Nanotechnology Science and Applications
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Lecture - 10
Impact of the Nanoscale on the Hall-Petch Relationship

Hello, in this class we are going to look at the Impact of the Nanoscale on the Hall-Petch Relationship. We have been in the last couple of classes building up to this discussion, we have looked at the idea of those mechanical properties and what kind of properties we are interested in, we have also looked at the experimental process that will need to be involved for us to do this kind of a study to I mean understand the set of effects, that are going to show up when you go to the nanoscale if you are trying to look for mechanical properties.

So, with that background of both the mechanical properties as well as the experimental approach, now we look at the effect of the nanoscale on the Hall-Petch relationship.

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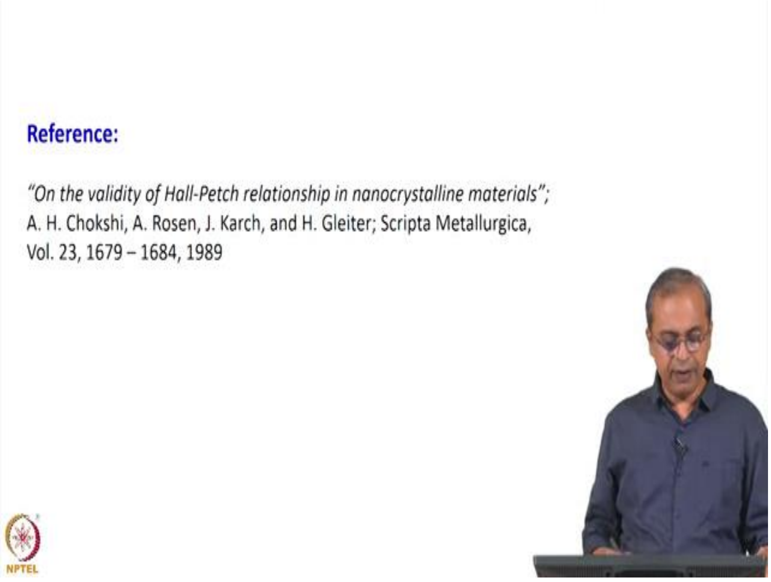

Reference:

"On the validity of Hall-Petch relationship in nanocrystalline materials";
A. H. Chokshi, A. Rosen, J. Karch, and H. Gleiter; Scripta Metallurgica, Vol. 23, 1679 – 1684, 1989

So, this is a very important reference in this context, this is the original work which basically highlighted this effect that we are talking about; it is called on the validity of the Hall-Petch relationship in nanocrystalline materials. It is a scripta met publication, you can see its a 1989 publication in the sort of the earlier days of studies into nanomaterials and nano technology and so on.

The authors are here Chokshi, Rosen, Karch and Gleiter and Chokshi is I mean this work is actually a very heavily cited work because it is very important contribution to some very fundamental aspect of what is happening at the nanoscale with respect to mechanical properties. So, I will draw your attention to this reference; please go look up this reference in your library if you are interested in more details of this work. It is the original work some of the discussion that we are having relates to ideas that were developed through this work.

So, if you want to see the original work, this is the original work that you should take a look up.

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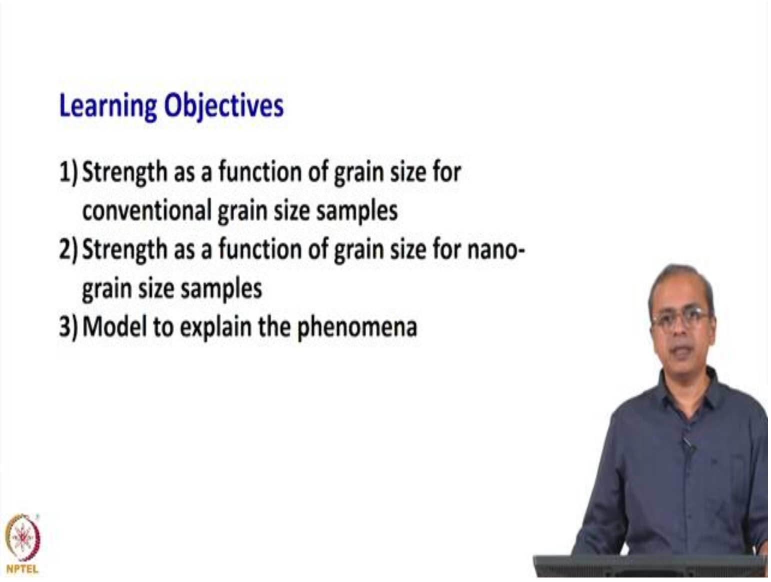

Learning Objectives

1) Strength as a function of grain size for conventional grain size samples
2) Strength as a function of grain size for nano-grain size samples
3) Model to explain the phenomena

So, our learning objectives for this class are to look at the strength as a function of grain size for conventional grain-sized samples to also look the strength as a function of the grain size for nano grain-sized samples. So, both conventional grain size samples as well as nano grain size samples and we already saw the process some of the experimental processes, that you can utilize to create these conventional grain size samples as well as to create these nano-sized grain size samples.

So, now we would like to look at the strength as a function of those grain size in both these regimes and once you see some data and you see some trend in the data etcetera to think of a model to explain that phenomenon. So, this is the idea that we would like to discuss through this class.

