

Nanostructures and Nano Materials: Characterization and properties
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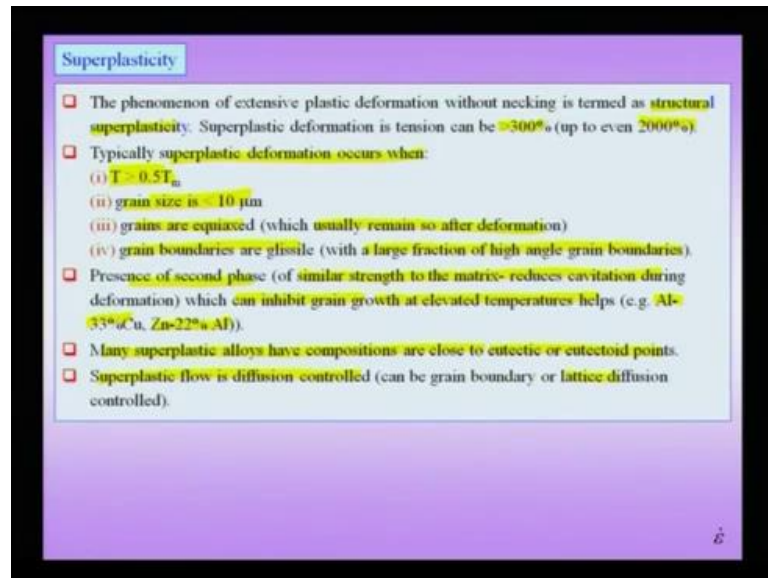
Lecture - 18
Defect Structure and Mechanical Behaviour of Nano Materials

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- Basics: ● Superplasticity ● Creep (mechanisms of creep)
- Testing of nanostructures and nanomaterials:
- How to synthesize bulk samples which can be tested easily?
- Grain boundaries in nanocrystals
- Intergranular glassy films
- What kind of mechanical behaviour should we expect in nanomaterials?
- Deformation of nanomaterials:
- Grain size and strength (Hall-Petch relation and the inverse Hall-Petch effect)

In normal plastic deformation suppose I take aluminium at room temperature or copper or one of the ductile materials. Then typically I get elongation of about few tens of percent.

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But there is a phenomena known as structural super plasticity in which case I can get elongations in tension up to more than 300 percent. And there are even reports of getting about 2000 percent of elongation. That means, this is really a drastic effect and as we shall see later that, the nanocrystalline solids or bulk nanocrystalline materials, we expect that, this effect is going be enhanced. Typically super plastic deformation takes place when the temperature if high, when the grain size is less than about 10microns that means,we are not really talking about nano scale grain size, but we are talking about micron scale grain size.

The grains, if they are equiaxed it helps and especially, so if they remain so during and after deformation and the grain boundaries are glissile. That means, they are pinned and typically that means that we have a large fraction of high angle grain boundaries. So, these factors tend to promote super plastic deformation in materials, so to summarize these factors, it is typically more than about $0.5 T_m$, which is we call the recrystallization temperature. The grain size is in the micron scale, the grains are equiaxed and we have a large fraction of glissile grain boundaries.

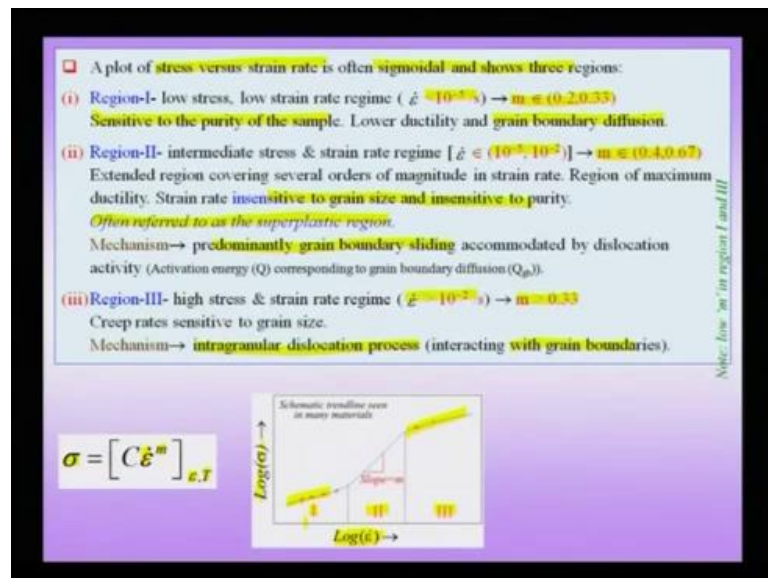
Presence of a second phase of similar strength to the matrix reduces the cavitations during deformation, and this which also can inhibit grain growth at elevated temperature, and this helps in obtaining super plastic deformation. Because even though I may start with an micron size grains if during deformation, because we are at high temperatures.

There is a tendency for grain growth, then what happens is that, we are going to have large size grains, and this would inhibit super plastic deformation or further plastic deformation.

Typical alloys, which are found to have super plasticity or are aluminium 33 percent copper, zinc 22 percent, aluminium alloys. Many super plastic compositions are close to the eutectic or the eutectoid points; that means having a eutectic or eutectoid composition helps in super plastic deformation. And typically super plastic deformation is diffusion controlled and this diffusion can be either lattice diffusion or can be grain boundary diffusion.

So, here briefly we have summarized some of the aspects, which contributes to super plastic deformation and they include material parameters, they include process parameters. Material parameters include their composition, the kind of grains we have got, the grain size, the process parameter, obviously includes temperatures. And we shall see that, it usually low strain rate, which actually promotes super plastic deformation.

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And if you look at typical materials, and you plot a stress versus strain rate curve, then you would notice that log of stress versus strain rate. And of course, you would plot normal stress or you could actually plot shear stresses, shear stress model behaviour. And this is typical of many-many materials though not all materials, and such a log stress versus strain rate plot shows 3 regions, region 1, 2, and 3.

In region 1 and 3 typically, the strain rate sensitivity is small. Of course, the way of obtaining such a curve would be to do an experiment at a certain strain rate and find a stress for a given strain, fixed strain, and then I would like to plot the result of such many-many experiments in the form of a log strain rate versus stress curve. And if I do so this is now result of many experiments, I would notice that there are 3 regimes, the region 1, where the strain rate sensitivity is small region 3, where there is an again strain rate sensitivity is small, but in the intermediate regime. But there is a region 2, where actually the strain rate sensitivity is high.

This region 2 is often referred to as the super plastic regime and herein we actually get the maximum elongation. And we also have to note that, the x axis being log strain rate, the region 1 corresponds to low strain rates, region 2 corresponds to intermediate strain rates, and region 3 corresponds to high strain rates. In normal materials, suppose I employ very high strain rates, then I would expect that there is going to be reduction in a phenomena like super plasticity.

The mechanism, underlying mechanism between these regions also change and the kind of sensitivity to purity of the sample also change. For instance in region 1, the sample purity plays an important role, it is very sensitive to sample purity. While in region 2, the sample purity and grain size are not, the material is not that sensitive to that, when I am saying sensitive it implies that there is a dependence, but it is not sensitive. In region 3 for instance, again the material is not that sensitive, it becomes again sensitive to the purity of the sample.

Now, the underlying mechanism for instance could be grain boundary diffusion as in the case of the region 1, it could be predominantly grain boundary sliding. And this grain boundary sliding is of course accommodated by dislocation activity and also some amount of diffusion, but that is region 2 mechanism. Well, in region 3 inter granular dislocation process with these dislocations interacting with the grain boundaries is expected to play an important role in the deformation of the material.

Therefore, if you look at to summarize this slide therefore, I am looking at a plastic deformation of a super plastic material, and I know that the curving equation is now at constant strain and temperature. That means, it is high temperature is the material, I am plotting here; that means, I can write stress as a strain, a strain rate power m , where m is

the strain rate sensitivity. And in the high, if the strain rate sensitivity is high, then I get long super plastic elongation large percentage elongation and this is the middle region in the curve.

Now, a very related kind of a phenomena to super plasticity is the phenomena known as creep. In creep 2 sometimes, we get long elongations, but the essential difference between, if you look at even the mechanisms often, the mechanisms between super plasticity and creep are very-very similar.

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Creep

- ❑ In some sense creep and superplasticity are related phenomena: in creep we can think of damage accumulation leading to failure of sample, while in superplasticity extended plastic deformation may be achieved (i.e. damage accumulation leading to failure is delayed).
- ❑ Creep is permanent deformation of a material under constant load (or constant stress) as a function of time. (Usually at 'high temperatures' → lead creeps at RT).
- ❑ Normally, increased plastic deformation takes place with increasing load (or stress)
- ❑ In 'creep' plastic strain increases at constant load (or stress)
- ❑ Usually appreciable only at $T > 0.4 T_m$ → High temperature phenomenon.
- ❑ Mechanisms of creep in crystalline materials is different from that in amorphous materials. Amorphous materials can creep by 'flow'.
- ❑ At temperatures where creep is appreciable various other material processes may also active (e.g. recrystallization, precipitate coarsening, oxidation etc.- as considered before).
- ❑ Creep experiments are done either at constant load or constant stress.

Creep can be classified based on

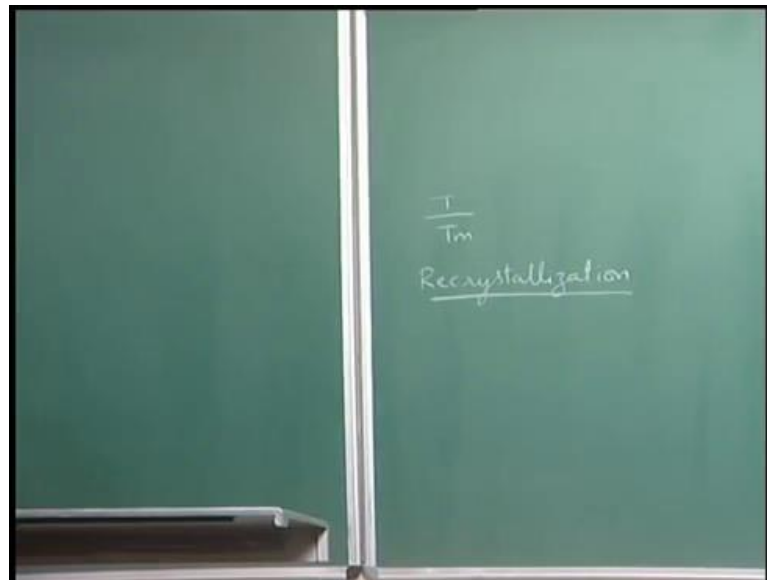
- Phenomenology
 - Harper-Dorn creep
 - Power Law creep
- Mechanism

And therefore, we can think of creep and super plasticity being as related phenomena. And typically these are again low strain rate phenomena, they are usually typically high temperature phenomena. But the important difference being, in creep we can think of as damage accumulation leading to the failure of the sample, while in super plasticity extended plastic deformation can be achieved. That means, accumulation of damage leading to failure is delayed in super plastic deformation.

