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Lecture - 16 Defect Structure & Mechanical Behavior of Nanomaterials (C3)

(Refer Slide Time: 00:14)



In the discussion of mechanical behavior of materials, we will take up a overview of some of the properties, how they arise, the mechanisms behind these properties. And further, we will try to discuss how these properties change when we go from the bulk to nano materials or nano structured materials.

(Refer Slide Time: 00:39)

> Overview&> Nanomater	ials
Density and Elastic properties Plasticity by slip Motion of dislocations & dis	locations in finite crystals
Strengthening mechanisms	Grain boundaries in nanocrystals
Twinning versus slip	Grain size and strength
Superplasticity	Nanocomposites

We will also take up issues, regarding artifacts, in testing artifacts, in the properties which we observe and try to describe that how we can develop better strategies of testing materials. And also coming up with properties which has specifically peculiar to nano materials. Some of the properties, which we will be talking about are elastic properties, plasticity. We will also talk about strengthening the mechanisms, we will talk about the switch over from twinning to slip. We will talk about important properties like super plasticity and creep in nano materials and also about the role of green boundaries in a structured materials. In the whole process, we will also take up some hybrids like nano composites, which are lot of research is being conducted in these areas nowadays.

(Refer Slide Time: 01:26)



So, we will alternate between the basic property in bulk materials, the description of the property, and then take up specific properties of nano materials. Now, it is important to start with a broad overview of mechanisms by which a material can fail. Now, this can be mechanisms which are physical, they can be electro chemical or they could have other origins from which failure can be, material can fail. In this context, failure has been defined as a change in the desired performance, which could involve changes in properties and or shape.

As you know there is a component, like a gear wheel, which is meshing into a system with other gears in the system, then if there is a change in the shape of the gear, then automatically this is constituted as failure. Often, elastic deformation is not included in failure, but it is obvious that suppose I have a spring board from which a diver is going to take a dive into a pool. If the spring board deflects too much, even though this would come under the class of elastic deformation, needless to say this would be a failure of the desired performance. And therefore, it would constitute failure by elastic deformation.

The common other methods are failure would consist of plastic deformation, even if slip is one of the important mechanisms of plastic deformation. Fracture where in the material cracks propagate in the material leading to failure, fatigue could be one of the reasons behind such a failure, and fatigue could also lead to cracking in the material. There is creep, and we will see that there are many creep mechanisms, which can actually lead to failure.

Micro structural changes itself can lead to failure. Like for instance suppose I can think of twins and stresses related to twins, phase transformations, grain growth particle coarsening which we have taken up in detail already. All these can be micro structural changes, which would constitute failure. Needless to say chemical or electro chemical degradation of material, which includes corrosion, and which includes oxidation etcetera, would also can, or can also lead to failure in the material.

And therefore, because once we have corrosion, that means that the material is getting degraded on the surface. And surface being an important part of the whole material can lead to desired. I mean undesirable change in the properties of the material. Physical degradation, like where an erosion can also lead to failure. And this would be very-very important, when you have two components in contact, like the gear wheel, where in surface wear could be an important property, which we need to take into account.

Suppose you talking about blade operating under water, which is propelling a ship, then erosion from particles in the medium could be a serious issue. And therefore, that also need to be protected against. Having got a broad overview of the mechanisms by which a material can be and actually fail. We will take up some of these during the course of this lecture, wherein we will see that how some of the properties have a beneficial effect when we go to the nano scale.

And therefore, we can actually improve the properties when you work in nano structured materials. Parallely we will also highlight some of the problems in using nano structured materials. And therefore putting together this problems and the advantages, we of course design strategies for improving the performance of materials and components.

(Refer Slide Time: 04:31)



The first property we take up is the physical property, which is density, but we take the sub, because this is closely related to some of the mechanical properties, like the elastic properties. Now, suppose I am taking a bulk material, then the fraction of grain boundaries in such material and the fraction of what you might call triple lines is very small. And therefore, we can ignore them in terms of the overall contribution to the elastic properties.

Of course, we cannot ignore grain boundaries, when we are talking about plastic properties and we will take up those important contributions later, but as far as elastic properties go, we can often ignore the grain boundary contribution. The problem with nano structured materials or nano structured bulk material is a challenge, because often full density or close to the theoretically density cannot be obtained and residual porosity can affect the density.

So, in our arguments, we always have to keep in mind that when you are talking about density of nano structured materials, there could be an issue of porosity and this porosity could drastically affect the properties, and one, and one of the properties. And we would like to get rid of this artifact which is coming from this specimen processing or specimen preparation. Now, before we take the elastic properties of a nano crystal, it is important to note that, what is a grain? What is a grain boundary? And what are the higher order entities in a grain structure?

Now, I can visualize that of course, we have a single crystal, then you have only one defect in the material, which is the surface. Suppose, I have a multiple grain material and I draw it schematically here.



(Refer Slide Time: 06:02)

Then I can notice that, each of this is a grain and one grain can be differentiated from another grain. So, this is grain one, and this is grain two, another one grain can be differentiated from another one by the orientation difference across the grain boundary. Let me highlight the grain boundary by red lines.

And we have already noted that grain boundaries are regions of lower coordination as compared to the bulk. So, both this were FCC copper crystal, then the grain would have a coordination number of 12, but the grain boundary would have something less than 12 and therefore, their regions of extra free volume and lower density. Now, apart from this grain boundaries, as you can see there are higher order terms here or higher order structural entities, like this is what you might call it triple line. So, in two dimension of course, it looks like a point, but in the third dimension, this is a line and therefore, this is triple line. So, you have grain boundaries and triple lines. Further you can also conjunct their heights that is four grains are meeting at a point, then that would constitute a quadruple junction.

And in terms of the energy and bonding, you can think of the grain interior being of the lowest energy. The grain boundary being of a little higher energy, the triple lines being

of even higher energy and finally, quadruple energy being of the highest energy. If you take bulk material, then the volume fraction of each one of them is going to be small and it can be ignored, but in nano structured material, this grain boundary. When I am talking about a nano structured material, I am talking about a bulk nano structured material. It means that the grain sizes of the order of nanometers, so this is of for the instance may be a 10 to 100 nanometers.

