Nanostructures and Nano Materials: Characterization and properties

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Lecture -19

Defect Structure and Mechanical Behavior of Nano Materials

We had previously seen that when we use a composite structure or a hybrid then, we can get beneficial properties, which are neither found in neither the one of the components, which gone to make the hybrid or the composite. Additionally, we had seen that how a polycrystalline material can be thought of as a composite of green boundaries, the crystal, the triple line junctions and quadruple junctions.

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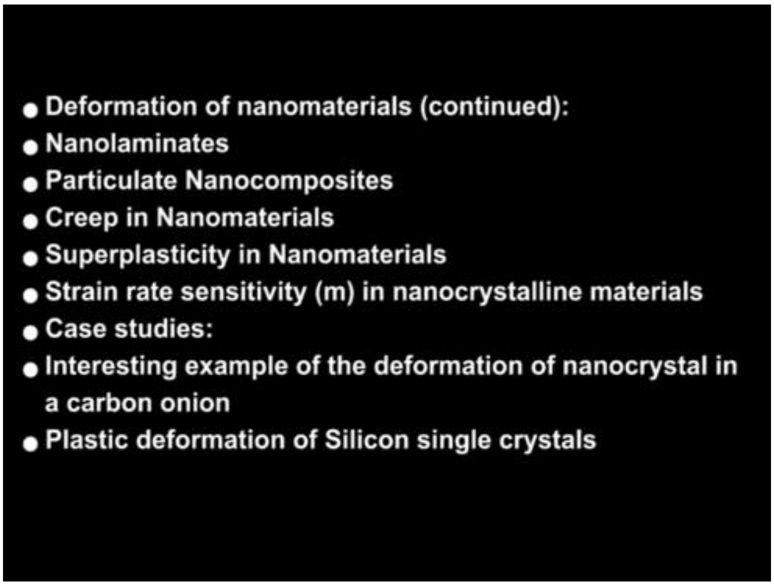

- Deformation of nanomaterials (continued):
- Nanolaminates
- Particulate Nanocomposites
- Creep in Nanomaterials
- Superplasticity in Nanomaterials
- Strain rate sensitivity (m) in nanocrystalline materials
- Case studies:
- Interesting example of the deformation of nanocrystal in a carbon onion
- Plastic deformation of Silicon single crystals

We had also made a calculation on the upper bound and lower bound on the elastic modulus, when we use this concept to understand polycrystalline materials especially at the nano scale. We had also seen the relationship known as the hall petch relationship in which we had described the increase in yield stress with decreasing grain size. And we had seen that the relationship if you plot sigma y versus d power minus half, then you will find a linear relationship.

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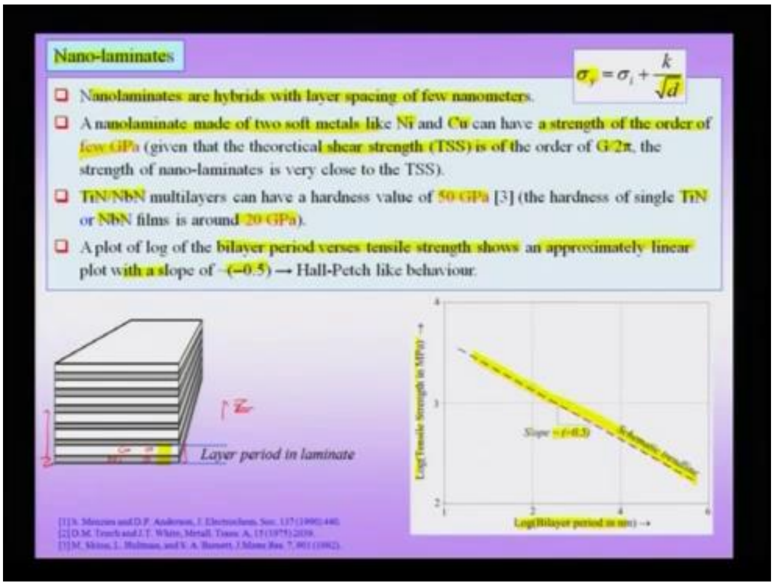

Nano-laminates

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

- Nanolaminates are hybrids with layer spacing of few nanometers.
- A nanolaminate made of two soft metals like Ni and Cu can have a strength of the order of few GPa (given that the theoretical shear strength (TSS) is of the order of G/2π, the strength of nano-laminates is very close to the TSS).
- TiN/NbN multilayers can have a hardness value of 50 GPa [3] (the hardness of single TiN or NbN films is around 20 GPa).
- A plot of log of the bilayer period verses tensile strength shows an approximately linear plot with a slope of (−0.5) → Hall-Petch like behaviour.

We had also pointed out that it is actually the grain boundaries, which are responsible for such a relationship and one of the common models used to understand the hall petch effect is known as the dislocation pile up model. We had also noted in that context that actually that this model though it is a popular model that often electron microscopic evidence is not available in support of this model.

Even though this kind of a behavior is seen in a wide class of a material across large variation in grain size, but we had also noted that, when we gave down very small grain sizes, actually the hall petch relationship breaks down, just what is expected? We noted that there could be regime in a below about 20 nanometer grain size wherein we could have an altered strengthening with decreasing grain size.

We could have no strengthening with decreasing grain size or we could also have what you might call in inverse hall petch effect, which is absolutely no concepts, which is coming basically in the grain size being in the below about 29 meter, which is especially new for nano crystalline materials. Now we will consider a hybrid and we will also explore the possibility of the applicability of hall petch relationship in nano laminates and particulate composites.

Nano laminates are hybrids with layer basic few nano meters. A schematic is shown below in which you have two materials. In the examples considered one material could be nickel and another could be copper. Of course, you could take wide variety of materials for instance, you could have germanium layer followed by germanium silicon solid solution layer. You could have gallium arsenide layer and indium gallium arsenide layer, but anyhow you can form a bi-layer, which is basically a 2 d nano crystal and you can start them one on top of the other to obtain a laminate structure.

The two layers could actually be coherent with each other, they may be incoherent or they could also be semi coherent. In the process you actually have a long periodicity or you have a periodicity in the z direction. So, this is my z direction. The important point to note is that of course, this is my layer period that, this is my unit cell parameter along the z direction. Now, this implies there are two length scales in this problem, one length scale is related to the lattice parameters of each one of these crystals.

Suppose I am talking about nickel and copper then, the lattice parameters of the individual components is one length scales in the problem. The second length scale is of course, the individual layer periods and if I take them to be equal then, I need to talk about the periodicity along the z direction, which i just described which is an additional lattice parameter in the structure. Now, such a structure can we called a super lattice because now and is the super lattice in the z direction.

The reason that you tend to form such kind of composites is because you get additional benefits, which are not found in either one those individual components. Now, in the case of nickel and copper if I make a nano laminate that means, the periodicity is of the order often or 20 or 30 nano meters. Then, it is found that the nano laminate formed from two soft metals like nickel and copper, nickel and copper both are f c c that implies that, triple stress in these structures is small and they easily plastically deform.

Then this nano laminated can have strength of the order of a few g p a that means, we are approaching the theoretical shear strength, which is order of g by 2 pie in nano laminates. This is very beautiful strange effects that mean, that we are getting very high strength in the nano laminate while, each one of those components nickel and copper actually are very soft metals. In titanium nitrate, niobium nitrate by multi-layers that means, one layer is titanium nitrate, the other layer is niobium nitrate.

We can have a hardness value approaching that of about 50 g p a and if you note the hardness of the individual layers are like titanium nitrate and niobium nitrate, that is much lesser than this value of 50 g p a. The important point to note in this context is that not only are we getting this kind of hardening effect, but suppose if I studied the hardening effect as a function of the bilayer period. And for now I assume that the individual layers made up of either titanium nitrate or niobium nitrate or the nickel copper system either, made of nickel and copper are equal thicknesses.

I do not vary that thickness I keep it constant, but then I vary the overall periodicity or the layer thickness. Then, if I plot a log of the bilayer period verses tensile strength and often in such systems either, you measure the tensile strength or you may even measure the hardness. Then, you find an approximately linear relationship with a plot showing a slope of about point minus 0.5; this is like a hall petch behavior.

That means that now if I am plotting log bi-layer period versus the log of the tensile strength I find approximately linear plot, which shows a slope minus 0.5 which means that, we have seen the effect which is very similar to the hall petch effect. That means that in the hall petch relationship we originally pointed out that typically we have plot yield stress and yield stress follows this relationship. We had extended to say that even hardness follows this relationship. Now, we are saying not only is the grain size d which, follows this relationship, but could actually be a bi-layer period in a nano laminate or a laminate structure. So, this is a very interesting effect.

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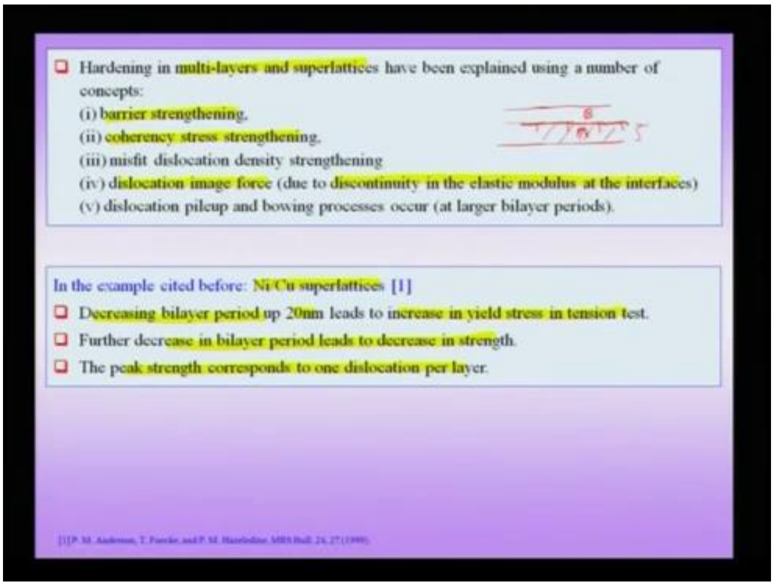

- ❑ Hardening in multi-layers and superlattices have been explained using a number of concepts:
  (i) barrier strengthening,
  (ii) coherency stress strengthening,
  (iii) misfit dislocation density strengthening
  (iv) dislocation image force (due to discontinuity in the elastic modulus at the interfaces)
  (v) dislocation pileup and bowing processes occur (at larger bilayer periods).

In the example cited before: Ni/Cu superlattices [1]

- ❑ Decreasing bilayer period up 20nm leads to increase in yield stress in tension test.
- ❑ Further decrease in bilayer period leads to decrease in strength.
- ❑ The peak strength corresponds to one dislocation per layer.

[1] P. M. Anderson, T. Foecke, and P. M. Hazzledine, MRS Bull. 24, 27 (1999).

Well a little deeper about this nickel copper super lattices, you would notice that in a decreasing bilayer period of 20 nano meter leads to an increase in the yields stress in tension test. Further, decrease in bi-layer period leads to a decrease in the strength. The peaks strengths correspond to about one dislocation per layer. So, this linear trend is of course followed in a certain regime as I pointed out and would not be followed in a very large period. But the interesting thing is that the peak strength corresponds to about one dislocation per layer.

Of course, we will soon see how what is the mechanism which has been attributed to this kind of a strengthening. To summarize this slide, we can not only have nano scale materials, but we can have nano hybrids in which case, the two components forming the composite or the hybrid structure are both of the nano scale. In this case individual layers for instance nickel and copper or in the nano scale. This kind of a nano laminate actually shows very high strength even though it may be made of material are actually soft like nickel and copper.

This can approach almost the theoretical shear strength of the material and that means the yields stress could be order of giga Pascal's. And additionally you also observe a hall petch kind of a behavior in a certain grain size or a bi layer period regime. Now, the hardening in such multi layers and super lattices has been explained using a number of concepts. We just list them here we do not go into the details of some of these. Because some of these are still debated upon which is the correct mechanism, which is the dominant mechanism and one kind of a system is correct kind of a mechanism.

Some of these we list here and we may make a few additional comments. They are talking about increase in barrier strengthening which is giving rise to this kind of an extraordinary strength in the nano scale. There is expected to be some kind of a coherency between the two layers. Suppose, I am talking about two layers, this is my layer A and this is my layer B. So, it is expected that this interface between layer A and layer B could be a coherent interface.

That means, it is there is an epitaxial relationship between this A and B layers and which gives rise to certain coherency stresses. These coherency stresses and these coherency stresses are going to modify your local stress rate, which is coming from an externally applied shear stress or a tensile stress. It is also assumed that if this bilayer period becomes large and if you start, what you might call a coherent system then, it will no longer remain coherent for large thickness. And in fact you may obtain misfit dislocations decorating the interface.

So, it typically you could have certain decoration or misfit dislocation along the interfaces which, implies that the system is partially coherent. And this misfit dislocation would impede the motion and this misfit dislocation as we have noted before is a structural dislocation. It is not a statistically stored dislocation in the bulk of the crystal and such a misfit dislocation would tend to give rise to certain hardening effect, which is seen which could attribute to the additional hardness of such a material in the nano scale.

Additionally there is the concept of the dislocation image force, which we have encountered before. This is due to the discontinuity in the elastic modulus at the interfaces. A few words may be necessary here because this is not the classical image force.

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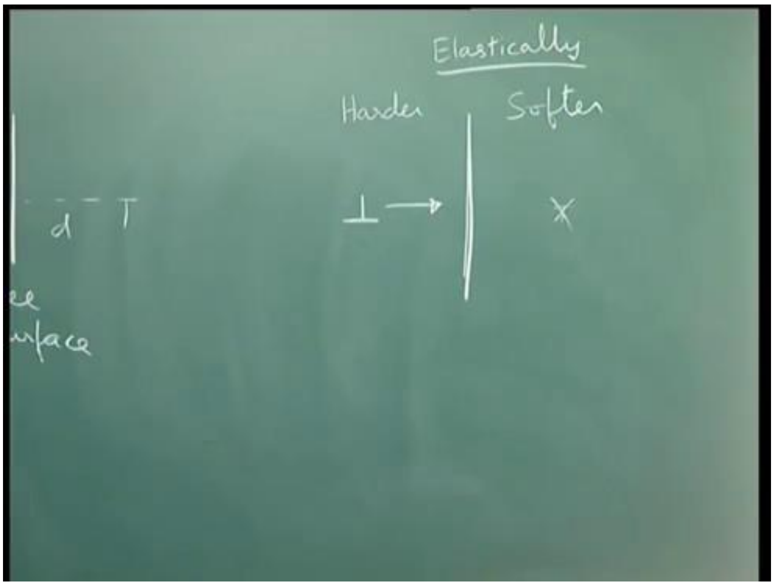

In the classical image force we have noted before that you have a free surface and there is a force which is attractive force towards the free surface. Now, we can extend this concept of an image force. In this case of course, I can make image construction and therefore, the attractive force between the two is called the image force, but I can extend this. This kind of a force is called a configurationally force because this is coming not because of an individual mass particle being attracted toward individual mass particle, but because of t h configuration of the entire system.

