Nanostructures and Nanomaterials: Characterization and Properties

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Lecture - 2
Introduction to Nanomaterials (CI)

Before proceeding further, let us briefly review the concepts, we have considered so far we asked the question that, what determines the properties of materials, and the answer we gave was it was a combinational decomposition of the material.

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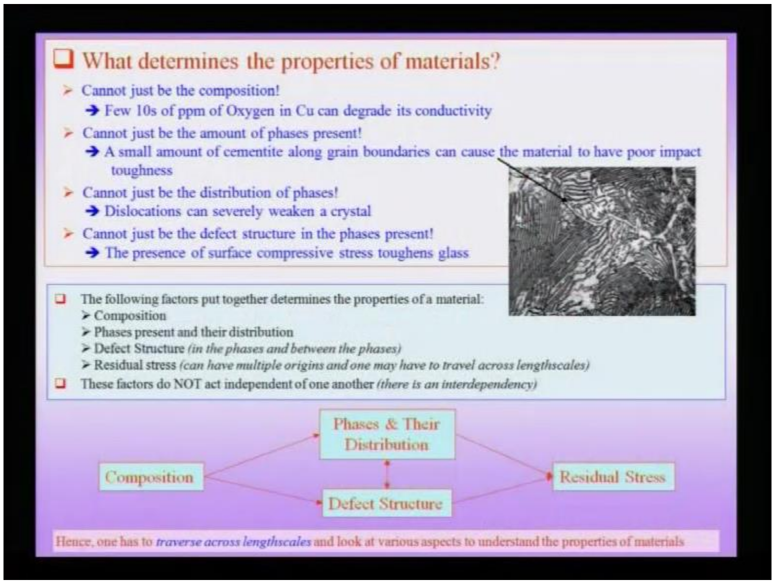

❑ What determines the properties of materials?

- ➢ Cannot just be the composition!
  - ➔ Few 10s of ppm of Oxygen in Cu can degrade its conductivity
- ➢ Cannot just be the amount of phases present!
  - ➔ A small amount of cementite along grain boundaries can cause the material to have poor impact toughness
- ➢ Cannot just be the distribution of phases!
  - ➔ Dislocations can severely weaken a crystal
- ➢ Cannot just be the defect structure in the phases present!
  - ➔ The presence of surface compressive stress toughens glass

❑ The following factors put together determines the properties of a material:
- ➢ Composition
- ➢ Phases present and their distribution
- ➢ Defect Structure *(in the phases and between the phases)*
- ➢ Residual stress *(can have multiple origins and one may have to travel across lengthscales)*

❑ These factors do NOT act independent of one another *(there is an interdependency)*

Hence, one has to *traverse across lengthscales* and look at various aspects to understand the properties of materials

The phases present in the material and their distribution we have to consider the defect structure. The definition formal definition the defect structure, which we will consider soon and last, but not the least we have to consider the presence of residual stress in a material which is present even in the absence of any external loading or constraints.

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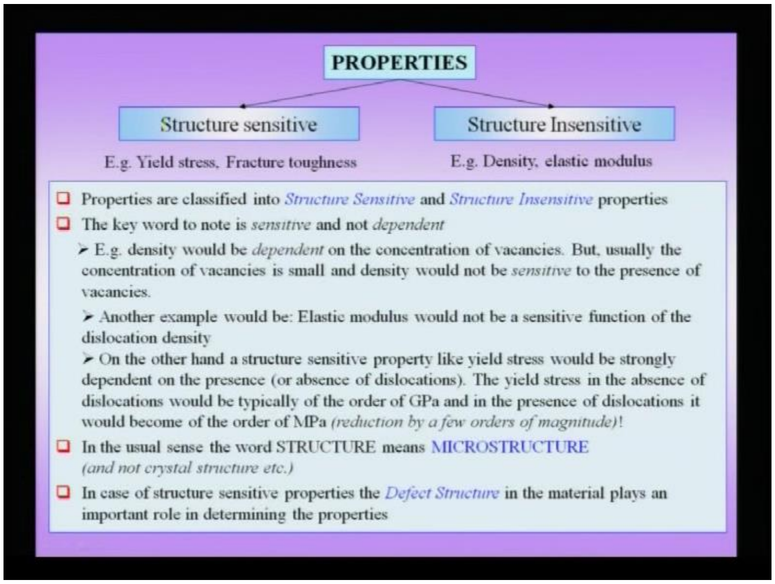

PROPERTIES

Structure sensitive

E.g. Yield stress, Fracture toughness

Structure Insensitive

E.g. Density, elastic modulus

- ❑ Properties are classified into *Structure Sensitive* and *Structure Insensitive* properties
- ❑ The key word to note is *sensitive* and not *dependent*
  - ➢ E.g. density would be *dependent* on the concentration of vacancies. But, usually the concentration of vacancies is small and density would not be *sensitive* to the presence of vacancies.
  - ➢ Another example would be: Elastic modulus would not be a sensitive function of the dislocation density
  - ➢ On the other hand a structure sensitive property like yield stress would be strongly dependent on the presence (or absence of dislocations). The yield stress in the absence of dislocations would be typically of the order of GPa and in the presence of dislocations it would become of the order of MPa *(reduction by a few orders of magnitude)*!
- ❑ In the usual sense the word STRUCTURE means MICROSTRUCTURE *(and not crystal structure etc.)*
- ❑ In case of structure sensitive properties the *Defect Structure* in the material plays an important role in determining the properties

We said that this becomes especially important when we are talking about structure sensitive properties like: yield stress and fracture toughness. And as an example, we had considered the micro graph shown on the right hand side wherein there is a steel with a cementite network all along the prior assonate grain boundaries. We had also asked the question that, if you are talking about phases in the distribution what kind of phases exist and we had classified phases based on the geometrical entity or the physical property.

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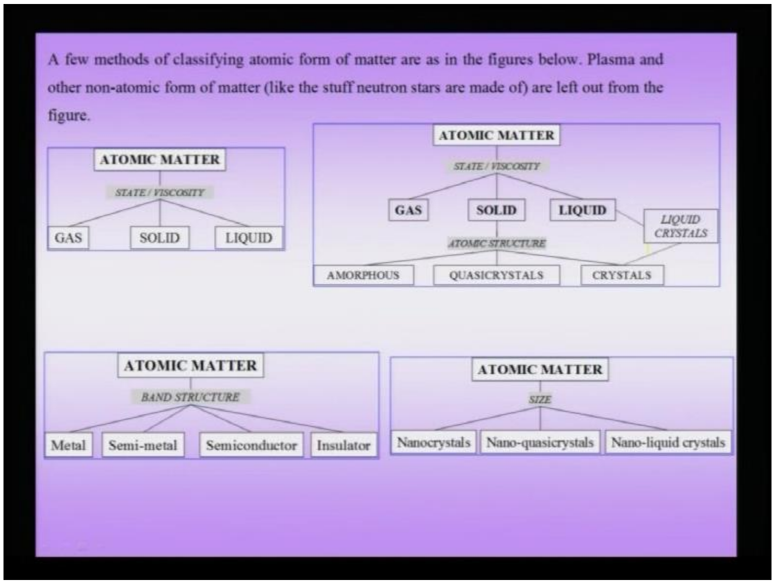

A few methods of classifying atomic form of matter are as in the figures below. Plasma and other non-atomic form of matter (like the stuff neutron stars are made of) are left out from the figure.

ATOMIC MATTER
STATE / VISCOSITY
GAS
SOLID
LIQUID

ATOMIC MATTER
STATE / VISCOSITY
GAS
SOLID
LIQUID
LIQUID CRYSTALS
ATOMIC STRUCTURE
AMORPHOUS
QUASICRYSTALS
CRYSTALS

ATOMIC MATTER
BAND STRUCTURE
Metal
Semi-metal
Semiconductor
Insulator

ATOMIC MATTER
SIZE
Nanocrystals
Nano-quasicrystals
Nano-liquid crystals

We would also consider various ways of looking at atomic form of matter and we had come across important concepts like the atomic based structure which is can be classified into crystals: quasi crystals and amorphous phases. We also said that, based on band structure we can have metals, semi conductors and insulators. And from this course perspective we had talked about a size based classification which gives us nano crystals, nano quasi crystals, nano liquid crystals etcetera.

We had also gone ahead in defined what are crystals in a very simplistic way and we had said that crystals are ordered and periodic. And anamorphous phases on the other extreme are neither ordered nor periodic.

