Surface Engineering for Corrosion and Wear Resistance Application
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Lecture – 01
Structure of Solids

Hello dear students, let me get started this particular course is on Surface Engineering. But at the beginning, what I intend to do is to lay the foundation of the course which would mean that, we will dwell upon the fundamentals of engineering solids, its classification, structure, micro structural, evolution, various properties related to primarily to the surfaces of the solids. And then we will try and understand as to how this surface dependent properties can be tailored by various processes which are known as surface engineering.

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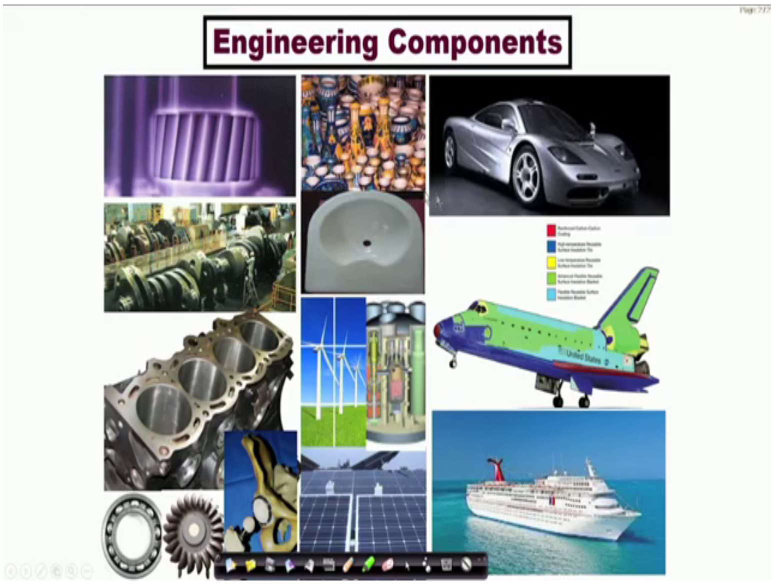

Engineering Components

To begin with let me tell you that this when you look at the slides the first very slide actually gives you a collage of various components; I mean, they are very not at all connected with each other we are talking about. For example, our gear component here, a camshaft an engineer an engine block a bearing assembly then these are all metallic components.

Here we are talking about ceramic components; these are colored ceramics glazed tiles then polymeric materials, semiconducting materials, solar harvesting panels the and at the last column I wanted to show you examples of complete engineering systems. For example, an automobile you never can say whether it is made by a single engineering discipline or a particular mechanical engineer or a design engineer or electrical engineer any way essentially need input from all branches of engineering to make a complete engineering systems. So, when you look at all these either individual components or a complete system, you realize that an engineering product which is standalone will certainly have components made from various origin and made through various processes.

So; obviously, when the manifest has a complete system they have both compatibility and non compatibility issues. Now when you are an engineer and trying to design a complete component or a system what kind of material are you dealing with or what material do you choose. So; obviously, the question comes what kind of materials do you have at your disposal.

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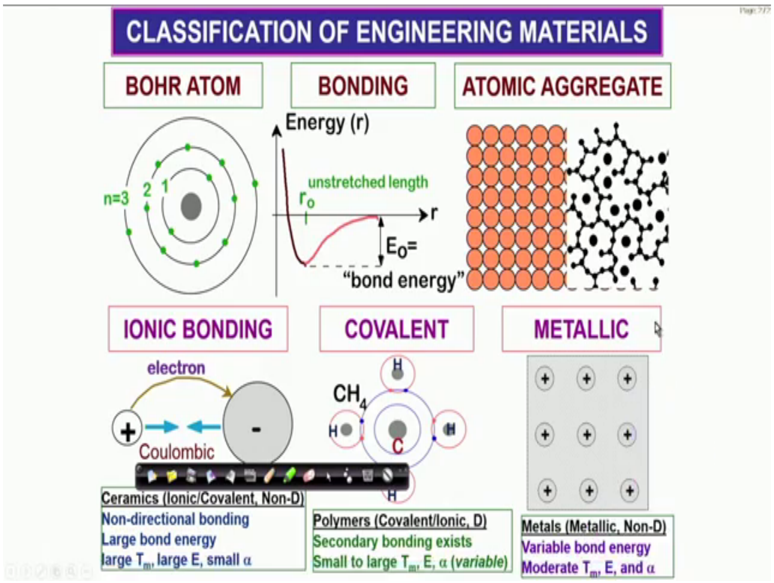
CLASSIFICATION OF ENGINEERING MATERIALS

BOHR ATOM

BONDING

ATOMIC AGGREGATE

IONIC BONDING

COVALENT

METALLIC

Ceramics (Ionic/Covalent, Non-D)
Non-directional bonding
Large bond energy
large T_m, large E, small α

Polymers (Covalent/Ionic, D)
Secondary bonding exists
Small to large T_m, E, α (*variable*)

Metals (Metallic, Non-D)
Variable bond energy
Moderate T_m, E, and α

If you think of solids of all possible types then these solids actually can be broadly classified uniquely in three major fundamental compartments and this is what I have said here as we all know basically and these are called the metallic materials, the polymeric materials or ceramic materials. But whereas, where is this classification coming from we are not going by certain traits which are we are going actually by certain traits which are absolutely unique.

