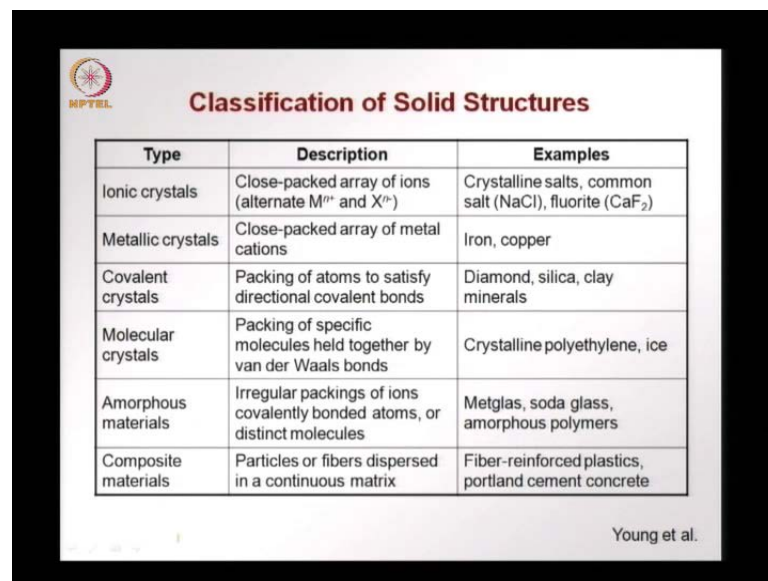


Modern Construction Materials
Prof. Dr. Ravindra Gettu
Department of Civil Engineering
Indian Institute of Technology, Madras

Module - 2
Lecture - 3
Structure of solids - I

Welcome to the third lecture on Modern Construction Materials. We looked at atomic bonding in the previous lecture; we looked at how chemical bonds are formed and these chemical bonds lead certain structures in materials that we are going to discuss later. Today we are going to look at structure of solids; as you know, they are different phases of matter solids liquid and gases. We are going to look now at the crystalline structure of certain materials. Later on look at defects that occur in these crystalline structure, and we will also look at materials which are not crystalline that is they are glassy are amorous.

(Refer Slide Time: 00:57)



Type	Description	Examples
Ionic crystals	Close-packed array of ions (alternate M^{n+} and X^{n-})	Crystalline salts, common salt (NaCl), fluorite (CaF_2)
Metallic crystals	Close-packed array of metal cations	Iron, copper
Covalent crystals	Packing of atoms to satisfy directional covalent bonds	Diamond, silica, clay minerals
Molecular crystals	Packing of specific molecules held together by van der Waals bonds	Crystalline polyethylene, ice
Amorphous materials	Irregular packings of ions covalently bonded atoms, or distinct molecules	Metglas, soda glass, amorphous polymers
Composite materials	Particles or fibers dispersed in a continuous matrix	Fiber-reinforced plastics, portland cement concrete

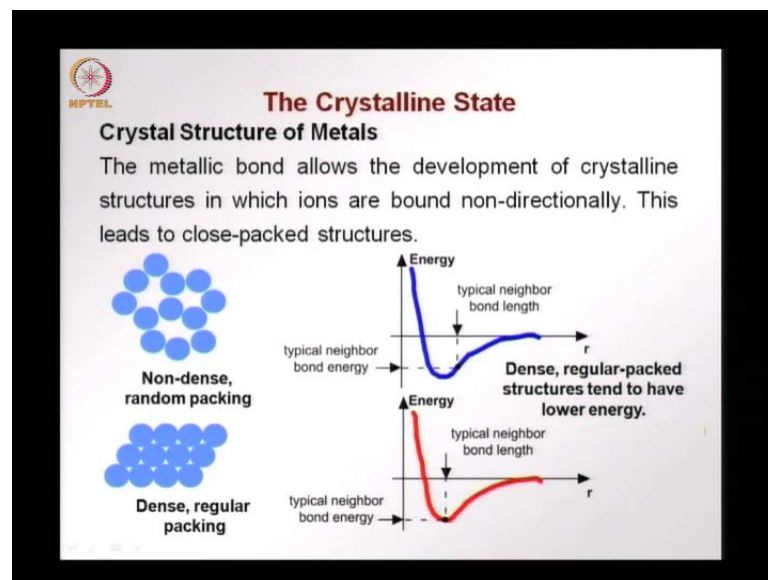
Young et al.

When we look at the different types of solid structures, we have ionic crystals materials, which form through ionic bonds, where we have arise of ions of different chargers positive and negative charged ions, and these form ionic crystals such as those that we find than salts like common salt fluorite and so on. In metallic crystals, we have metal cations that are closely packed, and this is what we see in metals including iron, copper

and so on. In covalent materials also, we can have crystalline structures, where we have chains sheets are three dimensional networks, where there is packing of atoms and this gives a crystalline structure, the examples are silica diamond clay minerals and so on.

We can also have molecular crystal, where we have molecule held together by Van der Waals by hydrogen bonds they are packed together in specific configuration, and this we find in plastic such is polyethylene and other material such as ice. One thing that is common in all crystalline material is that there is an ordered structures, there is an arrangement that is repetitive, and there is a dense packing. There are other material which are not crystalline, and they are generally called amorphous materials, there you do not see a regular packing, but there is an irregular arrangement of ions, atoms or molecules, examples are glass, polymers that are amorphous. And also some other materials which are generally crystalline could be transformed to amorphous materials such is metglas here. The last class of solid structures or composite materials, where we have different phases mixed together like one setup particles of fibers dispersed in a continuous matrix like we have in fiber reinforced plastics or we have aggregates are particles disposed in a cementation matter like we have in portland cement concrete.

(Refer Slide Time: 03:35)

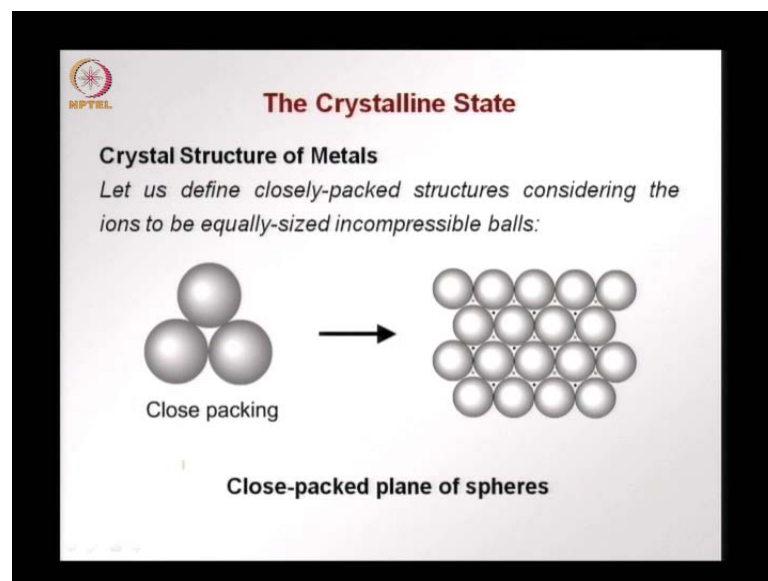


We will start with the crystalline structure of metals. The metallic bond as we saw in the previous lecture allows the development of ordered structures, crystalline structures which are cations - positively charged ions that are bound in a non-directional manner;

that means that they are formed symmetrically and they grow in all direction, and this can lead to close packed structures. So, here we have a structure that is not so closed packed, see you see here that there is an not a dense arrangement, it seems to the a random packing, and if you go back to the Condon-Morse diagram that we looked at in the previous lecture. We find that here, we would not be at the bottom most points of this curve which signifies the minimum energy, but the separation now between the particles is more.