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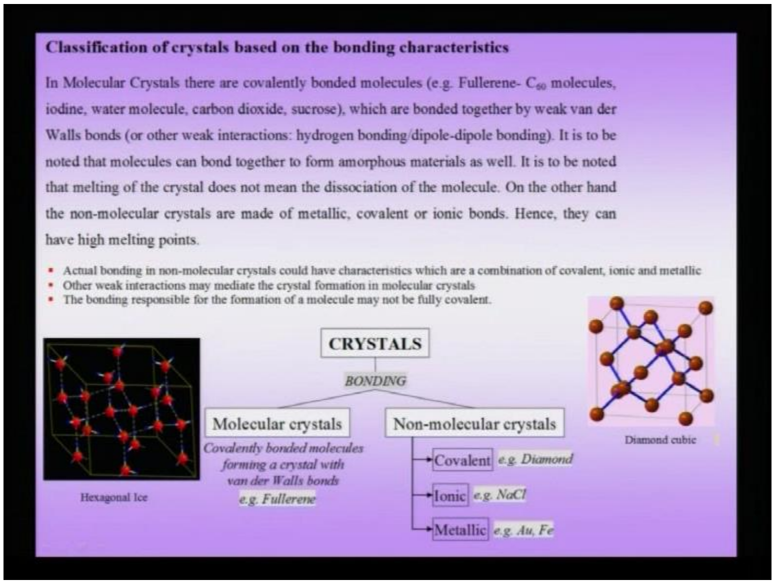

Classification of crystals based on the bonding characteristics

In Molecular Crystals there are covalently bonded molecules (e.g. Fullerene- C_{60} molecules, iodine, water molecule, carbon dioxide, sucrose), which are bonded together by weak van der Walls bonds (or other weak interactions: hydrogen bonding/dipole-dipole bonding). It is to be noted that molecules can bond together to form amorphous materials as well. It is to be noted that melting of the crystal does not mean the dissociation of the molecule. On the other hand the non-molecular crystals are made of metallic, covalent or ionic bonds. Hence, they can have high melting points.

- Actual bonding in non-molecular crystals could have characteristics which are a combination of covalent, ionic and metallic
- Other weak interactions may mediate the crystal formation in molecular crystals
- The bonding responsible for the formation of a molecule may not be fully covalent.

CRYSTALS

BONDING

Molecular crystals

Covalently bonded molecules forming a crystal with van der Walls bonds

e.g. Fullerene

Non-molecular crystals

- Covalent *e.g. Diamond*
- Ionic *e.g. NaCl*
- Metallic *e.g. Au, Fe*

Today let us consider classification of crystals based on the bonding characteristics. Now, based on bonding a substance could be for instance belonging into a certain type like an ionic crystal. But based on the atomic order the same thing could be glassy in other words it could be amorphous like before we had considered that 1 way of classification will not clash with another way of classification.

The bonding characteristics of the material play a very important role in all the properties which we think of. So, based on bonding we can classify crystals into 2 types: the molecular crystals and the non-molecular crystals. In molecular crystals there are covalently bonded molecules like for example, in fullerene we have the C60 molecule in water molecule we have the H2O molecule. Another example of molecular crystals are crystals based on carbon di oxide molecule, sucrose molecule etcetera. The bonding within the molecule is of one of the is typically of the covalent type, but the intra molecular bonding which actually gives rise to the crystal is usually of a weak type. It is a non-covalent interaction typically they could be of Hydrogen bonding type or dipole bonding; a detail list of which we will soon consider.

As we have seen that molecules can not only form crystals, but these molecules can also get order in amorphous form or you can even think of a quasi-crystalline order for these molecules. So, but the important thing in the molecular crystal is that the bonding within the molecule is covalent type and the bonding between the molecules which gives rise to the order or the lack of it is typically of a weaker type which we can be for instance an Hydrogen bonding type or a dipole-dipole kind of an interaction.

On the other hand, there are these familiar types of crystals which we are which you might have been exposed to before which are the non-molecular crystals and examples of non-molecular crystals are: the covalent crystals and example of which could be our diamond carbon based diamond. The ionic crystals the common salt or the Sodium Chloride it is a nice example of an ionic crystal or the metallic crystals like gold, ion, aluminum, copper, etcetera.

The kind of bonding characteristics will reflect in all properties which we can think of for example, if I am talking about the melting point of a material. A molecular crystal will typically melt at a low temperature. Because, the kind of interactions holding together the molecule which gives rise to this atomic order in the form of a crystal is of a weak type and therefore, such a crystal will typically melt at a low temperature.

On the other hand, a non-molecular crystal like for instance diamond which is covalently bonded you would have a very high melting point for such a material, not only that if I am talking about the what you might call the plastic behavior of a material typically, the latest parameter of example and covalently bonded crystal or a metallic crystal would be small.

And therefore, what I am considering here is the usual kind of covalently or metallically bonded crystal and I am not taking into account for now. Those kinds of crystals which are, which can have a large lattice parameters the usual 1s like: gold, silver or diamond have a reasonably small lattice parameter. And therefore, we will be having a small Burgers vector which means that my inner head lattice résistance to the motion of dislocations would be small which would translate into easy plastic deformation of especially these metallic crystals.

But on the other hand, molecular crystals typically suppose I am talk of fullerene is made of large molecules and the Burgers vector will be very large. Now, the bonding characteristics with respect to for instance the pearl stress which otherwise called the inner and lattice resistance can be compared between the covalent and the metallic crystals also.

In the case of a metallic crystal the pearl stress is typically small while in the covalent case of the covalent crystals, the pearl stress is very large. And typically therefore, covalent crystals are not that plastic especially at room temperature or low temperatures which means, below the 0.5 of the melting point of the material. So, these all these properties are naturally coming out of the bonding characteristics.

In ionic crystals for instance, if I am talking about plastically deforming an ionic crystal like Sodium Chloride typically it will fail by fracture rather than plastically deforming. That is plastically deforming by slip; the reason being that a ductile material is 1 for which the yield stress is lower than the fracture stress.

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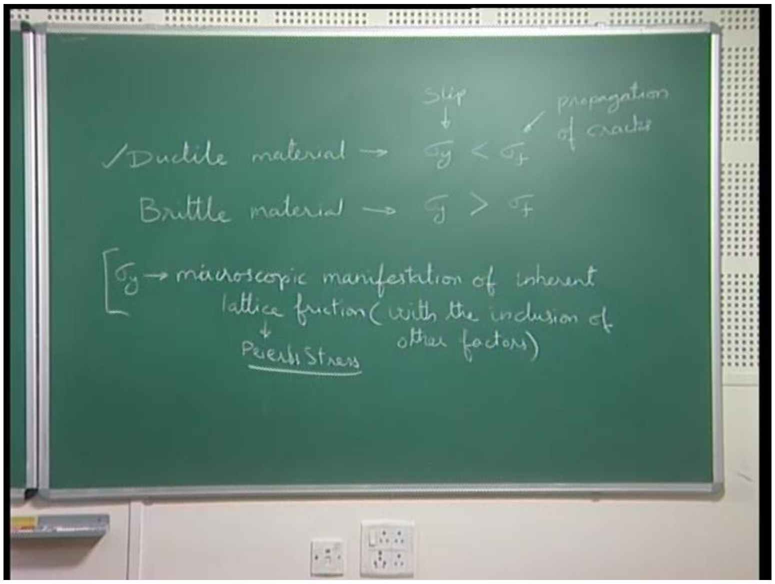

Slip
propagation of cracks

✓Ductile material → $\sigma_y < \sigma_f$

Brittle material → $\sigma_y > \sigma_f$

[σ_y → microscopic manifestation of inherent lattice friction (with the inclusion of other factors)

↓

Peierls Stress

So, if I am considering a ductile material a brittle material on the other hand, is 1 whose yield stress is larger than the fracture stress. So, a ductile material will yield first before fracturing. In other words, the yielding we are taking here is especially by a mechanism known as slip and fracture is caused by propagation of cracks. So, when I have 2 competing mechanisms which can take up my external loading 1 being slip, which is listed here.

And the other being propagation of cracks and if my yield stress is smaller than my fracture stress then the material is called ductile; yield stress is a macroscopic manifestation of the inherent lattice friction which is otherwise called the Pearl Stress or pearls in a Barrow Stress. So, other factors would come into picture when I am taking my inner and lattice friction which is otherwise, I call the pearl stress.

I will take my pearl stress and go to a macroscopic gross property like yield stress. So, this pearl stress is a strong function of the bonding characteristics of the material. A covalent material typically has a high pearl stress and therefore, has high yield strength and a tip. Therefore, if I am trying to plastically deform a covalent material like diamond then it turns out.

It is difficult and typically an ionic material which again has the scenario of high pearl stress would fail by brittle fracture rather than plastically deform. Therefore, if I am looking at any property then the bonding characteristics become very, very important in determining the properties. On the left hand side, there is an example of a hexagonal ice which is a molecular crystal.