See as materials engineer or for that matter engineers, we do not deal with single atom that is the domain of the physicists and chemists where they actually would like to go into subatomic particles and deeper inside at much smaller length scale. As engineers we do not deal with single atom, but we deal with aggregates, and when we talk of aggregates of atoms or molecules or ions, they actually can manifest themselves in two possible ways. One is this three dimensional periodic aggregate which we call crystalline, and other possibility is when they do not maintain three dimensional periodicity we call them non-crystalline or a amorphous and even a subset of that is for glassy materials.

Now, in all these cases particularly saying crystalline material we know atom to atom distance is fixed under a given thermodynamic condition. So, this fixed distance of equilibrium separation is because of forces of attraction and repulsion we all know and when this is repeated in all three possible dimensions and maintaining a certain periodicity, that is what gives rise to this crystalline aggregate and the lack of that gives rise to this a periodic or non-crystalline aggregate.

Now, whether it is crystalline or amorphous all these solids can have atom to atom bonding in three possible ways, one is when the electrons are transferred from one species to the next; so, the cation donates electron to that anion and in turn what we have is called ionic bonding. And these ionic bonding are characterized by non-directionality fairly large bond energy as a result of which you actually have large melting temperature, large elastic modulus and very small coefficient of thermal expansion.

In comparison you can also have situation where the neighbors decide to share their electrons and when they share in a particular way where the electron spends most of its time in the overlapping, orbit then we end up getting what is known as covalent bond bonding, and this covalent bonding leads to the classes of materials which we call polymeric materials.

So, here we are talking about directional bonding, fairly large to very small all the both are possible and because of which actually you are likely to see fairly small to fairly large, so a band of melting temperatures, variable coefficient of thermal expansion and also variable elastic modulus. And finally, when you discuss materials where you have a very unique situation which is like you have cations at periodic array and permitted by free electron cloud. In such a situation what you end up getting is known as metallic bonding and as a result of which you have a fairly variable bond energy, but moderately large melting temperature elastic modulus and coefficient of thermal expansion.

The most important thing is all the traits, all the material properties that we can think of they actually can be easily explained by the nature of the bonding that these primary or the pure classes of materials enjoy. In other words if we are dealing from the very beginning then as an engineer we should first know whether we are dealing with metallic covalent or ionic bonded materials, and as a result all the properties that are manifested in the bulk or even in the surfaces would be fairly easy to explain.

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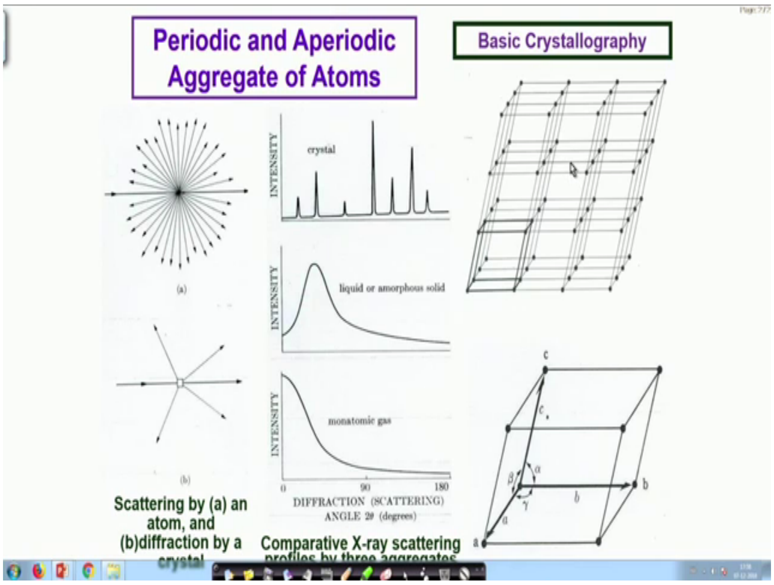

Periodic and Aperiodic Aggregate of Atoms

Basic Crystallography

Scattering by (a) an atom, and (b)diffraction by a crystal

Comparative X-ray scattering profiles by three aggregates

So, having said that now let us imagine that we are dealing with initially set of atoms or a aggregates of atoms, and when you scatter these atoms with some electromagnetic radiation where the wavelength would be of same. Periodicity, as the repeat distance of the atoms or ions or molecules, then you can have actually one of these three possibilities.

If you have a crystalline aggregate where I said that they are essentially characterized by three-dimensional periodicity you are likely to see a fingerprint like this whereas, where most of the ah; so, this is essentially intensity versus angle of a incidence. So, accordingly only at very specific angles of incidence you see very large peaks; which means that coherent the diffraction or a constructive interference is taking place only at this angles of incidence which is typically; which is typical of the metallic typical of the crystalline materials.

Now, instead of that if you do not have crystallinity along with periodicity, you are likely to see such broad hallow fairly broad without having centered on a very particular angle like in case of crystalline materials. So, these are amorphous materials and when the matter is in a gaseous state practically having very large distance of separation then you are likely to see a profile like this. So, in a situation wherein you actually are dealing with aggregates so, we now can imagine that, when we are dealing with crystalline aggregates which are likely to give you such diffraction patterns, you characterize them in terms of a repeat unit which is called unit cell.

So, now imagine that in three-dimension if you have array of points or essentially addresses where an atom or molecule or ion can sit. So, if you imagine these points are now distributed in space at some regular intervals both along x, y and z direction, then essentially what you have is a cage of these points and you call them essentially a point lattice.

The smallest building block of the point lattice is called the unit cell which is characterized by six possible parameters and we call them lattice parameters. So, unit cell is nothing but essentially the smallest building block which when repeated in three-dimensional then you give back you get back this three-dimensional point lattice.