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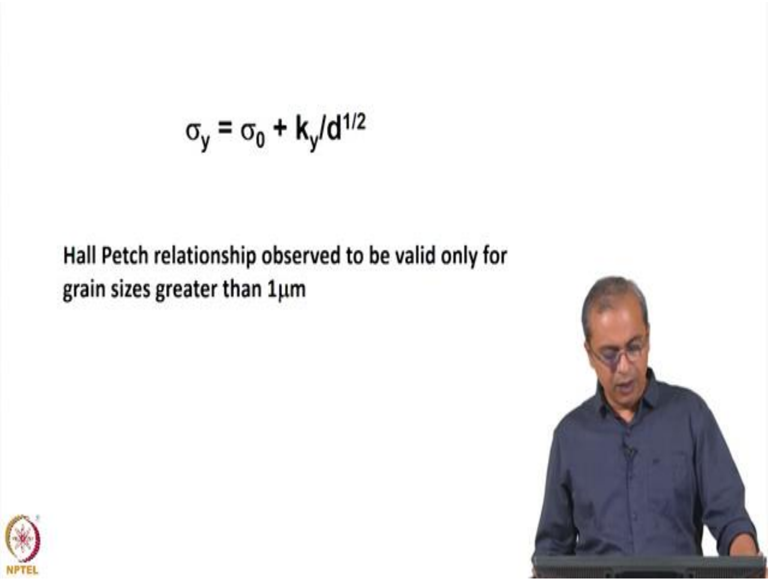

$$\sigma_y = \sigma_0 + k_y/d^{1/2}$$

Hall Petch relationship observed to be valid only for grain sizes greater than 1μm

So, we as we noted earlier this is the Hall-Petch relationship and it gives you the yield strength as a function of the grain size and there are constants here, there is a constant here and there is lattice friction constant here and so, those are two constants that we have. What is generally true and known of this relationship is that it is valid over a wide range of grain sizes.

However, generally, it has been observed that it is valid only till about a grain size of about 1 micron. So, if you go below this 1-micron grain size this relationship does not hold very effectively and that is an observation that people have had and, but that is the Hall-Petch relationship it is a very important contribution by itself to the field of material science because a lot of the treatment of materials.

So, that they will have the kinds of properties that we desire in a final product and which relate to cold working, reducing the grain size and so, on are related to this understanding that if you reduce the grain size, your yield strength will go and so, therefore, this is a very important relationship. And therefore, any deviation from this relationship is also very important for us to recognize and to also understand and that is the idea of this activity.

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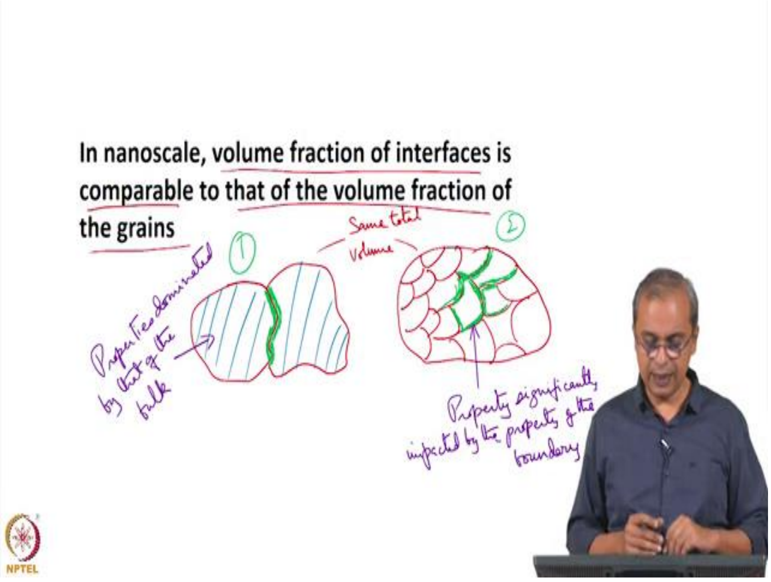

In nanoscale, volume fraction of interfaces is comparable to that of the volume fraction of the grains

So, what is special about the nanoscale and why should it matter at all with respect to say mechanical properties or any other properties? The idea that is relevant to the nanoscale which is what is mentioned here is the primary idea that makes a difference from the perspective of size scales. And, that is that the volume fraction of interfaces volume fraction associated with the interfaces is comparable to that of the volume fraction of the grains itself.

So, now if you take two grains if it, if I take grain that size and I take another grain here; so, then this is the boundary area that we have, the interface that we have between these two grains. And if you have a sample that is full of such grains, then you will have interfaces of that nature and of course, the final exterior surface would also be a surface of interest, but this is the interfaces that we have. Now if you associate a certain volume an interface by definition is a two-dimensional structure, it is just the point of contact between two solids that is a interface.

But generally, if you look at it at atomic level what happens is, you have perfect atomic order here and you also have perfect atomic order here. But as you get close to the interface, as you approach the interface itself the atomic order begins to start getting bit disrupted and if you do see I finally, at the interface you have some bonds which are sort of broken and they are not complete and so on.