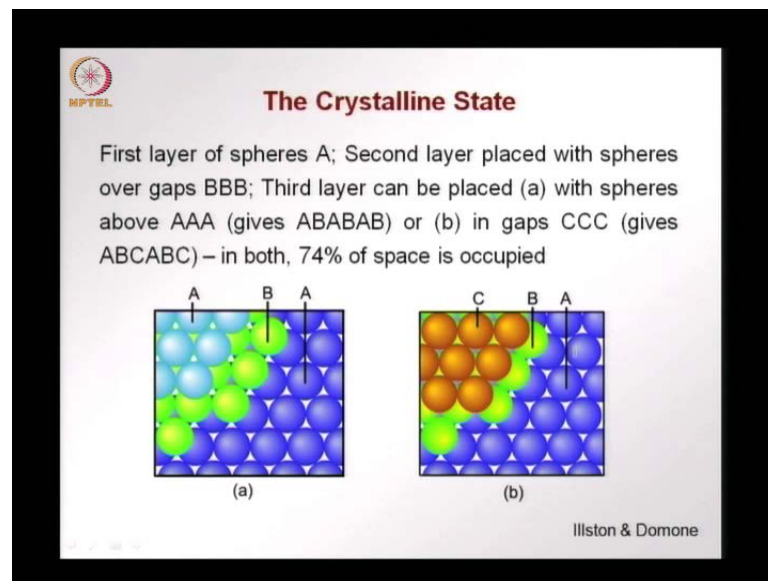
So, we find that the inter particle separation is not r_0 corresponding to the minimum energy, but little bit higher. A material will always try to reach the minimum state for stability, this always happen in all materials. When we look at the structure, the structure will try to get the minimum energy level possible that makes it more stable. So, if we compare this case to another case, where there is a dense regular packing; you see that the particles are closer to each other. And when we go back to the Condon-Morse diagram here that we have in red, we find that he will have a lower energy because the particle packing in such that the inter particle spacing is lower and you reach the most stable state or the minimum energy level. So, this is the reason why, we have dense structures, because we have regular packing that is leads lower energy, because each particle is surrounded by several neighbors and the packing becomes regular and dense.

(Refer Slide Time: 06:01)



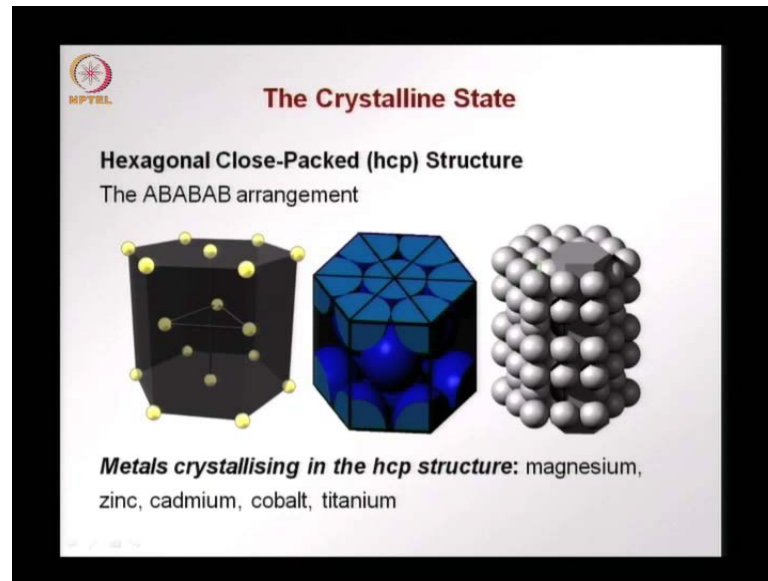
Now let us see how the packing can achieve such a structure. Suppose we take ions and we represent them by spheres, and we try to see how they can closely packed like we see in this diagram. We for simplicity, we are considered things all the ions to the equal sized and incompressible balls, and we can now put the layer or a plane of spheres like this. So, this would be what happens in one plane to have achieved a very compact structure which will give the least energy possible.

(Refer Slide Time: 06:42)



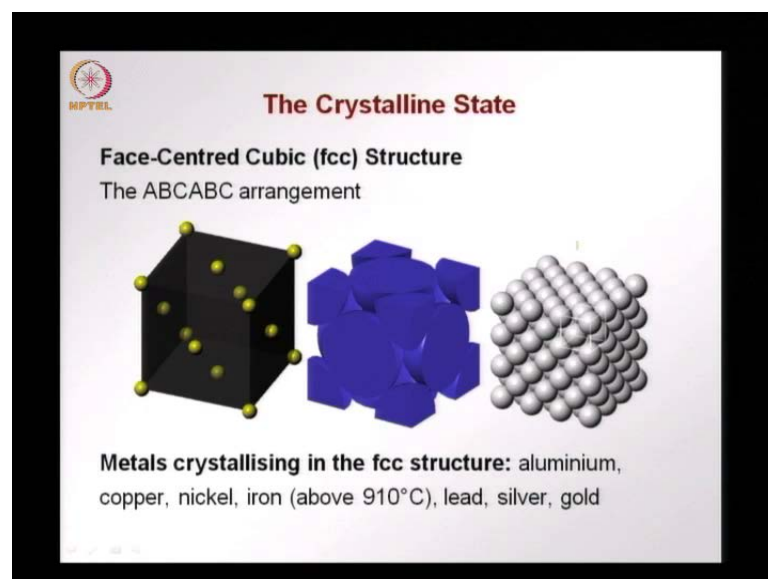
Now we have to have other layers. So, we can have couple of cases, let's say in the first one we have what we looked at in the previous slide, this spheres aligned together in one layer that is the layer-a. We can have the next set of balls placed over the gaps in the layer-a that is the layer-b; after that we can have two choices, one could be putting the next layer on top of position of balls in layer-a, so that is what is called a structure ABABAB. So, this is the repetitive A and B structure. Or you can have this case, where we put this spheres over the gaps on b, so that gives the spheres located in CCC giving a structure what is called ABCABC. So, these are two possible structure, where you can have dense packing, both these cases 74 percent of space is occupied. So, this is one way to get dense packing.