So, what is creep? Creep is permanent deformation of the material at constant low. Previously, we had seen the uniaxial tension test, in uniaxial tension test we know that to cause further plastic deformation or to cause further even elastic deformation, we need to increase the load. That means, it is deformation with increasing load. But here in creep, actually the whole test is carried out at constant load or sometimes at constant stress. And you slowly progressively accumulate strain, but at constant stress or load.

And this with therefore, a typical result of such a creep experiment, we have plot of time versus strain. So, we are accumulating strain with time and therefore, you have a what is known as a creep curve. And this is as I pointed out is a high temperature phenomena, but we have to remember now we are talking about homologous temperature.

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That means, the relevant temperature is nothing but T by T_m . And if I am close to the recrystallization temperature or above it, then I would expect phenomena like creep becoming very important. Therefore, if you look at lead, lead is even room temperature is high temperature. Therefore, if you hang a load on lead wire, then actually lead will creep at room temperature.

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Creep

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Creep can be classified based on:

- Phenomenology: *Harpes-Dorn creep*, *Power-Law creep*
- Mechanism

Normally, increased plastic deformation takes place with increase in load, but in creep plastic deformation takes place at constant load. So, this is the basic definition of creep and this has to be kept in mind. And creep rates become appreciable only about 0.4 or 0.5 T_m .

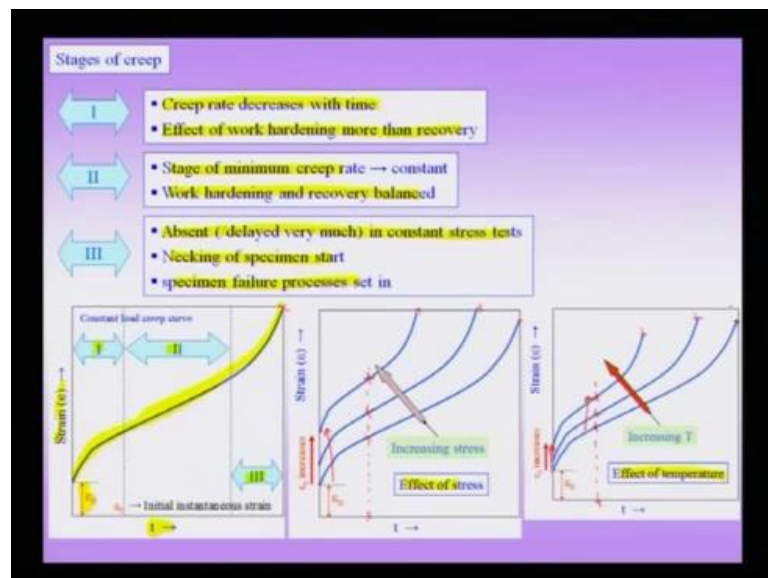
Mechanisms of creep in crystalline materials is different from that in amorphous materials, and for now we will restrict ourselves to creep in crystalline materials. Because, in amorphous materials, typically you have the mechanism of creep could be very similar to what we call viscous flow or Newtonian flow. While in crystalline materials we will see there are many mechanisms, which can contribute to creep and we will have a next slide, which will actually give a broad over view of these mechanisms.

It is important to note that at temperatures where creep is appreciable various other material processes may also become active. And these of course, may contribute to creep, they may what you call lead to failure, they may actually what you meant corrupt your creep data. But it is important to note that high temperature is a region of what you might call, all kind of thermally activated process taking place like this could be oxidation, this could be precipitate coarsening, this could be recrystallization, etcetera. And therefore, when there are parallely many-many process taking place, it becomes what you call complicated or difficult to ((Refer Time: 09:56)) you.

The pure effects of creep, these are the other effects, which can come in like oxidation, which could actually corrupt your data. Creep experiments as I pointed out are conducted either at constant load or constant stress, and creep can be classified based on either phenomenology. That means the kind of constitutive behaviour in which case you would call them power law creep or harper dorn creep some of these names come in.

But here we will focus on the mechanistic classification of creep, which is we will of course, consider in the side after this, but first we will take as I pointed out what happens when I load a material at constant load, of course and plot the strain with respect to time. So, similar to the case of super plasticity of course, there the axes were very-very different, there it was a plot of log strain rate versus log stress.

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But here I am plotting time versus strain and you get what you might call the 3 regions of creep. So, at time strain curve is the creep curve, and you typically observe 3 regions, region 1, region 2, and region 3. Initially of course, when you subject a material to a load, you will get some elastic deformation, which is the initial strain ϵ_0 , but with time this strain grows and therefore, you get a creep curve.

In region 1, the creep rate decreases with time, you can see the slope is downwards sloping; that means that the creep rate decreases with time and the effect of work hardening is more than recovery. That means that here the work hardening is

contributing to the increase in the strength of the material, which is actually leading to a decreasing creep rate.

In region 2, this is called a region of minimum creep rate and typically you can consider that as a constant rate of creep, because you can think of this as a linear portion in the curve and therefore, you can think of it as a constant creep rate. That means, that here the work hardening and recovery are approximately balanced. That means, whatever strength you are gaining by work hardening is sort of lost by the recovery processes and therefore, you are having a constant creep rate.

In region 3, which is the region leading finally, of course, if you want to draw it to a region where finally fracture takes place wherein, cavitations other damage accumulate to such extent the material actually fails. Then, you would notice that, this of course, region 3 could be absent or delayed in constant stress test. So, if you are doing a constant stress test this, this region may not be observed and if you do a constant low stress you may actually observe this. Herein, the necking of the specimen starts as many as I pointed out failure process like cavitations, etcetera.

And finally, this is the region where you would not like to operate your material in, because it is tending towards failure. Now, you can study the effect of stress and the effect of temperature on creep. And it is noticed that of course, if you load a material with increase and increasing stress it or more load, then you would see that the initial elongation increases. So, you have an initial elongation, which is increasing, which is now the elastic elongation with more stress.

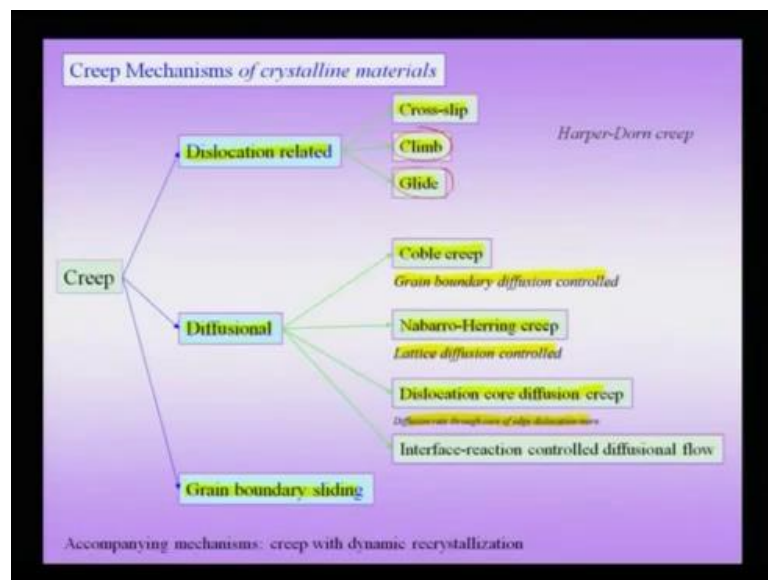
Additionally you would notice for a given time suppose, I draw a time axis here with increasing stress you would actually obtain an higher amount of strain, which is what is expected; that means, the material is going to fail in a shorter period of time. Suppose, this is my failure line and actually the material would fail at shorter time when you increase the stress, which is what is of course common sense expected?

On the other hand, the effect of temperature is very much similar to the effect of stress and herein, again you would notice that you have an increased initial elongation. Of course, the reason for this initial elongation is that, the elastic modulus actually decreases with an increase in temperature. Though this is not very-very sensitive to temperature

increase, but definitely there at least a 10 percent reduction elastic modulus is seen when you heat a material from room temperature to say, its melting point.

Therefore, this decreased modulus would imply that my initial elongation is going to increase, though it is a smaller effect than stress for instance on the initial elongation. And similar to effect of stress, you would notice that for a given time for instance I draw the curve for a given time. That means, in an increased temperature test actually I would have an increased strain, that means strain would increase at a constant time if you increase the temperature. That means, creep is going to proceed faster and which also implies that your specimen is going to fail sooner.

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So, this is the brief overview of super plasticity and creep, and later on we will actually get back to understanding that, why these kinds of creep and super plasticity is expected in the case of nano materials. And of course, we will also address a question how far the expectations are fulfilled. Now, what are the creep mechanisms, which can give rise to failure?

There are 3 kinds of mechanisms, which are important. The dislocation related mechanisms, the diffusion related mechanisms and grain boundary sliding mechanisms. And later on, we will see that when you go to nano scale materials, the deformation mechanism would actually change switch from slip to grain boundary sliding. And therefore, you can see that, why creep would be expected to become important in nano

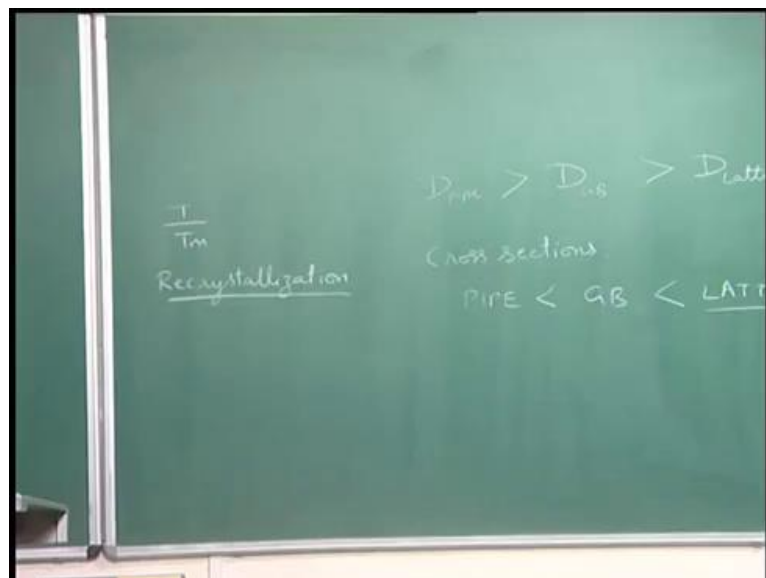
scale or nano grain sized materials. When you are talking about dislocation related mechanisms, there are 3 important phenomena, one is cross slip, one is climb and other is glide.

And as we know that glide requires, climb requires higher temperatures, because that involves vacancy diffusion and here, I am talking about climb of edge dislocations. Then, glide can also become more and more thermally activated. Therefore, at high temperature this is also glide is also going to get predominant. Diffusional mechanisms on the other hand, can involve either grain boundary diffusion or lattice diffusion.