And therefore, in such a material, the effect of these on a, the density and elastic properties cannot be ignored, obviously needless to say their effect on plastic properties and fracture and other behavior also cannot be ignored. Therefore, let us see how these entities affect my density. The coordination number and packing close to the grain boundaries and which also includes triple lines, which I short form call TL, quadruple junction the QJs. And this quadruple junction some time in literature is also called corner junctions, is and is expected the coordination number and packing is expected to be lower than the bulk in or if you compare it to the single crystal.

This implies that, on decreasing the grain size, the density of the sample will decrease. Though this effect is expected to a marginal effect, this is not going to be a drastic effect, but nevertheless when you decrease the grain size. In other words you increase the amount of grain boundaries and triple lines per unit volume, then you expect that the density would actually decrease for a poly crystalline nano structured material. However this effect, that is, that is the reduction in density with grain size is expected to become noticeable, when the grain size is reduced in the nano scale regime. And this is an important effect which sort of like shows this prominence, only when you go to the nano scale regime as we shall see shortly.

Now, how to understand effect of these? The way to understand is that, we assume a certain grain morphology and then from that grain morphology, we can assume that there is a distribution of triple lines, quadruple junctions and we can. Therefore, now calculate the density based on the distribution of these. One of the most common ways of understanding grain structure and grain boundaries the way it is modeled, is to assume models of the form which I am showing here. In this case you can see that, there are two kind of standard packing of grain structures, which are used.

(Refer Slide Time: 10:15)



This is using something known as the tetrakaidecahedron, sometime also referred to as Kelvin's tetrakaidecahedron, which is a space filling solid and here I have brought something known as the rhombic dodecahedron, which is also a space filling solid. Now, we can see that how these rhombic dodecahedron, tetrakaidecahedron can monohedrally implies using a single tile, a single shape can fill space.

Now, the reason for using these shapes is that, this is mathematically easier to model. That means I have a single shape, and I can use the entire crystal to be made of, grains of all the polycrystal, to be made of grain of this shape. And the difference in choice comes, because this solid even though it is a preferred choice for a grain structure, some people also prefer to use a rhombic dodecahedron, because every phase has identical shape which is a rhombus. In this case, there are two type of phases, one is hexagonal phase and one is a square phase.

And therefore, there are two choices which are classically used for modeling grains and to calculate effective entities from grain boundaries and also the mechanical behavior of grains. But in the calculations as we shall show now, we will use a different kind of a shape for a grain, and this shape we are going to use is a cube. The reason to, for us to use a cube is to make it mathematically simple, to actually calculate the various quantities which we are interested in.

(Refer Slide Time: 11:38)



As a first approximation, we shall assume that the grain boundaries have a similar character in nano structured material. So, this is a very drastic assumption, but we will make the assumption that, even though we are going to nano structured material. The overall crystal structure of the grain, the grain boundary structure, the grain boundary widths, etcetera remain very comparable or very similar to that in a micron size material. So, this is a drastic assumption we are making, but this will help us make a simplification in terms of the calculation.

Additionally we will assume that, we will the value of a grain boundary thickness, which is now a very, what you might call a quantity which is based on a definition. The region close to a grain boundary where there is a disturbance of the atoms from the expected lattice position. I call it a grain boundary region, and this is typically less than about 1 nanometer, but for simplicity here, we will assume that it is about 1 nanometer. And in metals typically it has been found that, it is of the order of about three atomic layers.

So, to proceed further, we will make two assumptions, number 1 is that the grains are all cube shaped, which is of course, a very drastic assumption. Because as we said, the closest they actually can come to is something like the Kelvin's tetrakaidecahedron and definitely not close to a cube. The second assumption we will make is that, the character of the grain boundaries, the character of the triple lines and quadruple junctions do not change as we go from a micron size material to a nano size material. The third

assumption we will make is that the grain boundary thickness is, which is the region of disturbance around a grain boundary or triple line is of the order of 1 nanometer. Making these assumptions, we will go ahead and make a model to calculate the fraction of grain boundaries with decrease in size.

Now, we had talked about porosity, we will be ignoring porosity in all these calculations. But as we pointed out that in some materials, when in so called bulk or fully dense material as reported in later age, would actually have about 3 to 5 percent porosity. And this 3 to 5 percent porosity would actually dominate over some of the effects we will be talking, regarding grain boundaries and triple lines.

But nevertheless, we will assume for now it is absolutely theoretically dense, except for this green boundary and triple lines, etcetera. And there is no contribution of porosity to the overall effect of reduction in density or therefore, it is influence on elastic properties. Now, therefore, now I have cube shaped grains which is filling space and the region between these cube shaped grains, is the grain boundary and additionally we of course, have triple lines, which we can plot like this.

So, these are triple lines. And the region between the grain boundaries, is the grain this of course, this is the grain boundary region and this model and we are showing a two dimensional cross section of the three dimensional crystal structure. So, this is my size of the grain and this is my thickness of the grain boundary. Now, you can see that, this such a structure can be described by unit cell, which consists of this yellow region and the blue region around it. So, this is the unit cell which is styling to give rise to the entire structure.

(Refer Slide Time: 14:41)



The fraction of grain boundaries and of course, and of course, triple lines and quadruple junction depends on the grain morphology. For, simplicity we have assumed that the cube morphology is the one to make our calculations very simple. And in cube grains, triple lines can also be referred to as triple junctions, as often done in literature. The fraction of triple lines and quadruple junctions become important, when the thickness, for about thickness of about 1 nanometer, when the grain size is of the order of 10 nanometer or below, which we shall see very soon from the plots and the way we make the calculation. The fraction of grain boundaries as a function of the size of the grain, which we have shown here d. And the size of the grain boundary which is t can be written as d cube divided by d plus t the whole cube. This is the pure geometrical calculation based on the cube morphology.

The fraction of the grain boundary region can be written as d cube by d plus t the whole cube one minus this value. The fraction of quadruple junctions can be given as 6 t cube divided by 8 into d plus t the whole cube. The fraction of triple lines can be given as 6 t square d divided by 4 into d plus t the whole cube. Therefore, I have definite formulae for the fraction of the grains, the grain boundaries, the quadruple junctions, and the triple lines.