In other words, in the ice crystal there are covalently bonded water molecules H2O molecules, which form a crystal via the Vander walls bond. If you want to talk about bonding characteristic based on the type of bond like: non covalent, non molecular crystals like covalent ionic and metallic this what you might call are the end pictures. And a real bonding characteristics could be somewhere between all these extremes possible.

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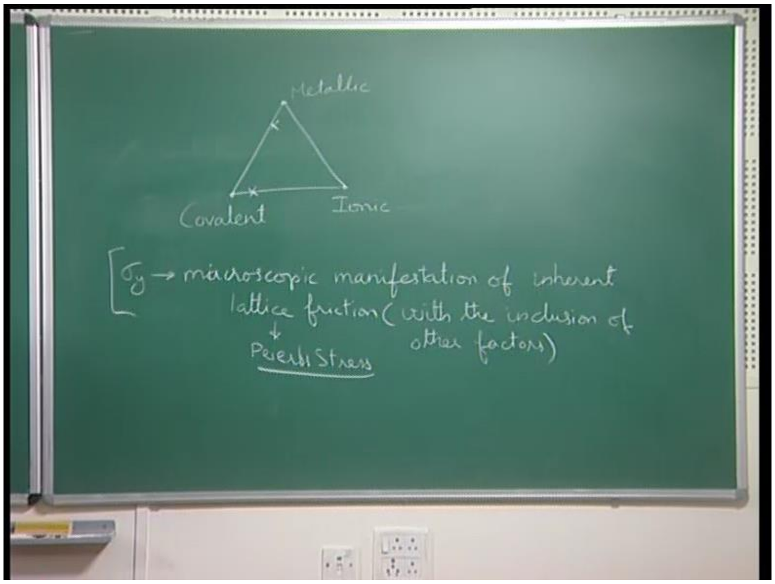

σ_y → macroscopic manifestation of inherent lattice friction (with the inclusion of other factors)
↓
Peierls Stress

So, these 3 extremes the metallic, the covalent and the ionic represents 3 extreme bonding characteristic and a given material for instance could actually falls somewhere between the triangle it could have some covalent characteristics. But a little bit of ionic characteristic and therefore, in this triangle it could lie here. Certain metallic crystals could also, have a certain amount of covalent character and therefore, they would not be on the extremes which are the metallic covalent or ionic extremes.

But would lie somewhere in this what you might call a turnery looking plot. Therefore, real crystals have characteristics which have a bonding which is a combination of covalent, ionic and metallic characteristics. We will consider in the next slide that there are other weak interactions which can mediate the formation of crystal and molecular crystal apart from the Hydrogen bonding which is responsible for the formation of the ice crystal.

Therefore, the kind of bonding which we are considering here forms a important basis for the properties that the crystal exhibits. And therefore, it is important to note if the crystal is some molecular crystal or a non-molecular crystal and given it is a non-molecular crystal which, will form much of the considerations in this course for instance. We have to consider if it is a covalent crystal and ionic crystal or a metallic crystal.

Now, we will briefly consider here various kinds of interactions in molecular crystals the weak interactions though we will not go into detail an interested read. And actually want to refer to details, for various individual molecules or various individual crystals as to which bonding is responsible for the formation of the molecular crystal.

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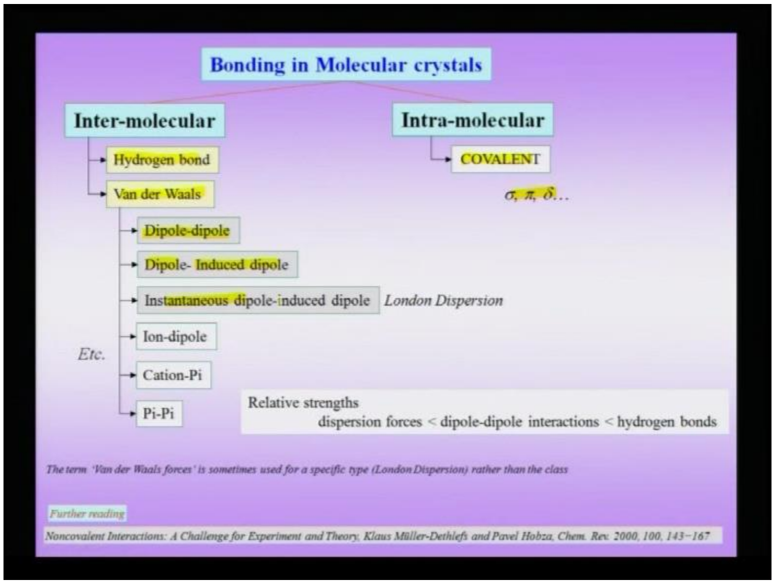

Bonding in Molecular crystals

Inter-molecular
- Hydrogen bond
- Van der Waals
  - Dipole-dipole
  - Dipole- Induced dipole
  - Instantaneous dipole-induced dipole London Dispersion
  - Ion-dipole
  - Cation-Pi
  - Pi-Pi

Etc.

Intra-molecular
- COVALENT

$\sigma, \pi, \delta\ldots$

Relative strengths
dispersion forces < dipole-dipole interactions < hydrogen bonds

The term 'Van der Waals forces' is sometimes used for a specific type (London Dispersion) rather than the class

Further reading

Noncovalent Interactions: A Challenge for Experiment and Theory, Klaus Müller-Dethlefs and Pavel Hobza, Chem. Rev. 2000, 100, 143−167

Typically in this molecular crystal as I told you, it is covalent interactions which give rise to the molecule. These are typically given symbols like sigma Pi delta, the inter molecular interactions which is responsible for the crystallization could be the Hydrogen bond or what is called the Van der Walls bond which includes Dipole-dipole interactions. Like here we are talking about permanent dipole-permanent dipole interactions or it could be a permanent dipole which actually induces any dipole in the neighboring molecule.

Therefore, you have a Permanent dipole, Induced dipole interaction which can also give rise to some bonding or there could be an Instantaneous dipole- Induced dipole interaction which is typically called the London Dispersion force. And there other forces like the Ion-dipole to the Cation-Pi and Pi-Pi interactions and all these various interactions listed here like the Hydrogen bond, the Van der walls bond etcetera are actually weak interactions.

The typical relative strengths of some of these bonds are the dispersion force that the weakest the Dipole-dipole interactions, that is the Permanent dipole-Permanent dipole interactions are usually stronger and the Hydrogen bonding is usually stronger than the Permanent dipole-Permanent dipole interactions. The book on non-covalent interactions is a interesting is an exhaustive study of these interactions and an interested or the paper on in chemical review would be a good reading place for other for students to learn further about these non-covalent interactions.

Now, we have to ask ourselves that we have talked about phases, but there is a larger picture beyond the phases when a material is given to you. Typically for instance I am holding a pen here; you can see that this pen is not made of a single kind of a material there is plastic, there is there are some metallic parts and other parts which are hidden away inside.

So, such a material or for instance your cell phone your typical cell phone is what made call of course, it is an entire device. A device has many components and each some of these components may actually view what is called a hybrid. It is not a single material which goes on to make your entire cell phone or some of its components. Now, why is that this consideration is very important or the question that, why what kind of a bulk materials exists is an important question is. Because, later on we will see when we talk about nano materials that not all components of the nano material may be nano in size only a few of these components and some of this may be even property related, may be actually nano sized and remaining of the components may actually be bulk like.

And those bulk like components will continue to have the properties which you normally expect for bulk materials. Therefore, it is a very important consideration that what kind of bulk materials exist and therefore, which of these components of these bulk materials can actually get into the nano scale, which is going to give us the interesting properties which we were interested in the study of nano signs and nano technology. Now, when you are talking bulk materials on 1 hand as I told you, there is a scale of the component for instance it could be a the scale of the component, could be of the orders of centimeters or even meters.

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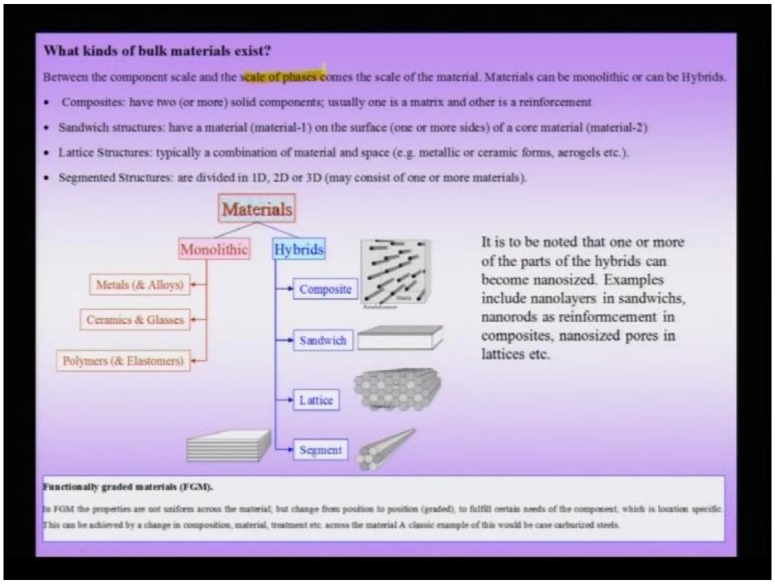

What kinds of bulk materials exist?