And as it is obvious in a fine grain material, the grain boundary diffusion is going to become more and more important. And grain boundary diffusion phenomena for creep is called coble creep wherein the grain boundary diffusion is controlling the creep phenomena. And wherever the lattice diffusion is controlling the creep phenomena, it is known as the Navarro herring creep.

Additionally, diffusion at the core of this location which is called pipe diffusion can also influence creep. And the diffusion rate through the core of edge dislocation is more, because that is a region of free volume. Though we should notice very important thing that, when you are talking about lattice diffusion though.

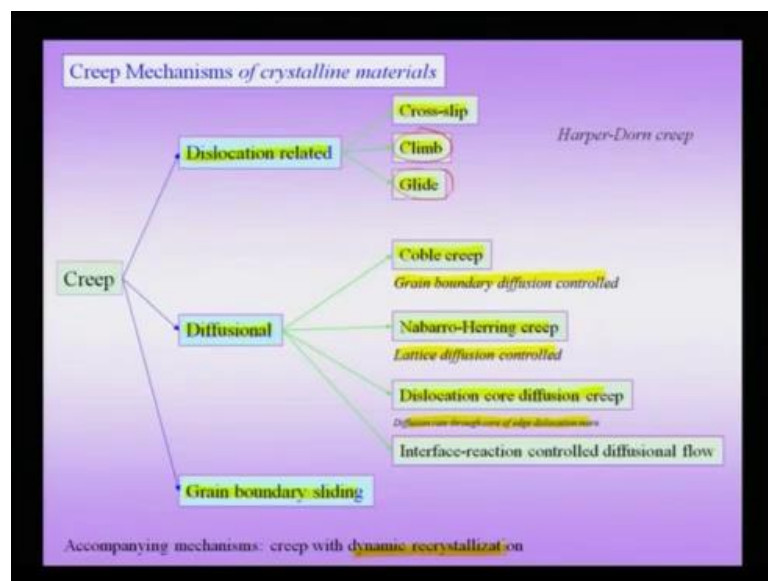
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And if I want write the diffusivity for these 3 phenomena, I can write down diffusivity of pipe being greater than the diffusivity of grain boundary diffusion, which is greater than the diffusivity of lattice diffusion. But this does not imply automatically that, the amount of matter transported by pipe diffusion is going to be more than the grain boundary diffusion, because the cross section of these is different. And typically in a normal material you will notice that, dislocation cross section for pipe is the smallest followed by grain boundary followed by lattice.

So, in normal materials, you would notice that it is lattice diffusion, which is going to sort of be prominent at normal grain sizes and normal temperatures. But, then at different rates of different strain rates, and different temperatures other phenomena can also become important especially in nano crystalline materials. And there it is important to note like in the case of creep, plastic we have pointed out and creep we have pointed out.

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There are accompanying mechanisms, which cannot be ignored like dynamic recrystallization, which play an important role. And finally, so we just to summarize this slide. There are three kinds of important mechanisms, which we need to enlist those contributing to creep, one is dislocation related mechanisms wherein, you have dislocation phenomena like cross slip of screw dislocations, climb of edge dislocations, and glide of screw and edge dislocations.

Diffusional mechanisms like, grain boundary diffusion, dislocation core diffusion, which is called pipe diffusion, lattice diffusion and also interface reaction control diffusional flow. Finally, of course grain boundary sliding is also an important mechanism, which can contribute to creep. Now, we will highlight a few points regarding these various mechanisms.

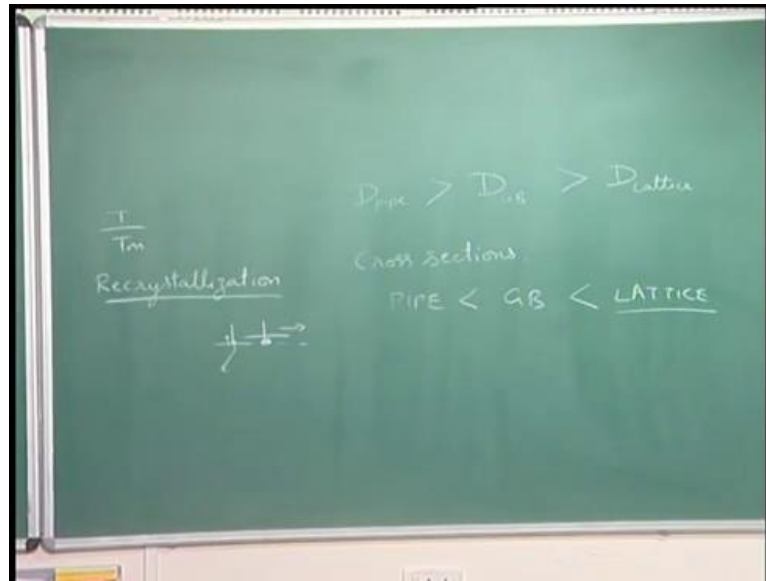
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The slide is titled 'Cross-slip', 'Dislocation climb', and 'Grain boundary sliding'. It contains three sections, each with a title and a list of bullet points.

- Cross-slip**
 - In the low temperature of creep → screw dislocations can cross-slip (by thermal activation) and can give rise to plastic strain [as $f(t)$].
- Dislocation climb**
 - Edge dislocations piled up against an obstacle can climb to another slip plane and cause plastic deformation [as $f(t)$, in response to stress].
 - Rate controlling step is the diffusion of vacancies.
- Grain boundary sliding**
 - At low temperatures the grain boundaries are 'stronger' than the crystal interior and impede the motion of dislocations
 - At higher temperature (GB being a high energy region) becomes weaker than the crystal interior
 - Above the *equicohesive* temperature grain boundaries are weaker than grain and slide past one another to cause plastic deformation

Cross slip is typically predominant in low temperature of creep wherein, screw dislocation can cross slip by thermal activation and give rise to plastic strain as a function of time. So, essentially if you are working at low temperature and you are studying creep, then this would be an important mechanism to consider. Edge dislocation piled up against obstacles and suppose you are talking about dislocation climb, edge dislocation piled up against obstacle can climb to another slip plane parallel to it and cause plastic deformation, which means that as a function of time you are going to get strain.

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So, we here, we are talking about edge dislocations, and for now I will schematically show it has being piled up at some kind of an obstacle, and this is on this slip plane. Now, at low temperatures this will get, this will remain stuck, but at high temperatures this can actually climb this dislocation to a parallel slip plane and continue to move. This implies I can actually get plastic deformation from those dislocations, which had become sessile at low temperature.

And in this case obviously the rate controlling step is going to be the diffusional vacancies, because climb case only possible by diffusion of vacancies. And the other way of looking at it is that, the atoms at the core atomic core which was here at the core of the dislocation or near the core of the dislocation actually diffuses out. That means, the dislocation climb by 1 height. In grain boundary sliding if you look at it, at low temperatures the grain boundaries are considered stronger than the crystal interior and impede the motion of dislocations. This is what we know from normal and this we have, this in some sense is the reflection of what we have always known as the hall patch effect.

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Cross-slip

- ❑ In the low temperature of creep → screw dislocations can cross-slip (by thermal activation) and can give rise to plastic strain [as f(t)].

Dislocation climb

- ❑ Edge dislocations piled up against an obstacle can climb to another slip plane and cause plastic deformation [as f(t), in response to stress].
- ❑ Rate controlling step is the diffusion of vacancies.

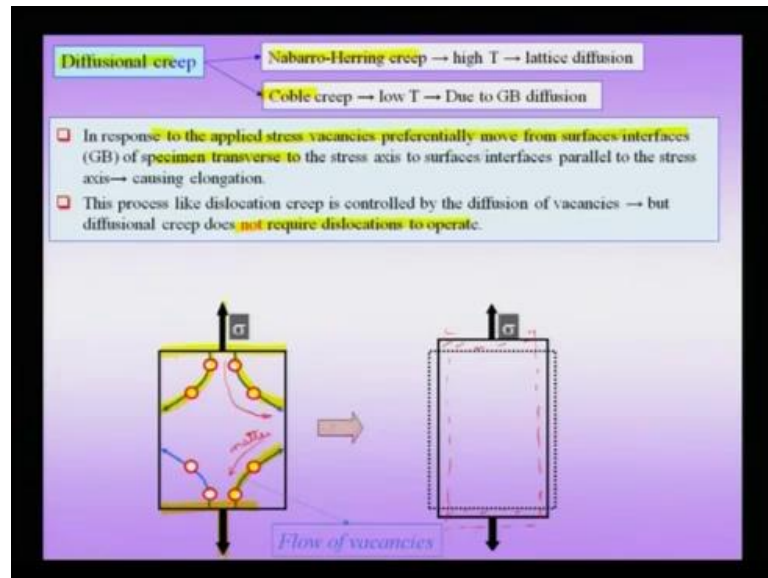
Grain boundary sliding

- ❑ At low temperatures the grain boundaries are *stronger* than the crystal interior and impede the motion of dislocations
- ❑ At higher temperature (GB being a high energy region) becomes weaker than the crystal interior
- ❑ Above the *equicohesive* temperature grain boundaries are weaker than grain and slide past one another to cause plastic deformation

At higher temperature, the grain boundary being the high energy region become actually weaker than the crystal interior and often sometime this is even described as the sort of a melting of the grain boundary at high temperatures. And this temperature where there is a crossover wherein, the grain boundary becomes weaker than the green interior or the crystal interior is called equi cohesive temperature.

And therefore, at high temperatures the grain boundaries can actually slide past one another to cross plastic deformation. So, inherently at high temperature, there can be switch in the mechanism of plastic deformation, and this we will is not only happening at high temperatures, but in equivalent way is actually reducing the grain size wherein, we observe a similar kind of effect in nano crystalline materials.

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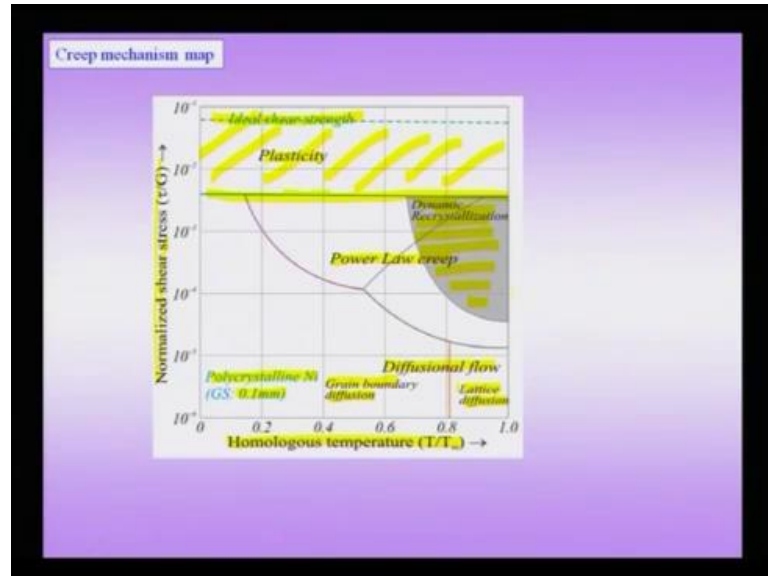
In diffusional creep, and we have already seen the 2 names associated with the Navarro herring creep, and the coble creep. In response to the applied stress, vacancies preferentially move such that, the specimen axis which is along the stress axis actually grows. And in effect what happens is that, so there is a diffusion of vacancies from the direction of tensile stress to the direction perpendicular, the face at perpendicular, which leads to a net elongation in the specimen that means I get this elongation purely by diffusional flow.

