sign will depends upon $\gamma_{sm} \text{ and } \gamma_{lm}$, very clearly. So, therefore, melting temperature in embedded particle, but when (1) If $(\gamma_{sm} > \gamma_{lm}) \longrightarrow T_m^{nano} < T_m^{bulk}$.

So, you have two situations here. You can clearly see, not one. In one case, you can have the similar situation like in the earlier, melting temperature nano particle will go down, in other case melting temperature can increase compared to bulk. That is very interesting, right. So, you can melt a particle nano size at a temperature higher than the bulk melting temperature. I know some of these things, we also do research in our labs.

So, this situation later one, now situation number 2, situation 2 is this one is known as super heating. Why it is called superheating? Because you are increasing the melting temperature

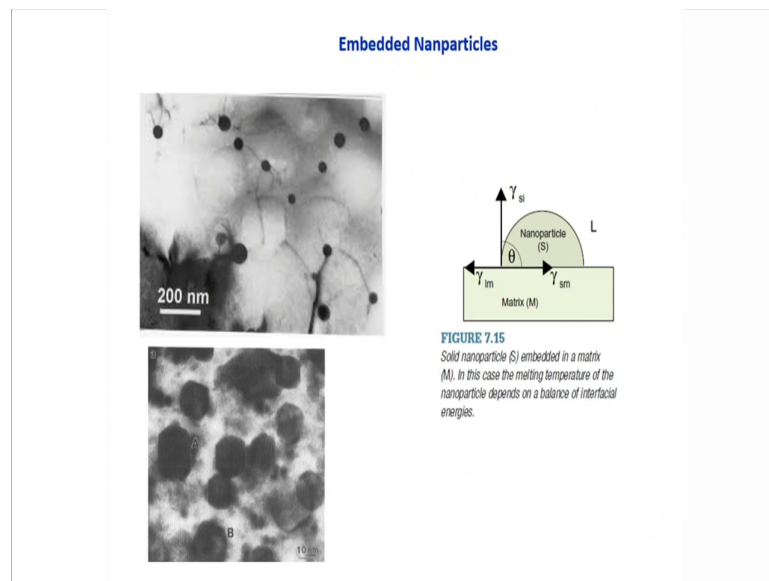
beyond the melting temperature of the bulk, ok. And see this you know, this mainly because of the interface between the matrix and the nanoparticle, ok.

So, you can see a γ_{sm} is what? γ_{sm} is matrix particle. So, matrix particle interfacial energy is lower than the liquid matrix interfacial energy ($\gamma_{sm} < \gamma_{lm}$). So, solid and particle, solid particle in the matrix interfacial energy is less than interfacial energy between the liquid and the matrix. So, liquid will not nucleate because liquid has there is a gain in keeping the solid in the solid form because energy is not gained by doing the process.

If I make that particle liquid, ok, we are not gaining any part of the energy because the system is saying that by keeping in solid form energy of the system will remain lower. So, that is why particle will try to remain solid as high as possible temperatures. And that is why the particle will get super heated. This is nicely described in Ashby's book. And if whatever I said everything of that is written nicely in the Ashby's book, except the derivation which is supposed to do as a part of a assignments.

So, this derivation which I did, I think this is should be your assignment. And all of you need to submit the assignments. This is lecture number 20. So, in lecture 21, before I load the upload the lecture number 21, you must you know come up solution of the assignment then and you will be graded for that also, ok. So, that is something we discussed.

(Refer Slide Time: 45:14)



So, there are a lot of examples of this embedded nanoparticles. Here I am showing some of these, ok. You know this you can see that some of the particles are in the matrix or something, ok. And in fact, this is very common in this system. So, let me stop here. So, we have discussed quite a bit in this class about the melting temperature, the pressure.

And then how what are the two different situations we discussed, one is the free, others embedded nanoparticles. And I describe to you different kinds of situations in case of nanoparticles. So, in the next lecture, we are going to talk about thermal transport. Thermal transport, how thermal transport happens and how it can be dealt with mathematically.

Thank you.