And such a configurationally force can also exist between for instance a harder material and a softer material. If I put a dislocation in a harder material, it will be attracted towards the softer material and this is I am talking about elastically harder or softer. So, if I have a harder material and the dislocation sits in the harder material and there is an interface with the softer material then, the dislocation may feel a force towards the softer material.

This kind of a configurational force can of course, loosely be called an image force even though we should understand that actually, now I cannot have an image construction because this is not valid any more. This is not free surface, this is a softer material. Nevertheless, the dislocation will feel a configurational force towards the softer interface because now the energy of the system would tend to decrease as the dislocation, its position close and closer to the softer material.

That means that such kind of effects also seem to play an important role in the strengthening of these bi-layers. And they have also been attributed to give some effect some additional to the hardening which has in this bilayers, which we have seen approaches the almost the theoretical shear strength of the material.

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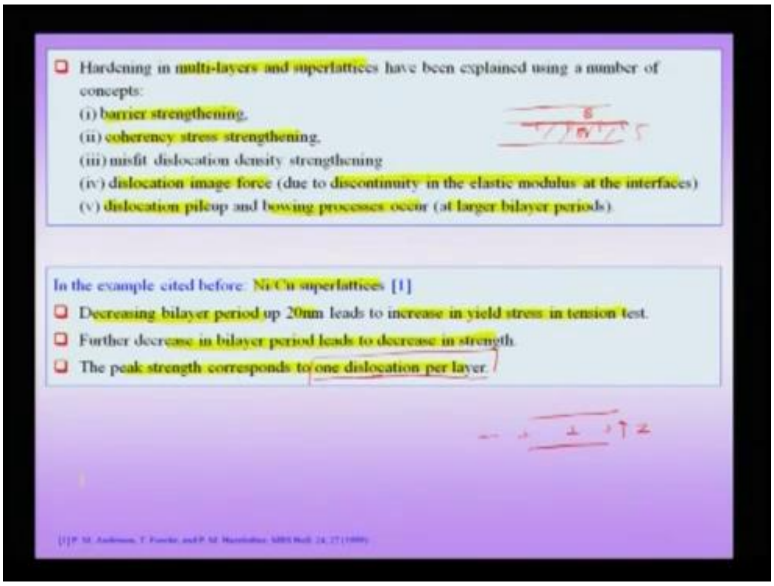

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Additionally of course, some common mechanisms which are observed in the case of large grain sized materials like dislocation pile up and bowing of dislocation, which is like the one bowing are also observed. Now, we have to note that this can only occur at larger bi-layer periods that mean, that in smaller bilayer periods we already noted that there is not enough space for a mechanism like a frank read mechanism or one bowing mechanism to operate.

We have already seen that in when you are talking about really small periodicity then, the whole region can only support only one dislocation per layer. That means that it is not possible to produce have put multiple dislocations. Of course, and I am talking about multiple dislocations, I am talking in the thickness direction.

So, there could be of course, many dislocations in the and of course, I am schematically showing here in the direction of the x or y, but in the z direction which is perpendicular or the direction of the periodicity of the laminate. You do not expect more than one dislocation and of course, you could have even smaller sizes when the system becomes completely dislocation free. In other words no dislocations are supported in the bulk of the two crystals, which make up the super lattice.

So, we see that in nano laminates we can obtain very high strength and to understand this we have to invoke a mechanism, which is now thickness dependent it is not independent of thickness. Therefore, if you go from larger bilayer periods to smaller bilayer periods, the mechanism may switch to a normal, what you call dislocation pile up or bowing mechanism.

The other kind of mechanisms which are operative like we just now saw the image force mechanisms etcetera at very small bilayer periods. Like we make a nano composite between as a laminate composite, we can also make nano composites the usual which is the particulate nano composites. Here in also we have of course, we see lot of beneficial effects of putting nano particles in a bulk matrix.

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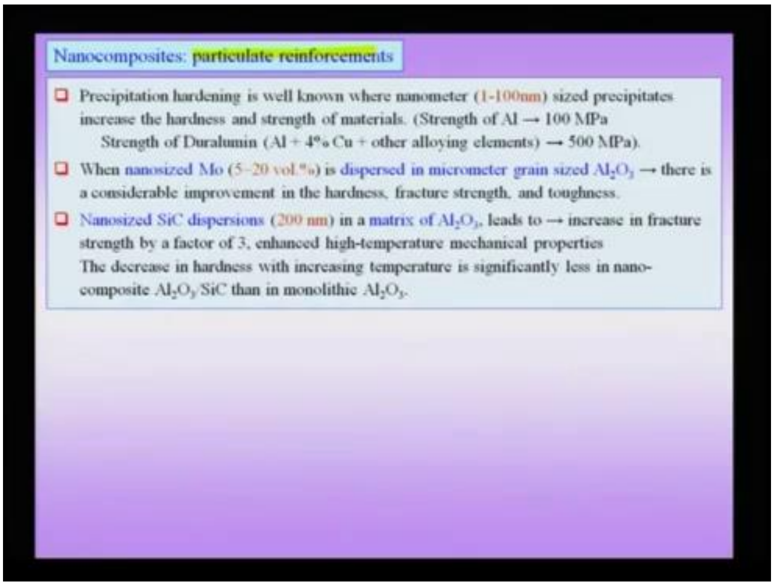

Nanocomposites: particulate reinforcements

- ☐ Precipitation hardening is well known where nanometer (1-100nm) sized precipitates increase the hardness and strength of materials. (Strength of Al → 100 MPa
  Strength of Duralumin (Al + 4% Cu + other alloying elements) → 500 MPa).
- ☐ When nanosized Mo (5–20 vol.%) is dispersed in micrometer grain sized Al_2O_3 → there is a considerable improvement in the hardness, fracture strength, and toughness.
- ☐ Nanosized SiC dispersions (200 nm) in a matrix of Al_2O_3, leads to → increase in fracture strength by a factor of 3, enhanced high-temperature mechanical properties
  The decrease in hardness with increasing temperature is significantly less in nano-composite Al_2O_3/SiC than in monolithic Al_2O_3.

The relevant nano entity in this whole system is the reinforcement. That means I could actually have a polycrystalline material and the grain size of this polycrystalline material is could be in the micron scale or tens or even hundreds of microns.

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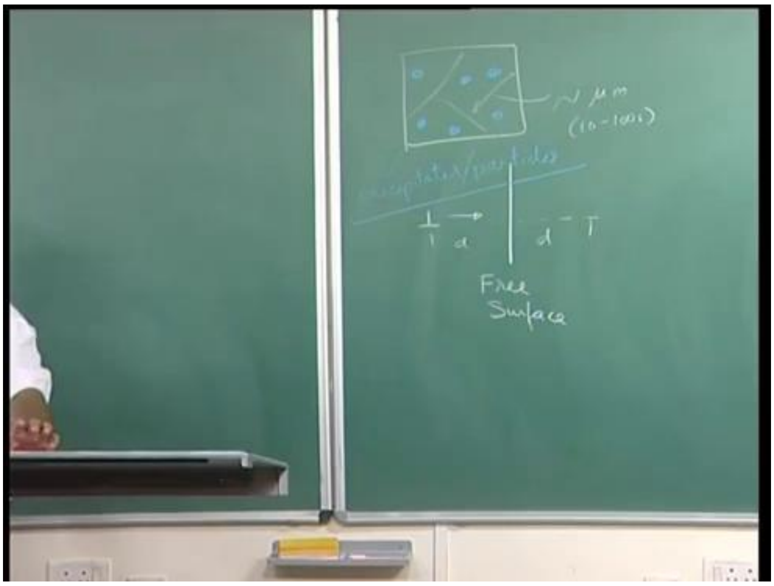

That means this is not the relevant nano scale dimension, but then I could put particles inside here, which are used as reinforcement. Now, I will draw schematically these particles as spherical particles though, there is no reason to believe they have to be spherical. These particles could also be precipitate and this nano scale dispersion of the second phase in a bulk first phase can actually give rise to tremendous increase in strength as shown in some of these examples here.

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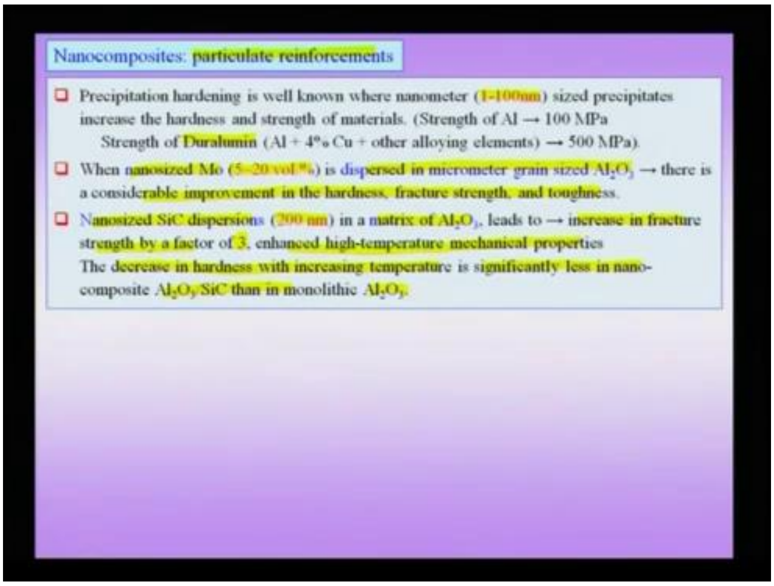

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We have already of course, talked in detail about the precipitation hardening system where in you have precipitates of the scale of 1 to about 100 nano meters. We will not repeat it here but, which is the case of the duralumin in which is a precipitation hardening system, but we will take up other examples like nano sized molybdenum in a volume fraction of about 5 to 20 percent. Then usual small volume fraction to a reasonable volume fraction when it is dispersed in a micrometer grain sized alumina that means, the grain size of alumina is no longer the nano scale.

It is only the molybdenum reinforcement which is in the nano scale there is considerable improvement in hardness fracture strength and toughness. So, you see that the properties are overall enhanced by putting nano sized molybdenum in a alumina. You know that alumina is ceramic that means that, it is prone to brittle fracture and its fracture toughness is expected to be small. Therefore, there is tremendous reason to add these kinds of particles, which would give you an increase in fracture strength and also the increase in toughness and toughness being the energy absorbed before fracture takes place.

Nano size silicon carbide dispersions, again we are talking about silicon carbide in the nano scale of about 200 nanometers in the same matrix, which is alumina matrix also leads to an increase in fracture strength by a factor of 3. So, this is very-very important because alumina as you know is being a ceramic being an oxide. It is in a stable state, so it is prone to it is resistant to some of those usual things with metals are not resistant like corrosion etcetera. It has a good elastic modulus as well, but the problem with ceramic as you know they are very intolerant to cracks. In other words they have poor fracture toughness.

So, by adding silicon carbide dispersions in nano scale you can get increasing strength factor of about fracture strength of about factor of 3, which is a pretty good increase. The high temperature mechanical properties are also pretty good and you know typically, the ceramic are do find applications in high temperature and this will be a good thing to add actually silicon carbide. The decrease in hardness with the increasing temperature which is what you expect because now, you have thermally activated motion of dislocation.

In other words in normal alumina at room temperature, the strength is very high because dislocations are not that glissile; the pearl stress is very large. Then when you go to high temperatures some of these will start showing plasticity, because now you can have thermally activated slip and also other mechanism like grain boundary, sliding may start to take place. Therefore, this softening effect is significantly reduced when you use an alumina silicon carbide composite rather than a monolithic alumina.

That means, you have benefits on all fronts, you have benefit in the fracture toughness, you have benefits in the high temperature strength and also in the case of molybdenum in alumina you actually have an increase in hardness and toughness. Therefore, it makes sense now to actually make some of these composites with reinforcements in the nano scale. We have already seen one example wherein a carbon nano tube has been used for reinforcement of alumina. We have seen that typically these are multi hole carbon nano tubes and by doing so you can actually get benefit in strength layer as well.

So, to summarize these slides we have of course, individual nano structures, which themselves so very good properties, but then we also have composites and hybrids where in at least one in relevant entity is in the nano scale, which can also give us improvement in the properties. Next we take up the issue of creep in nano materials, we had earlier talked about creep as a general phenomenon and we had also talked about various kind of creep mechanisms. We had talked about issues which will be highlighted when we go down to the nano scale.

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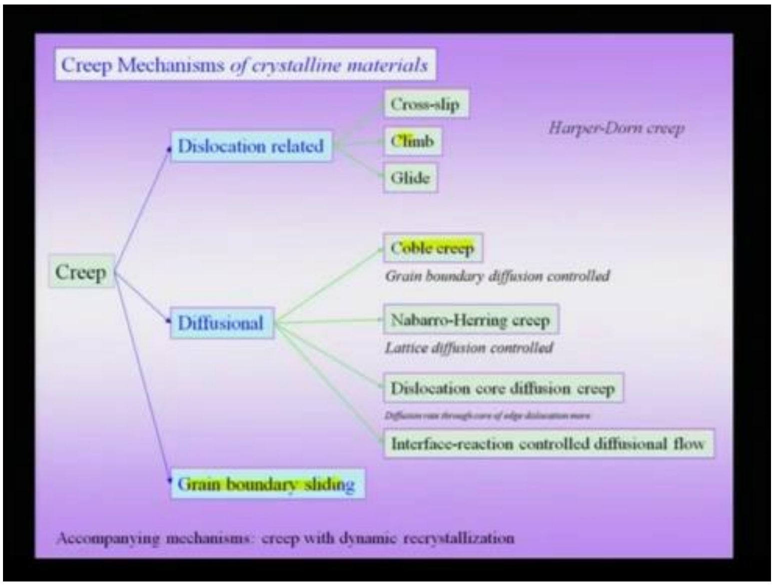

Creep Mechanisms *of crystalline materials*

- Creep
  - Dislocation related
    - Cross-slip
    - Climb
    - Glide
  - Diffusional
    - Coble creep
      Grain boundary diffusion controlled
    - Nabarro-Herring creep
      Lattice diffusion controlled
    - Dislocation core diffusion creep
      Diffusion rate through core of edge dislocation more
    - Interface-reaction controlled diffusional flow
  - Grain boundary sliding

Harper-Dorn creep

Accompanying mechanisms: creep with dynamic recrystallization

We say that some of these mechanisms have creep for instance when we talk about these diffusional mechanisms, when we talk about issues like climb. We said that when you go to nano scale, all these effects will be enhanced and therefore, you would expect certain high. What you call creep rates to be high additionally, we also noted one of the important mechanisms of creep is this grain boundary sliding and if you go down to A and we noted that for grain boundary sliding. In some sense, we have to cross the equi-cohesive temperature; decreasing the grain size in some sense is like increasing the temperature. Therefore, even at low temperature we said, we would expect some kind of a what you might call a behavior like a increased creep rate.