So, generally speaking even though the interface is a two-dimensional entity, we assume a certain small amount of thickness around that interface where the influence of that interface is very significant. And so, within that small thickness that you associate with that interface which I am just going to exaggerate here by putting this kind of thickness here. We will assume that in this thickness the impact of the interface is significant. So, some finite thickness basically it is not a zero thickness if there is some finite thickness associated with that interface over which the influence of that interface is significant.

And therefore, even though as I said the interface should ideally be thought of as a two-dimensional structure, we can assume a certain volume with respect to the interface which is the volume over which its effect is perceived or felt. Now clearly if you take a nanostructured material, where the same amount of volume I will draw this roughly the same amount of volume I am drawing here. And, I have a nanostructured material, I mean already something that is significantly smaller in size in crystal size.

So, if you have a slightly smaller structure like this, smaller grain size like this for the same volume that you are seeing here for basically these two have the same amount of volume, same total volume. Clearly, the amount of interface that is available here and I am just going to highlight a little bit of it, not all of it you can see here that you have interface here, you have interface here and so on. So, if you assume some volume for this interface, clearly in case 2 that that which I am just currently highlighting the amount of volume associated with that interface is significantly high for the same total volume. Same total volume the amount of volume associated with this interface is going to be much higher then so if this is 1 and this is 2.

In case 2 the volume fraction associated with the interfaces is going to be much higher than that in case 1 and if you continue this into the nanoscale. So, if the nano scale asset is the distance between atoms is only about two angstroms and so, if you take 1 nano meter you have only 5 atoms. So, if you take 1 nanometer you have only 50 atoms. So, once you have 50 atoms at in a 10 nanometer scale and you have crystals which are only about 50 nanometers across, then even if you assume like 3-4 nanometers across that, I am sorry 3-4 angstroms across the interface as being related to the interface you are already having a significant fraction of the total volume associated with that interfaces.

So, they become start becoming comparable therefore, normally in the macroscopic samples when you look at properties, the property is dominated by the presence of the in this case property. So, in case 1 the property that you measure is dominated by the property of the bulk or the bulk of the volume of that sample. So, the volume of the grain, therefore, dominated by the grain itself. In this case property is now significantly impacted by that, by the property of the. So, the property is now significantly impacted by the property of the boundary or these boundaries that are present.

So, that is the primary difference between the macro scale and the nanoscale and therefore, phenomena which were associated which are associated with the boundary even though they had some impact not zero impact non-zero impact it had even in the case where the grain sizes were large, but the extent of the impact was minimal. Here because the amount of volume associated with those grain boundaries is high, the extent of their impact on the overall property that you measure is also very significant. So, that is the idea of this nanoscale and that is also something that is now relevant with respect to the mechanical properties.

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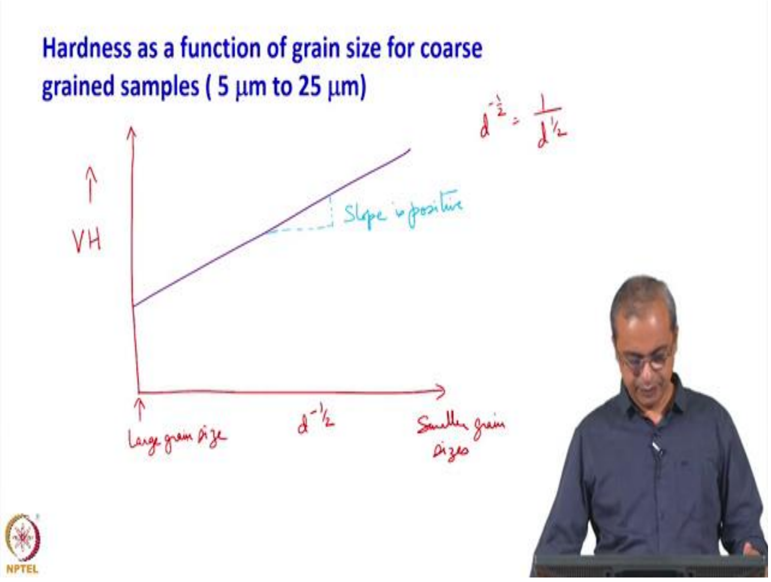

Hardness as a function of grain size for coarse grained samples (5 µm to 25 µm)

So, now if you look at, we just draw a schematic here, you can look up actual values for various systems in the literature including in that paper that we that I have mentioned the original paper where this work was carried out for the first time. So, if you look at hardness as a function of grain size for coarse-grained samples, where the grain size is 5 microns to about 20 microns. So, if you just draw here say Vickers hardness. So, I just write VH which increases that way and this is $d^{-1/2}$. So, if it is $d^{-1/2}$. So,

$$d^{-1/2} = 1/d^{1/2}$$

So, clearly when the and d is the average grain size. So, as the d increases $d^{1/2}$ increases and therefore, $d^{-1/2}$ decreases. So, therefore, this area this region here is large grain size and this side is smaller grain sizes. So, if you go from left-right, you are going from a large grain size to smaller grain size. If you do this then as you can expect from the Hall-Petch relationship, the plot that we see is something like this you see a linear behavior and you get a positive slope. So, you see linear behavior and you have a positive slope.

So, this is the classic Hall-Petch behavior that the most macroscopic I mean most samples which have coarse grain size in the range of 5 microns to 25 microns, they are going to show you this behavior and that is the behavior that you will see. And generally, it is as I said it is observed that if you go to 1-micron grain size and significantly below that, this relationship does not seem to hold. So, that is something that we see.