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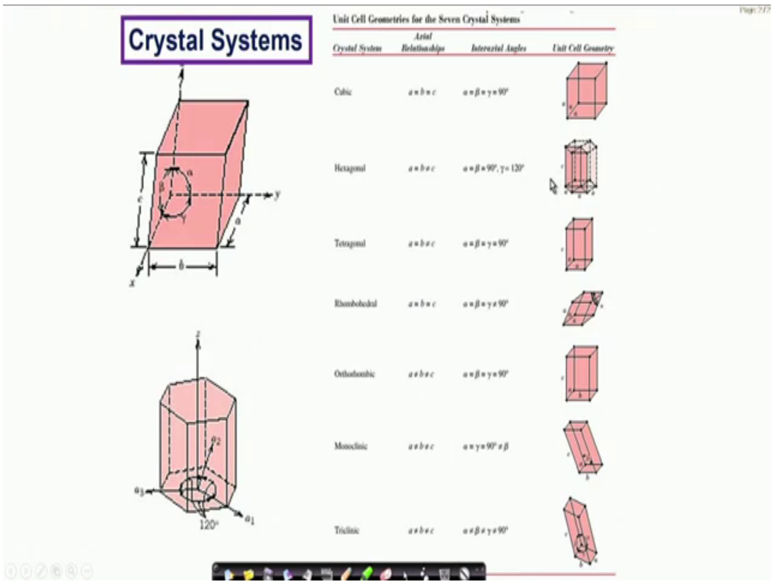

Crystal Systems

Unit Cell Geometries for the Seven Crystal Systems

Crystal System	Axial Relationships	Interaxial Angles	Unit Cell Geometry
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	

Now, when we go to ah; so, the as I was talking about these unit cell and I mentioned about six possible parameters now, if you can if you wish to vary them in all possible ways you will realize that there are only seven ways in which you can vary them. So, they the six parameters I should have mentioned actually are the six axial lengths and there is six axial angles.

So, if you vary the axial lengths and angles at random these are the seven ways you can vary them and these are all known to you that you actually can have these unit cells appearing as a cubic. So, the these are essentially also a solid block which essentially can manifest themselves as cubic or hexagonal or tetragonal rhombohedral, orthorhombic, monoclinic and triclinic and these names essentially refer to very specific combinations of these parameters the lattice parameters.

Again, this is something which comes straight from your class two physics so, we do not need to go into details of it, but what is important for us to know is that all crystalline materials will belong to one of these seven process possible crystal systems.

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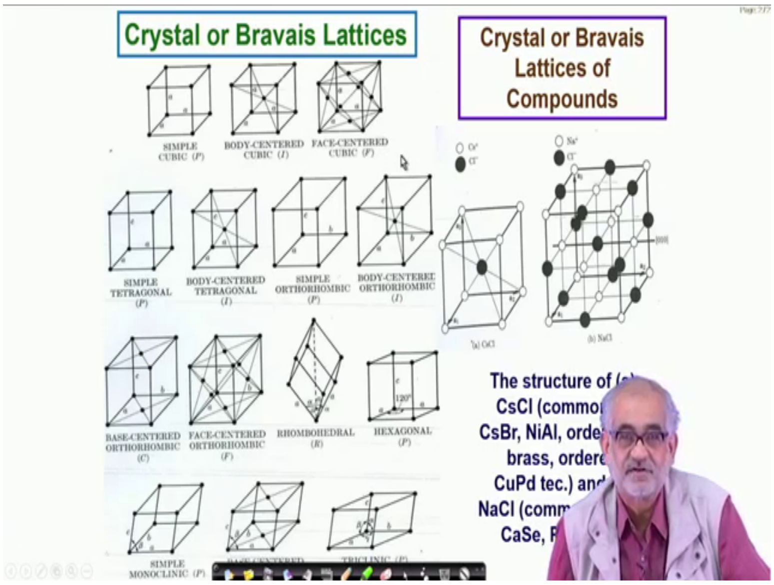
Crystal or Bravais Lattices

Crystal or Bravais Lattices of Compounds

The structure of (
CsCl (commo
CsBr, NiAl, orde
brass, ordere
CuPd tec.) an
NaCl (comm
CaSe, P

But, we must now clarify that when we talk of crystal systems, we are talking about atoms or molecules or ions which are allowed to sit only at the corners and not in that non primitive sites which could be the body center, based center or face centering positions, when you allow species to occupy these non-primitive sites then you actually add seven more possibilities. So, in the process now we have fourteen possibilities in which these individual atoms or ions can arrange themselves up and then manifest in three dimensional structures.

So, essentially now instead of crystal systems we are talking about crystal or Bravais lattices which are 14 in number and that number is unique. So, essentially it can be easily proven that any crystalline array must belong to one of these fourteen possibilities, but when you actually are; now, at until now we are talking about atoms or molecules of only one kind so, essentially we were talking about elemental crystals.

But moment you step into the realm of the compound crystals where you can have more than one species, you can have two or three or even more; obviously, their sizes will differ and as a result you end up you can end up getting a compound. So, in such a situation the situation the structural description becomes a little more complicated and you end up getting various kinds of a crystal structures.

So, the reason why I took time to explain these things which are which are possibly known to you already is because of the fact that we must be able to distinguish between the structural hierarchy starting from point lattices or space lattices to unit cell. Then lattice parameters of a unit cell variation of which give us these various crystal systems, the seven crystal systems and then from the crystal systems which are essentially primitive in nature having atoms only at the corners. When we go into crystal or Bravais lattices, then we are talking about atoms or ions or molecules possible to be located both at corners and non-corner sites or non-primitive sites.