Between the component scale and the scale of phases comes the scale of the material. Materials can be monolithic or can be Hybrids.

- Composites: have two (or more) solid components; usually one is a matrix and other is a reinforcement
- Sandwich structures: have a material (material-1) on the surface (one or more sides) of a core material (material-2)
- Lattice Structures: typically a combination of material and space (e.g. metallic or ceramic forms, aerogels etc.).
- Segmented Structures: are divided in 1D, 2D or 3D (may consist of one or more materials).

It is to be noted that one or more of the parts of the hybrids can become nanosized. Examples include nanolayers in sandwichs, nanorods as reinformcement in composites, nanosized pores in lattices etc.

Functionally graded materials (FGM).

In FGM the properties are not uniform across the material; but change from position to position (graded), to fulfill certain needs of the component, which is location specific. This can be achieved by a change in composition, material, treatment etc. across the material A classic example of this would be case carburized steels.

And then, there is a scale of the phases which could be of the order of microns or 10s of microns. And when if you want to classify materials we have to classify them as monolithic materials and hybrids. Monolithic materials are simple materials like for instance the word of course, has the route that monolithic means, single stone, lithic has a word origination, origin the word lithos which mean stone, which essentially in this contacts translates into a single kind of a material. For instance you could have a copper wire which is just pure copper of course, it is poly crystal line copper nevertheless it is a monolithic material.

For instance a ceramic, for instance your brick is also another kind of a material in 1 view in a more macroscopic view it can also be considered as some monolithic ceramic. But of course, if you go little deeper you would notice that the brick actually consists of lot pores and also lot of material. And therefore, truly speaking it will come into a structure which is known as the lattice structure, which is a subset of the hybrid.

Therefore, if I want to understand what bulk materials are I classify them into monolithic materials which includes metals and alloys, ceramics and glasses and polymers and elastomers and this classification is what is called the Usual Engineering Classification or the Usually Common

Practice; usual kind of classification wherein, you have monolithic metals, monolithic ceramics and glasses, and monolithic elastomers.

But we know that, instead of actually working with monolithic materials they can actually tap into the potential of a multiple materials in a single component or a single material actually having multiple components which can therefore, give us the benefits of presence of both kind of components and these are called the Hybrids.

Now, for instance suppose I am talking about the blade of an helicopter aircraft. The maximum bending just come on the surface of the blade and therefore, I may want to have a hard material on the surface. The interior of the material can be relatively softer as compare to the surface also; we know the surface is what is usually exposed to the atmosphere usually exposed to erosion.

Therefore, I would like to choose the material which is most appropriate for this purpose. And therefore, I can make a sandwich structure in which the outer layers the colored grey is the load varying or the more stronger 1, stiffer 1 and the inner 1 can be less stiff. Therefore, the philosophy in forming a hybrid is to tap into the potential of all the components to make a material which is actually having the benefits of both of those.

Now, what kind of hybrids exist hybrids can be classified into composites they can be classified into sandwich structures, they can be classified into lattice structures and they can be classified into segments. It should be noted here; that the word use that the word lattice is different from the use of the word lattice in the context of crystallography. Here the word lattice, implies a presence of a composite or a hybrid between air or vacuum and a material.

For instance in this example there are rods of a material and there are regions which are voids basically. We will also, consider soon an example wherein these voids are themselves in nano size and therefore, that can be a nano sized material or a nano structured material. In composites for instance, if I want a material which has good toughness at the same time has good strength then, I can use a load bearing reinforcement which has been shown in black and grey color here; a rod like structures here which is very stiff, but is brittle.

On the other hand, I can use the matrix which is not that stiff, but is ductile and it can take all the damage which might accumulate during the in service operation of the material. So, these reinforcements can be form in the form of a long rods they can be in the form of articles, they can be also in the form of plates etcetera.

In sandwich structures typically, we have the top and bottom constituting 2 different materials while inside is of a different kind of a material. We had seen that the lattice structure is 1 which is a combination of material and void. So, this hybrid of a material and a void is called a Lattice Structure and lattice structures have very important uses like for instance suppose, I want to impregnate certain lubricant into a material.

So, which is part of the material itself and plays the role in lubrication of the component then I can use the lattice structure. Suppose I want weight savings wherein, I do not want too much of I want a lot of volume of material, but actually of much less weight. Then, what you may call volume in this case is actually an effective volume then I can use the lattice structure.

These lattice structures sometime are also referred to as foams and you can have foams typically of metallic foams or ceramic foams, which have important roles to play in various kinds of engineering applications. Segmental structures again are in some sense and expansion or a of these sandwich in lattice structures where you can see clearly see that, there are multiple materials which are put together to form a segmented structure.

And this is of course, a 1 dimensional segmented structures, this is a 2 dimensional segmented structure where there are multiple layers which form go on to form the hybrid. Now, the important thing of considering this form of material in a monolithic material of course, you have a single phase like a metal and therefore, if I am talking about a nano structured monolithic material then I have to pick up certain lengths scale in the material, which can become nano structure.

For instance in a metal it could be the grain size which becoming nano scale.On the other hand, in the case of a composite just 1 of these components could be nano scale and of course, there is no stopping as from putting for instance 2 or 3 types of reinforcements. And therefore, 1 of these reinforcements could be in the nano scale or 2 of these reinforcements could be in a nano scale. Or for instance, suppose I am talking about reinforcements which are particles and rods then the particle size could be in nanometers the rod diameter could be nanometers, but not the rod length which could be much larger. And therefore, the important thing being here 1 of only 1 of the components could or 1 or more of the components could be in the nano scale and not the entire composite or the entire sandwich structure.

Therefore, this classification tells us, that once I have a broad overview of what kind of material exist then I know which of these can become nano sized. Further to this kind of a classification we have additionally another important kind class of materials which we need to look into which are called the Functionally Graded Materials.

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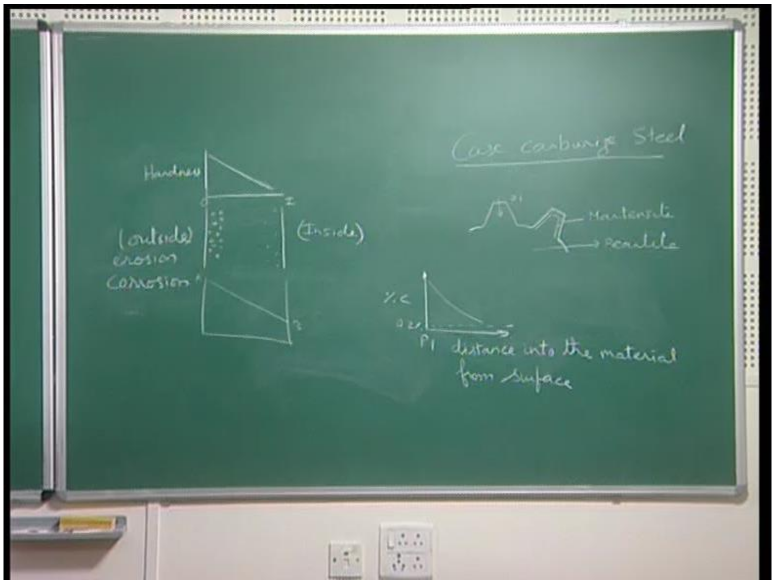

In a functionally graded material the concept is that, for instance in a component this could be the inside of the component where, the fluid flows and this could be the outside of the component wherein, for instance which could be exposed to erosion or corrosion. Therefore, even though I have a single material here I want to make it graded and I can make it graded in terms of the composition, I can make it graded in terms of for instance the precipitated density etcetera etcetera. So, that there is a gradation in the property for instance this surface could be harder and this surface could be softer and I am plotting my hardness with respect to surface. So, this is my outer and this is my inner and I can see the hardness could be varying of course, it need not be a linear variation nevertheless. Such a functionally graded material can perform a very important role that in a single component.