(Refer Slide Time: 07:57)



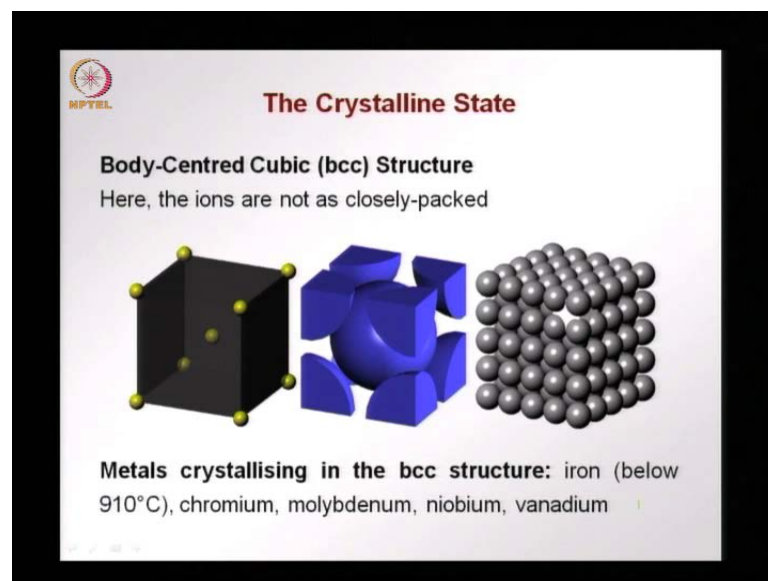
And this we see in many materials. The ABABAAB arrangement is called the hexagonal close packed structure or the hcp structure, we see this in metals such as in magnesium and zinc, cadmium, cobalt, titanium. You see the structure here, this is called hexagonal close packed structure - the h c p structure, where we have an arrangement in hexagonal nature and each particle is surrounded in its plane by six other particles or cations in the case of metals.

(Refer Slide Time: 08:39)



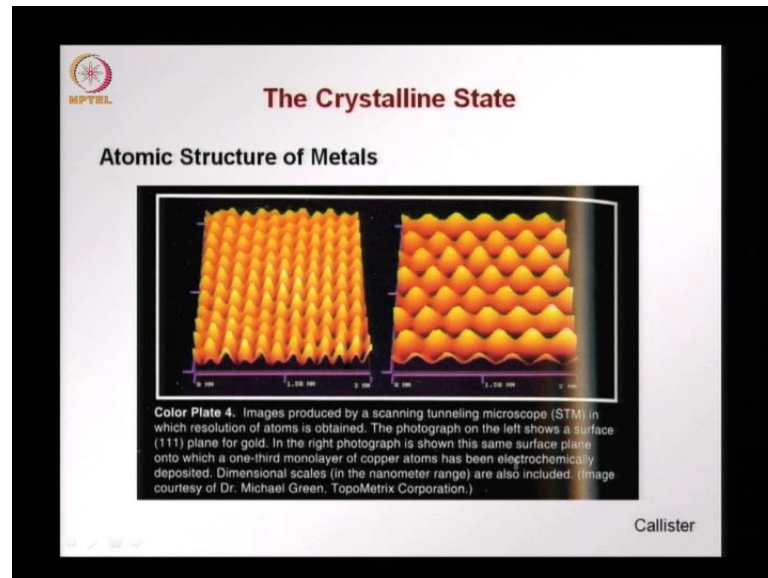
The other arrangement the ABCABC arrangement leads to what is called the face centred cubic structure, where we have any atom or particles surrounded by these particles on its plane and tops also. And if you see here you see a cubic formed here by the different particles, so this is called face centred cubic structure, and the metals that crystalline in the fcc structure include aluminum, copper, nickel, led, silver, and gold; iron exists in this structure above 910 degree centigrade. It goes through a phase change that 910 degree centigrade; above this temperature iron exist in the face centred cubic structure.

(Refer Slide Time: 09:39)



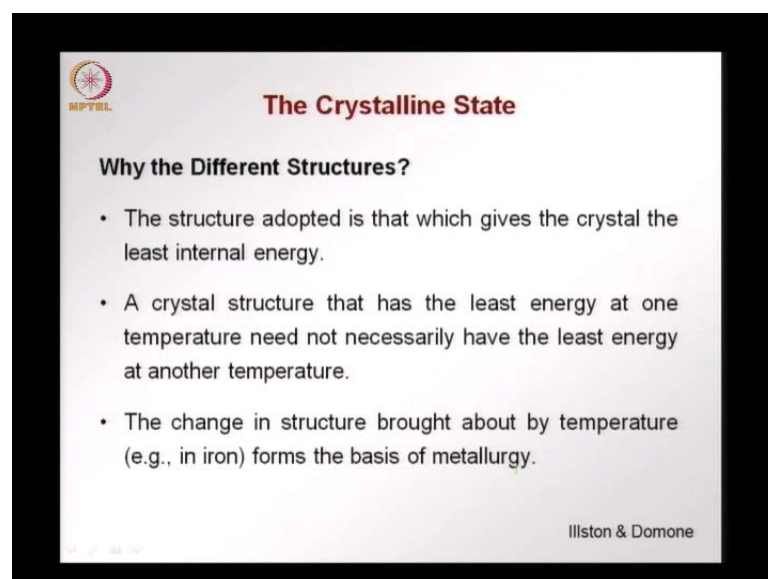
You can also have sometimes structure that and not as closely packed. We saw that in previous two cases 74 percent of the space was occupied when we consider spheres put together in the two structures what we discussed. We can have something called a body centred cubic structure, where we have each sphere touching eight other spheres below and above. So, these are the parts of the eight spheres that are touching it, this is called a body centred cubic structure, where we have a particle in the middle, and then you have cubic structure around it. Here the particles for the ion are not as closely packed as the previous two cases we saw. Metals that crystallizing in the bcc structure include chromium, molybdenum, niobium, vanadium, iron below the 910 degrees, as I told you before iron goes through a phase changed at 910 degree Celsius, below that iron also has bcc structure.

(Refer Slide Time: 10:53)



Now this is not just a model, but in reality, we have a evidence that the structure of the metals is of this nature. These are couple of pictures taken from the book of Callister, where we see images of atom produced by scanning tunneling microscope. Where we have on the left hand side a plane of gold, what you see there as bums or gold cations on the right-hand side again we see a layer of copper atoms, and again these satirical bums that you see are atoms of copper in the nanometers scale. So, this actually is the structure of metals and that has been visualized in the previous slide in the form of spheres to make the point about the crystalline nature.

(Refer Slide Time: 11:50)



Why do we have different structures, we already looked at different types of arrangement in crystals. Why do we have the difference structures? Well, the structure adapted is that which gives the crystal the least internal energy. If you remember the discussion on the Condon-Morse diagram we said that always this structure will be such that the lowest energy is achieved, and for that there is a certain inter particle distance or intermolecular distance. And the structure will be that which gives the crystal the least and internal energy for the condition that the crystal is in.