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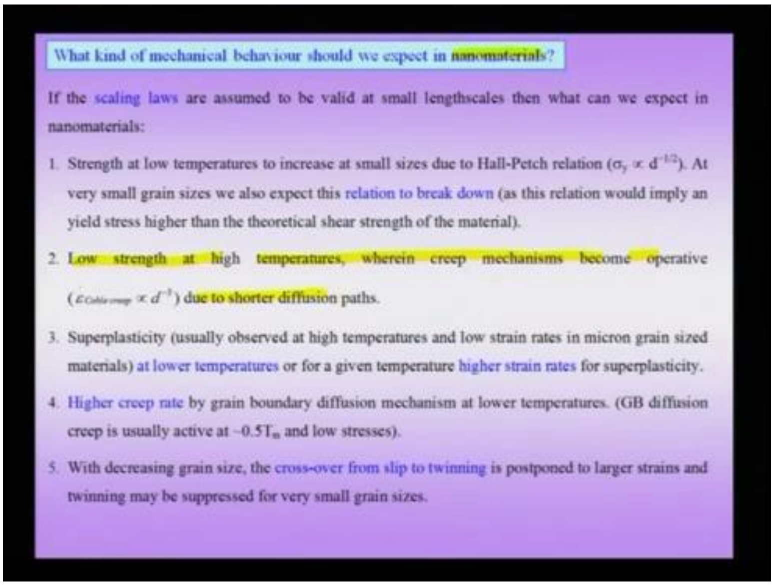

What kind of mechanical behaviour should we expect in nanomaterials?

If the scaling laws are assumed to be valid at small lengthscales 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 ($\dot{\varepsilon}_{Coble\ creep} \propto d^{-3}$) 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.

We have noted that we would expect nano structures in nano materials, high creep rates and that too at lower temperatures. So, this is what we had expected we had anticipated. Now, we will actually see how much of this is actually true when, you are talking about creep of nano materials.

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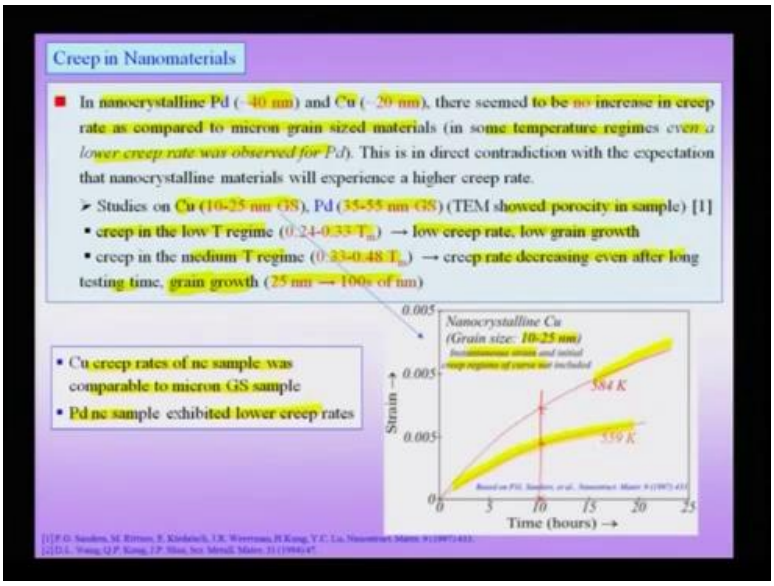

Creep in Nanomaterials

- In nanocrystalline Pd (~40 nm) and Cu (~20 nm), there seemed to be no increase in creep rate as compared to micron grain sized materials (in some temperature regimes *even a lower creep rate was observed for Pd*). This is in direct contradiction with the expectation that nanocrystalline materials will experience a higher creep rate.
  - Studies on Cu (10-25 nm GS), Pd (35-55 nm GS) (TEM showed porocity in sample) [1]
  - creep in the low T regime (0.24-0.33 T$_m$) → low creep rate, low grain growth
  - creep in the medium T regime (0.33-0.48 T$_m$) → creep rate decreasing even after long testing time, grain growth (25 nm → 100s of nm)

- Cu creep rates of nc sample was comparable to micron GS sample
- Pd nc sample exhibited lower creep rates

We will see in this case that in some systems we do expect, what our expectations were, but in many other systems we not only do not see what our expectations were, but we can even see effects opposite to the that what we had expected. So, if you talk about two important systems like nano crystalline palladium and copper, which have been pretty well, investigated. You can clearly see in these cases, the grain sizes of the order of 40 or 20 nano meters, which is extremely small. In this system there seem to be no increase in creep rate as compared to the micron sized counterpart.

So, this is pretty startling that we did expect that we would have increased creep rate, when you go down to nano sizes, but there was no increased creep rate. Of course, when we are comparing micron sized grain, we are using the same temperature as for the comparisons. And more surprisingly in some temperature regimes even a lower creep rate was observed in the case of palladium.

So, this is in direct contradiction of our expectations, which where we will be thought that there is going to be enhanced creep rate. Therefore, this is extremely surprising in the case of nano crystalline materials and the creep behavior studies on copper in the grain. Here we are talking about a small distribution of grain size, which is 10 to 25 nano meter and palladium 35 to 55 nano meters. Here in the 40 nano meters can we thought of an average in the regime between 35 and 55.

That means, again at the heart of the mechanisms, we have to keep in our mind that though there might be an average grain size reported in literature, but there is always a spread in grain sizes. More the statistical data we get we will actually find out what is the true distribution of grain size and t m in these structures showed there is porosity in the sample. That means, there was some damage, there was some and the question of course, arises as was this damage accumulated during the testing time or was it effect of the prior porosity in the sample. So, this is an important question.

I do not think the authors investigated that part. Creep in and then the creep study was done in two temperature regimes, one in the low temperature regime of about 0.24 to 0.33 t m and one in the medium temperature regime which is about 0.33 to p.5 t m. In this case there was low creep rate and low grain growth and in the case of the high or medium temperature regime the creep rate was decreasing, even after a long testing time and more importantly there was grain growth.

That means, that if I have grain growth I mean essentially changing the micro structure of the sample. Here we are not talking about small grain growth, we are talking about grain growth wherein the grain size increased by a factor of four or more. If this we are talking about the average grain size, which implies that the micro structure is continuously changing, maybe there is also porosity in the sample which is increasing.

Therefore, it is difficult to characterize creep in many of the nano crystalline materials because I cannot understand if this decreased creep rate is occurring because of the nano crystalline effect or is it occurring because of the increase in grain size, which is taking place during the test. Therefore, these are very serious issues associated with creep testing in materials.

There often we do see porosity often we do see lot of grain growth and therefore, it is difficult to separate out the effect, which is coming purely from the nano sized grains vis-a-vis the changing parameters structural parameter as the test is being conducted. Now, the below you shown for instance the studies on this copper material, which is has a grain size in the range of about 10 to 25 nanometers. In this plot the instantaneous strain, which is the elastic strain initially has been removed and the initial creep features of the curve also excluded in the plot.

If you observe this there are you see that at lower temperature of course, the overall creep strain at a given temperature. Suppose I take a temperature like time for about 10 hours. In 10 hours at lower temperature of course, you accumulate lower strain at higher temperature you accumulate higher strain, which is what is expected, but additionally you notice that the creep strains are continuously building up even after long hours of testing. To summarize this slide in copper, the creep rates in the nano crystalline sample was comparable to micron sized grain size sample, but in palladium nano crystalline sample actually, we could see certain lowered creep rate at certain temperature regimes.

So, this was extremely surprising as in the case of creep of nano materials, but this is of course, as I pointed out in the case of testing of nano crystalline materials. Even in cases where we are able to control the artifacts, the artifacts includes porosity in the initial sample artifacts include grain growth which we have just talked about even, when we are able to account for some of these effects.

There is no universality that means in some cases, you do observe a decreased creep rate, some cases you do not observe a similar creep rate to the micro crystalline counter parts, but there are other examples where in the creep rate increased with the decreased grain size in the nano scale regime. This was an alloy of nickel and phosphorous the creep rate of 30 nano meter.

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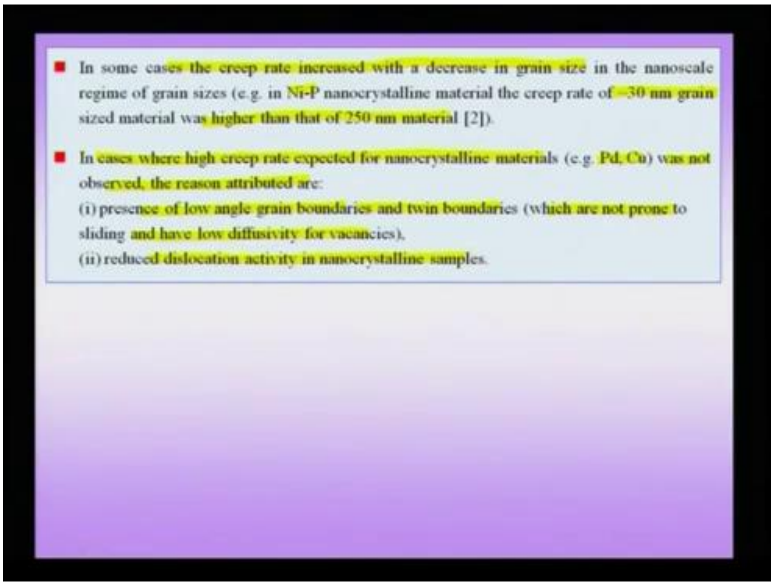

- In some cases the creep rate increased with a decrease in grain size in the nanoscale regime of grain sizes (e.g. in Ni-P nanocrystalline material the creep rate of ~30 nm grain sized material was higher than that of 250 nm material [2]).
- In cases where high creep rate expected for nanocrystalline materials (e.g. Pd, Cu) was not observed, the reason attributed are:
  (i) presence of low angle grain boundaries and twin boundaries (which are not prone to sliding and have low diffusivity for vacancies),
  (ii) reduced dislocation activity in nanocrystalline samples.

Grain sized materials was higher than the 250 nanometer grain sized material that means by decreasing the grain size. Of course, both these grain size are in the nano scale, one is 250 nano meters and one is 30 nano meters, there is an increase in the creep rate. So, we have seen that all three possibilities exist on reduction of the grain size. Of course, the comparisons are slightly different because in the first case we had compared in the case of copper. We had compared the nano grain sized with a micron grain size sample. Here we are comparing two nanometer grain sized samples and we see that there is actually an increase in creep rate as we decrease the grain size.

In cases where high creep rate expected for nano crystalline materials like we see for palladium and copper, which are nice metallic materials where the diffusion rate is high was not observed. The reasons are typically attributed to the presence of low angle grain boundaries and twin boundaries. These low angle grain boundaries are as you know low energy configurations. Typically low angle grain boundaries by the read shockley model are decorated by these structural dislocations, which actually accommodate the mis orientation.

These are not prone to sliding and have a low diffusivity for vacancies. Therefore, there is a predominance of these low angle grain boundaries. What is theoretical basis for understanding that why such a material in spite of being in the nano scale does not show high creep rate. Additionally low dislocation activity is also being attributed to this low creep rate. We had seen that even when there is grain boundaries sliding two other factors often come into the picture, one is dislocation activity and other is diffusion.

So, because we have just grain boundary sliding you will have triple junction cracks and this triple junction cracks have to be heeled by diffusion. Otherwise, what you call heeled out by plastic deformation which involves dislocation activity.

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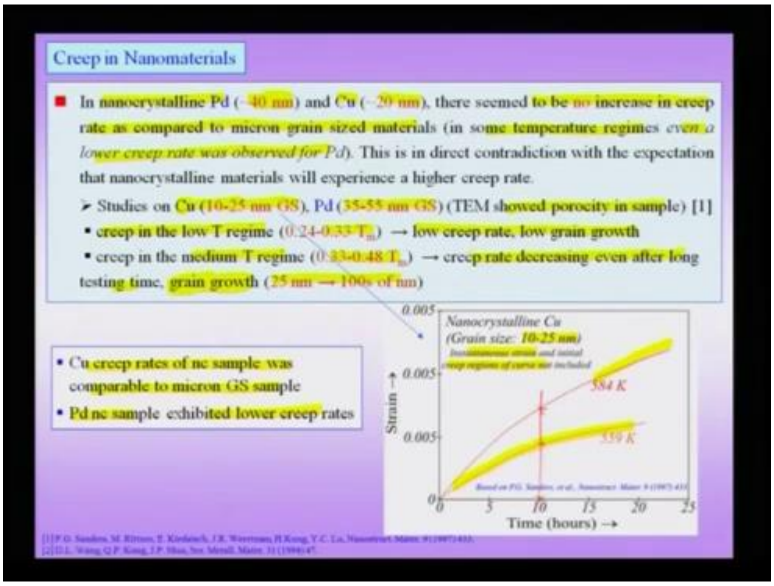

Creep in Nanomaterials

- In nanocrystalline Pd (~40 nm) and Cu (~20 nm), there seemed to be no increase in creep rate as compared to micron grain sized materials (in some temperature regimes *even a lower creep rate was observed for Pd*). This is in direct contradiction with the expectation that nanocrystalline materials will experience a higher creep rate.
  - ➢ Studies on Cu (10-25 nm GS), Pd (35-55 nm GS) (TEM showed porocity in sample) [1]
  - creep in the low T regime (0.24-0.33 T_m) → low creep rate, low grain growth
  - creep in the medium T regime (0.33-0.48 T_m) → creep rate decreasing even after long testing time, grain growth (25 nm → 100s of nm)

- Cu creep rates of nc sample was comparable to micron GS sample
- Pd nc sample exhibited lower creep rates

Therefore to summarize these two slides on creep of nano materials, we have cases where there is an increase in creep rate on decreasing size. There are cases where there is no not much difference to be talked about, but they are also cases where there is an increased creep rate on decreasing the grain size. One nice example where actually an increased creep rate with decreasing grain size was seen is in nano crystalline nickel and these are room temperature studies.

So, this is very interesting because now we have no this is something very close to the kind of expectation. We had earlier raised that we would have higher creep rate under two conditions perhaps under higher strain rate and at lower temperatures.

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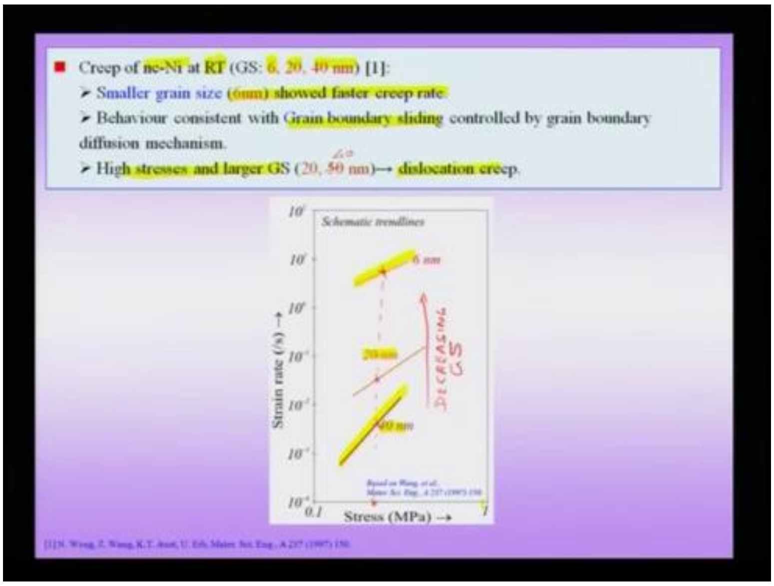

- Creep of nc-Ni at RT (GS: 6, 20, 40 nm) [1]:
  - Smaller grain size (6nm) showed faster creep rate
  - Behaviour consistent with Grain boundary sliding controlled by grain boundary diffusion mechanism.
  - High stresses and larger GS (20, $\overset{40}{50}$ nm)→ dislocation creep.