Actually I do not have 2 or more distinguishable component which can I can say this is a and that is b, but there is a continuous gradation of the properties. And I say that this gradation of the properties could actually come from change in variation in composition or it if I am talking about a composite then, I can talk about reinforcement density which is higher here for instance here I could have more particulate reinforcement while on this surface that is d could be little smaller. Or I could think of the composition here being rich in phase a and pourer in phase a and say go out from here; and this side could be pure b and this is almost pure a. So, there are various ways of making compositely graded materials. And the purpose here is to build in a single material a change in properties as you go from 1 special region to another and this could be a continuously varying property.

A classic example of this could be considered as the case carburized steel. In case carburized steel for instance suppose I am talking about a gear wheel and say this is my gear wheel tooth I can think of decreasing carbon composition from the outside to the inside. Suppose i am talking about this plane as p1 and this is going inward as I go from p1 I can actually have a carbon concentration which drops off. So, this is concentration of carbon.

Now, the important point is that I take a material with the certain amount of carbon in it for instance I have to take 0.2 percent carbon steel. Then, I would impose a carbonaceous atmosphere on the surface which will now allow carbon to slowly diffuse into the material and after sometime I will stop the carburization process cool the material later on take the material to high temperature and quench it.

In this process what would happen is that, the surface would have a high carbon marten site well the interior would have a micro structure which is like a pearlite. So, I have surface micro structure an outer micro structure which is and a interior micro structure is more like a pearlite. The reason for this variation in micro structure is related to the cooling rate, the surface feels a very high cooling rate or a high quenching rate which implies that the high carbon, which is in the solid solution.

The interstitial solid solution form forms a marten site well the interior is facing, which is facing a low cooling rate gives rise to pearlite. And this pearlite which on the interior side is also having lower amount of carbon which is similar to the original carbon which was there in the material; which I could call something like a 0.2 percent carbon. And therefore, I will have a in which the surface is extremely hard and the interior is stuff.

So, this structure which is now can be thought of as an classic example of a functionally graded material is having a gradation in the properties as you go form this surface to interior. And as you know the gear will actually measures with the remaining gears in system and therefore, it needs to be hard. The interior of the meal actually needs to be tough.

Because, the material has to be resistance against fracture suppose a material like we know that marten site is very hard, but very brittle. So, we do not want to have a material with which is throughout marten site because, such a material will be very brittle and would have a very pour impact and toughness in other words, very pour tolerance to presence of cracks in it which are un avoidable during actually the fabrication of a component.

The cracks you are talking about here typically here are micro cracks and not large size cracks. Therefore, in this example you can clearly see that I have my under my control the variable which is composition, I have under my control a gradation in composition, I have under my control the formation of the kind of phases like: the surface on the surface is marten site. The phase on the interior is more like pearlite it is actually not a phase, but a micro constituent.

So, I can have a gradation in the what you might call the formation of the phases in the micro constituents and therefore, I have a handle of the properties. We shall soon see that, how this concept of controlling composition or going from composition to phases to micro constituents can be thought of in the what you might call a functional definition of what we call a micro structure, which we will make an all in compassing kind of a definition which can actually give us a handle on the what we were defined before the micro structures sensitive properties.

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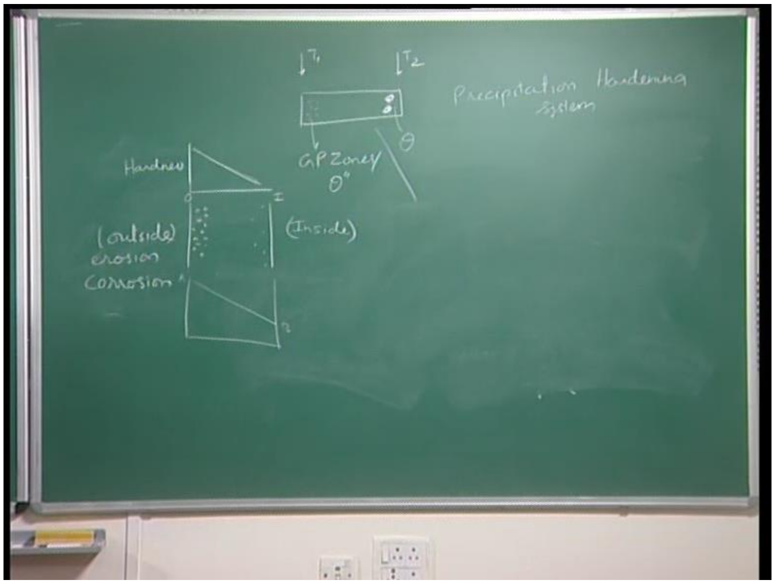

Another simple way of creating for instance, gradation based on precipitation which is what we considered here is to have actually, what you might call a precipitation hardening system. In the case of a precipitation hardening system, essentially what we do is the classic example of the aluminum 4 percent copper alloy system in which we take the system to high temperature.

So, where you have uniform solid solution we will quench the system to room temperature typically from a temperature like 550 degree Celsius which according to the phase diagram tells you is gives you a uniform solid solution of a copper and aluminum. When we quench it we actually at room temperature we have a super saturated solid solution of copper and aluminum additionally, the system will also be super saturated with respect to vacancies.

Now, I can age this system to at temperature like 180 degrees or lower, but around not as high as close to the equilibrium solves line and in aging, so I will produce a fine distribution of precipitates. Later on we will see an example, how this fine distribution of precipitate helps us in increasing the strength of a material.

But the important point to be noted here, suppose I use an ageing temperature which is T1 on 1 side and an ageing temperature T2 on other side then the kind of precipitate which is produced would actually vary from left to right. If T happens to the higher temperature then you tend to produce more of the equilibrium large size precipitates theta. So, I am schematically showing this large size precipitates as bigger circles.

On the other hand, the lower ageing temperature might produce fine GP Zones or theta double prime precipitate. So, I can now engineer a gradation in the kind of precipitate or the kind of phases which are produced during the heat treatments and in this process I can have a gradation in the properties. Therefore, I can have monolithic materials which of course, could have a variation in composition from 1 side to another.

We can have hybrids and added to that more importantly we can have hybrids and monolithic materials which can later on be what it might call made into more sophisticated version of these which is called the functionally graded materials; which is actually help in the actual engineering component. Wherein, I have a side specific property which will help me in better performance of my component.

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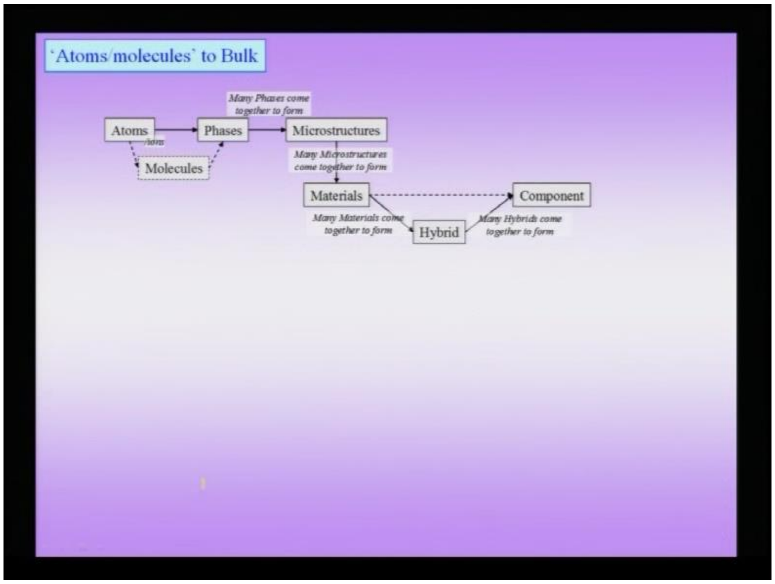

'Atoms/molecules' to Bulk

Now, when we had considered nano scale materials an important concept was that there are entities in the system, which are nano scale. But the more important thing to note is that, whenever we have a system we cannot understand its properties or we cannot understand entirety of the system without actually traversing across length scales.

Now, what is the length scales we need to consider is, what this diagram shows you and this also, tells you a bottom up approach towards what you might call assembling a component of course, this is more like a conceptual understanding of assembling a component. And in reality the component may actually be formed by a certain method like: casting or a welding or could be 1 of the other processing methods; which would in turn actually engineer the kind of micro structures which are produced or kind of phases which are produced.

But let us consider, this traversing across length scales and see how at 1 end of the spectrum you have atoms and molecules which are typically of the order of angstroms. And the next scale of the of the scale of the phases which could be of the order nanometers or could be of the order of microns. Then, we have the scale of the micron structures wherein multiple phases come together, to form a micro constituents and multiple micro constituents you may come together to form a micro structure.