If I plot these functions as a function of the grain size, you would notice that, this is the main function, which is the fraction of the grain and the fraction of the grain seems to

reduce below as you go down to smaller and smaller grain size. So, that means that, if the fraction of the grain is reducing that means that the remaining of the material is going to increase, which is now going to be the fraction of the triple lines, the fraction of the grain boundary, and quadruple junction, which you can normally see that they are increasing.

The important point to note from this graph is that, it is only below about 10 or 20 nanometers. So, I can draw some vertical lines around this, 10 nanometer or 20 nanometer. So, in this regime which is below this size, that grain size effect start to dominate on these other entities of the crystal. That means if I am at a larger grain size of about 50 nanometers and I am in a larger grain size, then I can safely ignore the contribution of these two densities or as a, because the volume fraction is going to be small then therefore, I can ignore them.

Now, what happens to these quantities when you are in the small grain size regime and we already defined this small grain size regime to be about less than about 20 nanometers. You notice that, the grain boundaries already start to play an important role when you are already less than about 30 nanometers. While the importance of triple lines and quadruple junctions become very important, only when you are below about 10 nanometers. I can see that these function start to dominate only in this regime.

This is very-very important, because when you are talking about nano crystalline materials with a grain size of 10 nanometers, which are plastically deformed. You will notice that, you cannot anymore ignore the presence of triple lines and quadruple junctions and they will play an important role in the plastic deformation of the material. And of course, first before we reach that stage, we will of course, going to talk about the elastic deformation of materials with these kind of entities in them.

To summarize this slide, and to summarize the lesson so far. With decreasing grain size the importance of quadruple junctions, grain boundaries, and triple lines is going to increase. So, the grain boundary can be thought of as a 2 d structure, the triple line can be thought of as a 1 d structure and the quadruple junction can be thought of as a 0 d structure. So, you can see that these 2 d, 1 d and 0 d structures actually start to play a prominent role, only when the grain size is below about 50 nanometer or more specifically about less than about 30 nanometer.

The grain itself is a 3 d entity as we know, but more specifically the role of triple lines and quadruple junction the 1 d and 0 d entities in the structure start to dominate only below about 10 nanometers. And the important point is that, we can actually, these calculations are coming from assuming a queue morphology and we are assuming a grain boundary thickness of about 1 nanometer. And then, we can write down the fraction of these various entities given by these formulae by a pure geometrical calculation, which is easy to perform.

Therefore, I can have a fraction of these entities and I can actually calculate how these fractions start to change. And the overall trend is that whenever, whatever fraction is lost from the grain, goes into either the grain boundary, or to the triple line or to the quadruple junction. Now, what effect does this have on the density of the material, because we already noted that the bonding the coordination number are actually small are lesser as compared to the bulk in the grain boundary or the higher order entities. Therefore, now this is going to affect my density and as expected, this density is going to be prominent about 10 nanometers or of that order.

(Refer Slide Time: 19:48)



Now, I can write down the density of the material using the formulae that rho is equal to 1 minus fraction of grain boundary, fraction of triple line, fraction of quadruple junction, into density of the grain. That means if I take out all the other entities, what I am left

with the fraction of the grains, and that fraction I can multiply by the density of the grains.

And then I can multiply the relative fractions of all the other entities, like the grain boundaries, the triple line quadruple junction with respect to their relative densities. And I will get the density of the entire composite of or now the polycrystal, so nanocrystal I will get. I will get the density of the nanocrystal. Now, to get this number I need to know the values of f GB, f TL, and f QJ. I need to sorry, I need to know the value of rho GB, rho TL, and rho QJ. Having I have already calculated the f', the volume fractions already in the previous slide.

So, I need to know these entities, and this can be, for this of course, you need to do some detailed modeling, may be some kind of an atomistic modeling or molecular dynamics modeling. But from some kind of a reasonable estimate, which is arrived at by looking at various models and also experimental results is that, it is assumed that the grain boundary densities about 0.95, the density of the grain. That means now I am talking about the relative density of the entity with respect to the grains.

So, both the relative density implies the density of the polycrystal divide by the density of the grain. So, for the individual entities, grain boundary has a 0.95 relative density with respect to the grain, the triple line is about 0.90 and the quadruple junction is about 0.81. That means, as you go reduce the dimensionality from grain boundary to quadruple junction. So, this is 2 d, this is 1 d, and this is 0 d, then I see that the density actually decreases.

Now, these numbers of course, as you, as I just pointed out, are not sacrosined numbers and it depends on the model depends on the material system, it depends on the what you define as a the grain boundary region etcetera, and how you calculated the density. But for now, we will assume some kind of a numbers to arrive at, what you might call a qualitative picture of wherein can I see a change in relative density which finally, of course, I want to correlate with the reduction in the modulus of the material.

And again I want to point out that, we are actually ignoring porosity in this whole calculation, because if porosity is present, that is going to be the dominant factor as compared to some of these effects which we are talking about. Needless to say the fractions of all these put together has to going to be one from which we have actually used to calculate this number at the top.

Now, if I plot this relative density using these values for the grain boundary triple line and quadruple junction, I notice that the relative density actually decreases with grain size and you see that below about 20 nanometers, this effect tend to dominate. So, when I am below about 20 nanometers I see that I have to worry about the presence of grain boundaries and triple lines in the calculation of relative density. That means now the density of a bulk crystal if I is 1, then the density of a 10 nanometer grain size crystal, is going to be about or let me take a little smaller number.

So, that here is a going to be about a 98 percent, that means point about 2 percent reduction in density has taken place. Purely from the fact that now I have a polycrystal in which there are going to be a higher density of grain boundaries triple lines etcetera. Therefore, now I have a polycrystal what you might call a porosity free or an artifact free polycrystal, purely from the internal geometric structure, which involves grain boundaries. There is a reduction in the relative density and this relative density reduction can be pretty high, if we are going to smaller and smaller sizes.