Therefore, you can have creep that means, strain accumulating as a function of time. And again like the case of the dislocation climb, this whole process is controlled by diffusion of vacancies. But obviously it is needless to say, for this mechanism to operate we do not require dislocation. Dislocation are not required for purely diffusional creep however, if you want climb mechanism for creep to take place, there has to be diffusional flow. Now, just to summarize this slide, in diffusional creep purely diffusion that means, diffusion of vacancies from the face at which has been loaded here, for this I am loading here to the face at which is perpendicular, so I have of diffusional flow of vacancies.

In other words, I can think of it as matter being transported along the opposite direction, so this is the direction of transport of matter. And this implies that, I am going to get an elongation purely diffusional flow that means, the material is going to progressively get longer in this direction. And of course, these are all exaggerated views, so the material

gets longer in this direction, the direction of the tensile axis, and therefore you can have accumulation of strain with time.

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Typically there is a map called the creep mechanism map, which puts together data from very many experiments and tries to identify regions of various mechanisms, which are operative. And typically, such a map would have a homologous temperature with normalized stress. There are other axis also possible in a creep mechanism map, but I just chosen one as an illustrative example. Wherein, I plot homologous temperature or of course, natural temperature with shear stress or normal stress and I would notice for this is a creep mechanism map for polycrystalline nickel.

And you can notice that, the grain size is large, it is of the order of 0.1 millimetre. I can see that there are various regions wherein, different mechanisms operative like of course, at high stress values plasticity. So, this is the line above, this is the dividing line above which you will have plastic deformation, which is the plastic deformation you expect that means, this is not typically a region of creep.

And of course, at even higher stresses, you have the ideal shear strength to the material, but if you look at high temperature regime and the low stress regime, which is the region below this plasticity regime, you have, for instance the region where you can have power law creep. You can have region, which is wherein the diffusional flow creep is taking place, And at very high temperatures, you have lattice diffusion dominated creep, but at

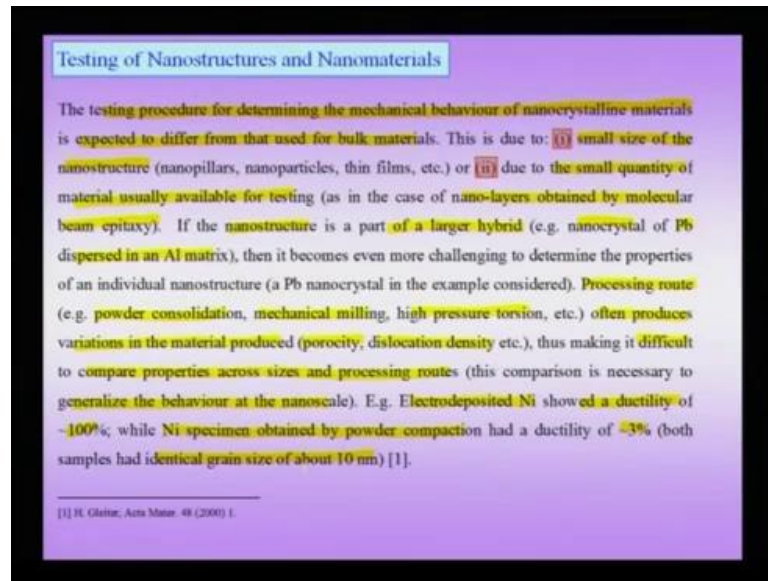
lower temperatures you have the grain boundary diffusion dominated creep. And there is a whole region, which is marked in grey, which is the region of what you might call dynamic recrystallization.

Therefore, I can put together data from various experiments, and I can identify mechanisms and such a map is called the creep mechanism map. And such maps are very-very useful, if have to understand the creep phenomena. Now, let us switch to the topic, to a different topic wherein, we will talk about testing of nano materials and nano structures. So far we have of course, talked about some basics regarding plastic deformation, we have talked about super plastic deformation, creep etcetera. But one important thing we have to remember is that, inherently bulk materials there are very standardized testing procedures over decades and they have been standardized.

And therefore, we know how to do tests on these bulk materials, we know how to interpret the data. But when it comes to testing nano structures and nano materials, there are very important issues, which is still being addressed. Often in many cases, there are no standard procedures like the ASTM available for testing such materials. And therefore, two things become important, how do I test these nano materials? And second thing, how do I interpret the data I get from each one of these test?

Like for instance suppose, I had a thin film, then I may do a hardness test on a thin film. On the other hand, I have a nano wire and I may do a tensile test or some kind of a nano tensile test on a nano wire. How can I compare these 2 data is an important question. And still of course, science is grappling with some of these questions and trying to correlate the results.

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So, let us address some of the important issues involved in testing nano structures and nano materials, and see how we can get around understanding the results of such tests. The testing procedure for determining the mechanical behaviour of nano crystalline materials is expected to differ that used for bulk materials, this is needless to say. And this is due to the small size of the nano structure, like there are some structures we have already noticed, they do not have any bulk counterpart at all. Like something I am talking about carbon nano tube, it does not have a bulk counterpart at all.

Suppose, I want to test nano pillar, then I may not be able to grow that nano pillar into large sizes in the form or with the properties I am looking for and therefore, they exist only in the nano scale. Secondly, the amount of material available for me, available for testing could be very-very small, like for instance suppose, I have nano layers obtained by molecular beam epitaxy. Typically you will have these nano layers in the nano, few tens of nano meters at best going to sub-micron regime, but typically this molecular beam epitaxy is such a slow process that we do not make bulk materials out of MBE.

And the problem gets even more complicated, if this nano structure or a nano crystal is part of the larger hybrid. That means, suppose I have a lead nano crystal embedded in an aluminium matrix, and we have already seen that we could produce such a material, but actually melt spinning lead along with aluminium. Then, it becomes challenging for me to determine the properties of this lead nano crystal.

Suppose, I am interested in the melting point of this lead nano crystal or I am interested in the for instance in the modulus of this lead nano crystal, and I want to isolate the property of this lead nano crystal from the matrix. That means, now it is embedded in a matrix and therefore, I may not able separate out the properties, which are coming from interface and embedding effects from the pure material properties. So, this is an interesting problem, as we have seen that a free standing crystal if you approach a nano side are always going to melt at lower temperature that means there is going to be a depression in the melting point.

But an embedded nano crystal as we have seen in some cases based on the interface energy can actually you can observe super heating. Therefore, it becomes difficult to separate out the effects what is coming from the nano crystal or the embedded nano structure, and what is coming from the, what you call embedding material or the matrix around it. The processing route can play a very-very important in determining the properties.

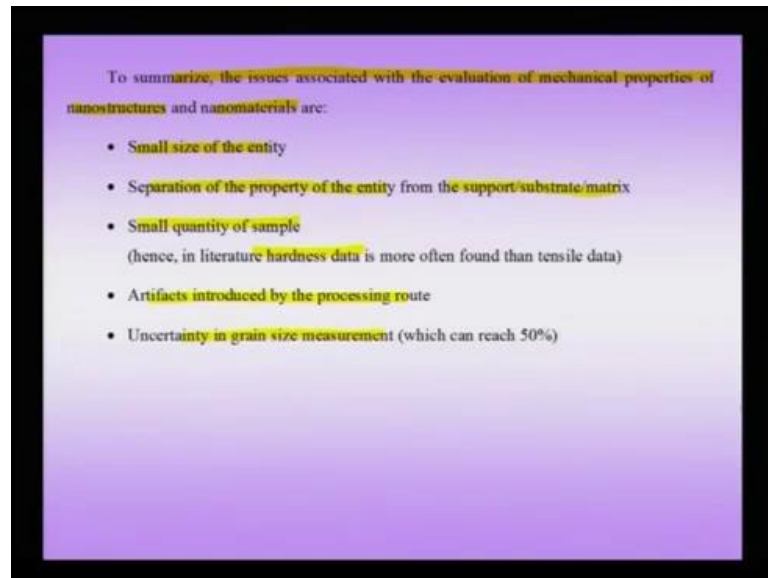
For instance, I may have materials obtained by powder consolidation, mechanical milling, high pressure torsion, etcetera. Each one of these process the kind of defects introduced into the material, the kind of amount of material produced by these materials, the amount, the shape of the particles produced by these processing routes, each one of them is going to be different. And this often produces variations in the properties of the materials. Like for instance, the porosity could be higher even I produced using powder compaction while dislocation density could be high when I do it by mechanical milling or high pressure torsion. That hence, it becomes actually difficult to compare the properties across sizes and processing routes.

So, this is an important challenge in studying bulk nano structured materials that, on one hand I do not have sufficient nano material available for my testing, but then every material cannot be produced by every processing route. And therefore, have a variation in properties coming as which is hand from the processing route itself. Therefore, it becomes difficult to find a way of generalizing the behaviour at the nano scale.

I have to give an example suppose, I have an electro deposited nickel, it showed a ductility for about 100 percent that means, a very good ductile material. While the same nickel, if produced by powder compaction, which had a very little ductility of 3 percent.

And in both cases the grain size was seen to be identical about 10 nano meter. Therefore, my processing conditions or processing parameters or the processing route is now going to affect the properties that nano material I produced. And this becomes an important challenge that how do I compare now for instance, an electro deposited nickel with a nickel produced for instance by powder compaction.

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So, this is an important challenge in the study and determination of the properties of nano structures and nano materials. And even when you are talking about a single carbon nano tube, it is obviously not easy to isolate a single carbon nano tube, make sure it is a defect free carbon nano tube.

Then, actually if I want to produce for instance, and frequency through it or try to study tensile strength, it becomes actually a challenge when you are actually operating at the nano scale, wherein you need to isolate the carbon nano tube, put it between say 2 contacts and maybe I want to measure its conductivity. And in the process also I make sure that I am measuring the inherent of the nano tube and I am getting rid of all the contact effects, etcetera. Hence, to summarize the issues associated with the evaluation of mechanical properties of nano structures and nano materials, we have a problem of small size or limited quantity.