So, let us briefly explore this pathway which will actually form the bases for this large broad spectrum understanding of materials and their sub components. So, we have atoms or ions as a case may be and they could combine to form molecules. Many of these molecules or if directly I can go from atoms can give rise to phases and we already considered what kind of phases we are talking about possibility of many kinds of phases.

These phases may come together to form micro constituents and further the micro structures. And I am using micro structure so far in what we what you might simplified engineering usual use of the word sooner we will define micro structures in a more specific functional way. But for now, we will expect the usually understood meaning of the word micro structure.

We could have multiple micro structures coming together to form a material, we could have multiple materials coming together to form a hybrid and further. Multiple hybrids could come together to form a component and of course, this component could be in the scale of few 100s of microns or it could be much larger or it could be even talking about a much larger component which could be of the order of centimeters.

And we all know form a everyday experience that actually most of the components we are we actually see in application are actually hybrids. For instance a pen cap could actually be having a metallic part and a plastic part further; the metal metallic part also could have some layer quoted on top of the metal to give it a certain shine.

Therefore, we have already talking about a multilayered material or what you might call hybrid material and that hybrid material going in association with another kind of monolithic material like plastic which finally, gives rise to a simple pen cap. But we go to larger and larger components; we will see that there could actually be many, many hybrids which come together to form a component or many, many materials directly forming a component as the case may be.

Therefore, I need to understand the properties of the component which I am really interested in comes from many many things which sit below in the hierarchy of the length scales which I have to consider. For instance suppose I start with atoms which are heavier; obviously, the component is going to be heavier. Suppose I start with magnesium which is a lighter metal then my component is going to be lighter.

But the story does not end there right for instance, suppose I am interested in a property like as we just know. So, wear resistance then if I can make a hybrid in which I can quote my magnesium with certain harder phase or have a selectively a harder phase which is impregnated on the surface then actually I can get a harder component. And therefore, I need to worry about all these length scales which are there, between the length scale of the atom and that of the component. The design of the component itself is very very important as far as the performances goes. For example, if I have a component which has sharp bends then those sharp bends can actually give rise to stress concentration which could be regions of failure. And I may want to design the component with high radius of curvature wherever possible.

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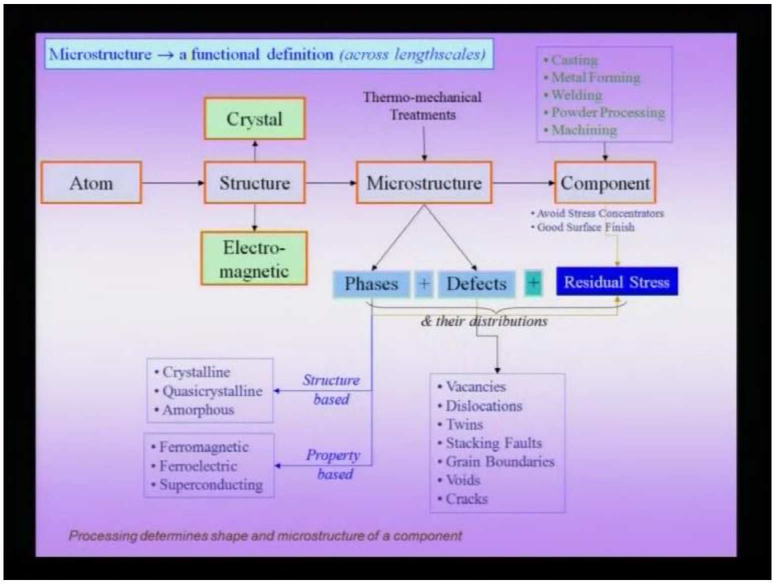

Microstructure → a functional definition *(across lengthscales)*

- Casting
- Metal Forming
- Welding
- Powder Processing
- Machining

Thermo-mechanical Treatments

Crystal

Atom

Structure

Microstructure

Component

- Avoid Stress Concentrators
- Good Surface Finish

Electro-magnetic

Phases + Defects + Residual Stress

& their distributions

Structure based

- Crystalline
- Quasicrystalline
- Amorphous

Property based

- Ferromagnetic
- Ferroelectric
- Superconducting

- Vacancies
- Dislocations
- Twins
- Stacking Faults
- Grain Boundaries
- Voids
- Cracks

Processing determines shape and microstructure of a component

Now, we are in a position to actually define the term micro structure and define it in a functional way as we have covered sufficient background to actually now go ahead and understand it a micro structure. We will define it based on 2 important considerations which are listed there it is going to be a functional definition and it is going to be a definition which includes multiple length scales.

First I will give a justification, why you need to define micro structures this way. Now, suppose I am looking the classic definition of micro structure would be that this structure I would see under an optical microscope which would typically go up to 1000 x magnification. Now, suppose I am looking under transmission electron microscope then I could be having a magnification going up to 1000 kx or 50 kx.

In this case, I may have to define a new term as nano structure or some additional term will have to be defined for those lengths scale which are even smaller than that. Therefore, I will have to be introducing multiple new terminologies whenever I am changing the scale of my viewing. This scale of the definition of micro structure as viewed under high magnification typically 1000 x is the satisfactory or what you may call the usual general excepted terminology.

The way we are going to define micro structure could actually be called could have been given a new name. But since the most important thing we are interested is what is called the micro structure property correlation therefore, we do not want to introduce new terms. But, instead use them term of micro structure, but built into it these 2 aspects the functional aspect and also the aspect which covers all length scales.

And as we shall see, by this very definition of this micro structure as defined here we will be including all length scales of the problem. We have already seen that advantage of the spectrum of the building block of atom sets and the other end of the spectrum is the spectrum of the component. The component typically as you know is formed by various kind of forming material manufacturing process like: casting, metal forming, welding, powder processing and machining etcetera.

These are typically some of the typical 1 so metal. But there are other 1s which can use the ceramics that is still more which shall use for polymers. And in the component forming methodology obviously, you could have a material synthesis aspect followed by aspects which actually shape it into the form of a component. So, there are multiple steps which could be involved in the formation of a component.

The next scale after the atom is the scale of the crystal structure or the structure as you might call and we already seen that, for instance how atomic structure can be classified. Now, when you are talking about structure we could be talking about the atomic order based structure or what you might call the crystal structure or more importantly the electromagnetic structure of the material. In other words, I could be talking about the electron densities, I could be talking about the orientation spins or the magnetization vectors of individual, atoms, ions etcetera. The next scale after this structure or what you may call the structures scale where, in the electro structure and the electromagnetic structure reside is the scale of the micro structure.

Important thing is that, this micro structure can form by those processes which actually are used to form the component for instance. In other words, what are the processes key features of those processes will give rise to the micro structure or for instance the component are the thermo mechanical treatments.

In other words, I could be talking about a material heating the material or I could be talking about forming the material like for instance I could use exclusion, I could use rolling or I could use the combination of both, I could use the high what we might call a thermo mechanical process where, I could actually do the rolling at a higher temperature.

Therefore, the bases for formation of the micro structure is very similar to the bases of formation of the component of course, I may desired to form the micro structures first for the material and they later on do additional processing to form the components. So, that is the possibility, but essentially the thermo mechanical treatments which under take to actually make the component or make the material itself would give rise to a micro structure.

Further of course, I could use the series of these thermo mechanical treatments to engineer my micro structure even further like, the example we had considered this just now. Wherein, we took an aluminum copper alloy which could have been form by melting and further we did a certain set of heat treatments which can give us which might call a thermal treatment.

So, which could be desired micro structure and more importantly we even considered a gradation in the micro structure, which can give rise to a gradation in the properties and therefore, the gradation performance of the material. At the component scale we already saw that we need to avoid stress concentrators which would in fact, be very could prove deleterious for the operation of the component. Now what is this word micro structure mean, what are its components and how each 1 of these components give rise to a handle on the properties is the important question we are going to answer next.

We can think of a micro structure as phases under distributions defects and we will soon introduce a term called defect structure. So, defects and the distribution and last, but not the least residual stress and their distributions, so we have 3 important components to a micro structure the phases, the defects and the residual stress. And not only these 3 components we have to consider, but we have to consider their distributions.

So, we need to understand the terms used in this definition and also, what do we mean by the term distributions you have to note that residual stress can be an integral part of the micro structure itself or can be on coming from a larger scale like when we form the component. So, there could be multiple origins of residual stress, but more importantly once the residual stress is present in the material it might actually play a performed role in the properties of the material.

Now, we already seen what kind of phases can exist for instance, we had already seen structure based definition of phases like: the crystalline, amorphous etcetera. We had also talked about a property based definition of phases like: the Ferro electric, Ferro magnetic etcetera. Therefore, we are have a clear understanding of what these term phases mean.