Now a crystal structure that has the least energy at one temperature, need not necessarily have the least energy at another temperature, we already saw the example of iron which changes its structure at 910 degrees centigrade having an structure above and one structure below the temperature. So, a crystal structure for one temperature need not give the least energy for any other temperature, and this changes structure for example, what we saw in the iron formed the basis of the metallurgy which deals with the transformation of the structure and forms of materials.

(Refer Slide Time: 13:15)

The Crystalline State

Ionic Solids: Ions of the same charge

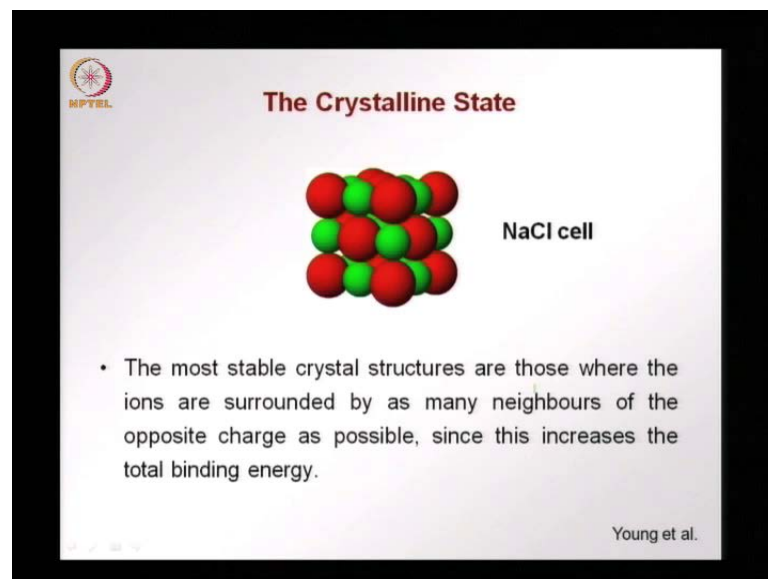
- Ionic crystal structures are packed arrays of anions with cations located in the holes of the array.
- The geometries depend on the radius ratio,
 $R = r_{\text{cation}} / r_{\text{anion}}$

$r_{\text{cation}}/r_{\text{anion}} > \text{ideal}$ $r_{\text{cation}}/r_{\text{anion}} = \text{ideal}$ $r_{\text{cation}}/r_{\text{anion}} < \text{ideal}$
 Stable Stable Unstable

Ionic solids also have crystalline arrangement. In ionic solid, what we have ions of same charge packed in layers. So, you have in ionic crystal structures arrays of anions add with cations in the holes of the array. So, the arrays are made of anions and the cations fit into the whole between the anions. The geometry then which result depends on the ratio of the radii of the cations and anions that is this ratio between the radius of the cations and

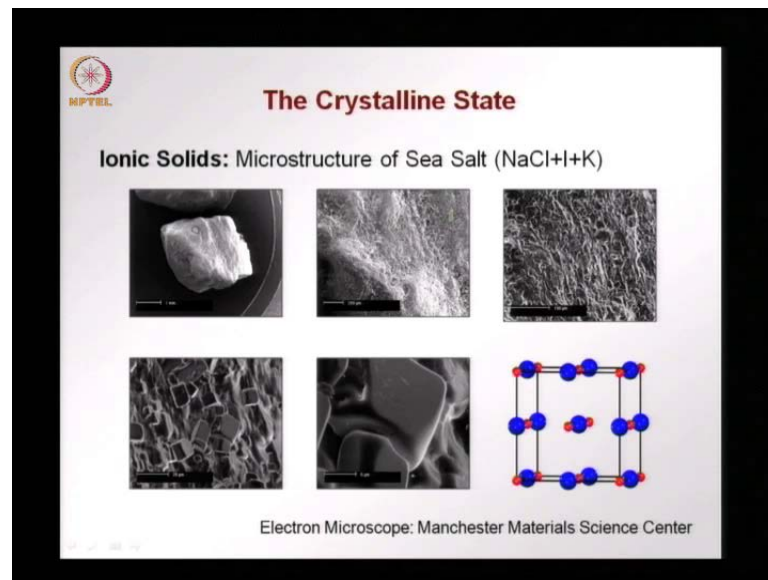
the radius of the anions. The best case or the most stable cases this, where you have the cations fitting exactly in the hole between the anions. So, all the particles are touching each other, so it gives a close packing and a stable structure with the least energy. This is also stable, because there is not much possibility of movement, but this is above ideal, the ratio is above ideal. This is an unstable situation, where you have cation, which is much smaller than the space between anions and this give rise to an unstable structure and this will not last for a long time.

(Refer Slide Time: 14:51)



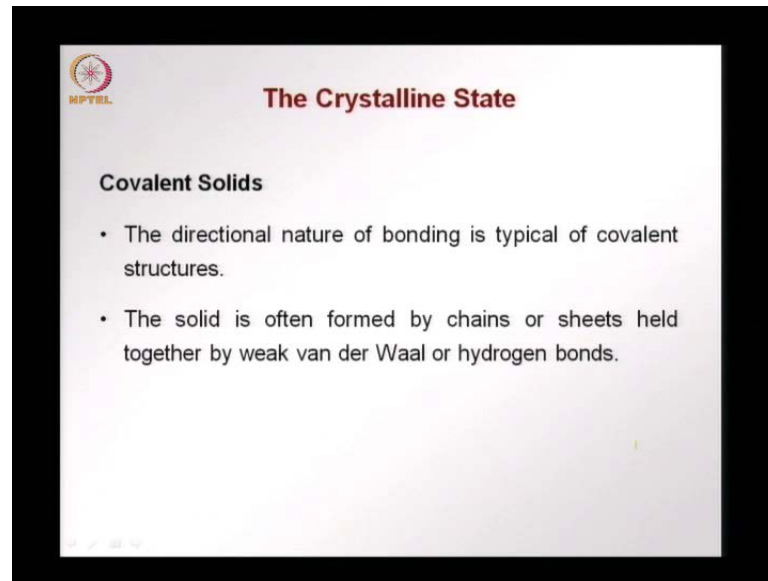
So, when we continue to look at ionic materials and example is sodium chloride - common salt, where we have the sodium and the chloride ions distributed in an orderly structure. And the most stable structures are those whereas as I said before the ions are surrounded by as many neighbors as possible of the opposite charge as this increase the binding energy, this increase the attractive energy that keeps the solid together. It increases the total binding energy and it decreases the potential energy to a minimum that is when the material is most stable.