We have a problem of the separation of the property of the entity in question from the supporter substrate. And we know that many nano structures cannot be obtained in a

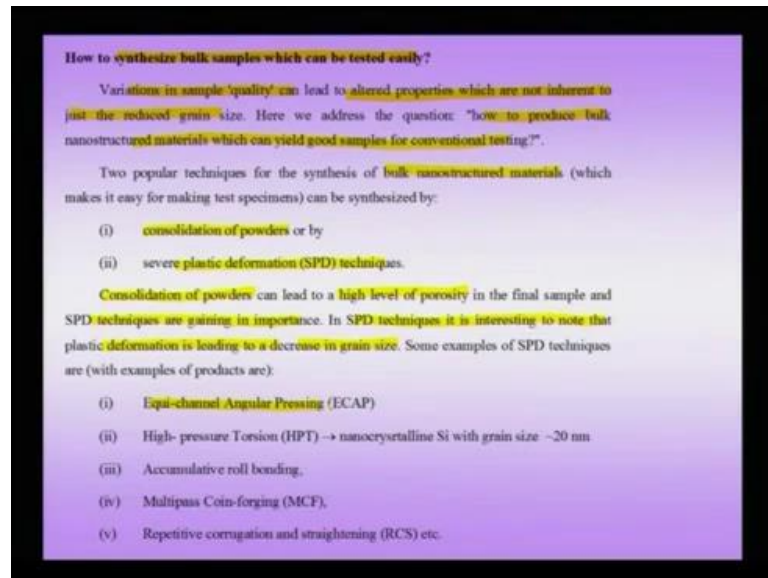
support free fashion. That means, suppose I am wanting to produce a 5 nano meter thin film, typically I would grow it on a substrate, a glass substrate, or on a ITO substrate, or I may grow it on an sapphire substrate. And therefore, there is a substrate embedding, which is going to determine some of the properties.

I have a problem of the small quantity of sample in many cases and therefore, the small quantity of sample implies that there is abundance of hardness data and very little of tensile data on these material. While in bulk materials it is very easy to make a tension or ((Refer Time: 30:55)) or tensile specimens and actually find out the tensile data. Then, I there are artifacts introduced into the processing route, and we will have a few little more things to say about the artifacts, which are induced by the processing route and hence, how these artifacts can be controlled. Therefore, I am now not seeing the property of the that means, I can obtain the inherent property of the material and not that arising from the artifacts.

And there is an additional problem in a bulk nano structured materials is the uncertainty in the grain size measurements. Many-many research reports would actually report an average grain size, but not report the grain size distribution. And this grain size distribution could be very large that means, that there could be a variation of about 50 percent around the mean grain size. Suppose, a person says that the average grain size is 50 nano meter, what actually could be the scenario is that the grain size could vary from about 20 nano meter to about 80 or 90 nano meter.

So, what the property I am seeing is of a poly crystalline aggregate with very different many different grain sizes rather than its mono disperse grain size. And obviously when you go to very small grain sizes, you will use certain and techniques and in some cases the study could be transmission electron microscopy. In which case I am sampling a very little volume of the material and therefore, I do not have a bulk estimate on the grain size. That means, grain size variation is not well studied or well characterized, and this is often the case with much of the case in literature as well. Therefore, I have many-many problems associated with you know testing nano materials and get, trying to get true property of the nano material. Now, that implies that I have to find ways of synthesizing bulk samples.

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And of course, when I mean bulk sample, I am talking about materials like bulk nano structured materials, and I am not really referring to, I cannot make a bulk counter part of a nano tube. So, that I can test the sample easily and I can, so variation in sample quality can lead to altered properties, which are not inherent to just the reduced grain size and this is very-very important as you have seen.

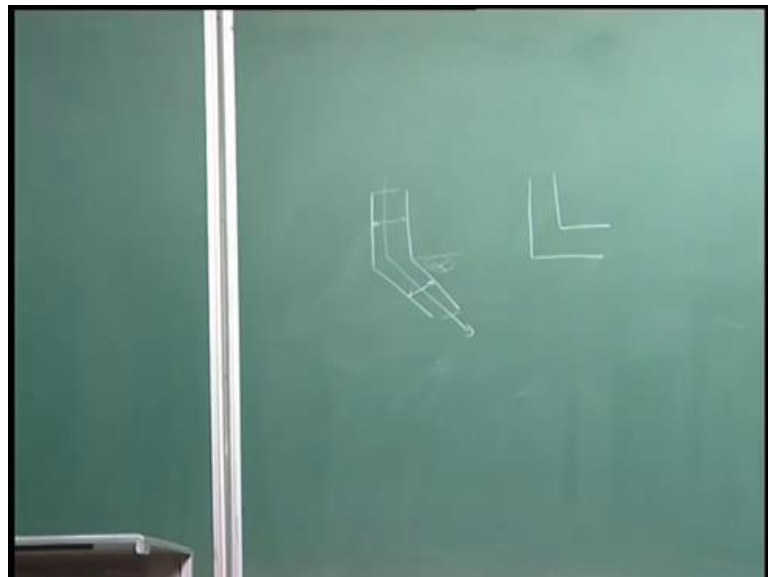
Therefore, we know how to produce bulk nano structured materials, which can yield good samples for conventional kind of a testing, so this is an important problem we are talking about. And there are 2 popular techniques for producing bulk nano structured materials, and these are consolidation of powders, and by severe plastic deformation technique.

So, these are techniques which have become popular in the last 20 years, wherein, I am, people are addressing the question that, how do I produce these bulk nano structured materials such that I can put it to some of the common test, which like tensile testing or hardness testing. Such that I am able to obtain the properties inherent properties of the material easily. The problem with consolidation of powders is that, it can lead to high level of porosity in the final sample. And this as lead to the popularity of a speedy technique, because as you know powder metallurgy and powder material science is being around for quite some time.

And very many important material like tungsten, etcetera are produced actually by powder consolidation. But, then when it comes to nano scale, this porosity can actually play havoc with the properties and therefore, people are worried about or trying to develop very many speedy techniques. In severe plastic deformation techniques, it is interesting to note that plastic deformation is leading to a decrease in grain size.

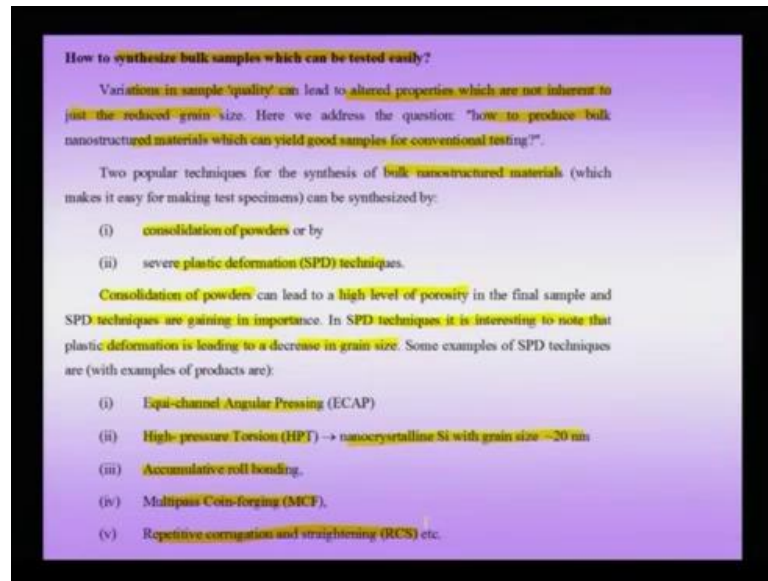
So, the automatically by plastic deformation you are actually getting a reduction in the grain size. So, this is with progressive deformation and here the technique is called severe, because typically the in a technique like equi-channel angular pressing, what you do is that you have a channel of a certain cross section.

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So, you have a channel and of course, this is you can have an angle of bend and this angle can be as severe as 90 degrees, and you extrude a material through this. And actually you can do multiple passes, you can send a material through this, put it back again, put it back again, so you can accumulate strain. And since, the channel diameter is or the cross sectional area is constant you call it an equi channeller, and, because of this angle you call it the equi channeller angular pressing. And by getting this kind of a repeated plastic deformation, you are accumulating strain in the material and this can lead to reduction in grain size.

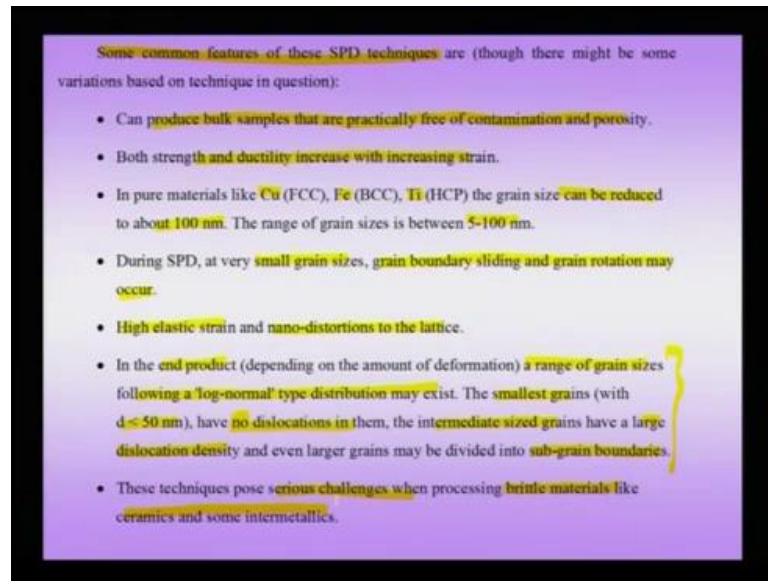
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There are other equivalent techniques like high pressure torsion and which has been used to produce nano crystalline silicon with about 20 nano meter grain size, accumulative roll bonding, multi pass coin forging, and repetitive corrugation and straightening. So, there are many severe plastic deformation techniques, which have been used to produce nano crystalline materials.

Typically, the grain size produced by these techniques is the order of 100 nano meters, and is usually difficult to go down to even smaller grain sizes, when you are using some of the severe plastic deformation techniques. Needless to say, when you produce a material with severe plastic deformation, you are going to have a often a very high dislocation density even if suppose a grain size of about 200 nano meters, you can have very high dislocation density. There is going to be a large what you call variation in grain size around the mean, but on the other hand the problem with consolidated powders is that you are going to have porosity problem.

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So, we will now take up some common features of this SPD technique, some advantages and disadvantages. Though we are trying to identify some of the common features, but we should note that technique to technique there are obviously variations, and these variations could be important for a given material. All these can produce bulk samples that are practically free of contamination and porosity. Both strength and ductility increase with increasing strain that means, we are decreasing the grain size with increasing strain and additionally we are increasing the strength of the material and its ductility, so this is the beautiful thing to be doing.

In pure materials like copper, iron, titanium, the grain size can be reduced to about 100 nano meters and typically the grain size range could be from what 5 to 100 nano meters. That means, there is large grain size variation even in a given sample and it is sometimes very difficult to decrease the grain size below 100 nano meters using some of these techniques. The important thing is that at very small grain sizes, when the grain size starts reduced, grain boundary sliding and grain rotation may start to take place. So, that means the mechanism of deformation switches, and we will see what is the reason behind this in some of the coming slides.