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	Moduli are bulk macroscopic properties and their definition is extended to be applicable to							
	these structures).							
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So, now what is the effect of this on the elastic properties, we will try to study that and for that we will have to invoke the concept of what is called the elastic properties of a composite. Because now I can think of my polycrystal as a composite between a grain and all the other structural entities we have just now talked about.

But before we go to that, let us talk about elastic properties as certain other nanostructures before we take up the elastic properties of the polycrystal as we just said. And there are some very interesting examples of nano structures and nano composites wherein elastic properties seems to play a very important role. We for start will assume an isotropic material that means the properties of the material do not change either with position or direction. And we know that for an isotropic material we can describe the elastic properties using two independent constants e and u or g and u.

And therefore, it makes our overall understanding pretty easy. If you, the introduction of an isotropic properties of course, brings richness to the system, but makes our understanding more difficult. Therefore, we will stick to isotropic properties for now. For a cubic crystal, we know that for instance in a, if you actually talk about the, you need three independent elastic moduli to describe the elastic properties of a cubic crystal. And if you go down to lower symmetry crystals, then you need more and more elastic moduli or elastic constants to describe the properties of an isotropic crystal.

And this assumption is drastic as we shall see for now, because we already noted that, if you take a polycrystal a nano polycrystal, the actually the density. And therefore, the modulus will vary from position to position, as you get close to a grain boundary expect a different modulus as compared to that in a bulk of the grain. Often, modulus of some nano structures as are, as reported below. It should be noted that moduli are bulk macroscopic properties and the definition is extended to be applicable to these structures.

So, we should note that modulus as, such as a property, is a bulk macroscopic property. That means it is an average over a large number of atoms or a collection of atoms. And if I am going to be describing modulus of a small entity, like a nanostructure, like a carbon nanotube, which could be a single walled or a multi walled carbon nanotube or I am talking about a zinc nanowire wherein the number of atoms are much limited. Then I am actually extending the definition of what is might call the bulk elastic modulus to some of these smaller entities.

But nevertheless having extended this definition, let us note that what are the interesting properties we can get by working with these nanostructures. Some of the values reported

in literature, that I am showing here below. Silica nanowires have found to have modulus variation in the order of GPa 20 to 100 GPa, zinc oxide nanowires from 140 to 200 GPa.

Multi wall carbon show the range of 11 to 63, and this obviously depends on the number of walls that the modulus is going to change. Single wall nanotubes have modulus which are very high, and which approach that of diamond. That means now, even though single wall carbon nanotubes can be thought of as folded graphing sheets. But their modulus when of course, pulled in the direction of the length, is get pretty high and in fact challenge that of diamond.

That means now I have a entity which is extremely strong, which is a single wall carbon nanotube, and people have even envisaged making ropes out of these single wall nanotube which can actually take lot of load, which is extremely, which is has very high modulus. That means that I can use it as a reinforcement in composite, and we will call such composites as nano composites. Even though we understand that the grain size is not in the nano, it is the reinforcement which is in the nano to actually obtain very good properties.

Now, to understand the modulus of composites, we need to understand that how if I mix two phases, then how would the overall modulus emerges. There are two ways of understanding this and this depends on if the state of stress in the presence of the composite.



(Refer Slide Time: 27:35)

So, now let me draw some schematics of composites that actually I could have a second phase, which is in the form of spheres. Or I could have a composite, in which the second phase in the form of long rods and these rods of course, could be aligned or they could be in other forms. And we can also think of laminates which form the composites. Now the important thing of course, is the interface between these first phase and the second phase, which I mark in red here. So, I have an interface.

So, it depends if this interface is actually transmitting all these strain, which means that it is in a state of isostrain condition, which means the strain in the metrics is the same as the strain in the fiber or the other extreme could be an isostress condition, in which case the stress in the metrics is same as the stress in the fiber. In the case of isostress, we can think of the two materials. Now, suppose this is material one and material two, which I draw in two different colors.

So I can think of two configurations, wherein the metrics and the fiber materials are as if in a parallel configuration. Another possibility is that the metrics and the fiber, which is the one of them is are in a series configuration. The parallel configuration is like an isostrain configuration, and the series configuration is like an isostress configuration.

(Refer Slide Time: 29:43)



And therefore, using either one of these two configurations I can calculate the modulus of the composite given the individual moduli of the fiber and the metrics. In the case of isostrain conditions, that means the strain in the metrics is same as the strain in the fiber, which is a strain in the composite. I get a formula that E c is equal to E f V f, which is V f is the volume fraction of the fiber and V m is the volume fraction of the metrics, which is nothing but the 1 minus the volume fraction of the fiber. Assuming that there are only two phases in a material, there is no porosity etcetera.

And this resistance in series configuration gives me a resistance the, what you call the modulus of the composites this kind of an averaging is called Voigt averaging and where I can get the modulus of the composite. The other extreme of a possibility is the isostress condition which I pointed out, which means the stress in the metrics is same as the stress in the fiber, which is the stress in the composite. And therefore, this is like resistance in parallel configuration which I pointed out, and this leads to what a formula like 1 by E c. The E c being the modulus of the composite is V f by E f, f, the subscript refers to the fiber plus V m by E m, m being the subscript referring to the matrix. And this kind of an averaging is called Reuss averaging.

Therefore, I have two extremes of the modulus of the composite with respect to the volume fraction of the material. Suppose I take any given volume fraction f, just for the sake I will call this f 1 here, this volume fraction is f 1. Then I have an upper bound given by the isostrain condition, which is nothing but the Voigt averaging and have a lower bound given by the isostress condition which is the Reuss averaging. Therefore, my modulus of the composite is going to lie between the upper and lower bound of the composite.

The reason that the real composite is not exactly one of the two is that, actually the matrix fiber interface could actually be partially be slipping, could actually not be contiguous in places. And therefore, not knowing fully what is fiber, each one of those fibers and their orientations, and their characteristics of the interface, I can only tell that the overall average has to be between the upper bound given by the isostrain condition and the lower bound found by the isostress condition.

