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## Module - 2 Lecture - 5 Part 1 of 2 Development of Microstructure – I

Welcome to the fifty lecture of modern construction materials. Today we're going to talk about the development of microstructure. We've already covered the bonding between different types of materials how the structure forms and in the last lecture looked at the movement of atoms through diffusion dislocation movement and so on. Now we're going to look at how the microstructure develops and will see what governs the microstructure formation and changes that can occur.

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In the microstructure know what is the microstructure details of the structure of a solid that can be seen only at high magnifications see under a microscope are called the microstructure. (Refer Slide Time: 01:04)

Formation of Different Kinds of Microstructures		
Conditions	Material	Remarks
Crystallization from melts	Metal Igneous rocks	
Precipitation or crystallization from solution	Hardened cement paste; Clays	Amorphous and crystalline components
Solidification without crystallization	Silicate glass Thermoplastics	Limited crystallization for some plastics
Solidification from gas phase	Silica fume Carbon black	Amorphous powders
Sintering of inorganic powders	Ceramics Bricks	May involve reaction between two kinds of powders, and/or partial melting (liquid phase sintering)

Now there are different kinds of microstructures that form in materials in solids you can have crystallization from a melts where you have a molten metal are molten rock that is crystallizing solidifying forming a crystalline solid. You can have amorphous and crystalline materials forming from precipitation from a solution or crystallization from a solution.

In the case of hardened cement paste you initially have a mix of cement and water. Cement reacts with water there is a precipitation of calcium silicate hydrates which is a amorphous material. You can also have solidification without any crystallization like in the case of glasses or thermoplastics. Silicate glass forms without crystallization through solidification.

You can have limited crystallization for some plastics that is some plastics can have some amount of crystal in the rest would be amorphous this is again something that we looked at a couple lectures back.

We can have solidification occurring from the gas phase also for example in the case of silica fume carbon black these are amorphous powders. Silica fume you would have heard of is a material that is very useful in concrete because it has a very high silica content and in this amorphous this makes it possible for this silica to react with calcium hydroxide that is there that is a byproduct of the reaction between cement and water.

The calcium hydroxide reacts with the silica fume to give us a form of calcium silicate hydrate which accesses the binding material in concrete. We also have sintering occurring we look at this when we look at diffusing in the last lecture. Sintering of inorganic powders occurs in ceramics and bricks were you have heating or partial melting it doesn't the temperature is not high enough to cause a complete melting; this gives rise to sintering between different particle which leads to bonding of different particle and a sintered solid. So these are the different kinds of microstructures which can be formed in solids.

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Metals , polymers and glasses solidify from melt so generally when you want a solid one of these types you start with a melt and go on to get the body are the structure with one of these materials. Now as we saw earlier solidification does not always involve crystallization in metals mostly. We have crystallization we looked at the example of metal glass which is different but in most metals we have crystallization; on the other hand we have glasses which are most often amorphous or non-crystalline. We also looked at polymers which are generally amorphous but you can have a solid structure which is partially crystalline due to the arrangement of the polymer chains.

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We discussed also in the previous lectures that most materials most substances including metals can be forced to form a glassy structure an amorphous structure, if the cooling rate is fast enough that is there is not enough time for nucleation to occur for the arrangement of the particles to form a crystalline structure to occur; that is if the cooling rates are fast enough you have a higher tendency for a glassy are amorphous structure to form.

However polymers can only partially crystallize because of the nature of the long chains that make up these polymers. So even if the cooling rates are slow enough polymers can only crystallize partially; you remember that we looked at different type of polymers like branch polymers and linear polymers.

We said that linear polymers would have a higher tendency to crystallize back to partially, because the chain start entangling themselves and it's difficult to have these chains align themselves in an orderly fashion. In cementations materials the microstructure is developed by solidification or precipitation from solution.

Solutions in this case are made up of a reactive solid and the liquid. In the case of hydrated cement paste we start off with cement a powder and water reactions between the cement and water want to form the hydrated cement-paste. The products are generally amorphous for

example in the case of port land cement or it can also be crystalline such as in the case of calcium aluminates cement.