(Refer Slide Time: 15:36)



Now again there is evidence of this that we can get from microscope, these are different energy is taken from the site of Manchester Material Science Centre. And here you see grain of sea salt at different scales; this on left top you see a grain of sea salt. And next to you it is an image that is closer the bar that you see here is about few hundred microns. This is a closer image, again you see you start seeing some of the grainy texture on the surface. When you go down this is now a scale of 20 microns, and you see near crystal cubic crystal of salt like what we saw before in the schematic diagrams, you see here the crystals offshore and this is now one crystal in the size of about 5 to 10 microns. So, you see here how the crystal of the sea salt it formed and this is similar to what we idealized in the diagrams before. So, there is quite a lot of evidence from micro scope how these structure exist in the micro scale and now from what we have learned in atomic bonding we can understand how this how the structure how the structure forms and how it can lead to crystalline or orderly structures.

(Refer Slide Time: 17:14)



The slide features a logo in the top left corner with the text 'MPTEL' below it. The main title 'The Crystalline State' is centered at the top in a dark red font. Below the title, the sub-section 'Covalent Solids' is written in bold black text. Two bullet points follow, describing the directional nature of covalent bonding and the formation of chains or sheets held together by weak van der Waals or hydrogen bonds.


The Crystalline State


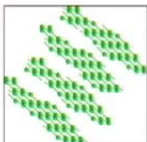
Covalent Solids

- The directional nature of bonding is typical of covalent structures.
- The solid is often formed by chains or sheets held together by weak van der Waals or hydrogen bonds.

We go on next to the third type of bond that we studied in the previous lecture covalent bond and covalent solids. We also know that covalent bonds are directional bonds as opposed to we saw in ionic and metallic bonding, covalent bonds are directional. And this is very typical of covalent structure. We saw in the previous lecture that covalent structure have seems are sheets to within the chains and sheets you have covalent bond and across them or between the chains and sheet you have weak Van der Waals or hydrogen bonds. So, within the chains, you have covalent bonds and between the chains and between the sheets, you have weak Van der Waals or hydrogen bonds holding them together. Only when there is an orderly structure of the chains and sheets we have a crystalline covalent solid.

(Refer Slide Time: 18:15)

 **The Crystalline State**

- Graphite is composed of covalently bonded sheets held together by van der Waal forces.
- The weak intersheet bonding leads to the softness of graphite (compared to diamond); graphite is an excellent dry lubricant.
- Graphite is a good conductor of electricity in two-dimensions.

Graphite is an example of where we have covalently bonded sheets. This is the piece of graphite and within a, we see that the carbon atoms are all aligned sheets in an orderly manner. These sheets now are held together by weak Van der Waals forces. These type of structure gives graphite a lot of interest in properties, one is the softness coming from the weak inter sheet bonding the sheet slip one over the other, and these make graphite an excellent dry lubricant because the weak Van der Waals forces can be overcome. The Van der Waals bond can be broken easily and start slipping one over the other. Now you can have carbon with covalent bonds forming a very hard structure also the example is diamond.

They you have a network of covalent a bonded atoms giving a hard strong structure opposed to the same element carbon in graphite, which gave a soft natured because the weight is form. So, reach up graphite is formed in this layers carbon within the layer you have covalent bonds and across from between one sheet and other we have because of this we have good electrical conductivity along the sheets and graphite is the good conductor electricity in two-dimensional that is along the sheets not across, but along the sheets.

(Refer Slide Time: 20:10)

Silica and Silicates

- The silicate tetrahedron is the basic repeating structure of silica and the silicates. The tetravalent silicon ion is surrounded by 4 oxygen anions, resulting in $(\text{SiO}_4)^{-4}$.
- The negative charge is neutralized when the oxygen anions are shared with other silicate tetrahedra or other cations.

The Silica Tetrahedron

Silicate chains

Legend: Oxygen (purple), Silicon (yellow)

The slide contains two diagrams. The first, titled 'The Silica Tetrahedron', shows a central yellow sphere (silicon) bonded to four purple spheres (oxygen) in a tetrahedral arrangement. A legend below indicates that purple represents Oxygen and yellow represents Silicon. The second diagram, titled 'Silicate chains', shows a series of these tetrahedra connected by sharing oxygen atoms, forming a chain structure.

Another set of material that are covalent solids are based on silicon silicates. The silicate tetrahedron that we saw in the previous lecture is a basic repeating structure in silica, and silicates the silicon ion is surrounded by four oxygen ions resulting in SiO_4 with a charge imbalance of minus four this charge is neutralized when the oxygen anions are shared with others silicate tetrahedral to form chains and sheets. So, this is the silica tetrahedron with one atom silicon in the middle surrounded by four atoms of oxygen and this can now link to form silicate chains.

(Refer Slide Time: 21:07)

Silica and Silicates

single chain

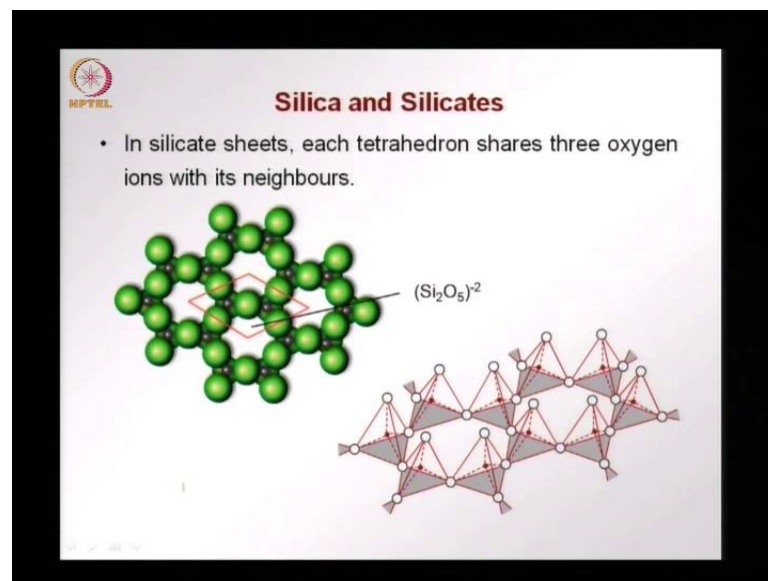
double chain

Certain double chain silicate structures form long thin crystals that can be bent and made into fabric, such as asbestos.

The slide contains two diagrams. The first, titled 'single chain', shows a series of yellow spheres (silicon) and purple spheres (oxygen) connected in a single chain. The second diagram, titled 'double chain', shows two parallel chains of these spheres connected to each other. Below the diagrams is a text box stating: 'Certain double chain silicate structures form long thin crystals that can be bent and made into fabric, such as asbestos.'