And of course, in typical composites, you do not add upto 100 percent of the fiber, usually the fiber concentration is about 5 percent, 25 percent, it is a smaller fraction as compared to the overall matrix in. Of course, exceptions we may go to higher volume fractions.

Therefore, for a given fiber fraction f, the modulus of various consumable composites lie between the upper bound given by the isostrain condition, and a lower bound given by the isostress condition. Therefore, now if I am making a composite, the modulus benefit I get, has to be between these two limits. And the composite we will be referring to very soon is going to be the nano composites, wherein we will be using reinforcement which is in the nanoscale. Now, one such example is the case of the multiwall carbon nanotube, reinforcement of alumina.

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Of course, it is better as you have seen that you reinforce the system with system wall carbon nanotubes. But it is easier in many cases to actually manufacture multi wall carbon nanotubes and reinforce that, and you can see that the grain size itself is in the of the order of microns. So, this is not a nano grain size alumina, but it is a micron grain size alumina and what is nano in this whole nano composite, is actually these carbon nanotubes which you see here in high magnification.

So, this multi wall carbon nano tubes have been used to reinforce alumina. The Young's modulus of such a composite has been found to be as high as about 570 GPa and the range typically has been found between 200 and 570 GPa. And this of course, depends on the nanotube geometry, its length, it is number of layers in the nano, multi wall nanotube, the quality of the nanotube and the porosity in the alumina. But if you note that the Young's modulus of alumina is actually smaller, then you actually can get a

considerable benefit in the modulus by adding a nanotube reinforcement to the ceramic. This additionally has been found to also give fractured toughness increment, which of course, we do not deal with here, but it is important to note that when you add nanotubes to alumina, there are other benefits which you get in the overall process.

(Refer Slide Time: 34:05)



So, this example of a carbon nanotube is nothing but a example of making a composite and therefore, enhancing the modulus of the material by making a composite.

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Of course, the reason for making a composite as you are aware, is that one or more of the properties see a beneficial effect with respect to just the individual components. Suppose, I use just alumina or just carbon nanotubes, then what about the properties I get, the composite actually gives me added beneficial property up and above each one of the components. And that is why I am justified in using a composite, because some of these composites are actually difficult to process and synthesize and actually use in routine industrial production.

Now, we had told that a nano polycrystal can be thought of as a composite between grains and grain boundaries and triple lines and other kind of a defects. Now, for a first order they can actually think of a nano polycrystal to be having, be a composite of the grains and these other defected regions in the polycrystal, which we saw just now, that has a lower density as compared to the bulk of the grain. These regions obviously are also expected to have a lower modulus, because the bonding is inferior as compared to the bulk of the crystal.

(Refer Slide Time: 35:19)



Now, we notice that there is a bulk change in modulus, only when the grain size is about below about 20 nanometers. And we had, we continue the modeling which we did before, we assume a cubic morphology and we also assume that the grain boundary has a modulus about 0.7 that of the grain. Here again, if to really determine the correct modulus of the grain boundary is a difficult task. There is obviously no such single number which can be thought about, because grain boundary itself we have seen is not a single plain, but it is a region in the material. And therefore, we have to assume some kind of number, and for now we assume that the E grain boundary is about 0.7 E grain.

And as before we ignore porosity in the material, because we as we shall see in the next slide, porosity could be a serious issue in very many problems and cause very many problems. Early result showed that, if there is a reduction in the modulus about, for about below even about 200 nanometers. That means that the region we already seen that where grain boundaries and other kind of entities do not play an important role, but they did observe some reduction in modulus when they were already below 200 nanometers.

And if you remember the slide from before, all the drastic changes need to happen only below about 30 nanometers, and not below about 200 nanometers. And in fact in the context bulk modulus of a polycrystal 200 nanometers can even be thought of as a bulk material, you can safely ignore most of the other entities in it, other entities implying the grain boundary, the triple lines etcetera.

These samples were perhaps, this result was perhaps, because of porosity in the samples and the investigators actually did not characterize a fully dense sample. So, we now can understand, perhaps in hind side that these were not really bulk sample, fully dense samples and that was giving rise to the change in modulus below 200 nanometers. And if you really using the value of E GB 0.7 E G, I, and I have a relative modulus defined as a E polycrystal by E grain. That means it is the reduction in modulus with respect to that of a grain and a plot the relative modulus with respect to grain size. I see that most of the changes seem to take place when you are around about 20 nanometers or below.

So, this seems to be the region, where actually these other entities seem to play an important role and there is a reduction in modulus. Since, I am assuming composite, I obviously have to have an upper bound and lower bound as shown here, the upper bound corresponding to isostrain and lower bound corresponding to isostress. And I see that for a 10 nanometer crystal for instance I can draw dot line like this.

The lower bound is about 0.9 and the upper bound is about 0.92 or 0.93. Therefore, by using my understanding of composites. I can actually calculate the modulus of a polycrystalline material and I see that the modulus of a polycrystalline material is

actually lower by about 10 percent, when you go down to small sizes which is about 10 nanometer or below.

But again I have to re emphasize that in such, in such cases actually synthesizing a porosity free material is actually difficult. And whenever porosity is present that is actually going to dominate the effect and not these other effects which I just now described.

(Refer Slide Time: 38:28)

 In early observations of clearly properties it was increase in any observations of the elastic moduli in multilayers. This phenomenon was termed the <i>supermodulus effect</i>. More work in this area have attributed this effect to artifacts or anomalies (it seems now that only about 10% enhancement in the elastic moduli may be real). Further work is needed in this area. 	In early observations of elastic properties if was actived that there is here (100%)
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There is another important clarification, which is required, because if somebody reads some old literature, it, there is some effect which is described as super modulus effect, which was observed and there was lot of excitement related to that. And this was these observations told that elastic properties as large as more than 100 percent enhancement elastic modulus multi layers.

.So, I am talking about thin film multi layers and they saw a huge increment in the modulus and they called this a super modulus effect. Now, later investigators of course,, could not confirm this super modulus effect, and this work showed that these could be, because of artifacts and anomalies.