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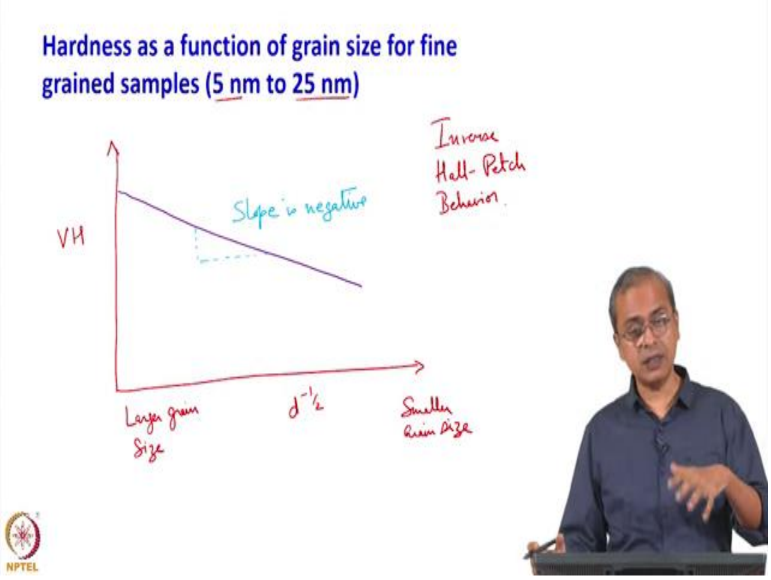

Hardness as a function of grain size for fine grained samples (5 nm to 25 nm)

Now, we look at a smaller grain size we are looking at say 5 nanometers to 25 nanometers previously we looked at 5 micrometers to 25 micrometers. So, now we are looking at 5 to 25 nanometers and if I make a similar plot; so, once again this is smaller grain size, and this is larger grain size and this is Vickers hardness. So, if you do this for these kinds of samples in the 5-nano meter to 25-nanometer range, you see a trend that looks like this. So, again the trend is linear, but the slope is now negative. So, the slope is no longer positive the slope is negative.

So, if you go back now you can see here this is the slope is positive, when you are in the 5 micrometers to 25-micrometer range, you are going from large grain size on your left-hand side to small grain size on your right-hand side. The slope is positive it means that as you reduce the grain size, the hardness is going up and we related hardness as approximately being related it's proportional to the yield strength. So, it also means that as the grain size is going down the yield strength is going up of that material and so, this is a very useful thing to know because you can make the material stronger by simply reducing its grain size and so, that is basically the idea that was captured by the Hall-Petch relationship.

Now the same phenomena when you study it for nano grain sized materials, we find the opposite the slope is negative; therefore, it means that when you are in this 5-nano meter to 25-nanometer size scale than when you go from about 25 nanometers to 5 nanometers. So, you are reducing the grain size which means you are going again from left to right on your on the axis that you see on the x-axis, these strength is actually coming down.

So, the slope is negative. So, this is referred to as the inverse Hall-Petch behavior. So, this is very useful and very important to know because in all of science that is basically what we do? We look at some experimental phenomena and we try to fit a theory to it. So, some experimental phenomena that has not been either not been observed before or it has been observed before it, but for which we do not have a good explanation.

So, we try to come up with an explanation we come up with a theory and so, the trend that was there in the grain size-related impact on yield strength was the phenomena that had been explained previously by the Hall-Petch equation. Now you see a trend that is opposite of that and therefore, that is a very significant deviation we are not looking at something that is a slope was high and, in the slope, slightly decreased under some circumstances it is not even like that. Even that would require some interesting explanation, but here that is within the same system.

Here for the same system, you may be going from something that has a positive slope to something that is the opposite trend which is the negative slope and therefore, when you say that the Hall-Petch relationship a relationship has now been inverted, that is a very dramatic change in behavior and therefore, scientifically very interesting to observe and scientifically very interesting to try and investigate and explain.

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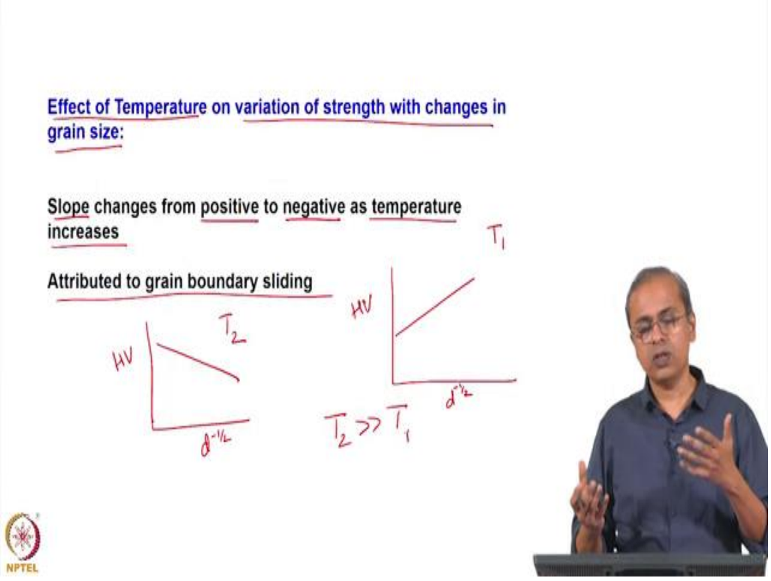

Effect of Temperature on variation of strength with changes in grain size:

Slope changes from positive to negative as temperature increases

Attributed to grain boundary sliding

So, to look at various possibilities associated with this phenomenon, if you as I said you can again look at lot of the discussion that is there in that original paper various ideas are looked at and so, one is the effect of temperature itself. To see where can you pick up the ideas to understand what it is that you are seeing here. So, first let us look at the idea of the effect of temperature. So, it is known that there is something called the equi-cohesive temperature.