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Crystallisati	on from Melts
The tendency for crystal gr to occur along prefere directions can lead to branched or <i>dendritic</i> structure	owth states a state of the states a
<ul> <li>The growth stops when dendrites meet. The point contact build irregular polyg surfaces(e.g., grain boundar)</li> <li>The solid acquires a gran appearance.</li> </ul>	the Dendritic structure of an antimony-lead alloy so of gonal fies).
Rosenthal	Crystal growth in preferred directions – dendrite (schematic)

Let us look at the crystallization from melts. We already saw that nucleation is the first phase then the crystal growth occurs and then the crystals are bounded by surface defects called grain boundaries, if you see here this is a that structure of crystallization in an alloy of and antimony lead what we see here is; what is called a dendritic structure. A branching structure as the crystal form and that is shown here this is the crystal growth along a certain direction, and we see here many of these dendritic structures within so the nucleation occurs then the rest of the dendrite structure starts form.

There is a tendency therefore for the crystal to grow along a preferential direction which leads to this branched or dendritic structure and when one then dendritic smeets another the growth stops and these points build-up join together to form a polygonal surface or a surface defect which is called the grain boundaries and finally after solification is over. (Refer Slide Time: 08:31)



The material now has a granular appearance as if it is made out of grains stuck together, so what I've told you know is represented schematically on the right hand side initially we have in the melt as the temperature decreases nuclei forming so there are spots were solidification is initiated from those points, you have growth occurring in this branch manner that is dendrites start to form.

These dendrites keep growing until they meet another dendrite they have to then stop growing in that direction the available space fills up and grain boundaries start developing to you have these grain boundaries which develop between that crystals or dendritic structures and that eventually becomes the grain boundaries and you have a grainy appearance to the material consequent, so first you have the formation of the nuclei. The growth of dendritic crystal in b and c. We have the meeting of the dendrites and this slow formation of the grains each dendrite has with form a different nuclei and for the crystallize, finally you have the grain boundaries forming and giving us a polycrystalline solid. Finally this is how you have the polycrystalline solid forming. (Refer Slide Time: 10:10)



So these steps are governed a lot by the temperature first the melt is at a higher temperature than the melting point as cooling occurs we reached a temperature of melting or the melting point. At this point there is an equal chance for a nuclear to be formed and to be melted that is there is as much chance for a nucleus to be absorbed by the melt as to be precipitated, so at this temperature solidification really does not start, because the nuclei can be precipitated and as well absorbed.

So nucleation at the melting point is nil or zero the rate of nucleation increases and goes beyond. The rate at which the nuclei being absorbed by the melt as the temperature is decreased feather that is the temperature has to be such that the melt is super cooled or under cooled to a critical temperature be critical only below this temperature we have nuclei forming and leading onto that dendrite structure that we talked about before and the grain storm.

Suppose you have impurities in the melt these can act as artificial centers of nucleation called seeds. In the case the seeds are present crystallization can occur above the critical temperature T critic that is closer to the melting point. If it is a pure material it has to be super cooled to the critical temperature T critical but if there are seeds then crystallization can occur above the critical temperature itself.

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What we see here on the right and is aluminum ingot about five centimeter wide which shows very clearly the crystallization process. We have on the outside surfaces crystals which are equiaxed that is we are having dimensions equal in all directions almost spiracle. This is because, cooling would have occurred very fast on the surface. So crystals equiaxed when the temperature of the melt is uniform.

However inside there is a gradient of temperature in a most we have a higher temperature outermost, you have cooling occurring, so the temperature is low, so there is a gradient across the radius of this ingot and in this direction ;we see crystals growing from outside, who has the center and we have these radial crystal occurring, so where ever the temperature is non uniform that is there is a temperature gradient .We have different sizes and shapes of crystals occurring like we see here.

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In the center again we have a uniform temperature and again the crystals can be equiaxed. Schematically this is what we have just discussed. Now if I have a molt and molten metal is poured into this molt and the molt is cooled very fast; the temperature drops radially outside it is coolest inside it is almost the temperature of the melt.