But we need to be introduced to the concept of a defect and more importantly the concept of a defect structure. And as I said it is not essential I only talk about defects, I need to talk about certain further considerations about defects like: the distribution of defects, association of defects etcetera. To have a first glance of what we mean by these defects.

These defects could imply 0 dimensional defects like vacancies, 1 dimensional defects like dislocations, twins, stacking faults, grain boundaries, voids, cracks, etcetera. You know, what is anything which sort of interrupts my perfect crystalline order and of course, I am now considering a crystalline material whichever interrupts my perfect crystalline order can be taught of as a defect in the crystal.

And suppose I am having an amorphous material then, in that case voids in the amorphous material or crystalline regions in the amorphous material could also be thought of as defects in the perfect or the existing amorphous kind of a structure. So, once I have an understanding of these 3 components of the micro structure the phases the defects in the residual stress.

Then, we can go ahead and try to understand how this micro structure is going to influence my micro structure dependent properties. And last once again to retreat the processing determines the shape and the micro structure of the components. In other words, the scale of the micro structure is intimately related to the scale of the component and of course, when we are doing certain processing that also tells us the kind of structure which is going to avoid.

For instance suppose, I am going to slowly cool a material I may get a crystalline material. If I cool it very fast then I may get an amorphous material and after cooling it very fast suppose I heat it again I may start to produce crystallines in the amorphous material. Therefore, I need to know the thermo mechanical history of the material if I want to know what kind of a micro structure has been obtained by this kind of processes.

Therefore, this is perhaps 1 of the important slides in this whole lecture or this whole course. Because, now we have now not said anything about the scale of the micro structures; we not said that it is only at the micron scale. For instance in the case of the GP Zones which we talked about which are essentially copper rich regions in an aluminum copper alloy matrix. They would have a length scale of the order of nanometers, not only that these GP Zones are coherent in nature; that means, GP Zones have a residual stress wheel associated with it.

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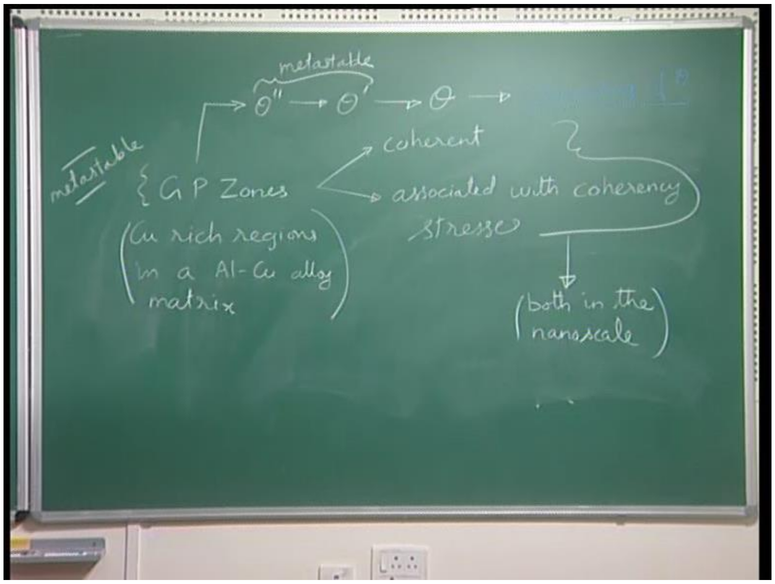

So, this is an important concept now that we have GP Zones. And these GP Zones are basically both the stress associated with the GP Zone and the copper rich regions the physical dimensions of that both of these are in the nano scale. And resistance of both of these is going to affect the property of the material the aluminum copper alloy which has these GP Zones.

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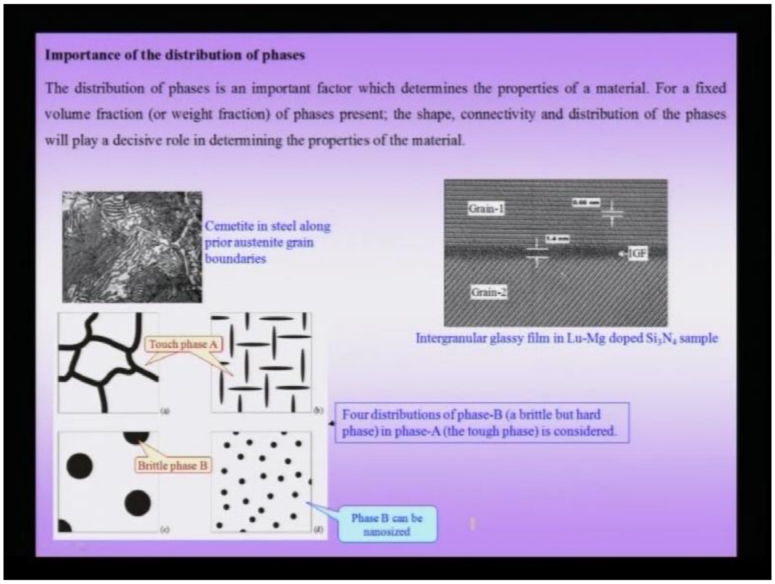

Importance of the distribution of phases

The distribution of phases is an important factor which determines the properties of a material. For a fixed volume fraction (or weight fraction) of phases present; the shape, connectivity and distribution of the phases will play a decisive role in determining the properties of the material.

Cemetite in steel along prior austenite grain boundaries

Intergranular glassy film in Lu-Mg doped Si_3N_4 sample

Four distributions of phase-B (a brittle but hard phase) in phase-A (the tough phase) is considered.

Phase B can be nanosized

I had mentioned that I have to worry about the phases present in the material, but along with it the distribution of the phases. We already seen 1 clear cut example and the example was, the presence of cementite in steel along the prior assonate grain boundaries that how the distributions can actually drastically alter my properties. So, for a schematic let me consider 4 distributions of phase b in a phase a.

And in this case let me, think of the phase b to be a hard, but, brittle phase and phase a to be more ductile kind of a phase, but not that hard. Therefore, the black phase the region which is shown by black which is right here; is my hard and brittle phase which as you can see has multiple morphologies as in the 4 schematic shown.

Therefore, when I am talking about distribution of phases I need to know the shape of this phase b, the way it is present I when I am talking about shape it could be needle like as in this case just typically the morphology observed in many cases, it could be spherical, it could be cylindrical, it could be irregular, it could be feather like etcetera. I need to worry about the connectivity of these phases.

For instances as you can clearly see in this example which is in the top you can see here; top example you can see that, the phase a is not connected to phase a, but phase b forms a continuous network. So, I need to worry about the connectivity of these phases suppose, I am talking about a lattice structure in this case I am talking about the lattice which is a hybrid. And suppose I want to use it for filtration purposes and therefore, in such a case I would want interconnected porosity in the material. So, the a fluid can actually be passed through this interconnected porosity or I want to store some lubricant in the system throughout the volume or I want to store some material throughout the volume then I need interconnected pores. And if the pores are isolated then that would not help in the filtration process.

Therefore, I need to worry about the connectivity of the phases. Then, I need to know the spatial distribution of these phases and suppose if this micro structure is evolving in time then I need to know the spatio temporal revolution of this micro structures. For instance in the example we just now took of GP Zones, if suppose this component which has GP Zones is employed in surveys at high temperature.

Then, what would happen is that these GP Zones will slowly transform into theta double prime precipitates which will later on terms theta prime precipitates. Then finally, you will get quilibrium theta precipitates these 2 are meta stable phases and GP Zones are meta stable as well. And therefore, they will transform finally to the equilibrium phase theta, but it will not stop there will be coarsening of theta.

In coarsening of theta what will happen is that, the larger precipitates of larger sized precipitates of theta would actually grow of small size theta, and in the end actually the average particle size would increase, but the inter particle or the inter precipitate distance would decrease.

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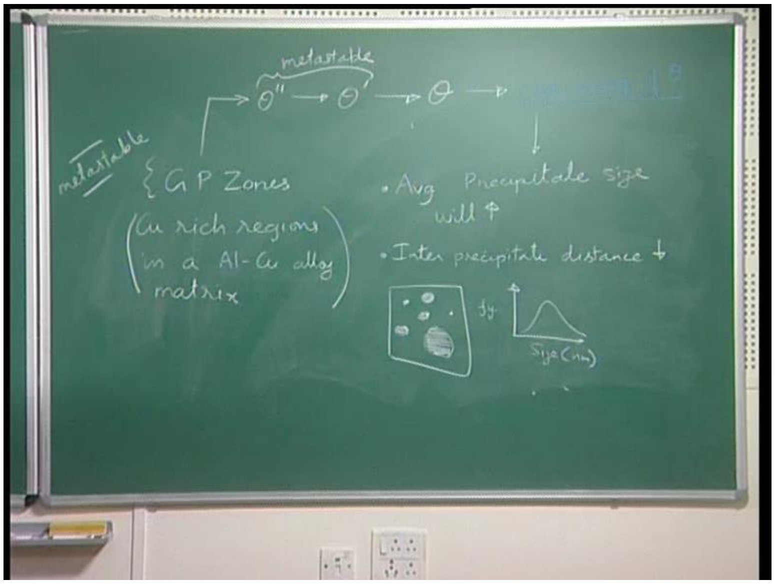

And we are talking about the average precipitate size, so during the coarsening process 2 thing would happen: the average precipitate size will increase and the inter precipitate distance would decrease. And in a later work numerical example later on we will see that this is actually going to be deleterious for the hardness of the material or distance of the material. Now, and as you have seen now that actually when you are doing the precipitation process some of the nucleation events would occur earlier and some of the nucleation events would occur later. And therefore, at any point of time suppose I freeze my micro structure and have a look then you would have a distribution of sizes.