So, for many materials, for most materials, there is something called an equi-cohesive temperature and generally it is observed that, if you are below this temperature the grain boundaries are stronger. So, grain boundaries are stronger than the grain, I when you are at temperatures below the equicohesive temperature and therefore, having grain boundaries in the material makes the material stronger, that is the implication having more grain boundaries in the material makes that material stronger.

So, that is the implication of having in situation where you are describing it as saying grain boundary is stronger than the grain. If you go to temperatures above this; so, if you go to temperatures above the equicohesive temperature, then it turns out that the grain boundaries are weaker than the grain. So, for the same material having more number of grain boundaries makes the material weaker at higher temperatures. So, the equicohesive temperature is a temperature where the term equi means something is equal it means that at t equicohesive temperature, the grains are roughly as strong or as weak as the grain boundaries themselves.

So, both of them the grain as well as the interior of the grain as well as the boundary have roughly the same strength or roughly the same contribution to the strength of the material. If you go below n temperature the grain boundary becomes relatively stronger than the grain, if you go above n temperature the grain becomes stronger than the grain boundary and so, correspondingly you see a difference in behavior. So, this was explained by creep diffusional creep and grain boundary sliding.

These are two phenomena which we will see to various levels varying levels of detail in this sense of sequent classes. Diffusion creep is creep of atoms and vacancies along the grain boundary and grain boundary sliding is where one grain slides with respect to the other for the shape of that sample to change as opposed to dislocations moving through the grain.

So, the boundary itself is sliding. So, this concept of equicohesive temperature was explained by taking these phenomena into account diffusional creep and grain boundary sliding. And so, this is the effect of temperature on a material which has a certain number of grains and grain boundaries. So, that is the situation that we are that that has been explained previously with this kind of a system. Now, if you look at another variation on this again people have studied this variation, which is the effect of temperature on variation of strength which changes in grain size.

Where whereas, previously we just looked at one particular possibility, grain size is fixed you are simply raising the temperature or lowering the temperature. Here you take a certain temperature you look at a variation of strength with changes in grain size. So, effectively sort of the Hall-Petch relationship at one temperature, then you look at the Hall-Petch relationship for the same set of samples at a higher temperature and you keep raising the temperature. You keep on raising the temperature, if you cross some temperature you start seeing you see that the Hall-Petch relationship in inverts.

So, at much higher temperatures you find that the Hall-Petch relationship seems to invert and the slope changes from positive to negative as the temperature raises and again this is attributed to grain boundary sliding. So, this kind of behavior has been seen. So, it means that you draw the Hall-Petch relationship and you see a trend that that looks like that. So, this is the hardness Vickers and d power minus half and this is a T1 and then you would draw the same thing at T2 and you see something like this and where T2 is significantly greater than t1 and you see that this relationship has changed.

So, temperature effects on the relative strengths of grain and grain boundary have been investigated at two different degrees and so, this kind of phenomena have been seen before., But what has been observed is that when you go to the nanoscale, you do not have to go to high temperatures at room temperature, at the existing same temperature you see a behavior where at larger grain sizes it shows the Hall-Petch relationship, it follows the Hall-Petch relationship and at very small grain size, it shows you the inverse of the Hall-Petch relationship.

So, there is some relationship with that concept and what is being seen at higher temperatures, but they are not I mean you cannot just take it and take the phenomena and put it at the room temperature because the other phenomena that people have studied are at much higher temperatures which is what we just discussed. So, there is some interest to see if the you some ideas of this nature can be pulled together to explain a phenomenon, that happens at room temperature. So, variation of strength with grain sizes at room temperature.

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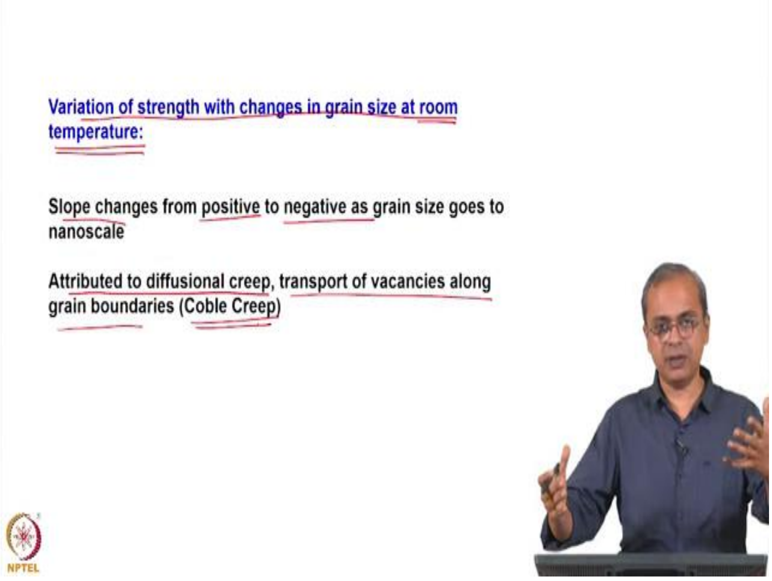