These are not perhaps true effects coming from the multi layered moduli, but there could be other effects coming, and a reasonable assumption perhaps today would be that there is an enhancement perhaps in these multi layers, but that is much smaller than the super modulus effect, which is originally described. But more work has to actually clarify that, how generally this trend of about increment in modulus, is it only related restricted to multi layers, or there are other effects which we need to take it into account? But clearly the super modulus effect is no longer attributed as a real effect in nano materials and therefore, it can be ignored. The next topic we take up after elastic properties is plastic deformation of crystalline materials.

(Refer Slide Time: 39:47)

	Plastic Defo	rmation in Crystalline	Materials
Slip Dislocation motion)	Twinning	Phase Transformation Grain bound	Creep Mechanisms
+ (Other Mechanis	Mas Vacance Disloca	ation climb

And often slip is considered as the most important plastic deformation mechanism. But we should note that, there are other important mechanisms as well. And some of these become important, like for instance twinning at low temperatures especially in materials like BCC materials, where in slip can be limited at low temperatures.

Additional mechanisms could be phase transformation, and here when I am talking about plastic deformation. I implying that there is permanent deformation in the material, that means even in the absence of the load, there is a deformation that is caused which is going to be permanent. And therefore, phase transformations can lead to permanent deformation and the shape of a material. There are creep mechanisms, like grain boundary, sliding vacancy diffusion and dislocation climb. And there are other mechanisms as well which can give rise to fine permanent or plastic deformation in a material.

Initially we will of course, start with slip, try to understand the role of dislocation motion in slip. We will understand also why crystals are weak, in for instance in a tensile test. And then later on understand how the behavior and of nano crystalline materials and nano single crystals are different from that of the bulk materials which we have been discussed.

We have to of course, note that in amorphous materials that the plastic deformation mechanisms could be very different. And this could involve sheer banding or even discuss flow, which is like almost like a Newtonian flow, liquid flow. And this typically in for instance bulk metallic glasses, it takes place above the glass transition temperature of the bulk metallic glass.

So, we have looking here at a broad overview of all the plastic deformation mechanisms and crystalline materials, but we will essentially focus on two or three of them. Initially on slip later on, on little bit on twinning and further down the lectures on creep mechanisms.



(Refer Slide Time: 41:36)

If I want to understand the plastic deformation by slip, the simplest test I can do on a material is the what is known as the uniaxial tension test. And when I perform a uniaxial tesion test of course, I get what is called a load stroke data that means I apply a load and I get basically some kind of an elongation or increase in length of the material.

Initially this load stroke data of course, can be plotted, as something known as an engineering strain versus stress plot, or it can also be plotted as a true stress versus true strain plot. There are two ways of plotting this data, and the way it is plotted can make the curves look very different, as you can see this curve on the left goes up the engineering stress strain curve goes up, then it finally starts to come down. And finally, there is a fracture while the true stress strain curve always keep going up and finally, till there is fracture.

Now, there are lot of important properties you can actually calculate from this uniaxial tension test, which includes for instance the yield strength, the ultimate tensile test strength, the fracture strength. And whenever the word strength is used in this context, it implies a fracture stress or ultimate tensile stress and you can also calculate for instance the elastic elongation, the elongation to the ultimate tensile strength. And finally, the elongation beyond which the material fails, which is called a elongation for fracture.

Now, the important things to note from this curve are, initially there is a linear region in this curve, which we call the elastic region and there is a corresponding elongation which is now my elastic elongation given by this value e u. Now, the value of e u and epsilon elastic, e elastic and epsilon elastic is very-very similar, because in small strains I can actually use the engineering strain as well as the true strain and they are equivalent. Only when the strains become large that I have to differentiate between engineering strain and true strain.

Now, if you want to divide this curve into parts, the linear part can be thought of as what is called the elastic region. But we have to note that, this elastic region is macroscopically elastic. In other words, if I really want to know truly microscopically elastic region, then that is related, that is only occurs to a very small strains of the order of about and I mark a point A here and this is the strain of truly elastic.

This strain is extremely small and therefore, beyond that the region, though the curve appears straight from A to Y. So, the point A to Y, the curve is straight, so this is macroscopically elastic, but at microscopic scale, there is actually some plasticity which is already taking place. The reason behind this plasticity we will see soon, is motion of dislocations leaving the crystal or the grain boundary.

Now, if I carry on my uniaxial tension test beyond this point Y, then I see that the curve goes up in the case of the engineering stress strain diagram and comes starts to come down. This peak is where we attribute the formation of a neck and this neck is forming, because there is localized deformation, that means that the deformation is not spread across the entire gauge length, which I can call L 0.

So, there is a localized deformation, and this localized deformation finally leads to fracture and the material separates into two halves. And then the ductile material typically you will observe something known as a cup and cone fracture and of course, an extremely ductile materials, you may even observe something known as a rupture where in the specimen thins down to a point and then it fails

Now, this region, blue region and the curve too often it is casually called a plastic region, we have to note that is actually elastic plus plastic and that it becomes obvious if I load from any point, like a point, like n or a point like n here. Wherein if I unload this curve, then the curve will unload parallel to my y axis and I will get an elongation. So, let me go down to the board and draw this again hence to avoid cluttering this diagram.



(Refer Slide Time: 45:45)

So, the elastic deformation I will exaggerate here, so that it becomes easy to visualize this straight region of the curve, this is the exaggerated actually the slopes are of the order of giga pascal.

And now, if I unload from a point say m in the curve, then of course, I can draw a vertical line and this is now my engineering strain, true strain, sorry engineering, true strain, true stress diagram. And I will now unload from point b and I can, I will notice that the unloading will take place parallel to this line that slope of these two lines will be same. And if I notice, then these are two similar triangles. At this implies that, this implies that, actually this region, which is the blue region.

That means by drawing similar triangles and unloading and unloading curve being parallel to this original elastic line. I observe that actually I recover more strain here as compared to if I unload from point y. So, in some sense, in the sense of the strain obtained, the so called plastic region is more elastic than even the elastic region. Therefore, I need to call this plastic, so called blue part of the curve as actually elastic plus plastic and not merely plastic.