If you look at the distribution of sizes there could be extremely small size precipitate particles as you may want to call them which are in the nano scale to precipitate which are in the micron scale. Therefore, there could be a range of sizes, so when I am talking about distribution of phases, I am talking about the spatial distribution of sizes and the frequency of occurrence of various sizes.

Therefore, you can actually plot until some point of time the size which could be measured in nano meters for instance and the frequency. And you can see that, there could be actually a variation which could also be thought of as a distribution of sizes. So, I need to worry about this spatial distribution of this phase I need to worry about the connectivity of the phase I need to worry about the frequency of occurrence of various sizes, I need to also worry about how the what is the shape of this phase particles.

Again, if I am talking about a temporary revolutionary system with the temporary revolution the shape these particles my also change. In for instance suppose I am talking about in some systems the precipitation of gamma and particles, precipitates. This gamma initially precipitates pherically, but later on when the precipitate becomes semi coherent or later on in coherent then it assumes a certain shape which could be cuboidal or a cube.

Therefore, this as spherical precipitate with time changes into a cuboidal shape and this is coming out because of the temporal revolution of the precipitate. And this is intimately related to the characteristics of the interface which could be which changes from coherent to an in coherent 1. Therefore, when I am using the term distribution of phases there are multiple parameters which I need to keep in view and all these as is towards understanding the properties of the material.

Now, another example for instance this is the right hand example there is an this is the example of Intergranular glassy fill in a silicon nitrates sample. This happens to be a Lutetium, Magnesium, doped silicon nitrate sample and you are noting that there are these crystalline regions in the top and bottom which is labeled as grain 1 and grain 2. But there is an amorphous region along the green boundary, which is very similar to the continuous network of the brittle cementite along the prior assonate grain boundaries.

Now, suppose the silicon nitrate sample is loaded sometimes in impact then it could so happen that the cracks may propagate along this glassy phase rather than actually propagating through the grain. And therefore, this material may have a characteristics which is brittle as compared to if the crack was propagating in an inter trans granular mode. Now, we had considered 4 schematic examples and in some sense it was this example a, which was simplified into this example of steel and in the case of silicon nitrate sample. 1 case of course, there was a crystalline phase like cementite along the prior assonate grain boundaries and a second case it was actually an amorphous fill.

If you look carefully the scale bar here; actually this fill actually happens to be in the nano scale while the silicon nitrate grains are actually large grains. And they are not nano scale only this inter granular glassy fill which is in this nano scale and that too in the dimension which is which has been marked in the figure. Therefore, I need to worry about the connectivity of the phase b its distribution etcetera.

If you look at the figure b here exactly the 2 phases are present which are present in the figure a, which is phase a and phase b. And for now we will consider that the volume fraction of phase b is also constant and the thing which is been altered is the shape and connectivity of phase b and of course, you could further go ahead and even make the micro structure more complicated by changing the sizes of the phase b as well.

But you can clearly see in the example b that the phase b is in this form of a needle or a lengths or what you might call a highly blade sphere spheroid in 3 dimensions. This kind of morphology would mean that at the tip of these precipitate, which I am marking here in yellow there will be actually high stress concentration. So, let me draw that here.

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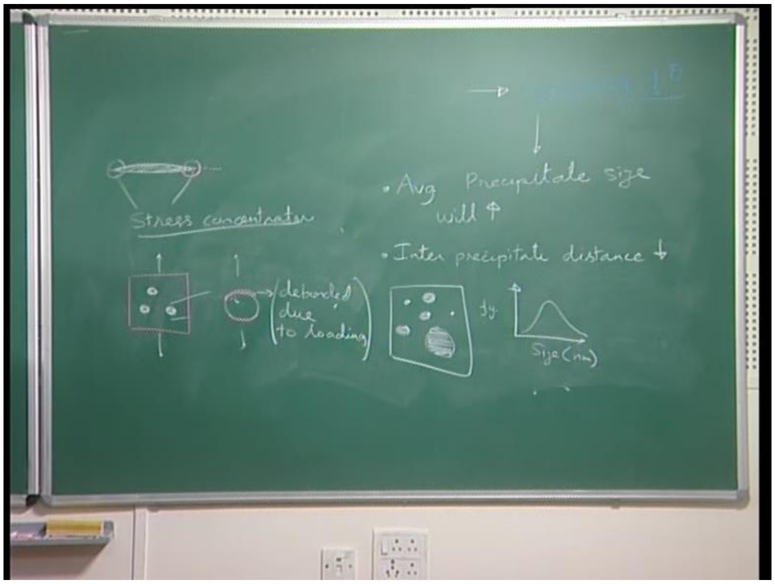

So, I have a precipitate which is like this and a head of the precipitate this region acts like. So, if this acts like stress concentrator then actually cracks may propagate cracks, may initiate at these regions which have been marked in this case by the circle. So, these cracks could nucleate here and therefore, propagate and lead to the failure the material.

On the other hand, suppose I consider the same distribution of b in a like in the case of c or in the case of d then you notice that the same phase is in the present form of a sphere of course, depicted as a circle in 2 dimensions. And in that case there is the stress concentration effect is much reduced and therefore, you would notice that such a material the propensity for crack nucleation at the phase practical would be reduced.

But now, I have 2 further examples or 2 distinguishable cases for even for the spherical case: 1 the case d which has been shown here and 1 the case c. In case c and case d the volume phase; volume fraction of phase b is same which as I told you is a brittle phase. But the size of the precipitate in the case of c is larger, what does this mean in terms of the properties. What are the now what is meant by size here?

Of course, we have to compare it with certain natural length scale in the material or a natural length scale in the component. So, for now we will restrict ourselves to the natural length scale in the material. So, automatically 1 of the natural length scales could be the lattice parameter of phase b or it could be the lattice parameter of phase a. And typically the lattice parameter as we have seen before could be much smaller than the length scale of the phase.

But there is an important another length scale which comes into picture, which is the length scale at which some of the defects in the material reside though we are not exposed to it at this point of time. But we will take a small pick ahead and we will see that, a distribution like in the case of a d actually will give rise to a better hardening in the material as compared to c and we will also, consider what is origin of this kind of a hardening effect coming in the case of a distribution like d. And more importantly from this point of view of the course, that suppose I keep on making the phase or the precipitate size smaller and smaller. Then, at some point of time it will become in the nano scale and therein lies lot of interesting effects which we will observe as we go along. Now, when considering this phases 1 important thing we have ignored is the interface.

So, 1 thing is that why is interface important is because we have talked about phase a its characteristics, we have talked about phase b and its characteristics. And we have been talking about characteristics; we have talked about things like connectivity shape etcetera. And we are inherently assuming that we also, know everything about the bonding characteristics of the material.

For instance when we talk about a brittle material, it is essentially we are reducing that that is coming from a comparison of the pearl stress or the inner and lattice friction with the fracture stress of the material. Therefore, we assume that I have an understanding of the bonding characteristics and I also, have an understanding of the way the phases are distributed.
But there is 1 important thing still left out before I can claim that I understand this distribution of phases, which is the interface between the 2 materials. Suppose I am talking about loading such a material which has the distribution of phases it could so happen that there are no cracks forming in material b, there is no cracks forming in phase a, but the interfacial bonding is so bad.

That suppose let me, assume this part out that actually an interfacial crack forms in other words; there is an interfacial de-bonding, because of this loading. So, this de-bonded region has been shown in right and therefore, in spite of a micro structure which might I am which is very desirable like for instance d which might I made use for some purpose. If the interface is not good then the properties may not be up to my expectations. Therefore, I need to understand the distribution of phases and also the characteristics of the interfaces. If I want to understand the complete picture of how this micro structure or actually how to put it tightly the first step of understanding of how micro structures will lead to properties naturally.