There are lot of nano distortion to the lattice, and there is a high elastic strain in the final product, which have produced using the severe plastic deformation techniques. The end product, which is the say for instance, I may use some 5 passes or 10 passes using severe

plastic deformation technique. A range of grain sizes following some kind of a log normal plot may exist, the smallest grains with d of less than about 50 nano meter may have no dislocations in them that means, they have become dislocation free.

The intermediate size grains may have a large dislocation density, and even larger grains may actually be divided into sub grain boundaries. And when I mean sub grain boundaries, we mean a low angle grain boundary, which is actually you know if you follow the read Shockley model consists of an array of dislocations. Therefore, when I am therefore, you can see those one of the problems associated with severe plastic deformations straight away.

But now there is a log normal distribution of grains and there is a range of grain sizes within, and the structure of each one of these grains, the micro structure is different. The smallest grains are practically dislocation free, the intermediate size grains have a large dislocation density, while even larger grains are actually divided into sub grain boundaries.

So, this variation is an important thing and therefore, when I am whenever I am using such a sample for determining the property I have to remember that, I have, I cannot say this is a single function of a single grain size, it is actually a distribution of grain sizes. And obviously needless to say that these techniques do not work well with brittle materials like ceramics and inter metallic, which are usually expected to be brittle.

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Grain boundaries in nanocrystals

- Grain boundaries and interfaces can comprise of about 50% of the volume fraction in a nanostructured material with grains size of about 5nm.
- Grain boundaries in nanostructured materials seem to be similar in structure to their bulk counterparts (except in specific examples).
- Both sharp and disordered grain boundaries (along with disordered triple junctions) were observed in Ti and Pd nanostructured thin films [1]. The region of disorder at the grain boundaries (with disorder) was about 0.5 nm. The most natural model to explain grain boundaries and triple lines is the disclination model.
- In a model by Suryanarayana [2], assuming a grain boundary thickness of 1 nm; when grain size is about 30 nm the volume fraction of grain boundaries is about 10% and that of triple lines (junctions) is ~1%.

[1] K. Rajanathan, R. Divakar and V. S. Rajanathan, Scripta mater. 44(2001)1188-1178.
[2] C. Suryanarayana, D. Mukhopadhyay, A. N. Parshetti, F. H. Poon, J. Mater. Res. 7(1992)2114

Next, we try to understand the grain boundaries in nano crystals. Now, so far we have seen that we are talking about reduction in grains, we have also seen that grain boundaries are expected to play an important role, when you go down to smaller and smaller sizes, not only grain boundaries, but triple lines and also quadruple junctions. So, these volume fraction of these increase, and you have seen that they play an important role in determining the density of the material especially below 20 nano meter crystalline size. We already seen that how the elastic modulus could change purely arising from the presence of these grain boundaries triple lines and quadruple junctions.

But we have an important question to arise, ask ourselves, are grain boundaries in nano crystals different from their bulk counter parts? So, we will try to understand this question and when we ask the question, what is a grain boundary? We said that, it is a region wherein, the atomic positions are in deviation with respect to the bulk or the crystal region and therefore, we even assumed a thickness for the grain boundary to be of the order of nano meter.

So, in other words in some sense in terms of disturbance to the atomic positions, even the grain boundary itself ((Refer Time: 40:12)) nano structure. But now we will take up the important question of can, are there really grain boundaries of the, of that thickness and, so to us ourselves ask the question that, are grain boundaries in nano crystal any different from that in bulk crystals?

We have already seen that grain boundaries and interfaces can comprise of about 50 percent of the volume fraction of a nano structure material, when the grain size comes down to a very small size, like about 5 nano meters. But so far studies have shown that in many cases the grain boundaries in nano structure material seem similar to their bulk counterpart.

So, this is a very important finding that, even though we are talking about grain boundary in a nano structured material, their overall character, in other words the thickness you can talk about the disturbance, their structure perhaps the models we will, I would, we would used to describe these kinds of grain boundaries in nano crystals. They seem to be very similar to their bulk counterparts, these are very-very important observation. In and lot of investigations have been undertaken in this area to understand grain boundaries in

nano structured materials. We will just consider couple of examples here to understand how they can be similar how they can be different.

For instance, if you look at titanium palladium nano structured thin films, we will see that both sharp and disordered grain boundaries are seen along with disordered triple junctions. So, that means that there are the sharp grain boundaries, which are very similar to the bulk counterpart, but there are also grain boundary showing considerable disorder. And this characterization was done by transmission electron microscopy.

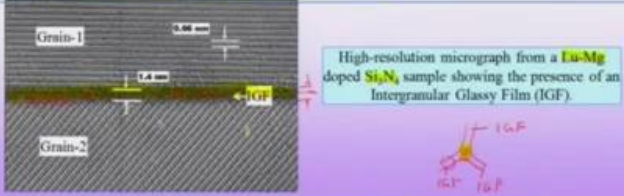
The region of disorder at the grain boundaries was about 0.5 nano meters. So, this is in the same order as the thickness, we assume previously for a grain boundary. And of most common model used to explain grain boundaries and the triple lines, what is known as a disclination model, because disclination is, then is associated with rotations. And therefore, typically people use either for large angle grain boundary, they use disclination model to understand grain boundaries. This aspect we will skip now, because the, we have already seen how with the volume fraction of grain boundaries, what is a fraction of triple lines, etcetera?

Now, to summarize this slide, we note that there could be disturbance, there could be differences in the grain boundary structure with respect to the bulk in very specific examples, like the titanium and palladium nano structured films. But even there were grain boundaries, which were very-very similar to their bulk counterparts. And in normal grain boundaries and nano crystalline grain boundaries, there is a region of disorder, which can be thought of the order of about 0.5 nano meters or order of 1 nano meter. But next we will take up an important example wherein, the grain boundary is truly a nano structure in its own right, and that is the case of the inter granular glassy film.

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Intergranular Glassy Films (IGF) → nanostructures in their own right

- ❑ GB are regions where order of one grain changes to order of another grain.
- ❑ GB can also have some degree of disorder.
- ❑ Special grain boundary structures are observed in specific materials like Si_3N_4 , Al_2O_3 , SrTiO_3 , etc. which have a thin layer of glassy material of constant thickness of about 1-2 nm [1]. These are called intergranular glassy films (or IGF for short). These IGFs are characterized by a nearly constant thickness which is basically independent of the orientation of the bounding grains, but is dependent on the composition of the ceramic. The IGF is resistant to crystallization and is thought to represent an equilibrium configuration. The presence of the IGF, along with its structure, plays an important role in determining the properties of the ceramic (as a whole).



High-resolution micrograph from a Lu-Mg doped Si_3N_4 sample showing the presence of an Intergranular Glassy Film (IGF).

[1] Anandk Subramanian, Chintugh T. Eark, Richard H. Cannon, Michael Stille, Materials Science and Engineering A 422 (2006) 1-18.

We know that grain boundaries are regions where order from one grain changes to another grain. And grain boundaries already we have seen can have some degree of disorder. But if you look at older literature below 19, before 1950 people even assume that grain boundaries in normal materials are like amorphous grain boundaries, but more and more observations have shown that they are, it is not true that grain boundaries are not disordered in the sense of amorphous.

And therefore, there are even structural unit models of grain boundaries, but these intergranular glassy materials are special class or international, intergranular glassy films are special class of green boundaries, which are observed in specific material. This is not universal, but there are specific materials found under specific processing conditions like you find them in silicon nitrite, alumina, strontium titan, etcetera. In which in these materials there is a thin layer of glassy material of constant thickness of about 1 to 2 nano meter.

This is very special boundaries found in very special materials, and the thickness if you look at this high resolution lattice fringe image at the bottom, there is a region below wherein, you find a region, which is about 1 to 2 nano meters, this is a thickness and this is the nano scale structure. So, in other words, this amorphous like region or a glassy material, the reason why it is glassy and we do not call it a glass, because its structure the glass, the structure of this intergranular glassy film is different from the bulk glass,

which can be formed from a similar kind of a material found in a for instance a triple pocket, which could be down the grain boundary.

So, if you have a triple pocket between 3 grains, then suppose these are IGF inter granular glassy films. Then, this triple pocket glass is to the bulk glass while these IGFs have a structure, which is glassy. In other words there is some partial order close to the boundaries, and these are self regulating in their composition. And therefore, they are different kind of a structure compared to the bulk glass. And they are in themselves a nano structured wherein, the grain size happens to be in the micron scale.

So, they are their own right a nano structure or a nano structured in a bulk material. These IGFs are characterized by nearly constant thickness, and it is basically independent of the orientation of the bounding grains except for special misorientations, which are called the CSL misorientations, you would find that the orientation does not determine the thickness of the glassy film.

But it is definitely dependent on the composition of the ceramic and this glassy film itself sometimes becomes a self regulating and its composition, but it suppose, you put more and more calcium, then it only retains a certain amount of calcium in the IGF region and the remaining calcium would actually go into the triple pocket, where there is glass.

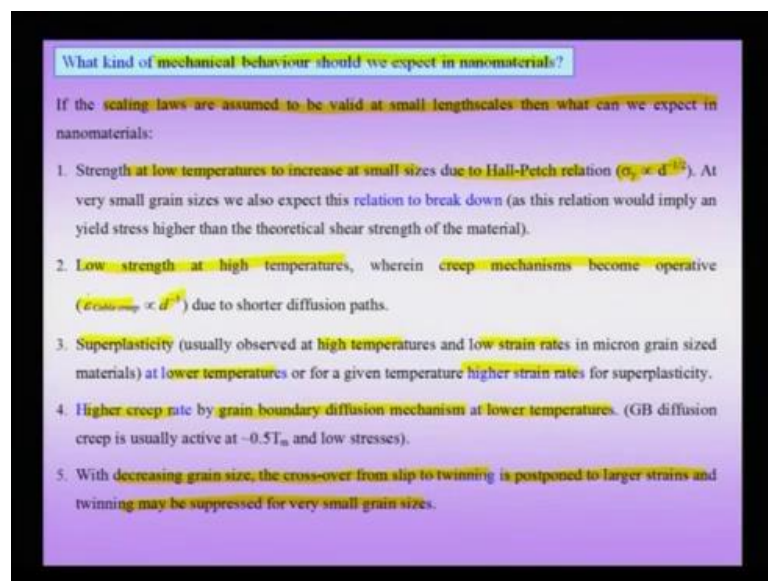
The IGF is resistant to crystallization and is thought to represent some kind of an equilibrium configuration. So, this is a very important kind of a structure, which is some kind of an equilibrium configuration. The presence of IGFs along with its structure plays an important role in determining the properties of the ceramic as a whole.

So, this nano structure, though it is a small volume fraction of the entire ceramic, but it plays a profound role in determining the property of the ceramic as a whole. Suppose, I tested this ceramic under impact, then it is slightly that the cracks would actually propagate in a granular mode inter granular mode, and the crack would grow along this IGF. And typically, it has even molecular dynamic stimulations as shown that the crack would tend to propagate along the interface between the glass and the ceramic or between the IGF and the ceramic.