So, altogether we have fourteen, but all these are imaginary structures and that is what is very important for us to note that until now; whatever, we have described are all imaginary in reality, we are dealing with atoms and for simplicity we considered them as hard spheres or simply marbles.

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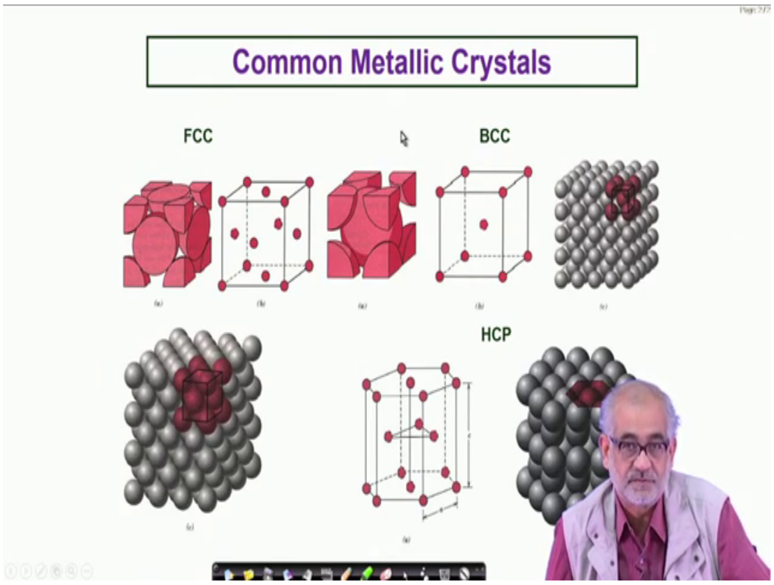
Common Metallic Crystals

So, when we are dealing with such real matter say for example, marbles then we are left with the fourteen possibilities. And out of these fourteen possibilities, if will be now place actually these atoms or molecules into those fourteen possible Bravais lattices, then we actually create infinite number of possibilities which we call crystal structures.

Now for metallic systems the situation is much simpler more than more than two-third of the metals, actually belong to one of these three possibilities the face centered cubic, the body centered cubic and hexagonal close packed. In fact, out of the out of the almost 75-80 percent of the metals that belong to one of; they actually belong to one of the two close packed structures the face centered cubic and hexagonal close packed, and out of the remaining majority are body centered cubic.

So, essentially as if you are metallurgist you are happy knowing only these three possibilities of unit cells or descriptions. But here is a little distinction that we need to understand, that when we talked about Bravais lattices 14. We did see hexagonal, but there was no mention of hexagonal close packed, and this is exactly what explains the difference between the Bravais lattices or crystal lattices and crystal structure.

So, hexagonal close packed is a crystal structure which is possible due to a particular way of packing or stacking of atoms, and which are not necessarily the hexagonal prism that we are seeing is not a unit cell. Actually, we have three unit cells which are juxtaposed with each other, as a result we see such a hexagonal prismatic structure, but the unit cell actually is one-third of this. Anyway, so let us not dwell more on this suffice to say that we should be able to distinguish between the point or space lattice the crystal system, the crystal lattices and then finally, the crystal structures.

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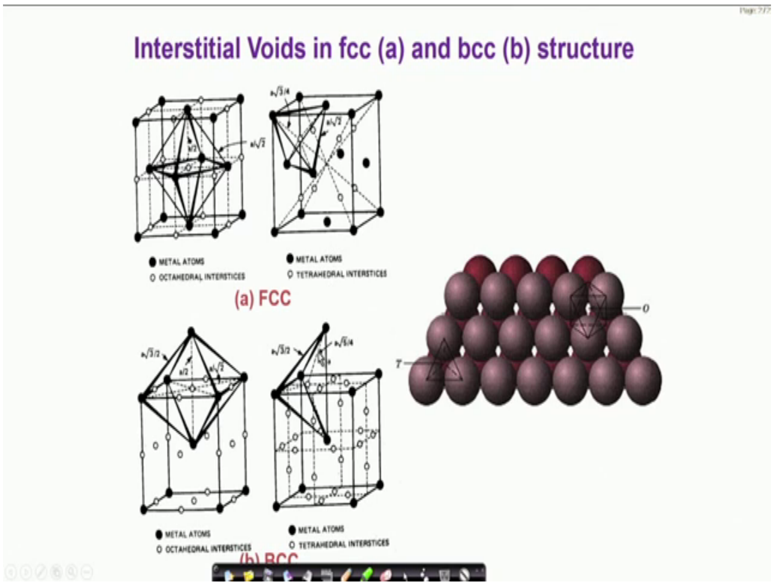

Interstitial Voids in fcc (a) and bcc (b) structure

While talking about crystal structures, when we have already understood that we are talking about specific location of atoms and for simplicity we assume that atoms are hard spheres. We all can know that, we cannot fill up a box; no matter what the size or shape is completely 100 percent with these solid spheres. So, there will be certain open spaces left, and that allows us to create the so, called concept of packing density and then we actually have packing density which is the packing density.

Actually can have very specific values depending on the structure or structural motive that we have ah; but, what is important for us is to realize that the open spaces will also have a very specific geometry just simply because the hard spheres have their own sizes. So, if the spheres are of same size then the packing density can take very unique values; for example, a maximum could be 74 percent or else it could be 68 percent if it is BCC and so on and so forth.