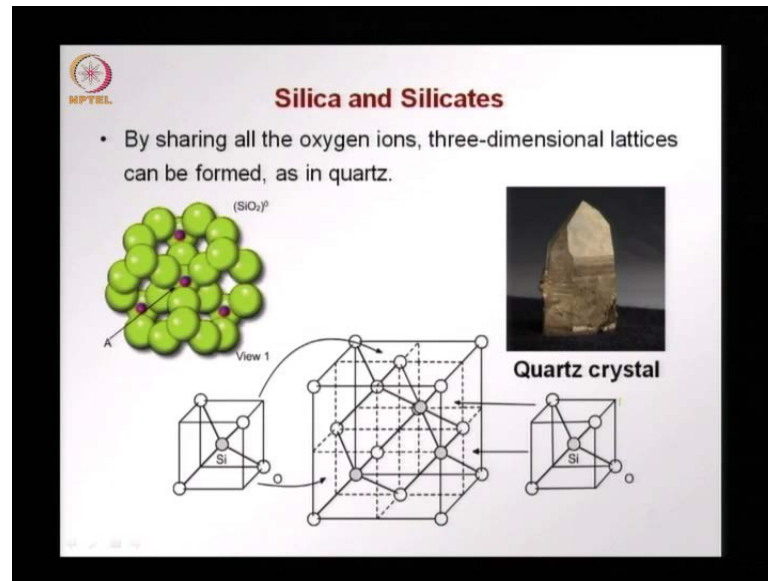
You have two types of chain that can form you have single chain or we can have double chain structure in either case what we find is long thin crystal are formed and this can be bent and the made into the fabric are a fabricate structure one example is asbestos asbestos as you know as been used for a long time in installation for reinforcing cement composition and. So, on how it is not much use because it is harmful to the health at one period time asbestos was very popular reinforcing material And insulating material that was now the tetrahedral can also form sheets. So, here you have sheets structure.

(Refer Slide Time: 21:51)



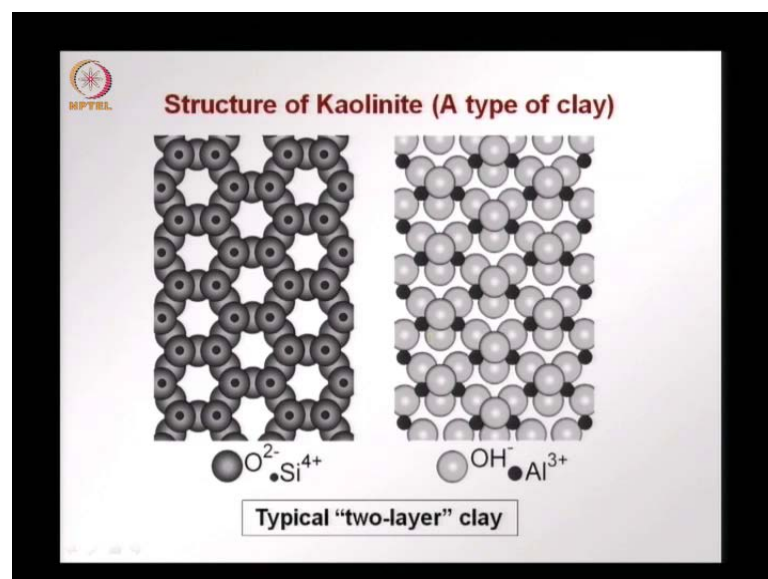
Where each tetrahedral now shares the oxygen ions with its neighbors forming these sheets can be quite whit. So, this structure of the sheets form by the tetrahedral.

(Refer Slide Time: 22:14)



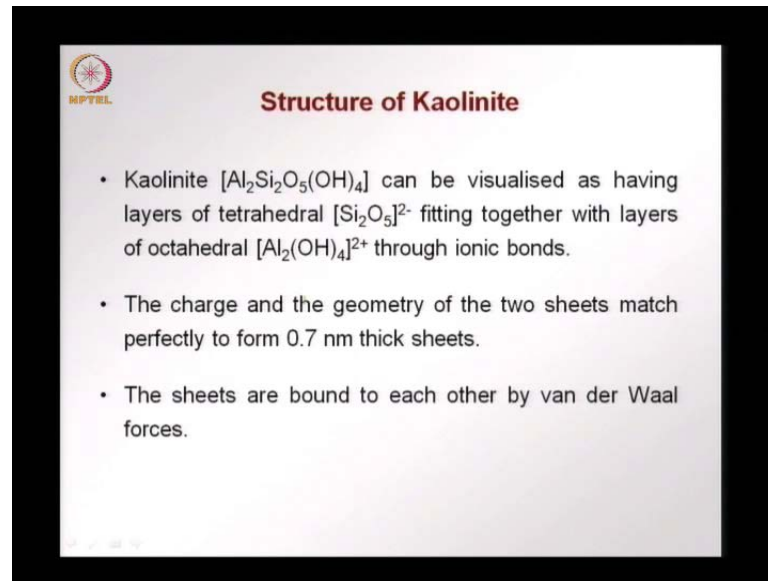
You can also have these tetrahedral making a three dimensional lattice this is one of the exceptional covalent material which as a three-dimensional structure the other being diamond which forms a three-dimensional structure with carbon now we have lattices of the silicate the tetrahedral which can form a network structure like in quartz. So, quartz is a crystalline material that is made up of this tetrahedron forming and network structure like this.

(Refer Slide Time: 22:54)



Now one type of crystalline material that we find in nature is clay this is the structure of kaolinite are type of clay which as a two layers structure one layer is made out of the silica tetrahedron this is that tetrahedral sheets on top of this we find and aluminum hydroxide sheet which is octahedral and this fix in and a takes care of charge imbalance. In and together the form units that is nuclear.

(Refer Slide Time: 23:33)



The slide, titled "Structure of Kaolinite", features the NPTEL logo in the top left corner. It contains three bullet points:

- Kaolinite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$ can be visualised as having layers of tetrahedral $[\text{Si}_2\text{O}_5]^{2-}$ fitting together with layers of octahedral $[\text{Al}_2(\text{OH})_4]^{2+}$ through ionic bonds.
- The charge and the geometry of the two sheets match perfectly to form 0.7 nm thick sheets.
- The sheets are bound to each other by van der Waal forces.

So, the kaolinite can be visualized this is the formal of kaolinite kaolinite can be visualized is layer of tetrahedral which are s i o two o five linking up with layers of octahedral aluminum hydroxide a l two o h four both have charge imbalance that tetrahedral a negative two charge imbalance octahedral aluminum hydroxide as plus to charge imbalance. So, they have an ionic bond which forms between the layers to give a single unit. So, that charge geometry fit the match each other and together the two sheets form a point seven nanometers thick sheet where thin sheets occurs within kaolinite now different sheets are bounded to each other by Van der Waals forces which is the weak point between the tetrahedral sheets and the octahedral sheets we have ionic bonds, but between this unit which forms the sheets and the next one we have weak Van der Waals forces which are not very strong.

(Refer Slide Time: 24:50)

Structure of Kaolinite

Si₂O₅²⁻
Al₂(OH)₄²⁺

Weak van der Waals bonding between layers

- Kaolinite crystallises as flat sheets. It does not absorb water but adsorbs it as a thin external layer.
- Halloysite [Al₂Si₂O₅(OH)₄·4H₂O] has a similar structure but with water between the sheets.