Variation of strength with changes in grain size at room temperature:

Slope changes from positive to negative as grain size goes to nanoscale

Attributed to diffusional creep, transport of vacancies along grain boundaries (Coble Creep)

So, that is that inverse Hall-Petch relationship that the work, that we have put our f given the reference to studied and brought out. So, this is at room temperature not at a higher temperature, and they also see that slope changes from positive to negative as grain size goes to the nanoscale. And since then lot of people have reported similar such behavior in variety of systems and that is basically the scientific process.

So, once that is why you get lot of credibility if you are the first to observe some phenomena that is very interesting and the first to explain it, because if that is a general concept if that is really something general to nature that you have discovered, then there is a good chance that in systems of similar concept you will see the same process being demonstrated. So, this is also attributed to diffusional creep and transport of vacancies along grain boundaries also referred to as coble creep.

So, except that now this creep, creep is a phenomenon where a material appears to have less strength and therefore, changes its shape at even relatively lower loads simply because the temperature is high at high temperature it keeps slowly deforming and that is called creeping. So, this is usually a high-temperature phenomenon, but in this case, we happen to be seeing it at room temperature, simply because you have a sample where the grain size is extremely small. So, you are sort of seeing a high-temperature phenomenon at room temperature, simply due to the presence of a very large number of grain boundaries.

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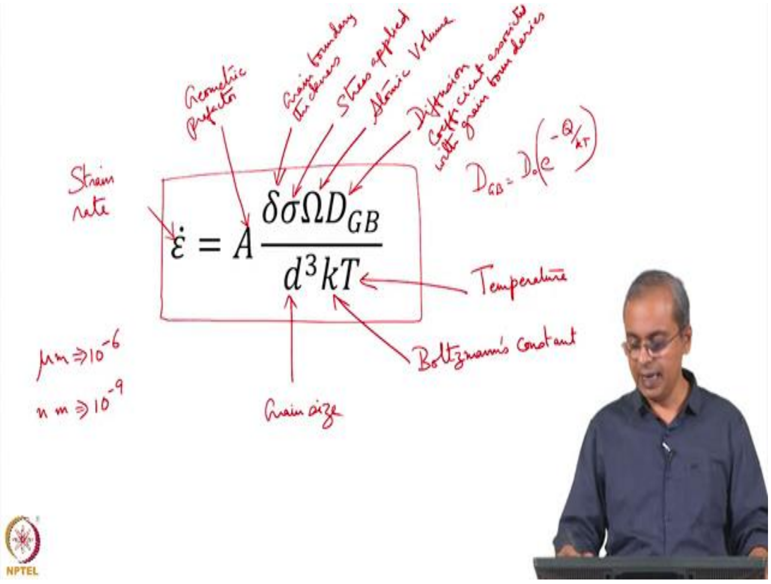

$$\dot{\varepsilon} = A\frac{\delta\sigma\Omega D_{GB}}{d^3kT}$$

To understand that let us look at the equation which is which sort of captures this idea of the coble creep or the diffusional creep. So, what you have here is the strain rate. So, that is epsilon dot, this is some geometric prefactor for this equation, this delta here is the grain boundary volume, grain boundary thickness sigma here is the stress that you have applied, this is the atomic volume omega capital omega is the atomic volume, this is the diffusion coefficient.

So, it is a diffusion coefficient associated with the grain boundaries this d there, this is the temperature t, this is your Boltzmann's constant, this is your grain size. So, we have lot of parameters here now we have to see the relative effects of these various parameters. So, clearly as your grain size goes down, what happens is the d is in the denominator. So, you have d^3 in the denominator. So, if you go from 10^{-6} which is the micron scale. So, micron-scale a micrometer is 10^{-6} nanometer is 10^{-9}.

So, d is now going down by three orders of magnitude and therefore, d^3 is now going to go down by 9 orders of magnitude and that is in the denominator. So, therefore, you are seeing a huge impact of it when you go from micro scale to nano scale. So, some something that is going down in is a parameter that is in the denominator, that is going down by several orders of magnitude its suddenly going to change the strain rate associated with the system. You will also find that t is in the denominator.

So, you will expect that at first glance, it looks like if the temperature raises it is actually going to reduce the strain rate associated for the same stress how quickly is the strain changing in the system in other words how quickly the material is deforming. You would it looks like because the temperature is in the denominator, if you raise the temperature perhaps the strain rate will come down, but actually you see the opposite effect at as the temperature rises, the strain rate actually goes up and that is because of the diffusion coefficient. The diffusion coefficient itself

$$D_{GB} = D_0 \times e^{-\frac{Q}{kT}}$$

So, it is a thermally activated process and so, as the atoms vibrate if they want to diffuse if they see a vacancy, they have to go past a barrier and a complete the movement and that is thermally activated. And so, as you raise the temperature the activation energy barrier comes down and you are able to, I mean for the same activation energy barrier you are able to push it past that barrier very easily.