[1] N. Wang, Z. Wang, K.T. Aust, U. Erb, Mater. Sci. Eng., A 237 (1997) 150

So, here the temperature is at room temperature and of course, we are now making comparisons of grain sizes in the extremely small regime. In the grain size of the order of 6 nano meter, 20 nano meter and 40 nano meter. Now, if you see the plot of these three grain sizes, so you have the highest grain size the 40 nano meter grain size here and you have a decreasing grain size as you go from here to here. Now, what you note that this is stress strain rate plot and for a given stress and for a given testing time, you notice that actually, the strain rate increased with decrease in grain size.

The smaller grain size sample the 6 nano meter sample shows a faster creep rate. And this behavior was attributed to grain boundary sliding and which is of course, accommodated by certain diffusion mechanism, but the high stresses and larger grain sizes that mean that if I go to the higher stress regime. If I am talking about like the larger grain sizes like the 20 nano meter or 40 nano meter of samples then dislocation creep seems to the important mechanism. So, we can replace this fifty by forty because this is the, which is originally involved in the study.

So, this is a very nice example the creep of nano crystalline nickel at room temperature wherein some of the initial expectations are actually fulfilled. And within this small grain size regime of about 60 to 40 nano meter we are actually seeing a switch in the mechanism. The small grain size seems to be actually seems to some sort of undergoing green boundary sliding accommodated by diffusion, while the larger grain sizes under higher stresses seem to undergo dislocation. We had noted some of these regions in the creep mechanism map, which we had seen earlier. So, the creep mechanism map we had noted that it is usually in the higher stress region, which is this axis that you tend to observe dislocation creep and in the low stress region you tend to observe diffusional creep.

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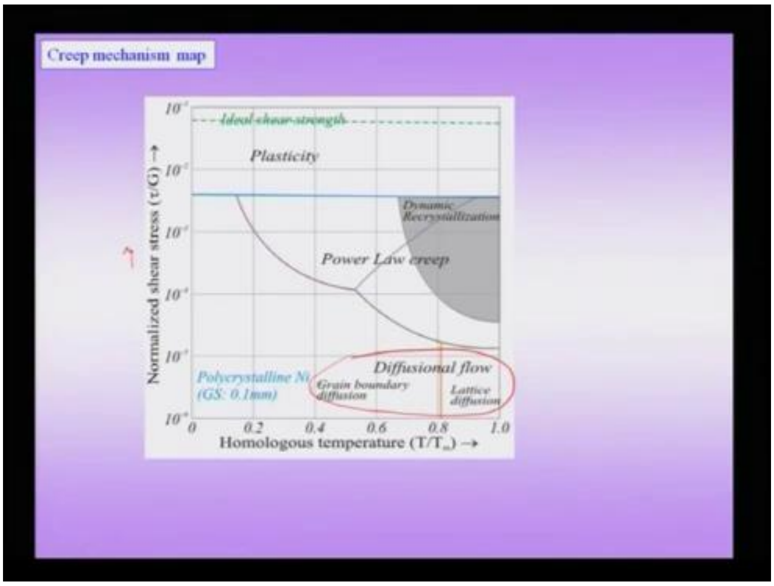

Creep mechanism map

So, you see that this is the region of the diffusional creep and in higher stress region, you actually obtain dislocation creep. So, this is a very interesting study again we have to keep a few things in mind that when you are talking about 6 nano meter grain size. We have to worry that obviously the grain size is not just one number like 6 nano meter, there is going to be a spread in the grain sizes. Nevertheless, keeping all the other artifacts away we notice that, this is a very interesting example where increased creep rate has been observed at room temperature.

The creep mechanism is consistent with our expectation that it is going to be grain boundary sliding at low grain sizes, but nevertheless in spite of 40 and 20 nano meters being a small grain size, that you see a switch in mechanism especially, when you apply higher stress. So, we have all kinds of material here we have pure palladium, pure copper, we have alloys like nickel phosphorus, nano crystalline material and we also have nickel. You see that each one of these though some of them are very similar like nickel and copper is f c c materials. We do see a very wide variety of behavior in the nano scale materials.

So, as far as the understanding goes today that there is no what may call generalized principle, which you can apply to understand creep of nano materials. Though we do understand some of the mechanisms which you would operate to a larger grain sizes and the mechanism, which would be operative at smaller grain sizes. We had made lot of observations regarding super plasticity in nano materials. We had also noted previously that super plasticity in some sense is a very closely related phenomenon to creep, except that in super plasticity damage accumulation does not lead to failure.

Therefore, you are able to get very long tensile elongations of the order of 350 percent to 2000 percent. Therefore, this gives us a beautiful mechanism by super plastic deformation. We can obtain nice shapes and we can use it as a nice production method.

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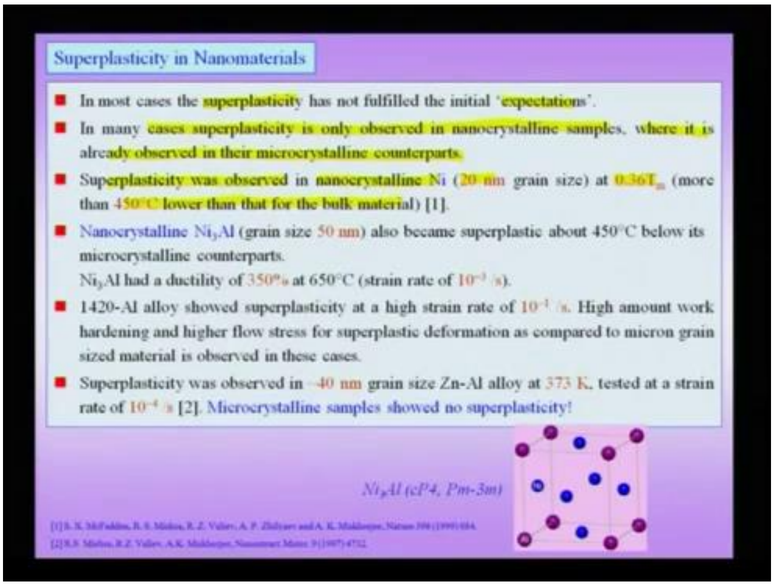

Superplasticity in Nanomaterials

- In most cases the superplasticity has not fulfilled the initial 'expectations'.
- In many cases superplasticity is only observed in nanocrystalline samples, where it is already observed in their microcrystalline counterparts.
- Superplasticity was observed in nanocrystalline Ni (20 nm grain size) at $0.36T_m$ (more than 450°C lower than that for the bulk material) [1].
- Nanocrystalline Ni_3Al (grain size 50 nm) also became superplastic about 450°C below its microcrystalline counterparts.
  Ni_3Al had a ductility of 350% at 650°C (strain rate of 10^{-3} /s).
- 1420-Al alloy showed superplasticity at a high strain rate of 10^{-1} /s. High amount work hardening and higher flow stress for superplastic deformation as compared to micron grain sized material is observed in these cases.
- Superplasticity was observed in ~40 nm grain size Zn-Al alloy at 373 K, tested at a strain rate of 10^{-4} /s [2]. Microcrystalline samples showed no superplasticity!

But in most cases it is observed that the initial expectations are again not fulfilled as far super plasticity nano materials is concerned. In many cases super plasticity is only observed in nano crystalline samples where, it is already observed in micro crystalline counter parts that mean, there is nothing very surprising. We have already seen that many cases; we see a completely contradictory behavior in nano crystalline materials as compared to bulk materials. Later on also we will see examples for instance, there are materials which are anti-ferromagnetic in the bulk, but which will tend to become ferromagnetic in the nano scale.

So, these are very surprising effects, but in case of super plasticity most of the cases it is seen that, super plasticity is only observed in cases where already the micron scales grain size sample you observe super plasticity. Super plasticity observed in micro nano crystalline nickel with a grain size of about 20 nano meter at 0.360 m that means it is more than about 450 degrees lower than the bulk material. So, I said that the initial expectations are not fulfilled. We will take up a few examples to see that where there are some interesting results.

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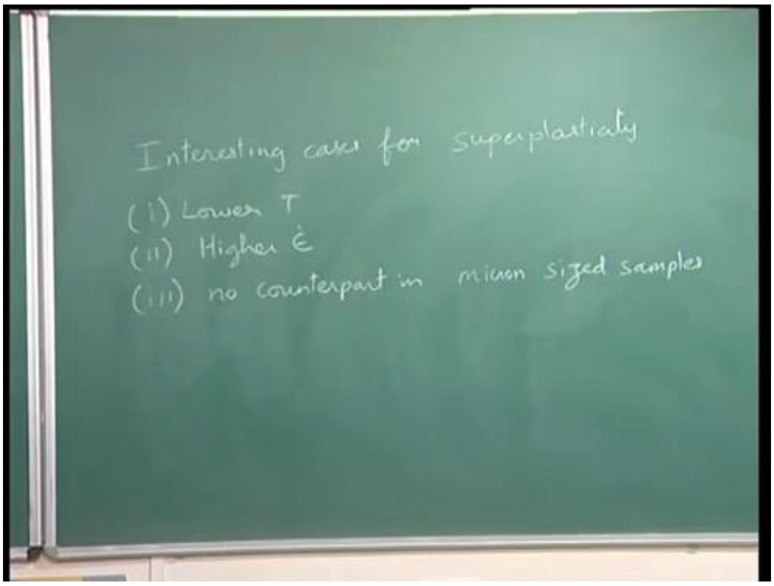

Interesting cases for superplasticity

(i) Lower T

(ii) Higher $\dot{\epsilon}$

(iii) no counterpart in micron sized samples

There are some examples where you did not observe super plasticity and in the micro-crystalline counterparts, but you did observe but, did it in the nano crystalline version. You observed it at a higher strain rate, which is also pretty good or you observed it at lower temperature. So, all three cases would be very-very interesting, so maybe I should write this down. So, we will take up a few examples to see some of these you might call interesting cases do exist when you are talking about super plasticity in nano materials.

The first one is a case of nickel, wherein the 20 nanometer grain size sample super plasticity was observed more than 450 degrees lower than that for the micron grain sized or larger grain sized bulk counterpart. So, this is very very interesting. In nano crystalline n i 3 a l and you know n i 3 a l is an inter metallic, which is got a structure of c p 4 and the unit cell of typical n i 3 a l unit cell is shown here at the bottom of the graph.

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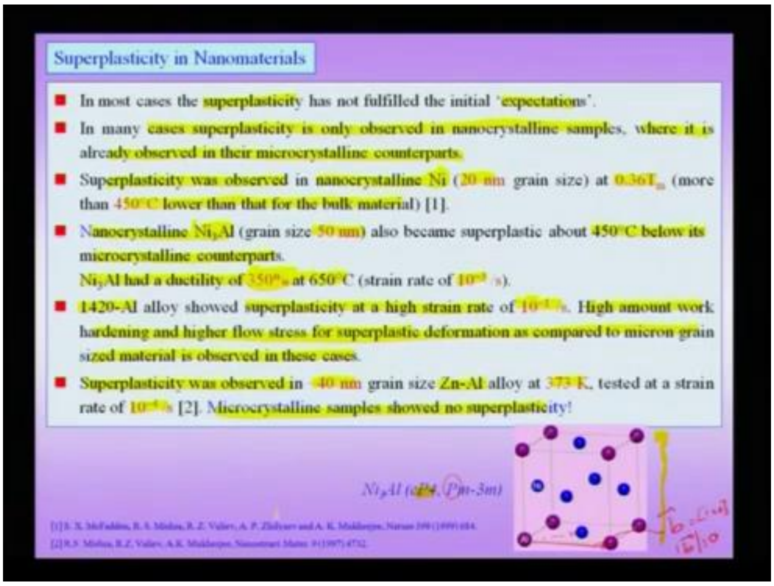

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When compared to the disordered alloy, you would notice that the burgers vector is larger in this structure. Now, the fundamental lattice translational vector because it is a primitive structure is this. If you had a disordered n i 3 a l, it would have been destructed which is as a length of root 2 by 2 while, in this case it root 2 by 2 a. In this case the burgers vector has a magnitude of 1 0 0 and therefore, the mode of the burgers vector is equal to a.

That means that the pearl stress in such alloys these ordered structure is going to be large and typically they would behave in a very brittle fashion and with very low tensile ductility at room temperature. So, if you observe super plasticity in these cases, it is actually is very-very surprising and the fifty nano meter grain size nano crystalline n i 3 a l became super plastic 450 degrees below its micro-crystalline counter parts.

So, this is again very beneficial that means that n i 3 a l is a technologically important inter metallic and therefore, if I am able to super plastically form n i 3 a l 450 degrees below its micro-crystalline counter parts. I have very important industrial applications for the nano crystalline sample. N i 3 a l had a ductility of 350 percent at 650 degrees at a strain rate of about 10 power minus 3 per second.

So, here and again we are not talking about very high strain rates of deformation. Reasonably what you might call so slow strain rates of deformation, but nevertheless we have a good ductility of 350 percent. Given the fact that these inter metallic normally tension in tested in tension would have very negligible ductility this is very good. You can see the temperature is also very reasonable for a industrial application.

So, we have therefore, we are able to see super plasticity at reduced temperature in a pure material like nickel. Also in inter metallic like n i 3 a l in the case of 1 4 2 0 aluminum alloy showed super plasticity at high strain rate of about 10 power minus 1 per second. High amount of work hardening and higher flow stress for super plastic deformation as compared to the micro size sample is also observed in these cases.

This implies that one of the at least the important expectations is fulfilled in the case of the 1420 aluminum alloy wherein, very high strain rates ten power minus one is typically, the almost like normal tensile kind of a test strain rate, which you in a slow test. You might want to perform and therefore, this is not typically the regime of super plastic forming like for instance 10 powers minus 3 or 10 power minus 4.

So, these are couple of orders of magnitude higher than what you would usually employ in a super plastic deformation. Still you are able to obtain a good deformation in the case of this aluminum alloy. The high amount of work hardening also implies that there is an accumulation of what you may call dislocation density actually, hardening the material. Here also you observe that the stress for super plastic forming is higher than its micron sized counterparts. Other interesting example is in the case of super plasticity in the 40 nanometer grain size zinc aluminum alloy. This example is interesting because this alloy showed super plasticity about 373 kelvins, which is a very low temperature and a strain rate as of course.