But, what about the open spaces; the open spaces are also very important and these open spaces are described in terms of the maximum possible shape circular spiracle shape. One can imagine and its diameter explains, what is the maximum size of species that you can fit into those inside this particular open spaces.

Now, so these are called voids or interstitial voids, and these interstitial voids have a particular location for example, depending on the symmetry or the coordination around these voids. For example, if this is this is nothing but an FCC unit cell, the body centering position is vacant so, here is an interstitial position and this particular interstitial position actually is going to have the maximum possible diameter.

So, when we try to describe certain properties of solids of crystalline solids so, we should actually try and develop, we should be able to describe what is the maximum size of such interstitial voids, or the diameter of such interstitial voids because that will allow or disallow whether a foreign atom is able to sneak into that particular open space or not.

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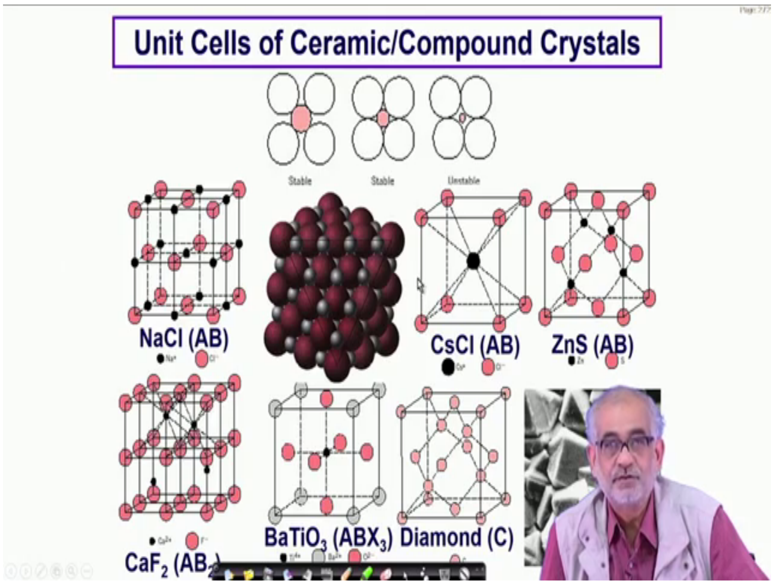

Unit Cells of Ceramic/Compound Crystals

I was talking about already the possibility where we can have a dissimilar species not just all elemental, but compound crystals. So, here is an example sodium chloride the obviously, this pink ones are the anions the chlorine and the smaller dots are the cations sodium. So, if you go into the details of this structure, one can easily explain that, this is nothing but an FCC unit cell. So, though it appears as if it is much bigger and which much larger number of ions unit, but it is structurally possible to explain that this is nothing but an FCC unit cells where per lattice site we have two ions or two species and an anion and cation.

We all are aware that for ionic crystals it is important also to maintain the charge neutrality, so in case of sodium chloride for every sodium there has to be another monovalent anion. So, this is how we actually can develop various compound crystals, ionic crystals, interstitial compounds or inter metallic compounds and so on which will have characteristics different than and somewhat in between metals and non-metals.

So, when you talk of structure of solids or properties of solids and we try to explain them in to and connect them with the structure. Then we should actually first understand that structures could be simplest in terms of elemental crystals, but fairly complex in case of compound crystals. And possibly, one of the most complex structural description, one can think of actually are available in the proteins particularly the DNA and RNA proteins that we all carry. But fortunately for engineers we do not necessarily deal with such very complex crystals all the time.

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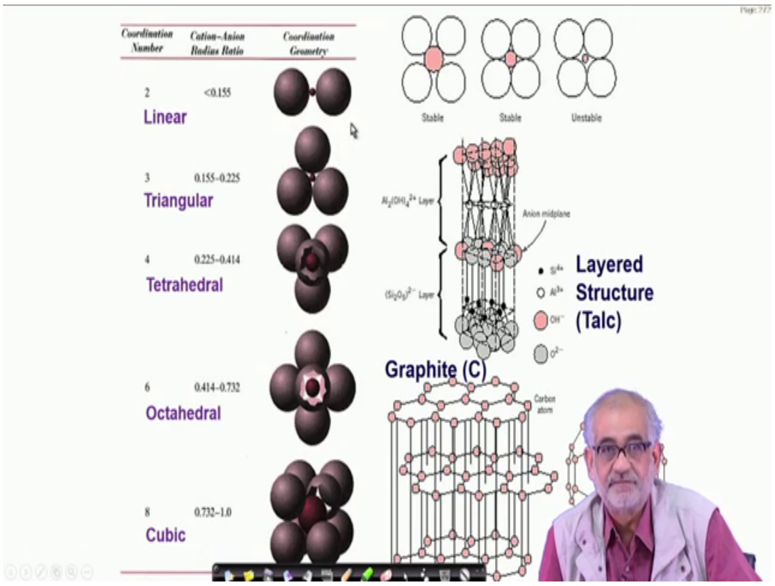

Coordination Number	Cation-Anion Radius Ratio	Coordination Geometry
2 Linear	<0.155	
3 Triangular	0.155–0.225	
4 Tetrahedral	0.225–0.414	
6 Octahedral	0.414–0.732	
8 Cubic	0.732–1.0	

Now, when we talk of the distinction between the imaginary and the real structures then we also have to realize that the way the atoms stack themselves or pack themselves in the form of a solid. That can start from the very simple linear description of stacking species one after another, to a situation where three bigger ones can actually leave a smaller hole inside whereas, smaller species can settle.