And therefore, this has a significant temperature component associated with it and since that is in the exponent its impact the impact of temperature there is significantly higher than the impact of the temperature in the denominator that you see. So, therefore, the impact of the temperature the denominator is not as much as the impact it has on the diffusion coefficient itself. So, you see that this is the equation that comes together and you can see here very clearly the impact of the d which is your grain size, and how it dramatically changes the situation when you go to extremely small grain sizes.

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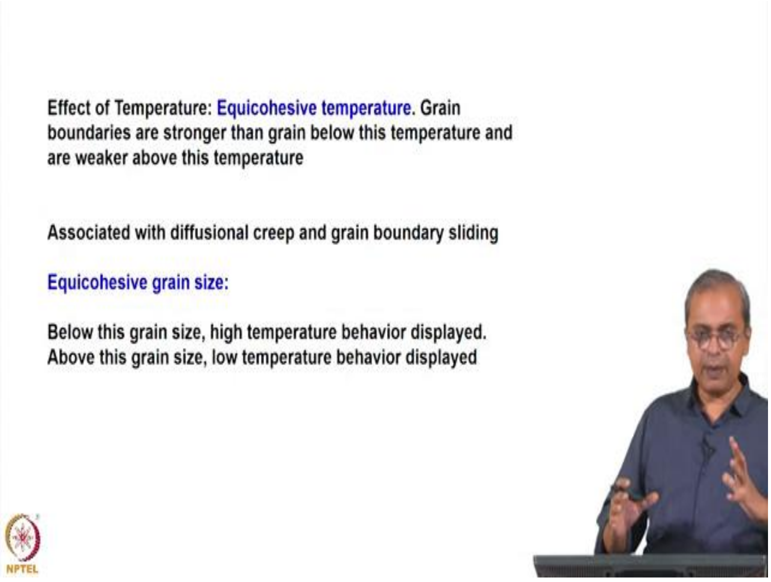

Effect of Temperature: **Equicohesive temperature**. Grain boundaries are stronger than grain below this temperature and are weaker above this temperature

Associated with diffusional creep and grain boundary sliding

Equicohesive grain size:

Below this grain size, high temperature behavior displayed.
Above this grain size, low temperature behavior displayed

So, if you bring these ideas together in some comprehensive manner, we see here that the effect of temperature is captured by this equicohesive temperature we already saw that. So, if you raise the temperature there is a temperature above which the grain boundaries are weaker than the grain, and below this equicohesive temperature the grain boundaries are stronger than the grain. So, that is an idea that we saw. And it is associated with the diffusional creep and grain boundary sliding. Similarly, the original work on this area suggest that you can even have something called equi-cohesive grain size.

An idea that they proposed where basically says that below this grain size high-temperature behavior is displayed, which means below this grain size the material acts as though it is sitting at high temperature which means creep is high, which means grain boundary is weaker than the grain. So, at high-temperature grain boundary is weaker than the grain and. So, having large number of grain boundaries makes the material weaker, but this is now happening simply because the grain size is very small at very small grain size it is showing behavior as though it is at high temperature at large grain size it is showing behavior as though it is at low temperature.

So, you can think of equicohesive grain size as a concept, where at grain sizes are smaller than this the material shows you behavior similar to what the material would display if it were at high temperature, and at grain size is larger than this it shows you behavior that is similar to what this material would show at room temperature or thereabout. So, this is the idea that is nicely sort of brought out by the level of thought and study of this phenomenon.

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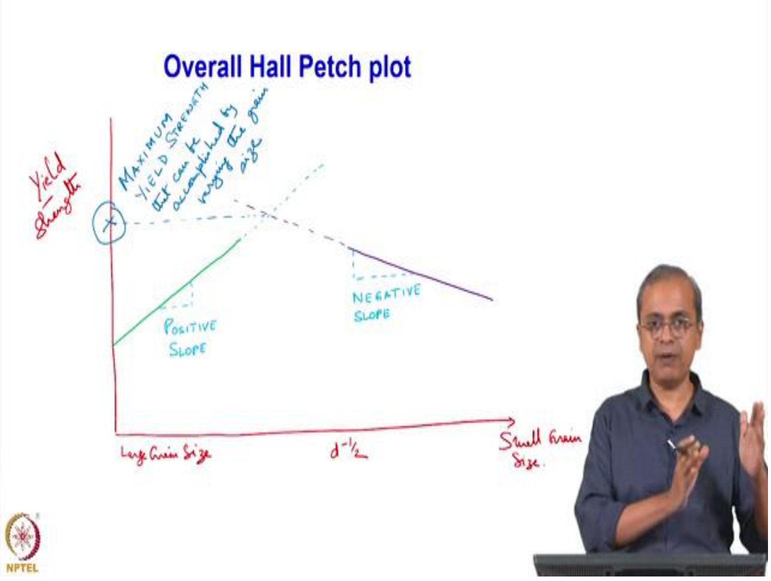
Overall Hall Petch plot

So, if you look at the overall Hall-Petch plot now. So, this is a yield strength and this as I said is large grain size, this is small grain size. Then what we see is a situation where you see that when you are going from large grain size and decreasing in grain size, initially you see early situation which where you are seeing a positive slope and the strength is increasing. So, you can sort of extrapolate that, and then when you go to very small grain sizes and you look at what is happening with respect to grain size as you change the, what is happening to the strength, as a function of increasing or decreasing grain size, then you see a trend that looks like this.