The important thing here the micro crystalline samples that mean the bulk counterparts of this showed no super plasticity. So, this is another very interesting example and therefore, we have covered a gamut of all the possibilities. We have covered pure materials like nickel, we have covered inter metallic like n i 3 a l, we had talked about alloys like zinc aluminum alloy and 1420 aluminum alloy. We have seen that super plasticity does take place in one of these cases at high strain rates.

In couple of these cases you observe super plasticity at what you might call much lower temperatures. Additionally you also observe super plasticity in cases where, there is no super plasticity in the bulk counterpart. So, this is a very interesting gamut of possibilities when it comes to super plasticity of nano materials. So, we need to now worry about what is the mechanisms underlying the super plasticity and what are the issues, which we need to address, if you want to understand the results correctly.

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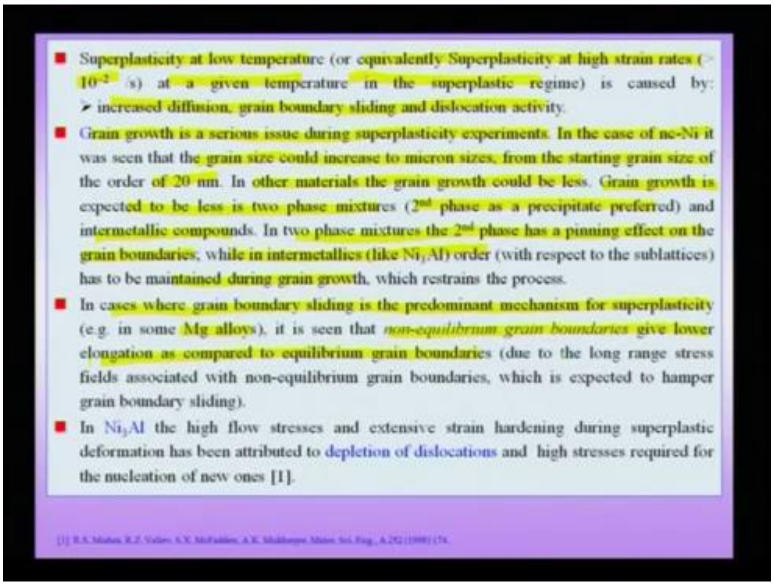

- Superplasticity at low temperature (or equivalently Superplasticity at high strain rates (> 10^{-2} /s) at a given temperature in the superplastic regime) is caused by:
  - ➢ increased diffusion, grain boundary sliding and dislocation activity.
- Grain growth is a serious issue during superplasticity experiments. In the case of nc-Ni it was seen that the grain size could increase to micron sizes, from the starting grain size of the order of 20 nm. In other materials the grain growth could be less. Grain growth is expected to be less is two phase mixtures (2nd phase as a precipitate preferred) and intermetallic compounds. In two phase mixtures the 2nd phase has a pinning effect on the grain boundaries, while in intermetallics (like Ni_3Al) order (with respect to the sublattices) has to be maintained during grain growth, which restrains the process.
- In cases where grain boundary sliding is the predominant mechanism for superplasticity (e.g. in some Mg alloys), it is seen that *non-equilibrium grain boundaries* give lower elongation as compared to equilibrium grain boundaries (due to the long range stress fields associated with non-equilibrium grain boundaries, which is expected to hamper grain boundary sliding).
- In Ni_3Al the high flow stresses and extensive strain hardening during superplastic deformation has been attributed to depletion of dislocations and high stresses required for the nucleation of new ones [1].

Super plasticity at low temperature or equivalently of course, super plasticity at a given temperature in the super plastic regime is caused by increased diffusion grain boundary sliding and dislocation activity. So, we have already seen that when you go down to nano crystalline sizes. It is usually the grain boundary sliding mechanisms which, becomes prominent and this grain boundary sliding is has to be accompanied by some diffusion and dislocation activity.

So, this seems to be the overall picture regarding, how the super plasticity is obtained in such kind of materials, nano crystalline materials at either high strain rates or at lower temperatures than what you expect for the micro crystalline counterparts. Like in the case of creep, grain growth seems as very serious issue during super plasticity experiments. If grain growth is going to take place and if you are expected super plasticity mechanism is grain boundary sliding then, obviously the elongations you are going to get is going to be limited purely because of grain growth issues.

In the case of nano crystalline nickel, it was seen that the grain size could increase to micron sizes starting from grain size of the order 20 nano meter. So, this is happening during the testing that means during super plastic forming. The grain size is increasing from about 20 nano meter to about something of the micron sized, which is a very serious issue in super plastic testing. That means that even though my initial material had this ability to deform to large extent, but during the test itself the grain growth would rather reduce my overall available ductility.

In other materials the grain growth could be less, I mean this was a very drastic example in the case of nano crystalline nickel, but in other experiments. In other experiments it is not necessary that the same kind of grain growth was the issue, but nevertheless grain growth could have taken place. You always expect that grain growth to be less in a two phase mixture, if the second phase especially is a precipitate. They are inter metallic compounds because in inter metallic compounds.

As you know they are very hard then and the grain boundary is less glissile. In two phase mixture the second phase has a pinning effect on the grain boundaries while, in inter metallic like n i 3 a l. The order has to be maintained as the grain growth has to take place. Suppose, I really want super plasticity retaining my grain growth and my final product have the same grain size as my initial starting testing sample.

That implies that I have to either work with a two phase mixture where, the second phase could be a precipitate or a kind of a dispersion, which will sort of impede my grain growth which, will have a pinning effect on the grain boundaries migration and therefore, leading to grain growth. I need to work with the inter metallic wherein the grain boundary migration involves also is impeded by the fact that now you have two sub lattices or more.

And for instance in the case of the n i 3 a l, one sub lattice is occupied by aluminum and the remaining threes sub lattices are occupied by nickel. Therefore, this sub lattice structure has to be maintained and this means that grain boundary motion is going to be more difficult. In cases where, the grain boundary sliding is the predominant mechanism for super plasticity. One example for that is typically magnesium based alloys, it is seen that non equilibrium grain boundaries give a lower elongation as compared to equilibrium grain boundaries.

This is expected due to the long range stress fields associated with the non-equilibrium grain boundaries, which is expected to hamper grain boundary sliding. So, this is an important effect wherein, you are talking about two kinds of grain boundaries that grain boundary, which is called an equilibrium grain boundary. When we use the terminology equilibrium, we have to remember that we are not talking about a global equilibrium because in the global equilibrium case, the system would not want to have a grain boundary. It would rather prefer to be a single crystal.

What do you mean by a equilibrium? In this case, a local kind of an equilibrium and what is implied by a non-equilibrium grain boundary is a fact that, there are additional dislocations which are not the structural dislocations, which resides close to the grain boundary.

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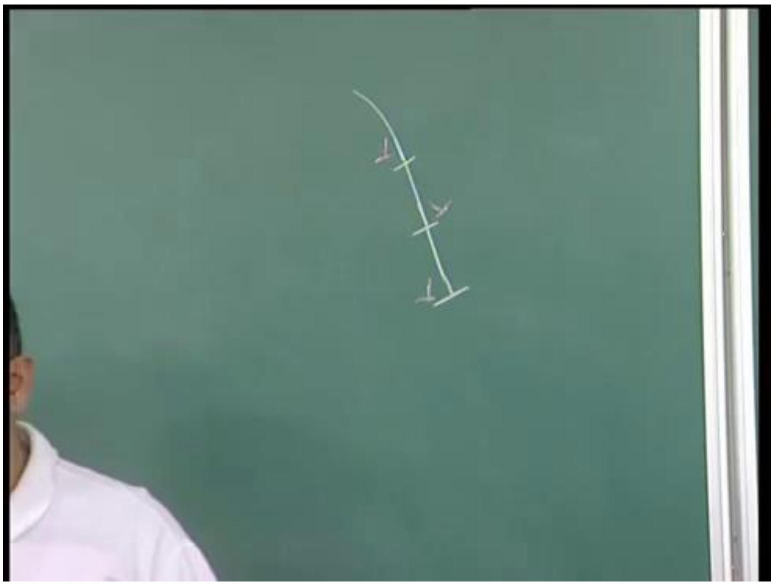

So, you have a grain boundary and this grain boundary itself may be by the read Shockley model may have certain dislocations, which are now the inter facial dislocations, but or the grain boundary dislocations. In addition to it this grain boundary may be associated with additional dislocations. These additional dislocations which I am drawing in red, which give rise to a long range stress feel for this grain boundary because this array of dislocation does not have a long range stress feel while, these red dislocation will give rise to a long range stress feel.

Due to this long range stress feels the associate with the non-equilibrium grain boundaries is expected to hamper grain boundary sliding. So, this is issue which is wherein, the people have gone into details of the mechanisms of how the grain boundary sliding take place. And what kind of a grain boundary would give you what you call an easy grain sliding versus a difficult sliding. It is seen that equilibrium grain boundaries would slide easier as compared to the non-equilibrium grain boundaries, which are associated with long grain stress field.

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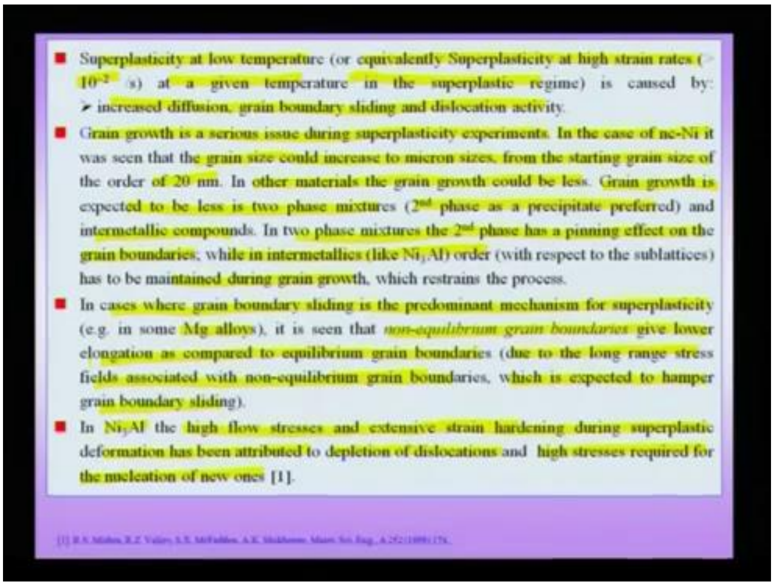

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[1] R.S. Mishra, R.Z. Valiev, S.X. McFadden, A.K. Mukherjee, Mater. Sci. Eng., A 252 (1998) 174.

In the case of n i 3 a l the high low **s**tress and extensive strain hardening during super plastic deformation has been attributed to depletion of dislocations and high stresses required for nucleation of new ones. So, we notice when we talked about the n i 3 a l structure and its super plastic forming here and we notice that you have super plastic deformation of 50 nano meter grain size sample.

It is observed here that the high flow stress is observed and additionally, there is extensive strain hardening during super plastic deformation that means, with progress in super plastic deformation, the stress has to be increased. That means the forming cannot take place at constant stress and this is attributed to depletion of dislocations and high stresses required for nucleation of new ones.

So, this is being the reason why n i 3 a l is difficult to form, but we have to also note the additional fact that n i 3 a l being an ordered structure, the dislocation structures. The kind of partials we are talking, the kind of stacking folds we are talking is going to be very different from that of a normal material like aluminum. For instance n i 3 a l would have something known as super latticed intrinsic stacking folds super latticed extrinsic stacking folds, which are not observed in the normal metallic counterparts. Next we take up the important issue. We had lot to say about a quantity known as the strain rate sensitivity.

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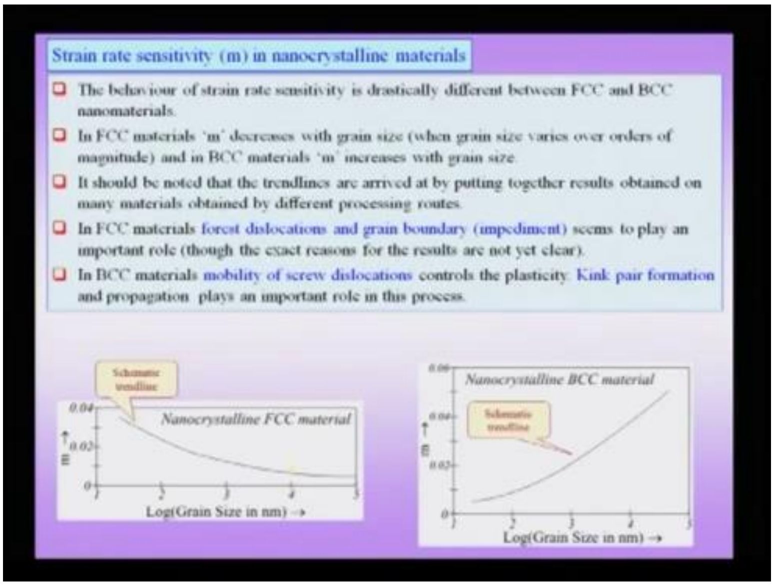

Strain rate sensitivity (m) in nanocrystalline materials

- The behaviour of strain rate sensitivity is drastically different between FCC and BCC nanomaterials.
- In FCC materials 'm' decreases with grain size (when grain size varies over orders of magnitude) and in BCC materials 'm' increases with grain size.
- It should be noted that the trendlines are arrived at by putting together results obtained on many materials obtained by different processing routes.
- In FCC materials forest dislocations and grain boundary (impediment) seems to play an important role (though the exact reasons for the results are not yet clear).
- In BCC materials mobility of screw dislocations controls the plasticity. Kink pair formation and propagation plays an important role in this process.

So, let us go back in review our sides wherein we have talked about this quantity called the strain rate sensitivity.

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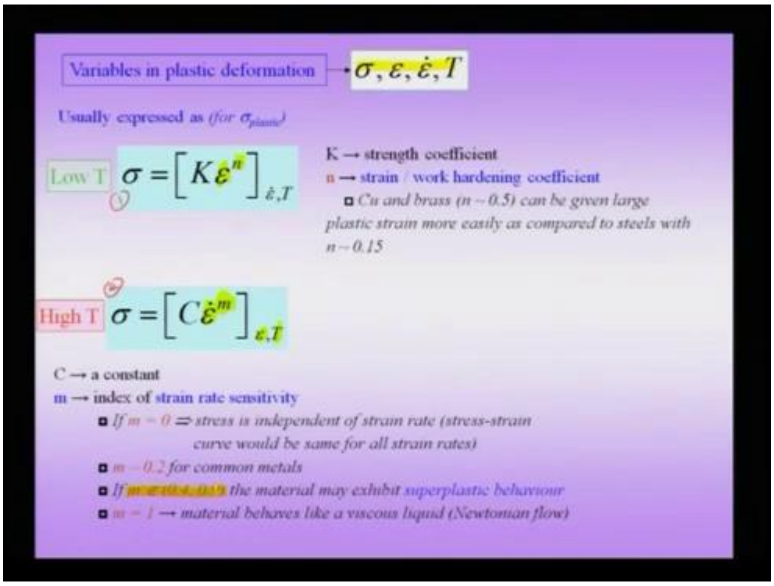

Variables in plastic deformation → $\sigma, \varepsilon, \dot{\varepsilon}, T$

Usually expressed as (for $\sigma_{plastic}$)

Low T $\sigma = \left[K\varepsilon^{n}\right]_{\dot{\varepsilon},T}$

K → strength coefficient

n → strain / work hardening coefficient

- Cu and brass ($n \sim 0.5$) can be given large plastic strain more easily as compared to steels with $n \sim 0.15$

High T $\sigma = \left[C\dot{\varepsilon}^{m}\right]_{\varepsilon,T}$

C → a constant

m → index of strain rate sensitivity

- If $m = 0 \Rightarrow$ stress is independent of strain rate (stress-strain curve would be same for all strain rates)
- $m \sim 0.2$ for common metals
- If $m \in (0.4, 0.9)$ the material may exhibit superplastic behaviour
- $m = 1$ → material behaves like a viscous liquid (Newtonian flow)

We had said that we can do deformation at low temperatures or high temperatures. When I mean low temperatures, we had said that temperature below the recrystallization temperature is about 0.5 t m or less. We had noted at low temperatures the important variable the relevant variable amongst the four important variable stress strain rate and temperature is strain at high temperature. In other system at low temperature system sort of becomes a build for energy. More and more dislocation densities tend to increase and the system is a battery, and if you spending some amount of energy part of this energy is stored in the micro structure in the form of increased point effect density and dislocation density. So, it becomes a battery.