(Refer Slide Time: 47:08)



There are few things we of course, we need to ask is that why is that this curve going up, the blue curve, and this phenomena that does stress actually required for flow increases with strain is called work hardening or strain hardening. And that means the material is getting harder and harder as I am plastically deforming it, till of course, we reach a point like fracture. The reason is as we peak ahead is, because of motion of dislocations and the increase in dislocation density that and this intersection of dislocations making dislocation motion difficult

Therefore, this is an result of what is known as a uniaxial tension test and to summarize the important points, there is truly elastic region from origin O to point A, there is a linear portion which we call the macroscopically elastic region. But between point e and y, this is, this specimen is actually microscopically plastic also. From Y to F, the material is undergoing strain hardening, which is nicely seen in the case of the true stress true strain curve, wherein the curve is constantly going up. There is a point n in the engineering stress strain curve after which the curve starts to stoop down and this is the point of onset of making, that means the deformation is very local.

And we will see that what are, later on the strain hardening exponent is going to play an important role in determining the amount of strain you are going to get after necking. That means the overall ductility is going be dominated by a factor, which is n, which we will see later, which is called the strain hardening exponent. Now, what are the variables in a plastic deformation.

(Refer Slide Time: 48:42)



So, here we are sort of like getting a broad overview and a general feel of the plastic deformation and materials the details of which of course, can be consulted to a basic course in the area. Stress, strain, strain rate in temperature, and normally the effect of strain rate comes into play, only when you increase strain rate by a few orders of magnitude. That means suppose I am conducting a test that is a strain rate of 5 per second and the double the strain rate into 10 per second, then this is not expected to

affect many of the properties including ductility or the ultimate tensile strength. But suppose I increase the strain rate by a few orders of magnitude from 10 to say 10 power four, then I do expect that the overall behavior of the material is going to change.



(Refer Slide Time: 49:25)

Temperature is a very important parameter in plastic deformation and when I am drawing curves like these, I am assuming that the temperature is constant. That implies that I am and this temperature at which that those stress strain diagrams are seen are typically at room temperature, and at elevated temperatures, you would notice that the behavior of the material is going to drastically change. Now, there are some standard or there are some standard equations, some kind of an empirical equation which can be written.

(Refer Slide Time: 49:58)



Connecting some of these variables important in a plastic deformation, at low temperatures you can write and this is one of the standard equation, stress sigma, which is now true stress can be written as a constant into epsilon which is the strain power n. And this we are assuming is conducted at constant strain test at constant temperature K is called the strength coefficient and n is the important parameter, which is called the strain or work hardening coefficient or the work hardening exponent.

For copper and brass n is about 0.5, that means that this material can be given large plastic strain much more easily as compared to steels, which is, which has a smaller strain hardening exponent. Now, what is the importance of the strain hardening exponent is that, if there is a localized deformation like necking, then there the strain there is larger. And that implies, because this, it is end it is exponential, that means the stress is going to be larger therefore, further plastic deformation. And this implies that the softer region of material adjacent to the region where you actually put more strain which became harder that means to draw schematically here.

(Refer Slide Time: 51:01)



Suppose I had a material like this with a neck, so this region has undergone more plastic deformation as compared to this region, and this implies if with larger end. This material be harder as compared to this region of material, that means this if, because this region is softer, the plastic deformation will tend to spread here rather than get localized here. Therefore, I will get more tensile elongation.

(Refer Slide Time: 51:36)



If I have a larger end, that is why a material like brass with a higher strain hardening exponent like 0.5 gives you more plastic strain in uniaxial tension as compared to steels

with a lower strain hardening exponent. At high temperatures, now when we are talking about high temperature, we are talking about a temperature above the re-crystallization temperatures of material. It is not strain, which is the important variable, but it is strain rate which becomes the important variable. And therefore, I can write an equation at for high temperature deformation as sigma is equal to C epsilon dot power m and of course, when I do these tests, I keep the strain and temperature constant.

For two specimens which have undergone tests, to have comparable values. C is a constant and m is another important index, which is called the strain rate sensitivity. This is very, very similar to m for low temperature tests. So in low temperature, the important variable is strain, and the important exponent is the strain hardening exponent. At high temperature it is the strain rate, which is the important variable and it is the strain rate sensitivity which is the important exponent.

Now, if m has a large value, then you would expect a behavior at high temperature, which is similar to having n having a higher value in the case of low temperature deformation. If m is equal to 0, that implies the stress is independent of strain rate and the curve would be same for all strain rates. If m is higher and typically for metals it is it has a value of about 0.2, then you expect that the material would strain rate harden more compared to the material of with lower strain rate sensitivity.

If m is in the range of over 0.4 to 0.9, the material may even exhibit super plastic behavior. We will of course, see what is super plasticity and under what condition do we will obtain super plasticity later. But essentially super plastic behavior implies that you are getting very large elongations of the even of the order of 400 percent, or 500 percent or 1000 percent, which is not seen for the case of a normal material like steel or even for aluminum.

That means strain rate sensitivity is going to be an important parameter for me in controlling, giving me the dictating, the amount of elongation I am getting at higher temperatures. If m is equal to 1 which is the extreme case, the material behaves like a viscous liquid or a Newtonian liquid which just flows.

(Refer Slide Time: 53:59)



Therefore, if the effect of strain rate sensitivity is very, very similar to that of strain hardening exponent, which is at low temperatures. To understand this effect of strain rate sensitivity, we will dwell well little deeper now. Now, we have already seen that, stress can be written as C epsilon dot power m and the test being conducted at constant range and temperature. Now, in some materials due to structural condition and high temperature, necking is prevented by strain rate hardening.

So, the effect as I told you about n at low temperature is the effect that, it actually uniformly spreads your deformation and therefore, localize necking is reduced. Similar role is played by m at high temperature, and we will try to understand that how it happens. So, we can of course, write C epsilon dot per m, load per unit area, which is the definition of stress of course.

And I can rewrite the same equation of, using this equation I can put sigma is equal to C epsilon dot power m. And therefore, I can write epsilon dot power m is P by C into 1 or power 1 by m and into 1 by a power 1 by m and from the definition of true strain rate, which is epsilon dot is sorry, this m should be cut out.