The temperature of crystallization is reached first at the sides leading to small equiaxed crystals covering the wall along the sides, then these crystals grow inward it is coolest on the outside. So they start there in the crystal grows inward in columnar grains, so here you seen these in this section these long grains which form from the outside towards the center. At the center again there is no temperature gradient and we have equiaxed crystals forming, this would be how the temperature gradient looks like? How the temperature distribution looks like?

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When we talk about crystallization from solution they're also the temperature plays important role crystallization; when it occurs from solution is governed by the degree of super saturation only; when the solution is super-saturated, you have nuclei occurring and the nuclei growing at saturation. The crystal is in equilibrium with the solution that is that the nuclei are dissolving at the same rate that which is causing the formation that is rate of dissolution is equal to the rate of crystallization. Temperature changes the level of saturation at higher temperatures.

More material can be dissolved and therefore at a certain temperature, you can have a different level of saturation, then another temperature once the crystal is form the rate of growth depends on the diffusion into the growing face. Once you have nuclear occurring and then you have a crystal growing this crystal grows as a function of how much diffusion can occur in the growing faces?

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Now we look at how face changes occur and for this we have to again look at what is a phase we discussed this previously and we said a phase is a homogeneous region within a system in which the properties are uniformed, so you have you can have a material existing within the total material ;which has different properties from the rest of the material or other phases.

Each phase as a specific composition an atomic structure and it can consist of one component or multiple components.

This picture of cast iron that we have seen before we have this cast iron made up of iron and carbon this four percent by weight of carbon in this and there are several phases. The long grief is that you see here are flakes of graphite with which is carbide. The rest the matrix is a mixture of iron bcc iron and iron carbide; which is the rest of the structure.

This graphite is a phase which has very different properties from the test and exists in an identifiable manner, so in materials we can have different phases occurring either the phase is introduced in the fabrication process or the phases occurred when solidification occurs from melt.

In concrete for example we have a phase which is the stone-phase other rock phase which are call the aggregates. These aggregates are mixed into a system which has cement-paste and the aggregates stay without changing their composition through the life of the concrete, so the aggregates from one phase and the hydrated cement-paste forms and other phase. In cast iron the phase is form as solidification occurs from the melt, since the quantity of carbon is very high this forms a separate phase of graphite within the cast iron.

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The changes of phases as a function of temperature is governed by phase equilibrium. We see here a simple case of an energy diagram here. We have on the y-axis the energy of the system. x-axis we have temperature this is an energy diagram for two phases alpha and beta say this could be two different packing's of atoms in a crystal or two different states of matter and we have here the energy for alpha as a function of temperature this is line this is how the energy will change as a function of temperature for beta.

Now what we have seen earlier is a material will always choose a structure that provides a lower energy that is the potential energy are the lattice energy should be lower, so in this case we see that until this temperature call the transition temperature.

Beta is stable; after this temperature alpha, become stable because in this region theta requires less energy to form and to stay that way then alpha, but beyond this transition temperature the energy required for alpha is less, so we say that this would be the stable path and the other are meta stable that is they have to be forced to occur otherwise the meta stable phases will not occur. So, phase alpha has a lower energy then beta at higher temperatures that is about the transition temperature and is then the table phase; whereas beta is stable at lower temperatures and therefore it is this stable phase below the transition temperature. At the transition temperature both energies are equal.

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The Meta stable phase will occur will exist only if some energy barrier is there for the nucleation of the stable phase otherwise it will not occur. Generally the Meta stable phase will not occur unless there is some reason, why the stable phase is not occurring and we are forcing the Meta stable phase to exist. The Meta stable phase can be induced to change to the stable phase leader by the application of additional energy this can be mechanical or thermal energy or by the addition of seed crystals otherwise always it will be the stable phase because the stable phase requires less energy when the other phase.

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Now let us look at when different phases are formed and for this we have to understand what a solid solutions, just like we would have solutions in the liquid form; we can have solutions in the solid form; when we have a melt of copper and nickel, we have liquid copper and liquid nickel are completely soluble in each other, so you have a mix of nickel and corporate atoms in the melt.