At high temperatures the micro-structure continuously renews itself that means, you have recrystallization recovery process taking place as the deformation is progressing. This is typically called dynamic recrystallization. Therefore, the micro structure is constantly renewing itself and therefore, the flow stress is not increasing with progressive deformation. So, here there is strain hardening and therefore, you have an exponent known as the strain hardening exponent.

At high temperatures the relevant variable is train rate and not strain and of course, you would do all these test to work on constant strain at a constant temperature. The important Para exponent here is strain rate sensitivity and of course, these two equations, the first one above and the second one which is relating the first one relates stress strain and the second one relates stress strain rate. Both are phenomenological equations typically found to for a certain broad class of materials and approximately true for the other kind of materials.

Therefore, at high temperatures the strain rate sensitivity becomes an important parameter. We had noted that when you have high strain rate sensitivity we typically expect super plastic behavior. We had seen examples of this high strain rate sensitivity in super plastic deformation. We had noted that in the case of super plasticity, the region with high strain rate sensitivity like between 0.4 and 0.67 is referred to as the super plastic regime in log stress strain rate.

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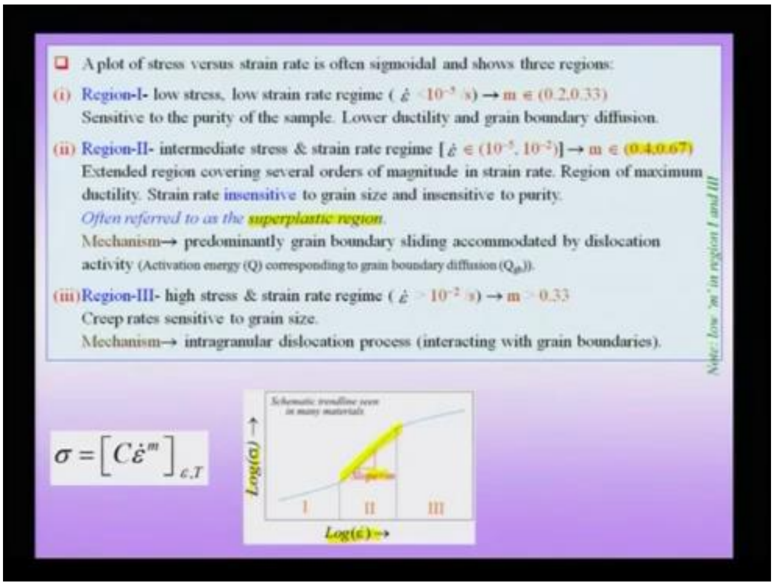

- ☐ A plot of stress versus strain rate is often sigmoidal and shows three regions:

(i) Region-I- low stress, low strain rate regime ($\dot{\varepsilon} < 10^{-5}$ s) → m ∈ (0.2,0.33)
Sensitive to the purity of the sample. Lower ductility and grain boundary diffusion.

(ii) Region-II- intermediate stress & strain rate regime [$\dot{\varepsilon} \in (10^{-5}, 10^{-2})$] → m ∈ (0.4,0.67)
Extended region covering several orders of magnitude in strain rate. Region of maximum ductility. Strain rate insensitive to grain size and insensitive to purity.
Often referred to as the superplastic region.
Mechanism→ predominantly grain boundary sliding accommodated by dislocation activity (Activation energy (Q) corresponding to grain boundary diffusion (Q_{gb})).

(iii) Region-III- high stress & strain rate regime ($\dot{\varepsilon} > 10^{-2}$ s) → m > 0.33
Creep rates sensitive to grain size.
Mechanism→ intragranular dislocation process (interacting with grain boundaries).

Note: low 'm' in region I and III

$$\sigma = \left[C\dot{\varepsilon}^{m} \right]_{\varepsilon, T}$$

So, this is where you get extensive super plastic deformation and this is a region of high strain rate sensitivity. Now, we will say a few more things about strain rate sensitivity especially the difference in the behavior of strain rate sensitivity between f c c and b c c materials.

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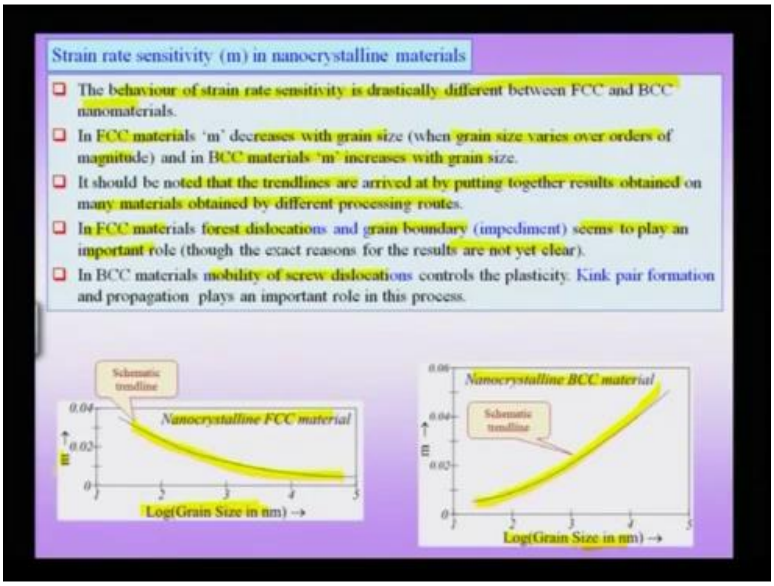

Strain rate sensitivity (m) in nanocrystalline materials

- ☐ The behaviour of strain rate sensitivity is drastically different between FCC and BCC nanomaterials.
- ☐ In FCC materials 'm' decreases with grain size (when grain size varies over orders of magnitude) and in BCC materials 'm' increases with grain size.
- ☐ It should be noted that the trendlines are arrived at by putting together results obtained on many materials obtained by different processing routes.
- ☐ In FCC materials forest dislocations and grain boundary (impediment) seems to play an important role (though the exact reasons for the results are not yet clear).
- ☐ In BCC materials mobility of screw dislocations controls the plasticity. Kink pair formation and propagation plays an important role in this process.

So, how is that the strain rate sensitivity is going to change in nano crystalline materials especially, as you change the grain size as shown in the plot below. First I will go to the plot and we will come back to the test very soon. If a plot strains rate sensitivity as a function of grain size and now I am in the nano scale regime.

Of course, I am plotting log of the grain size, you notice that for f c c nano crystalline materials the strain rate sensitivity decreases with an increasing grain size. On the other hands suppose I talk about nano crystalline b c c material like iron then, I notice that the strain rate sensitivity actually increases with an increase in the grain size. So, the effects are exactly opponent when you are talking about nano crystalline materials and the parameter of strain rate sensitivity.

That implies that the behavior of strain rate sensitivity is drastically different between f c c and b c c materials. There is some understanding, which we will see very soon, but the complete picture is not yet out. In f c c material m decreases with grain size and this grain size variation is over a few orders of magnitude. In b c c material m increases with grain size unlike in the f c c materials.

It should be noted that the trend lines, which we have seen below. These are trend lines and these are not exactly followed for one material or one testing condition are arrived putting together results obtain in many materials. These are obtained through many processing roots. We have already seen the important differences and important property differences, which can come from processing root itself. We had noticed that in the case for instance electron deposited nickel how different in properties it can be from for instance a powder it consolidated nickel.

So, we have seen that processing root can play a very profound role profound in a profound influence on the properties. Therefore, when we see such trend lines we have to keep that at the back of the mind. In f c c materials so far our understanding goes that, forest dislocations that means a singular dislocation cutting through a forest of other dislocations. Grain boundary impediment seems to play an important role and the exact reason for the strain rate sensitivity is not yet clear.

So, we will not discuss that aspect more, but this forest dislocation hardening mechanism and also the grain boundary impediment mechanism seems to play an important role in f c c materials in b c c materials. On the other hand mobility of screw dislocation seem to control the whole plasticity of course, this is true for any kind of b c c material. This strain rate sensitivity dependence also seems to have a very profound connection with this mobility of screw dislocations in b c c materials.

The reason being that in b c c materials, the edge component actually has a lower pearl stress as compared to the screw component in any material and in b c c materials. The screw dislocation actually has a core splitting along the 1 1 1 plane in three equivalent 1 1 1 kind of a direction three perpendicular directions which are one twenty degree apart.

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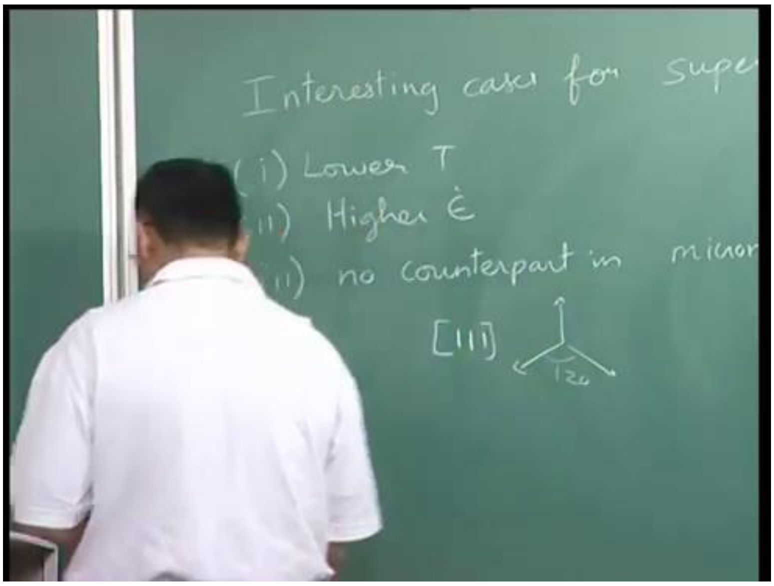

As you know, in screw dislocation in b c c materials or in the burgers vector is along the one one-one direction. The screw dislocation actually splits the core of the dislocation splits along three directions, which are 120 degree apart now. Of course, this kind of a splitting implies that if the screw dislocation has to move then, the core has to collapse and move to a new plane. This implies that the pearl stress for motion of screw dislocations is very large. Therefore, if I am doing the plastic deformation of the sample having edge and screw dislocations or more precisely having edge in screw components.

The edge component would actually leave the crystal, which implies that I will be left with more of screw kind of components in the material. This high pearl stress implies that instead of the entire dislocation line moving there is a mechanism, which is if you refer to the slide now known as the kink pair formation mechanism its propagation seem to play a very important role.

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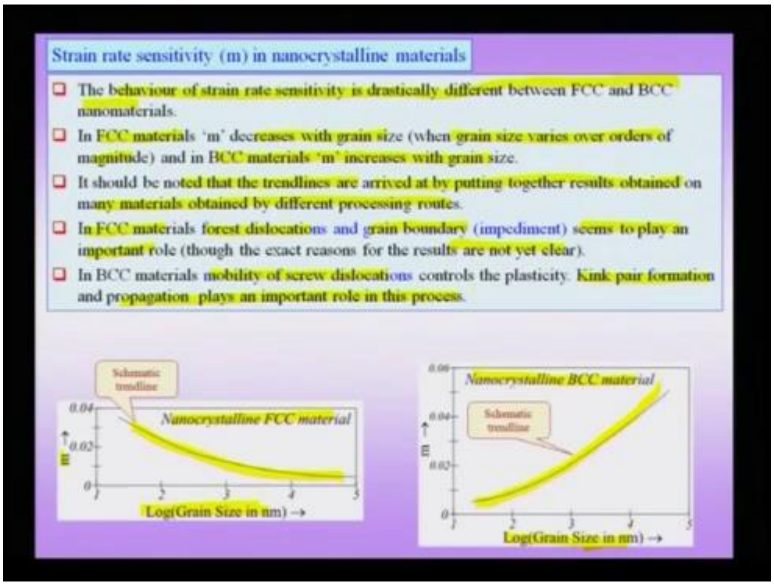

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So, I will briefly draw what is meant by this kink pair formation mechanism. Its propagation to understand plastic deformation in b c c materials. And also the case of which, is directly connected or which is given as one of the important reasons for this strain rate sensitivity.

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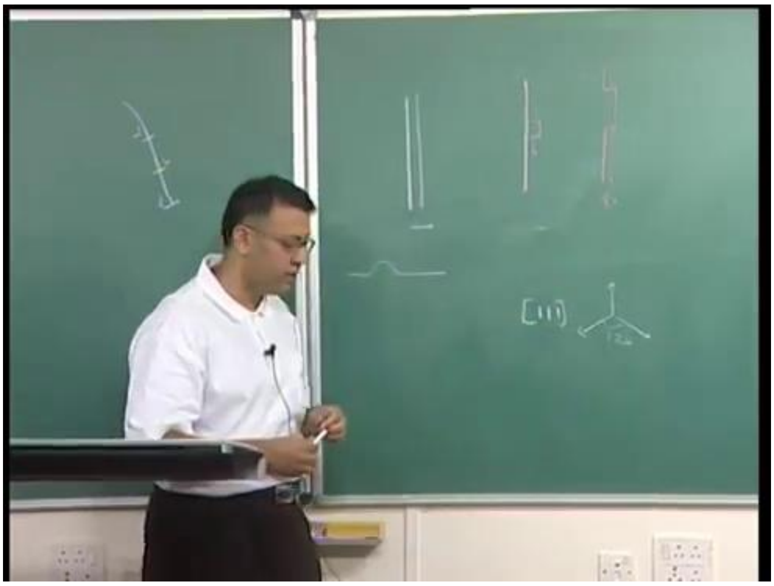

So, you have a dislocation line the entire dislocation line can move by a burgers vector and come here. The alternate possibility is that this dislocation line may actually develop a kink pair that means it can form a double kink like this and then this double kink can actually propagate. Now, the stress I need to apply is much smaller because I am only propagating a small segment. I am not propagating the entire dislocation by one burger vector.