We can think of a situation where four similar sized spheres can accommodate a smaller species in the middle in their centroidal position and that is what will give a tetrahedral coordination to the smaller atom in between. Or we can have an octahedral where we have 6 neighbors, nearest neighbors or a cubic coordination where we can have 8 neighbors.

So, this essentially is another way of looking at the structures with going into three-dimensional periodicity, if you just are given dissimilar sized species how can you stack them. So, if the size; if the radii of the small and the big the cation and the anion if the ratio is less than 0.155 then we expect simply linear stacking, because they cannot make a three-dimensional array simply. Because of the fact that the sizes are so different that the smaller one will actually rattle within the holes of the bigger ones.

We can think of slightly bigger size of the cation or the smaller species and that becomes if the size is between 0.155 to 0.225, then this species can actually enjoy a triangular coordination, not in three-dimension. As yet these two are still in two-dimension, then we go into the three-dimensional array and it begins with that, so called tetrahedral coordination.

And with more and more complexity, you can bring in octahedral or even cubic coordination where the size differences or the quotient between the cation and anion the ratio if it is between 0.225 to 0.414 you are likely to see tetrahedral, if it is 0.414 to 0.732 it is going to see give you octahedral coordination, and anything between 0.732 to up to 1 you are likely to see cubic.

And the most efficient packing which I already mentioned are manifested in the form of phase centered cubic and hexagonal close packed they are possible only when you have the similar sizes. So, this is going to be possible only for elemental crystals of only one single size of species and the maximum possible are the size difference as there is basically they are of the same size. So, the ratio is 1 and in only in that situation we can have the largest packing density.

You may; so, this is when you have complete crystallinity, but you may also have semi-crystallinity for example, you can have layered structures which we see in the natural crystal called talc, where we have these kind of layers and in between layers we have weaker bonds and also dissimilar species. So, as a result these kind of structures even including graphite actually are very good lubricants. So, you see complete crystallinity in plane, but across the plane the crystallinity is not continued.

We must realize that for all these descriptions, we essentially are trying to understand what kind of a structure essentially will be very stable and which is useful for developing crystals and developing solids even with non-crystals which are useful to mankind.

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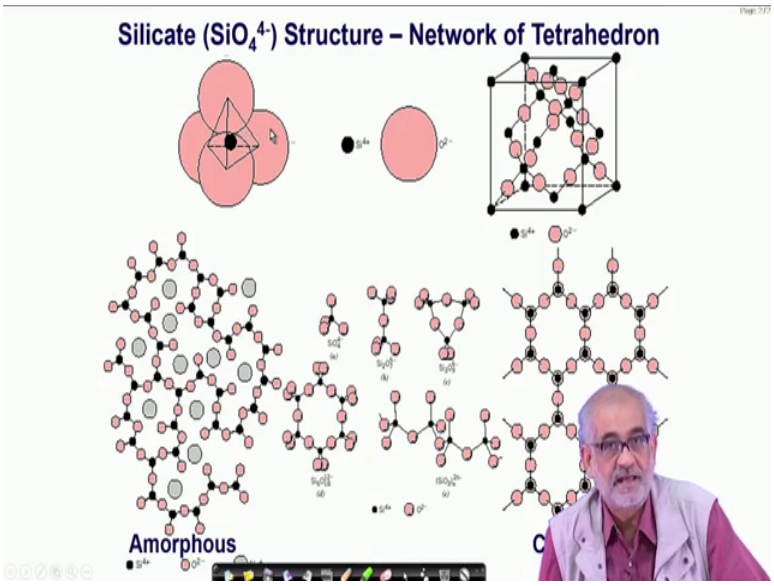

Silicate (SiO_4^{4-}) Structure – Network of Tetrahedron

Now, we are moving into non-crystallinity; say for example, you imagine that now we have a silica tetrahedra simply a tetrahedron where I have a smaller species in the middle and four bigger around. If this is a single unit, I can actually pack this unit in two possible ways. I can pack them such a way that the center this dark one coincides with one of these dark spots shown here in this particular cubic lattice cubic unit cell. Such that the other ones automatically follow a certain trend and in the process, the whole structure will manifest itself as a crystalline aggregate and this is how quads are very wasteful crystal. Actually shows its structure or essentially is arranged in the solid form.

But the same unit if it is not maintaining a certain trends or certain traits of reputation then it may end up giving you a situation which is non-cubic non-crystalline and then; that means, that this solid instead of crystalline now can manifest as amorphous. So, here is some interesting development, that the same solid, the same chemistry, the same bonding can manifest both as crystalline and non-crystalline.

So, when we talk of structure of solids and when we talk of properties of solids we have to be aware of not only the structure, but also various possibilities of structural manifestation and this is dictated by the thermodynamic terms to be more precise something called the Gibbs energy which essentially is derived from the intrinsic property of specific heat showing up in the form of enthalpy and entropy and contributions of relative contributions of enthalpy and entropy actually decides, what is the relative Gibbs energy of a particular phase in a given system.

And depending on the Gibbs energy relative Gibbs energy and to be more precise the chemical potential, one actually decides whether a particular phase is going to be stable or not and structure does play a role in determining such stability.