So, even though this is a small volume fraction of the material, its effect on the creep properties of the material, the fracture toughness, etcetera become profound. And

therefore, it is important to study these IGFs in their own right. And the example shown here, it is actually a high resolution micrograph for a lattice fringing image from a lutetium magnesium dot, silicon nitrate sample, wherein the grains have hexagonal shape and the IGF is of about thickness of about 1.5 nano meters. Now, we have talked about various aspects like super plasticity, creep, etcetera, and we also said that the role of grain boundary, the role of diffusion, etcetera is going to be more and more when you go along to the nano scale.

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What kind of mechanical behaviour should we expect in nanomaterials?

If the scaling laws are assumed to be valid at small length scales then what can we expect in nanomaterials:

1. Strength at low temperatures to increase at small sizes due to Hall-Petch relation ($\sigma_y \propto d^{-1/2}$). At very small grain sizes we also expect this relation to break down (as this relation would imply an yield stress higher than the theoretical shear strength of the material).
2. Low strength at high temperatures, wherein creep mechanisms become operative ($\dot{\epsilon}_{\text{disl-imp}} \propto d^{-3}$) due to shorter diffusion paths.
3. Superplasticity (usually observed at high temperatures and low strain rates in micron grain sized materials) at lower temperatures or for a given temperature higher strain rates for superplasticity.
4. Higher creep rate by grain boundary diffusion mechanism at lower temperatures. (GB diffusion creep is usually active at $-0.5T_m$ and low stresses).
5. With decreasing grain size, the cross-over from slip to twinning is postponed to larger strains and twinning may be suppressed for very small grain sizes.

So, the next question the obvious question is that, what kind of a mechanical behaviour should I expect in nano materials? Of course, the next question you will ask after this is that, having made these expectations that we are going to see in a nano material, how far are some of these expectations actually observed in nano materials, and in what cases we find that the expectations are not fulfilled?

If, I assume that the scaling laws are valid at the small length scales in the scale of nano materials, then I would expect that the strength at low temperatures to increase as the sizes of the grain decrease. That means, we know that from the whole petch relation, which will come a little more detail soon that, these yield stress varies as is proportional to $d^{-1/2}$.

And that means at very small grain sizes that you would actually expect the strength to become very high. But, then this increase in strength cannot go on forever, because you

know that the ultimate limit is of course, the theoretical shear strength, which means that at some small grain size, we would expect the whole petch relation to actually break down.

So, this is one important thing we would naturally expect that at very small grain sizes the whole petch relation would break down. That means, σ_y versus d plot d per minus half plot, which is going to be a straight line is going to break down. We also expect that there is going to be low strength at high temperatures, and we expect creep mechanisms to become operative. And for instance we, if we look at the strain rate for coble creep, it goes as d power minus 3 and, because of the short diffusion path I would expect, because the nano structured material, there is lot of interface diffusion, and the path length required for diffusion has become smaller.

Therefore, I would expect that creep like mechanisms should become operative, when you go down to small grain sizes. And we have said that creep in some sense is a counter part of super plasticity and therefore, I would also expect super plastic deformation to take place, which is usually observed at high temperatures and low strain rates to actually occur at lower temperatures and higher strain rates.

That means, now when I go down to nano structured materials, I would expect that I would be able to get super plasticity at lower temperatures. Previously we said that it is going to be about $0.5 T_m$ or more, but then now you would expect that it takes place at lower temperatures. And typically creep and super plasticity strain rates are of the order of about 10 power minus 4 or smaller. So, can I get super plasticity at much higher strain rates like 10 power 0 or 10 power minus 1?

And I also expect this higher creep rate to take place by grain boundary diffusion mechanism at lower temperature. So, the lower temperature part is a constant as we discussed before, and but then I would expect that mechanism of switch say for instance, from bulk diffusion to grain boundary diffusion this is another thing I would expect when I go down to nano scale.

Additionally, we have seen this and I just reiterate what we have seen before with decreasing grain size I would expect a switching mechanism for plastic deformation from slip to twinning. And in other words with decreasing grain size the cross over from

slip to twinning is postponed to larger strains and twinning may be suppressed for very small grain sizes, so this is what I expect.

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Deformation in Nanomaterials

- Deformation of nanostructured materials seem to occur predominantly by dislocations at interfaces (and not bulk dislocations). These dislocations have Burgers vector smaller than lattice dislocations. In some *in-situ* TEM experiments mobile dislocations were not observed when grain size is less than about 30 nm.
- In brittle materials like ceramics, at small grain sizes grain boundary sliding may be the predominant mechanism of plastic deformation.
- In some cases the nanocrystalline sample showed poorer ductility than their microcrystalline counterparts.
- Paucity of dislocations within the grain and difficulty in generating dislocations. For a mechanism like double ended Frank-Read source to operate to increase the dislocation density, two pinning points are required. As discussed before the maximum shear stress required (τ_{max}) for operation of the source is given by: $\tau_{max} = Gb/L$

Where, L is the distance between the pinning points which can take a maximum value of the grain diameter. In nanocrystals this value can exceed the theoretical shear strength of the crystal!

So, if I talk about deformation of nano materials, if we should notice that, deformation in nano structured materials seem to occur predominantly by dislocations at interfaces and not by bulk dislocation. And I am talking about grain size for instance of the order of about 30 nano meter or less.

We have already seen that when I am talking about large grain sizes more than 100 nano meters, there are dislocations and there is dislocation activity that implies dislocation related slip can give me plastic deformation. But when I go down to very small grain sizes of about of the order of 30 nano meters, then it seems that dislocations at interfaces, which have a burgers vector smaller than the lattice dislocations and these seems to play an important role in the deformation of the nano material. And in team experiments done, they observe that mobile dislocations are actually absent, when the grain sizes below about 30 nano meter.

So, this is an important switch in the mechanism, when you go down to very small grain sizes. In brittle materials like ceramics at small grain sizes, grain boundary sliding may seem to be a predominant mechanism for plastic deformation. But having seen this, in many cases we expected that the nano crystalline counterpart would actually have a higher ductility than the bulk grain sized material. But this is not seen in all the cases and

in many cases we see that the nano crystalline sample showed poor ductility than their micro crystalline counterparts. So, this is an important observation that it is not always that the nano crystalline counterpart is going to have higher ductility, and higher strength, but many cases they have poor ductility than their microcrystalline counterparts.

Some of the important things we observed regarding mechanism is the porosity of dislocations within the grain, which we already seen that in a previous slide that when you go down to a very small size of less than about 50 nano meter typically less than about 30 nano meter, we see that there is there not many dislocations within the grain. And additionally it is actually difficult to generate dislocations or multiplied dislocations, because for a mechanism like the frank read source to operate, which you already seen, the strength or the stress required goes as $1/L$.

And as the L decreases now, the grain size decreases that means, that we may actually exceed the theoretical shear strength before operating an actually a source like a frank read source. Therefore, when I go down to small scale materials to reiterate, the deformation mechanism is expected to change from bulk, what you call the dislocation present in the crystal leading to deformation to interface dislocation playing a predominant role. And also grain boundary sliding, what you call playing an important role. Additionally, multiplication of dislocations that means increase in dislocation density also seems difficult in nano crystalline material. We have been talking about the phenomena of grain size and strength.

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Grain size and strength

- ❑ In polycrystalline materials (e.g. polycrystalline Cu, Al or alloys) the dependence of yield strength (σ_y) on grain size (d) is given by the Hall-Petch relation.
- ❑ The relation states that as the grain size decreases the strength of the crystal increases.
- ❑ The reason behind this is that the grain boundary is an impediment to the motion of the dislocations (dislocation is a crystallographic defect and it ceases to exist where the crystallite ends). As the slip plane in one grain is typically not coplanar with the neighbouring grain, higher stress is required for a dislocation to initiate slip in an adjacent grain.
- ❑ The usual model to explain the grain size dependence on strength is the 'dislocation pile-up (at grain boundaries) model'.

Hall-Petch Relation

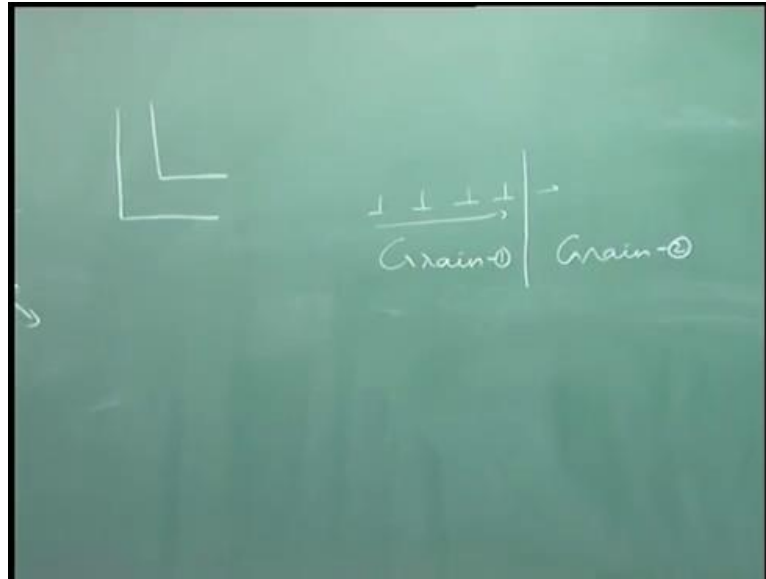
$$\sigma_y = \sigma_i + \frac{k}{\sqrt{d}}$$

- σ_y → Yield stress [N/m^2]
- σ_i → Stress to move a dislocation in single crystal [N/m^2]
- k → Locking parameter [$\text{N/m}^{3/2}$]
(measure of the relative hardening contribution of grain boundaries)
- d → Grain diameter [m]

And we said that the important relation governing the strength and the dependence of strength on grain size is known as the hall patch relationship which is given, which you already have encountered before, but we reiterate here to be as sigma y goes as sigma i plus k by root of d. Now, sigma y is the yield stress of the material, sigma i is the stress to move a dislocation in a single crystal and this is something like the inherent lattice resistance. k is the locking parameter, and is a measure of the relative hardening contribution of the grain boundaries. And d is the grain diameter.

In this hall patch relationship is some kind of an empirical relationship, which is true for polycrystalline materials and wide variety of materials studied over range of grain sizes have seem to be obeying this rule, which is called the hall patch relationship. Now, the relation states that, the grain size decreases as the strength of the crystal, I mean as you reduce the grain size, the strength of the crystal is going to increase. And typically, the reason behind this is given by a mechanism known as the dislocation pile up at the grain boundary model. So, this is the typical classical model called the dislocation pile up model, which means that grain boundary stops a dislocation.