So, epsilon dot is 1 by L, dL by dt and therefore, putting these two equations together, I can get a relationship of dA by dt, which is nothing but the decrease in the cross sectional area per unit time. So, that, because a negative sign there is a decrease, so it is a decrease in cross sectional area per unit time. That means, how fast is the necking

proceeding if, of course I the, if the overall specimen remains without necking. That means that the decrease is going to be small, but, because there is a necking taking place in a selected region. This implies that there is going to be a increased reduction in area in the localized region which we call neck.

Of course, dA by dt depends coming from these two formulae, putting these two formulae together, and arriving at this derivation is P by C power 1 by m, which are all constants of course, and 1 by A, power 1 minus m by m. If m is small, smaller the cross sectional area, the more rapidly the area is reduced. That means if I have a small strain rate sensitivity, then the smaller cross sectional areas will decrease even more rapidly and that is not a good condition for obtaining long elongations. Of course, if m equal to 1, we see that it becomes like a Newtonian viscous liquid, but between the value of small m to large M.

(Refer Slide Time: 56:25)



We will try to understand how this relationship can be understood better using plots. So, I have seen from previous relations of dA by dt can actually be related to A with the power 1 minus m by m.

So, if I plot dA by dt, which is the left hand side of this equation, which is the reduction in area per unit time versus A, and try to compare different materials with different m values. And these are of course, actual materials will have, will be close to one of these curves. If m is 1 by 4.25, and we said that this is something in the range where typical metals lie, which is about 0.25. We see that for a given area, the reduction in area is large.

On the other hand, if I had m of the higher value, that means that the increasing m curves are going from here, to here, to here along this dotted line, as you can see. That means for a given value of A, say for some value A 1 for instance and if I have a higher material with higher strain hardening strain rate sensitivity, then the reduction area would be smaller.

So, we will actually be on the lower curve rather than the higher curve. And if it is even higher like 3 by 4, then you will be on the even lower curve. This implies if I am going to compare different materials with different strain rate sensitivities, it is better for me to have a higher strain rate sensitivity, because in that case the reduction in area per, that means dA by dt, which is the reduction in area per unit time would be smaller. That means that now my deformation is not going to be localized.

And therefore, the deformation is going to spread across the sample and therefore, I can get higher elongations. Now, if you look at experimental results done on various specimens, you would notice that the curve on the left which I have drawn in the box here. You can see that the percentage elongation versus m, you see that, if m is larger. And now, this is now comparing various materials under various conditions there you can arrive at a schematic trend line that, if m is larger then you get larger percentage elongation

So, to summarize these few slides. Plastic deformation means permanent deformation, slip and twinning are two important mechanisms of that. In normal deformation like pulling of aluminum rod under tension, it is slip which is the dominant form of deformation. One of the simplest test actually we can do to understand the mechanical behavior of a material is a uniaxial tension test, which is typically plotted as a engineering strain, engineering stress diagram or a true stress true strain diagram.

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We can get important parameters regarding the mechanical behavior like elongation to fracture ultimate tensile strength etcetera from these curves. The curve can be understood as macroscopically elastic and elastic plus plastic regions.

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Variables in plastic deformation	n → σ,ε,έ, Τ
Usually expressed as (for σ_{plants})	
$\mathbf{\sigma} = \begin{bmatrix} K \mathbf{e}^n \end{bmatrix}_{\mathbf{e}^n}$	$\label{eq:K} \begin{array}{l} K \rightarrow strength \ coefficient \\ u \rightarrow strain \ \ work \ hardening \ coefficient \end{array}$
	Cu and brass (n = 0.5) can be given large plastic strain more easily as compared to steels with n = 0.15
$\operatorname{High T} \boldsymbol{\sigma} = \left[\begin{array}{c} \boldsymbol{\mathcal{C}}^{(n)} \\ \boldsymbol{\mathcal{C}}^{(n)} \end{array} \right]_{\boldsymbol{\mathcal{C}}, \boldsymbol{\mathcal{T}}}$	
$C \rightarrow a \text{ constant}$	
m -> index of strain rate sensitivity	
□ 1) m = 0 ⇒ stress is indepen	where of strain rate (stress-strain
a metals	
If me # 10.0 (the materia	il may exhibit superplastic behaviour
a material behaves	like a viscous liquid (Newtonian flow)

The important variables in plastic deformation are stress strain, strain rate and temperature. At low temperatures, it is strain, which is the important variable, at high temperatures it is strain rate which is the important variable. That means that I do not have to worry about the neck strain, the material does not accumulate strain, the material

is constantly replenishing its microstructure. Such that, at high temperatures you can, you do not have to worry about the strain in terms of hardening, it is the strain rate which is going to give you hardening.

Therefore, there are two empirical formulae which commonly used in literature, which is gives you the connection between these variables which is sigma is equal to K epsilon power n, where n is the work hardening or the strain hardening exponent. At high temperature, you can write down as C epsilon dot power m, which m is the strain rate sensitivity. And if I want to study the effect of strain rate sensitivity I can actually talk in terms of reduction in cross sectional area per unit time. And if I look at reduction in cross sectional area per unit time.

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One of I can I would have a curve for each one of the material I am studying and for a given cross sectional area, the reduction would be more for a material with a low m as compare to a material with high m. Therefore, higher the m, the smaller would be the reduction in the cross sectional area with time. Now this also can be understood by plotting experimental results for various materials, and you see that with increasing m, actually you are seeing that there is an enhanced ductility, which is obtained.

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And the explanation which is very-very similar to what I told you for n for small numbers, n for small low temperatures can be now thought of as m for high temperatures. That means, if necking is going to take place, there is reduction in area, there is a dA by dt term here, and if the, since there is a reduction here, the dA by dt here is going to be larger than the dA by dt here, where there is smaller reduction in area.

And this imply this region is going to get harder with respect to this region. If m is has a high value, which also implies that this the necking would now spread to other regions or the deformation would spread to other regions, and will not be localized to a region where the original reduction in area took place. That means now I will get longer elongation, and therefore I can understand the schematic trend line which is been drawn here for these materials.