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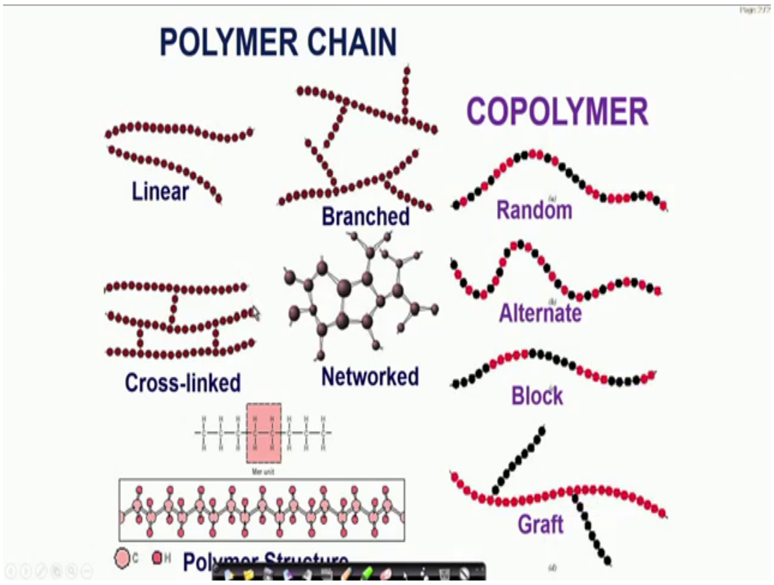

POLYMER CHAIN

COPOLYMER

Talking; we were so long talking about all mostly materials of inorganic origin, when you move into the covalent bond solids which are of covalent range which enjoy covalent bonding, there we can have these possibilities where these species to species bonding is primary which is covalent in nature. And, but the species that we are talking about here is no longer a single atom or a single molecule or a single ion, we are talking about a combination or somewhat like a radical which is called mar.

Now, these mars when they join with each other in a long chain they develop what is known as polymer and these polymers can actually be manifested in purer a form as linear polymers or branch polymers, cross linked polymer or network polymer. What we need to immediately understand is that, the along the length of the chain we have only one bonding and that is exactly of the same magnitude covalent or whose nature is covalent bonding where the electrons are shared between the nearest neighbors.

Now, just like we can add sugar to water and make a syrup or in solids we can add one type of atom into another lattice and create an alloy. In case of polymers also we can add different types of monomers and make a random co-polymer, alternate copolymer or a block copolymer and in some rare cases even graft copolymers.

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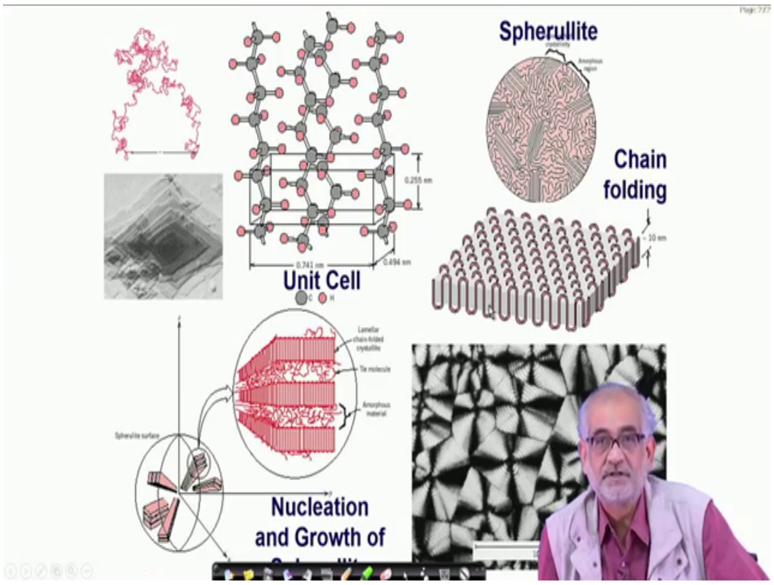

So, these are various structural manifestations, it is not very easy to imagine how these chains can actually go back and forth folding motion, and in the process can create such a structure which will have some semblance of repetition or periodicity. So, this is not again I must repeat it is not going to be very easy within a minute for us to appreciate, but it is important for us to know that polymers can develop crystallinity under certain thermodynamic conditions up to about let us say 70-80, even some rare cases over 90 percent.

But polymeric crystals are rarely 100 percent crystalline compared to the inorganic counterparts. But this crystallinity essentially is because of these kind of layers that are formed and these layers essentially; so, if we imagine that this is a long chain. And if we allow this chain to go back and forth motion chain folding motion then point to point there could be certain reputation of the species. And if you look from outside, you may see that certain types of atoms or molecules are being repeated at some regular distance in a given direction. And if this directionality continues in one-dimension and two-dimension and eventually even three-dimension then we end up getting such a crystallite are grown out of polymeric material.

So, the point I am only I am trying to say is that while metals could be 99 or more percent crystal with very little amount of crystalline defects, while certain types of ceramic materials. Particularly, the semiconductors or compounds semi compound ceramics can also manifest similar 99 percent crystallinity or certainly more than 90 more than 90 percent crystallinity.

Though of course, certain classes of ceramics like glasses can be non-crystalline, polymeric materials by and large are non-crystalline with little amount of crystallinity developed because of certain temperature pressure conditions and synthetically. One can convert polymers into predominantly crystalline aggregate a large part of it actually is happening. Because of such chain folding mechanism and the polymer crystallites like in case of metal ceramics, we call crystallites or grains the equivalent of that in polymeric material is called spherullite because they actually form such sphere like structure and a section of that sphere essentially will manifest as such spherullites.