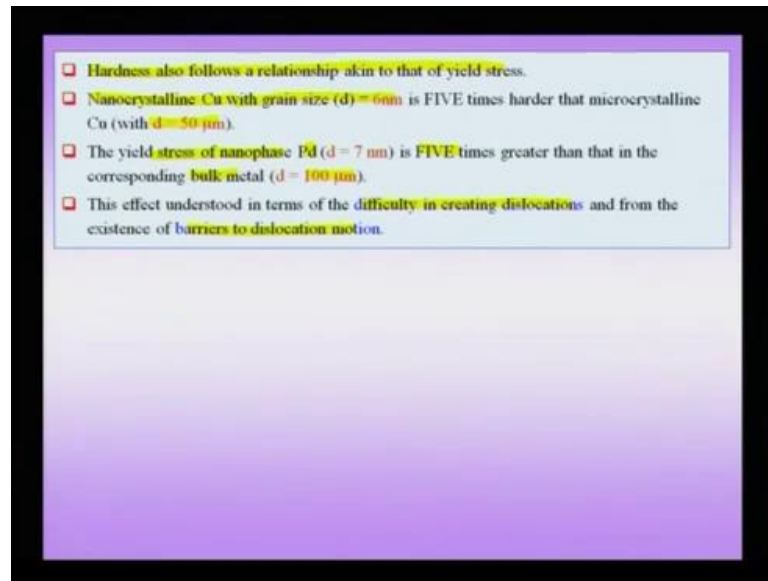
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Then, further dislocations are piled up at the grain boundary, and this pile up increases the stress on the grain boundary, and this can lead to further slip initiation on a neighbouring grain. Suppose, this is grain 1, then you can initiate slip. In other words, you effectively have a stress amplification by this pile up and you also see that there is an increase in strength, because of the impediment cause to the motion of dislocations by the grain boundary.

But the important point to note is that in many-many studies they could actually not observe a pile up and therefore, there are alternate theories, which have been proposed to understand the hall petch relationship, and but we do not want to go into details of the theory. But we note for now that across a size of grains in the micron scale to the even larger sizes and sub micron sizes, across very many materials this hall petch relationship is found to be true. And this is essentially coming from the fact that the grain boundary is an impediment to the motion or free motion of dislocations.

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And it additionally it is found that, the hardness also seem to follow a relationship similar to that for yield stress in the case of very many materials. In other words, I can write instead of σ_y , I can write the hardness of the material and still it will have an $1/\sqrt{d}$ kind of a dependence on the grain size the hardness.

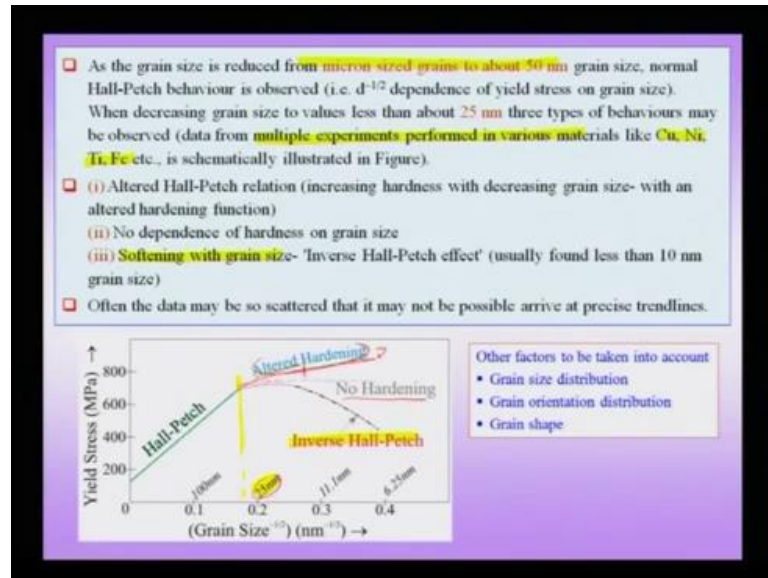
And as I pointed out that at means, if I go to smaller and smaller grain sizes, then I would obtain harder and harder material or material with higher and higher yield stress. And it has been found that in nano crystalline copper, the grain size is about 6 nano meters is about 5 times harder than material with about 15 micron meter grain size. And if you talk about yield stress of nano phase palladium, which is about 5 times harder than the bulk material with a grain size of about 100 micrometre.

So, all these effects typically are understood in terms of difficulty in creating dislocations and barrier to dislocation motion in this nano grain sized material. So, we have seen that, the strength increases with decreasing grain size. We also noted that we cannot keep on increasing the size with decreasing grain size, because some point of time we are going to exceed the theoretical shear strength of the material.

And also we noted that now, because the grain size is so small that actually it does not support, it is too small to actually support a pile up. Therefore, even if you look at the pile up mechanism or use the fact that now you are going to have very high strength, or we find that actually we cannot multiply dislocations like by a frank read mechanism at

these small sizes we expect that the hall petch relationship is actually going to fail. And this failure is typically occurs at very small grain sizes of the order of about 10 nano meter.

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But if you want to look at the broader picture what is, what is, what is that we expect, then when you go down to very small sizes. And now I am talking about very small sizes less than of about say about 25 nano meter. So, when you are going down to these small grain sizes and I am now talking about reduction in grain size from micron sized grain size to about 50 nano meter grain size, we do expect that the hall petch relationship is going to be altered.

So, what are the ways in which this can be altered, number 1 is that of course, that you may actually have an altered hardening that means, that the material tends to get harder and harder, but the rate of hardening actually is reducing. So, that means I can actually have an altered hardening. So, this is the red line here. So, even though that means that the deep our half relationship breaks down, but the material is still getting harder with decreasing grain size.

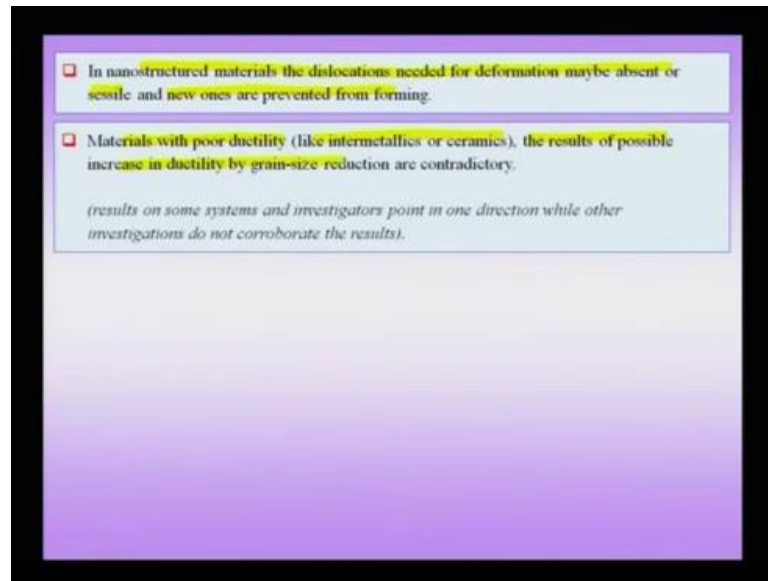
Of course, this is also cannot go on forever as we pointed out, but this can at least take place in a small regime close after between less than about 25 nano meter. The other possibility is that there is no hardening that means, the material's hardness tends to remain constant with grain size as you go down below 25 nano meter.

The third possibility, which is also seen in some kind of materials though it must be said that this is not been verified for a large classing materials or it has not been verified without much scatter in data. In other words, there is a considerable scatter in data whenever they try to do measurements at these small grain sizes. And again to point out the difficulty associated with this nano scale materials that, it is very difficult to obtain mono dispersive grain sizes. And also we not only want mono disperse grain sizes we do not want grain sizes grains, which are having very high aspect ratio, we want more equi axed kind of grains, so that our results are interpretable.

Therefore, getting such kind of specimens is very difficult and therefore, there is a large scattering data. But it has been seen that not only can you have altered hardening, you can have low hardening with decreasing grain size, but interestingly you can have something known as the inverse hall petch effect, which means that there is a softening with grain size. And this data has been accumulated by studying experiments performed on materials like copper, nickel, iron and titanium and this figure you are seeing below is actually a compilation of data of many such experiments.

And therefore, it is very interesting to note that, when you reduce a grain size below about 25 nano meters, you have 3 kinds of possibilities some materials show some kind of 1 effect, some other material show a different effect. But, then the most important effect you can see is that actually you may observe something known as the inverse hall petch effect wherein, actually the materials softens with decreasing grain size. So, this is a very interesting effect which has no counterpart or the bulk analogue, which is especially observed in very small grain size materials.

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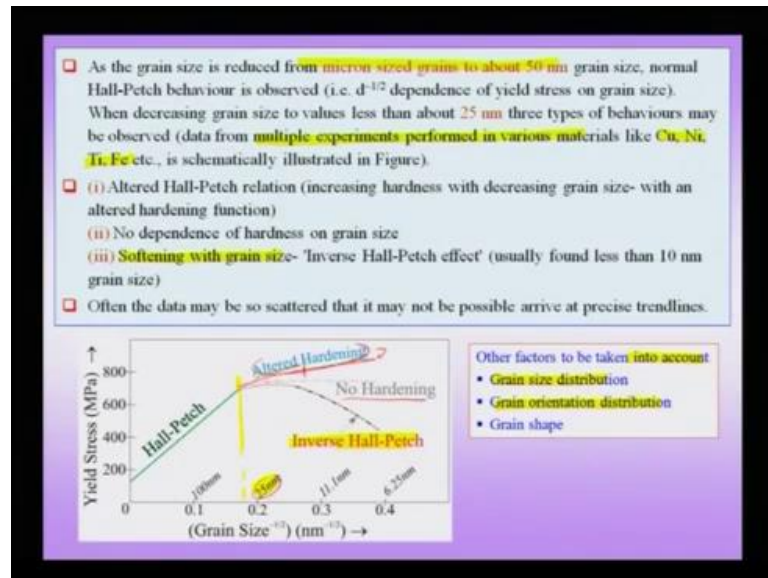


And we have already observed that the nano structured materials, the dislocation needed for deformation may be absent that means, or they may be sessile, and new ones are prevented from forming.

And if you look at test performed on materials with poor ductility like inter metallic and ceramics, the results of possible increase in ductility by grain size reduction are contradictory. That means, that there are materials wherein, still lot more research is to be done, lot more investigations have to be done to actually determine that by with decreasing grain size do I get additional ductility, what is exactly the mechanism of ductility, which is giving rise to? I mean reason behind the ductility etcetera.

So, even from the previous graph I showed you that the there is a little positive of data, there is scatter in the data, and there are issues related to as I pointed out, right from porosity to the method of manufacture or method of synthesis of these specimens. Therefore, still more work has to be done.

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But definitely there are very interesting effects when you go down to nano scale which includes the inverse hall petch effect observed in polycrystalline materials. And a precise what you might call a definition or a precise understanding of these kinds of materials can only arise, when we take in to account not only the grain size. But we also take in to account the grain size distribution, the grain orientation distribution, and additionally the grain shape, which is also going to play an important role in determining the deformation characteristics of nano structured materials.