So, this can actually propagate. Finally, of course, when the entire these segments would have left to the top, this segment comes down to the bottom. I would have the motion of dislocation stepped up by one b. Therefore, I can see that dislocation itself is a media medium by which actually you can actually avoid the shearing of the entire crystal. You reduce that problem of the shearing of the entire crystals to small regions in the crystal.

Typically the analogy given is a fold in a carpet that you actually make a fold in a carpet and role it. It is moving they are pulling the entire carpet I make a fold and roll down this fold down and to actually get a little elongation. I can make repeated folds to move the carpet. So, this is the analogy given to understand how a dislocation weakens a crystal, but this is a second order effect wherein even this whole dislocation need not go by one single burgers vector.

You can nucleate a kink pair and this kink pair can propagate orthogonal to the direction of the motion of the dislocation finally, moving the dislocation. So, I can actually have a second order mechanism operating, which is going to weaken my crystal, but nevertheless it is these trend lines we need to keep in mind.

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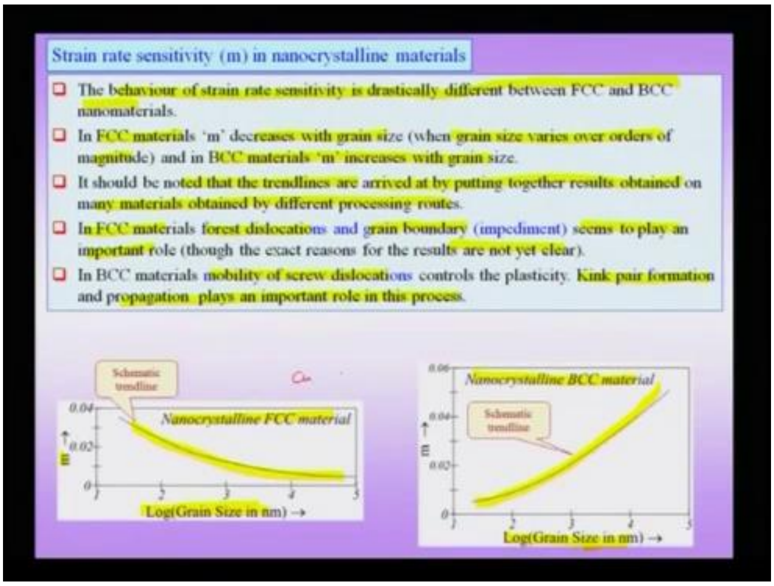

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We have exactly opposite trend lines when it comes to strain rate sensitivity of nano crystalline materials and this is for instance could be a a material like b c c, f c c copper. This could be a material like f c c iron and b c c iron. Additionally a few more points to be noted are the deformation in nano structured material seem to occur predominantly by dislocation at interfaces and not bulk dislocation you notice that.

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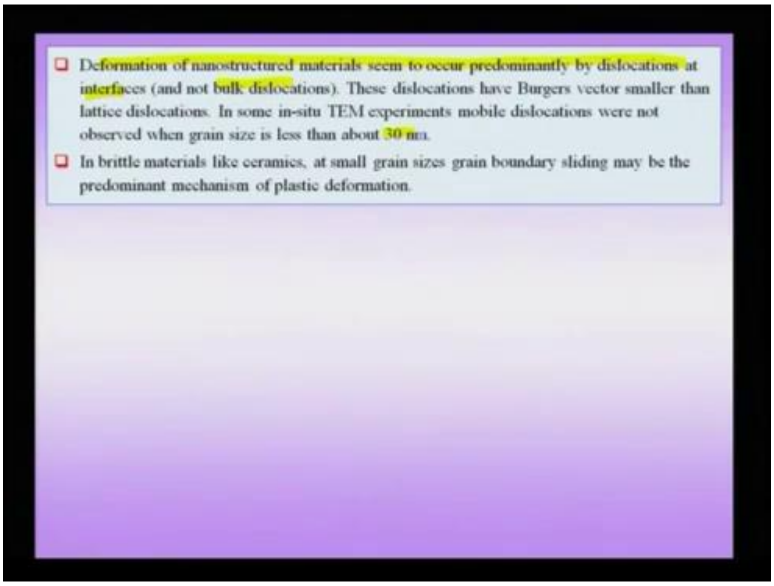

- ❑ Deformation of nanostructured materials seem to occur predominantly by dislocations at interfaces (and not bulk dislocations). These dislocations have Burgers vector smaller than lattice dislocations. In some in-situ TEM experiments mobile dislocations were not observed when grain size is less than about 30 nm.
- ❑ In brittle materials like ceramics, at small grain sizes grain boundary sliding may be the predominant mechanism of plastic deformation.

And this of course, we are talking about very small grain sizes of the order of about 30 nanometers. When you are talking about really large grain sizes where hundred nanometers and more where actually you can have bulk dislocations. You can continue to have pile ups, you can continue to have what you call orowan bowing and frank read mechanisms. You when go to really small grain sizes then dislocations at interface is seem to play a very-very important role. You when noted that an example here that these are some of the inter-facial dislocations grain boundary dislocations.

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Additionally, some of these gets closely associated which creates my non equilibrium grain boundaries. And if this dislocation sits exactly at the grain boundary, then they seem to have, they have a burgers vector smaller than the lattice dislocations.

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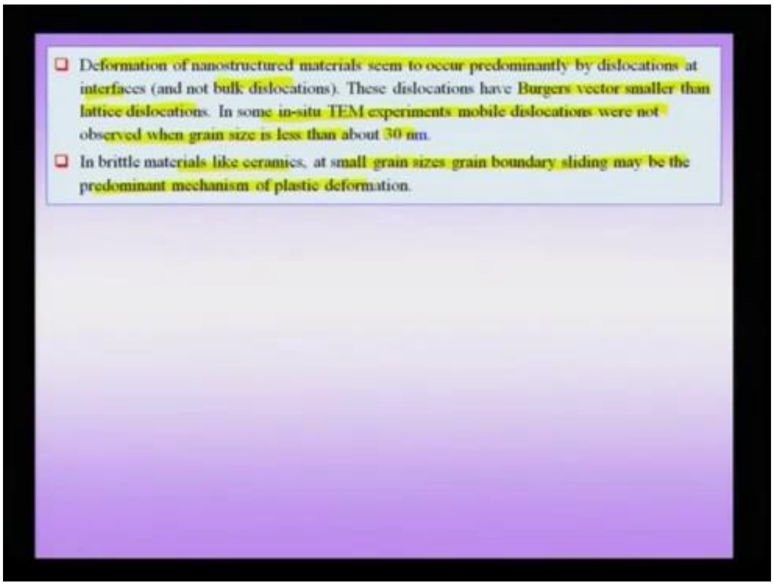

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- ☐ In brittle materials like ceramics, at small grain sizes grain boundary sliding may be the predominant mechanism of plastic deformation.

In some in situ t m experiment mobile dislocation observed were not observed when the grain size is below 30 nano meter. That means really t m experiments have confirmed the fact that when you go down to really small grain sizes like 20 nano meter and 30 nano meter, they seems to be positive of lattice dislocations. It is a grain boundary region, which becomes important from including from sliding perspective and also from the perspective of dislocation activity.

And in brittle materials like ceramics at small sizes grain, boundary sliding may be the predominant mechanism for plastic deformation. So, this already we have stated it before which is restating it that grain boundary is a region of activity and brittle materials like ceramics. Typically there is not much of dislocation activity at low temperatures and therefore, you expect that grain boundary sliding is going to be important phenomena.

However, we have been repeatedly saying some of the aspects. We just summarized this here that much more work has to be done to understand creep super plasticity and also plastic deformation in general in nano crystalline materials. We have already noted that in some cases the grain boundary structure is found to be similar to the bulk counterparts. Some cases there is a difference between the grain boundary structure in a bulk versus the nano.

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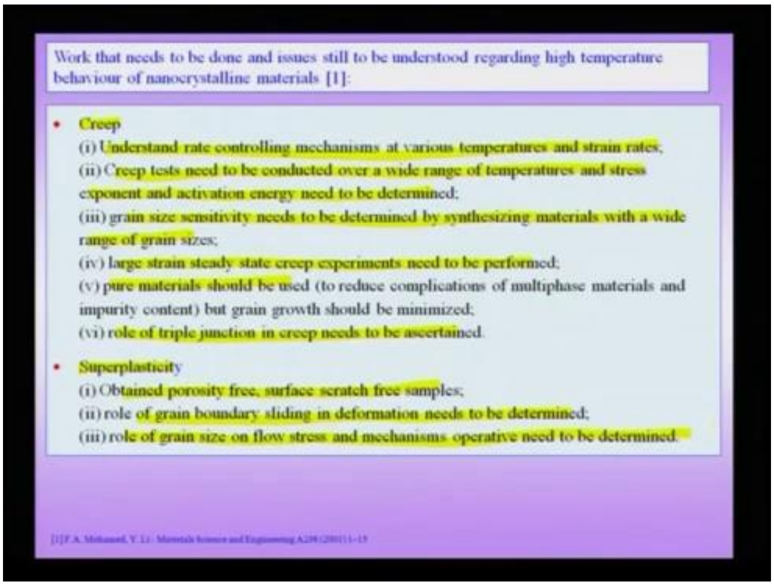

Work that needs to be done and issues still to be understood regarding high temperature behaviour of nanocrystalline materials [1]:

- Creep
  (i) Understand rate controlling mechanisms at various temperatures and strain rates;
  (ii) Creep tests need to be conducted over a wide range of temperatures and stress exponent and activation energy need to be determined;
  (iii) grain size sensitivity needs to be determined by synthesizing materials with a wide range of grain sizes;
  (iv) large strain steady state creep experiments need to be performed;
  (v) pure materials should be used (to reduce complications of multiphase materials and impurity content) but grain growth should be minimized;
  (vi) role of triple junction in creep needs to be ascertained.
- Superplasticity
  (i) Obtained porosity free, surface scratch free samples;
  (ii) role of grain boundary sliding in deformation needs to be determined;
  (iii) role of grain size on flow stress and mechanisms operative need to be determined.

[1] F.A. Mohamed, Y. Li : Materials Science and Engineering A298 (2001) 1-15

So, what is the work we need to be done so that we can now put creep and super plasticity and sound wherein, we can talk about a broader class of materials under one umbrella of under few our parameters of understanding? In the case of creep understanding rate control mechanism as various temperatures and strain rates needs to be understood. Creep test need to be conducted over wide range of temperature and stress. This stress exponent and activation energy needs to be determined.

Grain size sensitivity needs to be determined by synthesizing materials with the wide range of grain sizes. It is a very challenging problem and not only, when you are talking about very wide range of grain sizes, we are talking about close to mono disperse grain size. Large strain steady state creep experiment need to be performed, which is another area where lot of work needs to be done.

Pure materials should be used because typically in multiphase materials we have seen a few examples. Though there is an advantage of using them because grain growth is small, but the understanding the underlying mechanisms become difficult in multiphase materials. The role of triple junctions in creep also needs to be ascertained that means that we have already seen that triple lines and quadruple junctions are all very important. In the case of nano materials but, their role is poorly understood.

When it comes to creep in case of super plasticity, we need to obtain porosity free samples and surface scratch free samples because surface scratches can severely limit the overall super plasticity, which I am going to get. The role of grain boundary sliding in deformations needs to be determined that how much part of it is actually grain boundary sliding? How much of it is actually plasticity or dislocation related mechanisms? Role of grain size on flow stress and mechanisms operative also needs to be determined.

So though we have briefly listed some of the factors. It is also clear along with these. We are ought to talk about additional effects like for instance artifacts, which can come from the samples processing roots and etcetera, etcetera, which also always underlie when we are talking about. Some of these important effects, which need to be d-convoluted that means important effects, which we need to understand. So, I can understand creep and super plasticity and also general plastic deformation of nano crystalline materials.

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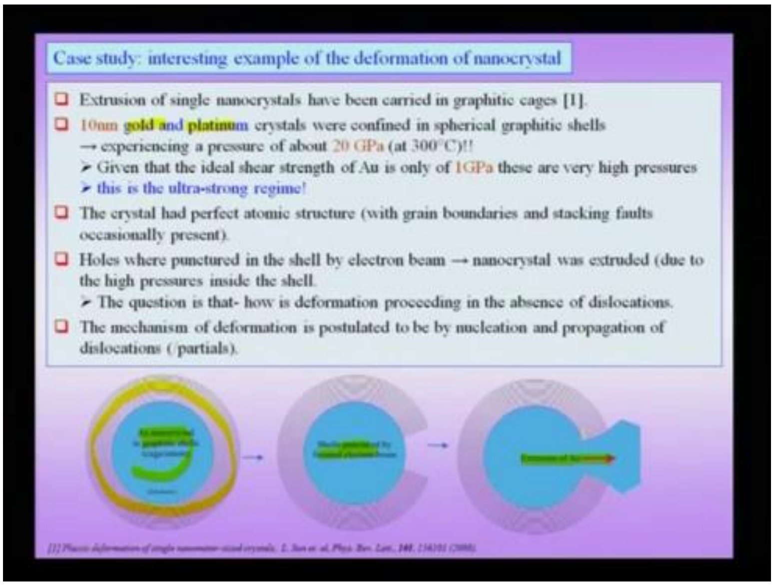

Case study: interesting example of the deformation of nanocrystal

- ❑ Extrusion of single nanocrystals have been carried in graphitic cages [1].
- ❑ 10nm gold and platinum crystals were confined in spherical graphitic shells → experiencing a pressure of about 20 GPa (at 300°C)!!
  - ➢ Given that the ideal shear strength of Au is only of 1GPa these are very high pressures
  - ➢ this is the ultra-strong regime!
- ❑ The crystal had perfect atomic structure (with grain boundaries and stacking faults occasionally present).
- ❑ Holes where punctured in the shell by electron beam → nanocrystal was extruded (due to the high pressures inside the shell.
  - ➢ The question is that- how is deformation proceeding in the absence of dislocations.
- ❑ The mechanism of deformation is postulated to be by nucleation and propagation of dislocations (/partials).

So, we will take up two case studies two interesting examples of deformation of nano structured materials or nano crystals. In one example, the first example I talk about. What was done is that a carbon onion. If you look at a figure below there is a carbon onion that means, there are multiple layers or graphite like shells inside, which there is gold nano crystal or in an experiment conducted. This could be gold or platinum nano crystal, which is enclosed within this cage. So, during the experiment what is done is that, so you have a gold which is a metal, which is inside this granitic or carbon onion shells.

This is punctured by a focused electron beam, the shells are punctured. Then this is extruded using this nano cage. Now, this is like a nano extrusion shell. So, you have a carbon onion which is punctured and this gold actually is extruded like you would do a bulk extrusion from this carbon onion cage. This extrusion has been studied.