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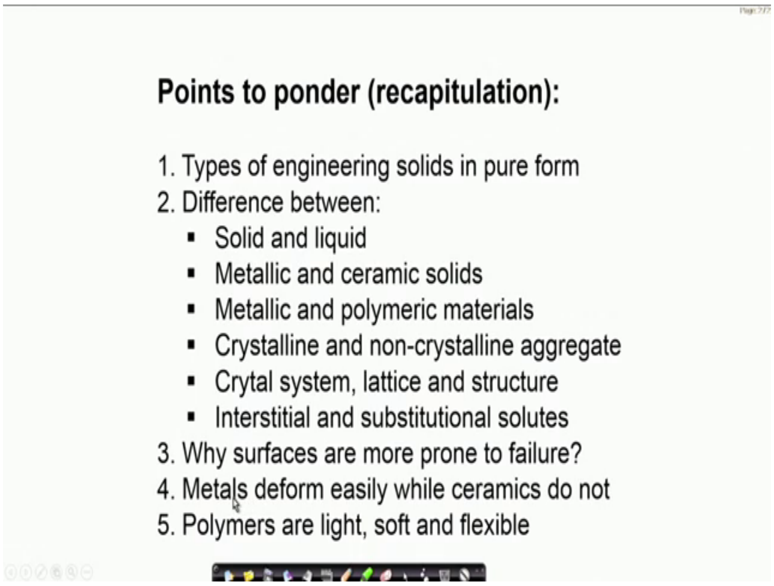

Points to ponder (recapitulation):

1. Types of engineering solids in pure form
2. Difference between:
    - Solid and liquid
    - Metallic and ceramic solids
    - Metallic and polymeric materials
    - Crystalline and non-crystalline aggregate
    - Crytal system, lattice and structure
    - Interstitial and substitutional solutes
3. Why surfaces are more prone to failure?
4. Metals deform easily while ceramics do not
5. Polymers are light, soft and flexible

So, what all we have done so far let us make a small summary. So, we try to understand that solids can manifest themselves in two forms crystalline and non-crystalline. We when most of the engineering materials which are useful to mankind they are essentially available in the solid form, but then we must realize what is the difference between the solid and liquid in terms of the shape and the rigidity. And though they have the same volume, but obviously, solids have a fixed shape where the liquids do not have and that is purely because of the strength of the bonds they enjoy within the species.

We try to understand the differences between metallic and ceramic solid similarly metallic and polymeric or polymeric and ceramic, and we realized that instead of going by certain traits or characteristics. The most important and the unique way of distinguishing various kinds of primary or pure solids would be on the basis of their bonding they actually enjoy, and it is because of this reason we can divide all possible pure solids in pre forms metal ceramics and polymers.

We should be now able to understand the differences between the crystalline which enjoy three-dimensional periodicity and non-crystalline aggregates which lack in such three-dimensional periodicity. We discuss about nuances of point lattices, then unit cell, lattice parameters, crystal lattices or Bravais lattices fourteen of them and then infinite number of crystal structures that eventually can arise out of these. But we must not forget that no matter how complex a crystal structure is if it is crystalline then it must be related to one of those fourteen Bravais lattices.

We talked about the open spaces available in solid crystals, though from outside we tend to believe that they are impervious and a 100 percent occupied, but because they are made up of these three-dimensional, made up of these spherical objects or atoms assumed to be hard spheres. We also have open spaces left in the lattice and they are called the interstitial voids.

And we understood that the largest diameter of the interstitial voids can be calculated because the crystal is completely periodic and we discussed a little bit about way they are stacked the way they are coordinated. And through which we actually can understand the evolution of various forms of solids.

The bonding characteristics will also allow you to understand why metals deform easily, but the ceramics do not, it will also allow you to understand why polymers are usually light soft and fairly flexible compared to the rigid metals and ceramics solids.

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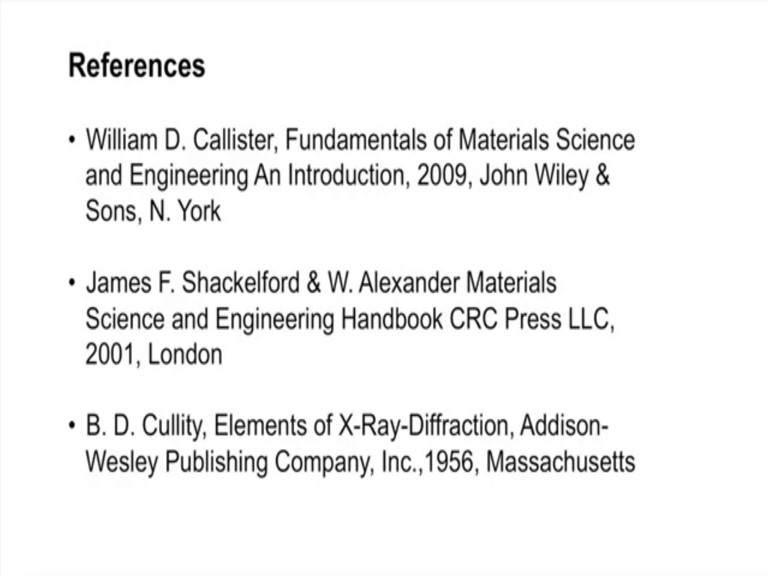

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So, with this we end the first lecture of this series on surface engineering and I must again clarify that there was hardly any mention to surfaces, because we are only talking about pure solids and structure of solids.

Thank you very much.