Young et al.

So, this is what shown. So, you have one unit made up of silicon five. And aluminum four and between this unit and next you will have weak Van der Waals forces which are not very strong force. So, that is why these sheets can split along this direction you can have the separation of these layers in kaolinite kaolinite crystallizes as these flat sheets, but does not absorb water, but it can absorb water as a thin external layer in the surface, but it is a type of clay which does not absorb water or expand another similar material which allows water between the sheets as opposed to what we see and

(Refer Slide Time: 25:47)

Structure of Kaolinite

Scanning Electron Micrographs

a: Kaolinite crystallises as flat sheets.

	Horizontal Plane	Vertical Plane
Highly Oriented Fabric		
Highly Random Fabric		

(a)

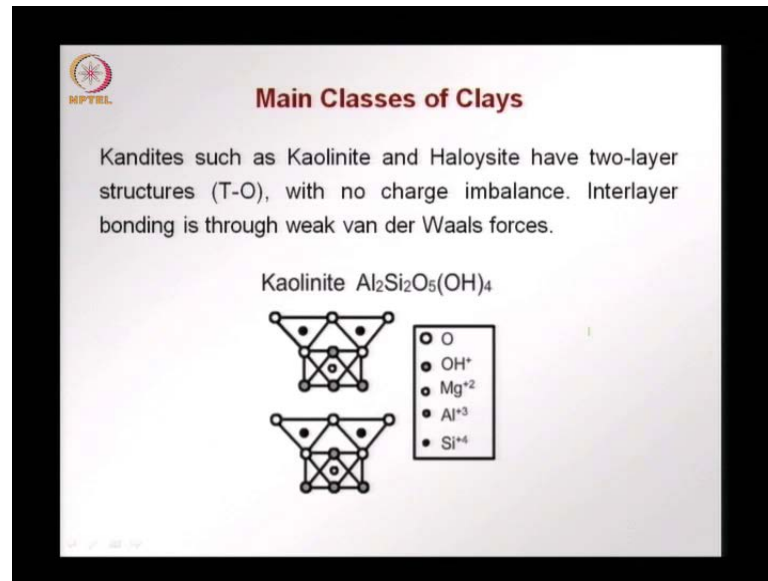
b: Halloysite sheets are rolled into tubes.

(b)

Bowles

These are some scanning electron micrograph as taken book of bowels where we see the small plate led's or crystal which form in kaolinite these are the small sheets which make up kaolinite halloysite is more a tubular structure we can rarely see here some tubular structure because the halloysite sheets or old like tubes whereas, kaolinite crystallises in the small flat sheets.

(Refer Slide Time: 26:22)



There are three main classes of clays what we have discussed up to now this the group called kandites which includes. Kaolinite and halloysite these are two layers structures that we saw before what is called the t over structure meaning tetrahedral octahedral structure without any charge imbalance that is they are stable as such and the differently layers of this material are bonded by weak Van der Waals forces which are which forces.

(Refer Slide Time: 26:59)

Main Classes of Clays

Smectites such as Pyrophyllite and Montmorillonite have three-layer structures (T-O-T), with some charge imbalance.

These clays readily adsorb water between the layers, which generally reduces the strength and causes swelling.

Pyrophyllite $Al_2Si_4O_{10}(OH)_2$

Legend:
○ O
● OH⁻
○ Mg⁺²
● Al⁺³
● Si⁺⁴

So, this is kind of than we have another structures called mactite which clays such as pyrophyllite and montmorilliinite which have a three layer structure called the t o t structure tetrahedral octahedral tetrahedral structure and having some charge imbalance. So, there is some charge imbalance in the structure and this makes it such that water is readily absorbed between the layers and once water goes in it leads to swelling of the clay. And reduction of strength the bond between the different layers or last and what a makes it such that this clay layers separate very easily this is in the structure.

(Refer Slide Time: 27:49)

Main Classes of Clays

Illites like Muscovite are three-layered (T-O-T) with K, Ca, or Mg interlayer cations, which prevent the entrance of water into the structure. Therefore, these clays are non-expanding.

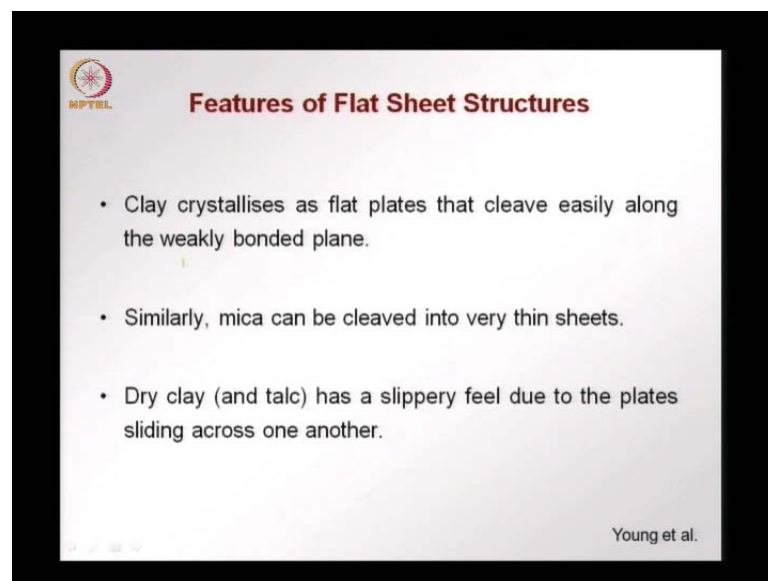
Muscovite $KAl_2AlSi_3O_{10}(OH)_2$

Legend:
○ O
● OH⁻
○ Al⁺³
● Si⁺⁴

Then we have a third class of clay called Illites muscovite is one of them which also as a three layers at t o t structure, but with potassium calcium or magnesium cations between the layers here you see the t o t structure are muscovite with potassium cations between the sheets again these potassium ions now fulfilled the charges imbalance, but now they do not let any water go in. So, this is the type of clay which does not.

Incorporate water and expands. So, this is the clay which does not expand this is the non-expanding clay even though at this similar structure to that of this material. So, what we seen is you can have a similar structure, but depending on the chemical nature of these structure they can be either expanding non-expanding that is important for us to understand when we looked at that foundation and will look at soil mechanics and we want to build structure and such soils.