Now, if you go back to an very early experiment going back to ajayan. What he did was he took such a carbon onion shell and without of course, gold inside. He put it under the electron beam of a 1.25 million volt electron microscope and to his surprise, he found that the core region of this carbon onion. See, we have this nice carbon onion shells.

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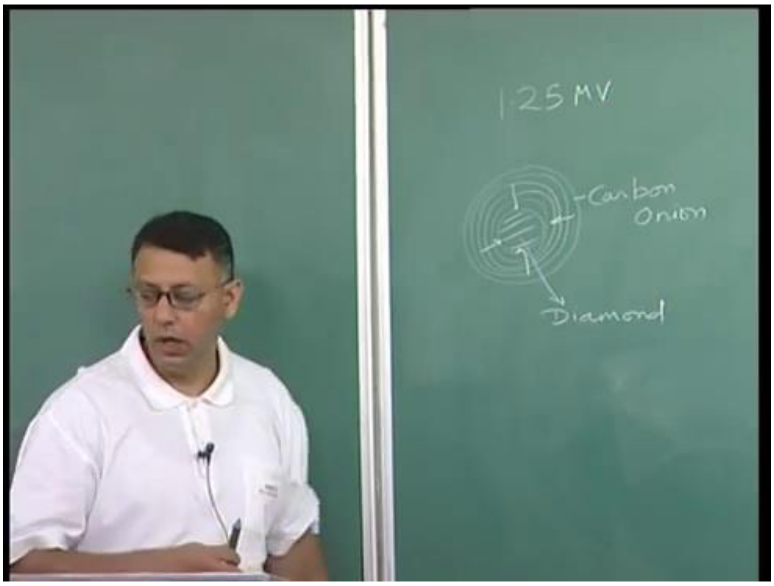

This is schematic he found that the core region purely under the electron irradiation. So, you are using electron microscopic with 1.25 million volt electron microscope. So, inside this these carbon onion and this is carbon onion here and this is became diamond. In other words under the electron irradiation and the intense pressure coming from these carbon shells, this interior of the carbon onion became diamond.

So, this is very interesting experiment, which was published in nature. So, you see that these carbon shells are actually imposing very high kind of compressive stress on the material inside. This is a later version of this experiment; where in this high pressure has been used for the extrusion of gold. So, in this experiment what they do is that they take carbon onion and then using this graphite stages they extrude gold or platinum. The size of this nano crystal is about 10 nano meter which is present inside; this blue color thing is about 10 nano meter.

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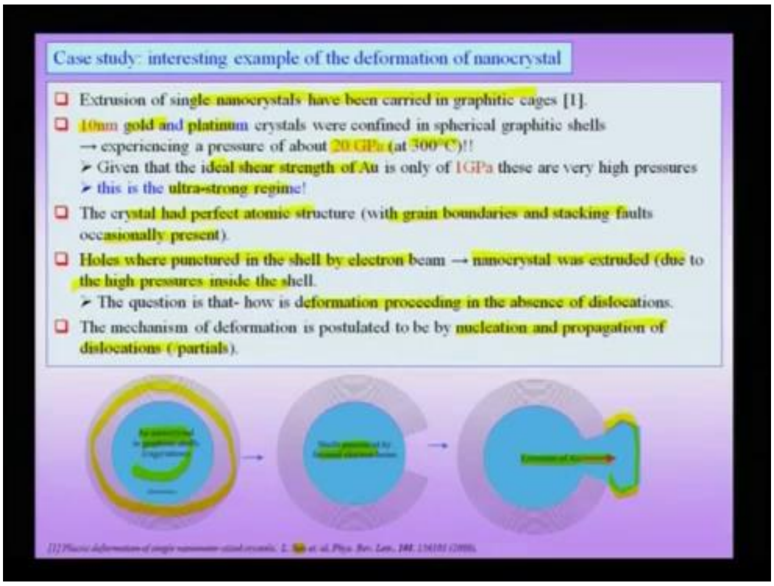

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This is a confined kind of a nano crystal the pressure experienced at about 300 degree Celsius is of the order of 20 g p a. So, this extremely high pressure, which is what this small carbon onion cages able to impose on this gold or platinum nano crystal. Given, that the ideal shear strength of gold is only about 1 g p a. You see that this regime can be actually called the ultra-strong regime. Therefore, you are actually extruding or keeping the material in the ultra-strong condition under this kind of a carbon onion shell.

The crystal had a perfect atomic structure with grain boundaries and stacking faults occasionally present, so the gold crystal when you observe it under electron microscope. Occasionally, you do see grain boundaries and stacking faults, but apart from that, these are a perfect crystal and because of the high pressure the lattice parameters actually smaller than the bulk lattice parameter. When holes are punctured by an electron beam, the nano crystal was extruded due to the high pressures inside the shell.

Of course, the important question to ask, if there are no dislocations in the material because you can see that there are grain boundaries and the stacking faults, but they are no dislocations. Then how is deformation proceeding in the absence of dislocation. Is it going to dislocation diffusional mechanism like a creep, which is operatively diffusional creep or is it some other mechanism?

The mechanisms which the authors of this paper which is sun eta. They have proposed is that, the mechanism is supposed to be because of nucleation and propagation of dislocations.

Though in the transmission electron microscopy observation, they did not observe any dislocation, but they did molecular dynamic study and per yearly they perform diffusion calculation to show the diffusional effects could be actually smaller. You do see that there is a fasting of the crystal when it comes out of the carbon nano tube, but this fasting cannot obviously take place without diffusion.

So, that means diffusion is playing a role in the overall process, but they ruled out diffusion as a possible mechanism for this plastic deformation or the deformation of this gold nano crystal through this graphitic punctured graphitic cage. They proposed that it is actually nucleation and propagation of partials of dislocations, which is responsible for this kind of a plastic deformation in the ultra-strong regime of crystals wherein, this material kept under pressure of 20 giga Pascal's.

So, this is one nice example wherein a nano crystal is placed inside a nano cage, which is extruded by a nano whole. So, this is a very nice kind of an experiment and you can clearly see that the kind of pressures we talking about, the kind of mechanism we are talking about, the kind of experimental issues in actually observing some of the effects is very difficult. We have to do secondary computation like molecular dynamics to actually sort of propose come up with the mechanism like a dis partials or full dislocations, moving through the crystals and causing leading to this extrusion.

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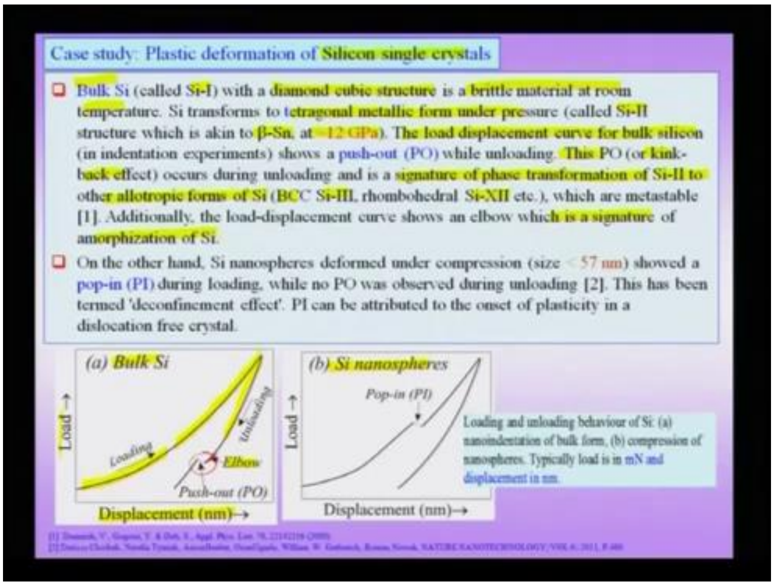

Case study: Plastic deformation of Silicon single crystals

- ❑ Bulk Si (called Si-I) with a diamond cubic structure is a brittle material at room temperature. Si transforms to tetragonal metallic form under pressure (called Si-II structure which is akin to β-Sn, at ~12 GPa). The load displacement curve for bulk silicon (in indentation experiments) shows a push-out (PO) while unloading. This PO (or kink-back effect) occurs during unloading and is a signature of phase transformation of Si-II to other allotropic forms of Si (BCC Si-III, rhombohedral Si-XII etc.), which are metastable [1]. Additionally, the load-displacement curve shows an elbow which is a signature of amorphization of Si.
- ❑ On the other hand, Si nanospheres deformed under compression (size < 57 nm) showed a pop-in (PI) during loading, while no PO was observed during unloading [2]. This has been termed 'deconfinement effect'. PI can be attributed to the onset of plasticity in a dislocation free crystal.

Loading and unloading behaviour of Si: (a) nanoindentation of bulk form, (b) compression of nanospheres. Typically load is in mN and displacement in nm.

In the second case is a case of a deformation of silicon single crystals. There are two examples we will take, one is the bulk silicon wherein there is an actually indentation experiment. There is also a compression experiment of silicon nano spheres. We will try to see the difference in deformation behavior between bulk silicon and which is an of course, indentation experiment. The second experiment is compression of silicon nano spheres in this bulk silicon, which typically called silicon one, which has a diamond cubical structure.

We know it is a brittle material at room temperature it actually transform to a tetragonal structure under high pressure, which is what is experienced under a diamond indenter. This structure which is tetragonal and which is a metallic form is called silicon tool. This structure metallic form of silicon is similar to the beta tin structure. We know that the tin also found in alpha tin and beta tin form and not only there is a crystal structure transformation, when its goes to alpha to beta, but there is also a change in the character of metallic character then alpha tin goes to beta tin.

This transformation in the case of silicon actually occurs at very high pressure about 12 g p a. Suppose, I plot the low displacement curve for bulk silicon and now this is load in indentation. This shows a very interesting feature and if you look at the load displacement curve here below for bulk silicon. You see that during loading there is a nice smooth curve, but while unloading, there are two important effects that the curve comes.

There is an additional effect, which is called the elbow that means, there is actually sort of a curvature change. Additionally there is an effect which is known as the push out or the p o effect, this is observed only during unloading. Now, what is the reason for this is at this p o or kink back effects sometime called occurs during unloading and is a signature of the phase transmission of silicon two to other allotropic forms of silicon.

So, you have silicon one which transforms to silicon two under high pressures, which is under the indenter, but when you actually unload that means, now you are relaxing the structure. This silicon two actually transforms to other allotropic forms like silicon three and, which is b c c or rhombo hedral silicon 12 structures, which are Meta stable forms of the silicon. Additional, this elbow part which, I mentioned that actually a signature of the amorphization of silicon. Some part of silicon also getting amorphized. Now, if you compare this bulk silicon indentation experiment, which is a deformation experiment with a deformation of silicon nano sphere. So, what I am doing here in the second case actually I am taking silicon nano spheres and putting them under two actually, doing a compression experiment on silicon nano spheres.

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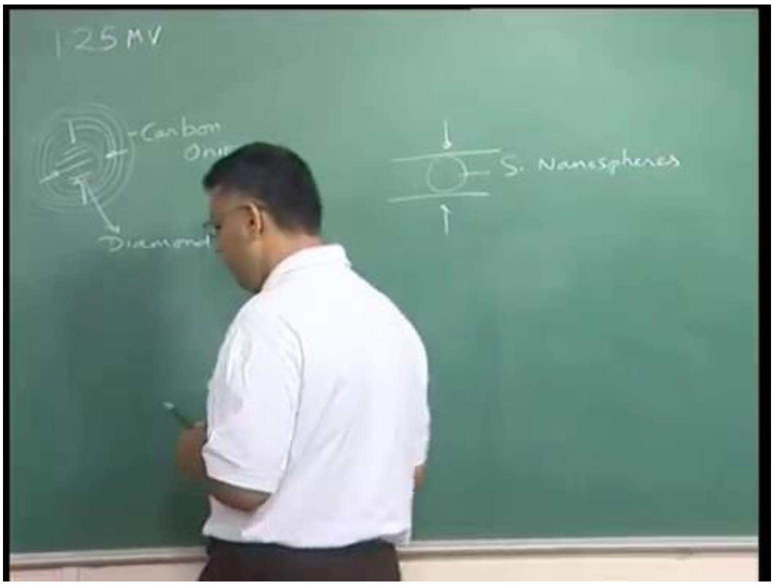

In that case you observe that the loading part of the curve and also the unloading part actually show us slight difference. In the loading part you observe something known as the pop-in phenomena and these nano spheres had a size of about 57 nanometers or smaller.

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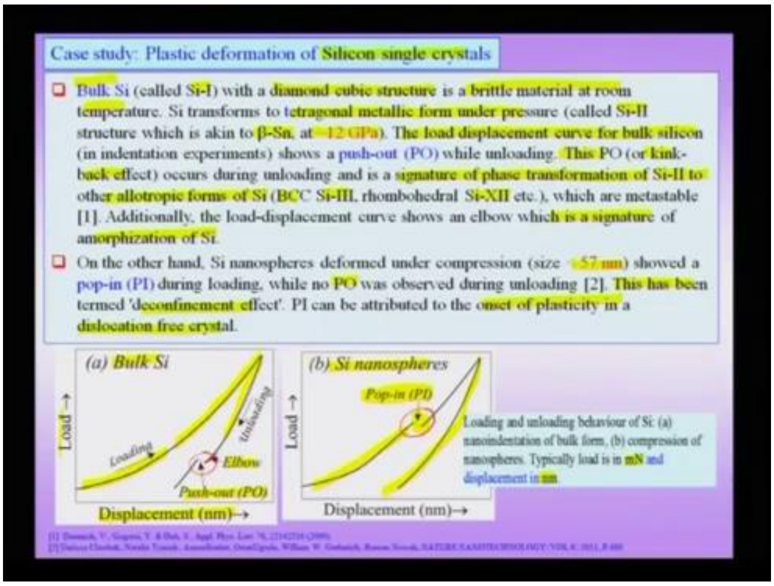

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- ❑ On the other hand, Si nanospheres deformed under compression (size ~57 nm) showed a pop-in (PI) during loading, while no PO was observed during unloading [2]. This has been termed 'deconfinement effect'. PI can be attributed to the onset of plasticity in a dislocation free crystal.

Loading and unloading behaviour of Si: (a) nanoindentation of bulk form, (b) compression of nanospheres. Typically load is in mN and displacement in nm

So, there was no pop out effect or push out effect, which we had seen during in the bulk silicon, so that part is the curve is smooth, there is no p o effect. When I am unloading the silicon so the difference comes in the nano sphere case is while loading. And this has been termed this pop in effect as a confinement effect. This can be attributed to the onset of plasticity in a dislocation free crystal. So, clearly there is a very significant difference when you trying to load bulk silicon indentation vis-a-vis compression of a nano sphere. There are important effects, which is technically called DE confinement effect, wherein you are actually seen onset of plasticity in a dislocation free crystal.

It should be noted in such experiments that the load is typically in the milli Newton range and the dis replacement in the nano meter scale. So, these are all very sensitive experiment done on silicon nano spheres with lot of care. You do then actually try to see how a deformation of a nano sphere is different from that of bulk silicon. And you do see a difference when you actually do such an experiment and the significant differences are in the loading stage of the curve.