So, you can extrapolate that. So, you can see here we have a positive slope here and we have a negative slope here. And can just extend this some more. So, that is what we have here. So, you can see here there is a certain maximum value, there is a certain maximum value that you can get here which is the value that you see here. So, in other words in most material systems to the extent that you can alter its mechanical property to the extent that you can alter its strength using grain size by manipulating the grain size, there is a certain maximum yield strength that you can get that you can accomplish by varying the grain size.

So, there is a certain maximum strength that you can accomplish by varying the grain size on either side of it is going to decrease on either side of it the strength of that material is going to decrease. So, this is some very useful information to have from as a material scientist, who is trying to maximize the property that you can get from material for some induce that you are trying to put it to and naturally most of the time we are looking for improved strength. And so, the maximum strength that you can get from the material using any process, that is available in the in that system is always a very useful piece of information to know and so, that is something that we can understand from this plot.

May perhaps similarly you can do for other phenomena, where you have conflicting or contradicting a process being displayed by the system where at some scale you are seeing someone version of the property. And, another scale you are seeing a different trend in the property, then you can do optimization and you can find that meeting point where you are getting the best possible behavior from that material for the purpose that you want to use it for. So, this is sort of the overall Hall-Petch plot which sort of captures both the Hall-Petch relationship and the inverse Hall-Petch relationship.

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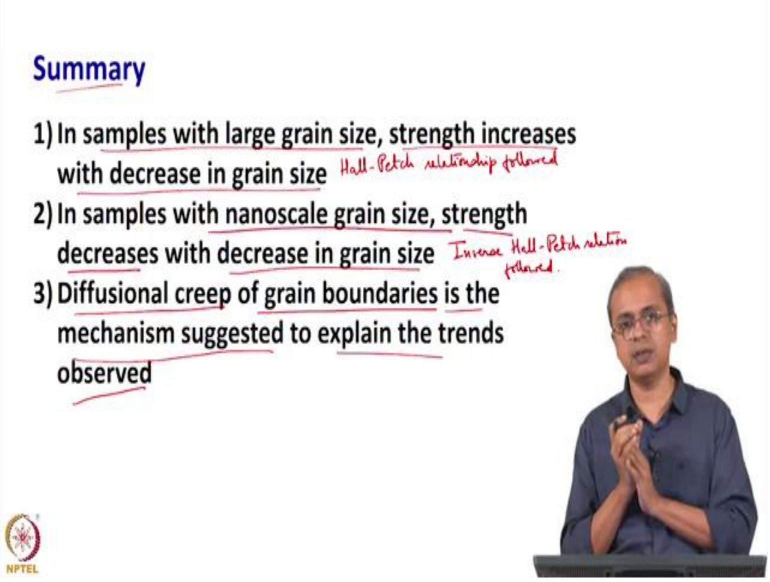

Summary

1) In samples with large grain size, strength increases with decrease in grain size Hall-Petch relationship followed
2) In samples with nanoscale grain size, strength decreases with decrease in grain size Inverse Hall-Petch relation followed.
3) Diffusional creep of grain boundaries is the mechanism suggested to explain the trends observed

So, in summary we find that in samples with large grain size strength increases with decrease in grain size and so, this has been seen before on many systems. So, this is the Hall-Petch behavior and this implies that the impact of the grain on the property is significantly more than the impact the grain boundary on the property Hall-Petch relationship followed. In samples with nano scale grain size strength is seen to decrease with decrease in grain size and so, this is inverse Hall-Petch relationship. And diffusional creep of at the grain boundaries is the mechanism that is suggested to explain the trends that are observed.

So, this diffusional creep is the creep of vacancies an atom along the grain boundary diffusional is creep that is occurring due to movement of atoms and vacancies along the grain boundary. So, atoms and vacancies can move through the grain as well as through the grain boundary, generally there are more defects at the grain boundary and therefore because there are incomplete bonds. So, therefore, the movement of atoms along the grain boundary is typically faster than it is through the grain.

However, in typical materials the amount of grain boundary that is available is less, therefore, if you total up the total number of atoms that are diffusing through the system, the fraction that diffuses through the grain boundary is less than the fraction that diffuses through the grain and that is how you see the overall diffusion coefficient of that material. But when you have more and more grain boundaries the fraction that is diffusing through the grain boundary, I mean keeps increasing at some point equals or supersedes the amount that is going through the grains and therefore, you see the creep associated with the grain boundary.

And therefore, if a phenomenon is being impacted by it, in this case, the strength is being impacted by it the strength gets impacted by this diffusion of grain. So, that is the overall summary for this class and it captures this idea of what changes are happening when you go to the nanoscale with respect to mechanical properties and as I said it is a very important and very interesting phenomenon to see because it brings out this idea that the nanoscale is something different.

As I said in one of our introductory classes, if you go to the nanoscale and you see no difference in trend you see no difference in properties if it is basically the same as what you would see in the microscale or the macro scale, then there is no great interest in the whole nanoscale. The interest arises only because we are seeing something which is significantly different sometimes even opposite to what you would see in the microscale and therefore, that whole process becomes interesting. So, that is what we have been able to highlight in these last few classes with respect to mechanical properties.

Thank you.