(Refer Slide Time: 28:56)

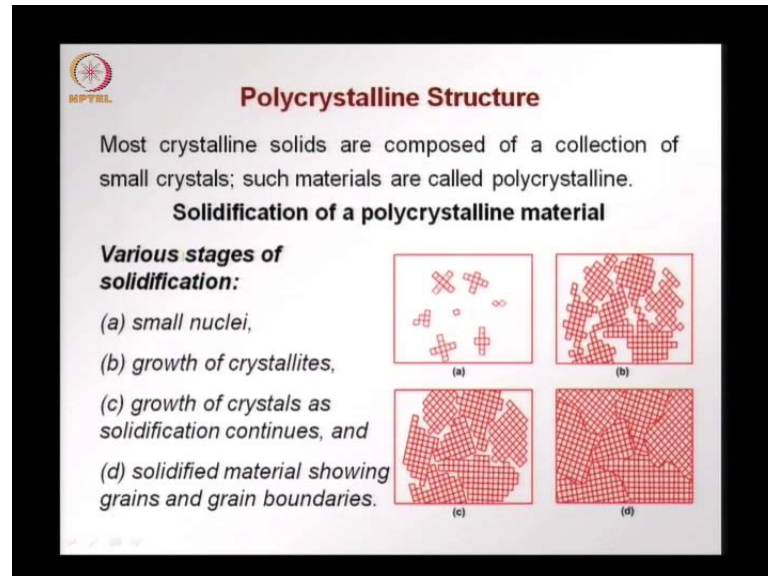


Be summarized about clays clayscrystallize as flat plates this can cleave easily cleave means they can separate easily along the weekly bonded planes and what are the weekly bonded planes those that are bonded by Van der Waals bonds the other bonds that ionic that we saw before. So, that does not break. So, easily, but the Van der Waals bond break easily and the plates of clay can separate similarly we also.

See in mica which can also be separated into very thin sheets or clayed into very thin sheets one evidence that this plates separately easily is when you take try clay and you rabbit with your finger and see a slipper feel same as talc cover we called it talc come

powder. So, the plate lets of clay slip over each other and that is why when you take clay powder in your between your finger you have a slipper feel.

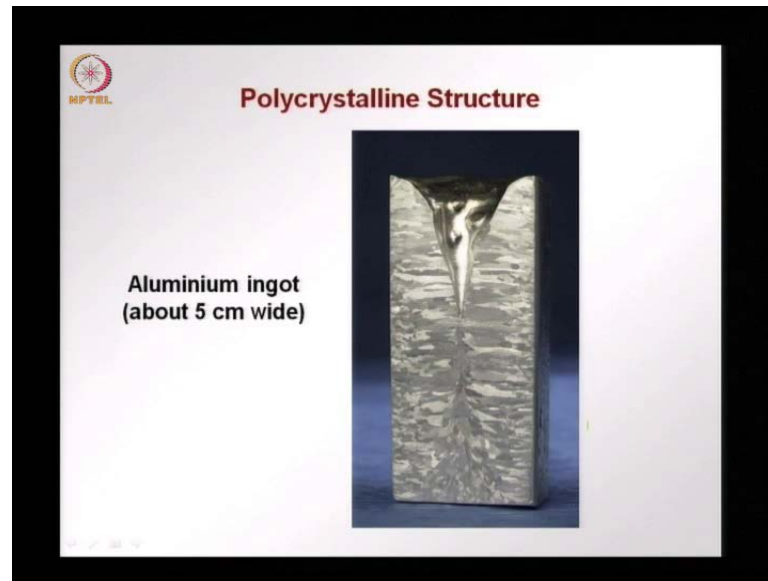
(Refer Slide Time: 30:00)



Now when we have materials generally they are polycrystalline like the whole solids is not made up of a single crystal that a collection of small crystal and therefore, they are called polycrystalline materials the diagrams below showing what are the difference stages of solidification when we have a melt and we start decreasing the temperature of the melt small nuclei start to solidify and around the nuclei we see the growth of the crystal. So, here we are seeing the other dense of some sort of growth around the different nuclei and as the.

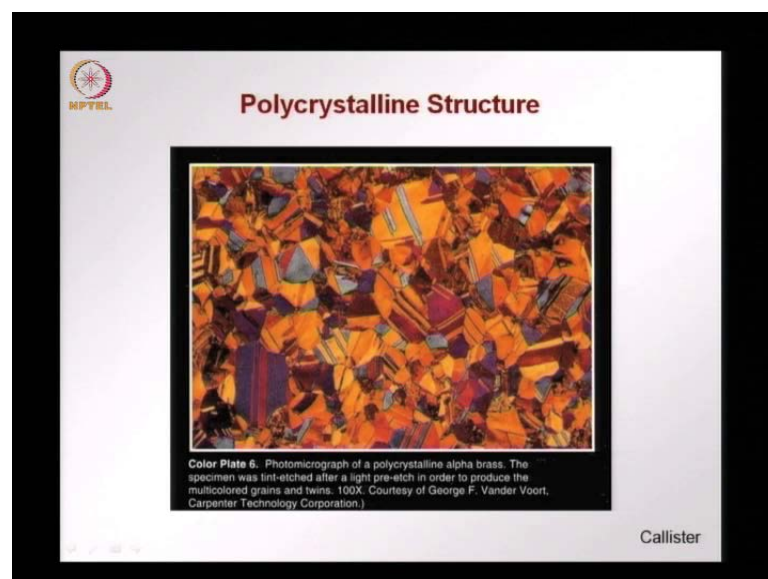
Solidification continuous each nuclei now grows into a large crystal and grows without any hindrance without any disturbance until one crystal needs another. So, when one crystal needs and another are does not have space to grow we have grain boundary within a grain the crystal structure is in a certain direction in the next crystal can have a different crystal direction or orientation eventually all the spaces filled up and you have there is grain boundaries that you see between the different crystals. So, each of this is the one crystal and between the crystal we have grain boundary.

(Refer Slide Time: 31:42)



This is an example of the grain boundaries and different crystals this is an image from the internet often aluminum ingot about five cm wide as it has solidified and you can see here that all of this is aluminum, but the different colors indicate the different crystals that have formed. This is an ingot which would've solidified first along the edges and then you have radial solidification. So, you have these elongated crystals which are formed and finally, is crystallization solidification in the center. So, these different colors indicate different crystals that have been formed.

(Refer Slide Time: 32:29)



Now this is an image from book of Callister again showing of micrograph of brass showing its polycrystalline nature again all this is brass and the different colors represent the different crystals which reflect light differently because of different orientation of the crystal planes and you see here how brass is made of different different crystal grains and between them we have the grain boundary. So, within one grain the crystal structure is uniform and begin one grain and other you will have a.

Discontinuity of the crystal structure to summaries in the first part of this lecture we are looked at different crystalline structure formed by either ionic metallic covalent bonding we also look at what properties can expect from such structures and we ended up looking at polycrystalline materials in the next part of this lecture we look at the defects that can occur in this crystals remember we said crystals.

Where materials which have orderly packing or regular structure now defects can also occur in this materials and this is what we look at when we continue with this lecture and later on we look at structures which are not crystalline they are either predicated or they are glasses. So, these are called amorphous structures which can form the amorphous structure by definition or irregular structure that can form in materials.

Thank you.