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So when the melt temperature is decreased we start solidification and a solid copper nickel alloy is form. In the case of copper and nickel you have complete solid solubility with copper and nickel atoms occupying random lattice sides that we see here, so there is a random distribution of nickel and copper atoms within the solid that means it is a solid solution.

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However we have other alloys which do not exhibit complete solubility for example in the case of copper and zinc were the zinc content is more than 30 percentage. We fine that instead of having a random distribution of copper and zinc atoms; we have a second phase forming this phase is a compound of copper and zinc, this separates from the solid solution of copper and zinc and can be identified as a separate phase that is occurring and this occurs when we have a high content of zinc beyond a certain limit in this case of 30 percentage.

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So, even solids we have solubility limit which are the maximum concentration of solute atoms that can dissolve in the solvent to form a solute solution, beyond the solubility limit be have a separate phase forming.

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In the case of zinc and copper be get this diagram which shows us as the blue line the limit of solubility as a function of temperature at lower temperatures. We have the limit of solubility of zinc and copper as thirty percent at higher temperatures. We can accommodate, we can mix in a little more zinc reaching about 40 percentage at four hundred degrees Celsius to the left of this curve.

We will have a solid solution of zinc and copper were, we will have atoms randomly distributed both zinc and copper atoms will be randomly distributed within the solid. However to the right we have one phase which would be the copper zinc compound another phase would be the solid solution, which would have a random distribution of copper and zinc atoms. So, this defines the solubility of zinc in copper the solid line represents as I said the solubility limit and when excess zinc is added the solubility limit is exceeded and now two phases coexist to the left we have only one phase to the right. We have two phase one the solid solution and the other that copper zinc comp. (Refer Slide Time: 26:14)



Now we come to phase diagrams, which you would have studied in ah first years of college there is the interaction of temperature pressure and composition in a material. The phase diagram is a graphical representation of the combinations of temperature pressure composition or other variable for which specific phases exist at equilibrium. In this case we have generic phase diagram on the screen with pressure on the y-axis temperature on the x-axis and we have different regions where different phases exist. So, the orange is the solid part that is within this orange area there is the existence of the solid-phase in the purple, we have the liquid phase, and in the green we have to gaseous phase. Now we find that between these areas of different colors we have lines where different phases can coexist that is along this line.

Now we can have the coexistence of both the solid and liquid-phase here, we can have the coexistence of the solid and gaseous phase here; we have along this line the coexistence of the liquid and gaseous phase this point which is called the critical point is up to where there is a clear definition of the different phases. Beyond this there is no clear definition of the amount of liquid an amount of gaseous phase that can coexist between these regions different phenomena can occur changing the phase from one to the other for example here, when temperature increases we can have the solid melting to form a liquid when the temperature drops we can have the liquid freezing to form a solid.

Now the liquid and gaseous phase, we can have the liquid boiling vaporizing evaporating to form a gas and when temperature drops, we can have the gas condensing to form a liquid; we can also have a change in phase from solid to gas and vice versa, when a solid becomes a gas it is called sublimation, where you have the gas occurring without passing through a liquid-phase a gas can become a solid ,we use the example of say silly co fume, where he said a gas can directly become a solid fine amorphous solid. In the case of silly co fume so along these lines as I said you can have two phases coexist, but there is always only one point call the triple point were all the three phases can coexist and that is called the triple point.

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So, let us see some examples of different systems and before that we'll have to define what is called the Gibbs phase rule, the Gibbs phase rule says that, if the number of degrees of freedom now in the previous diagram the degrees of freedom were pressure, temperature, if the number of degrees of freedom are represented by f and the number of phases that coexist by p and the number of components in the system by n then f plus p is equal to n plus 2.

So, this is the Gibbs phase rule at constant, atmospheric pressure the equation is slightly modified into f plus p equal to n plus one f being at n the degrees of freedom p being the number of phases n being the number of components, so this is when we take pressure out that is we assume that pressure is constant atmospheric pressure.

Gibbs phase rule is modified as such as an example, if you have to components that is n is equal 2 and a single phase molten alloy that is p is equal to one at constant pressure, would have f equal to 2, n is equal to 2 p is equal to 1, so f is equal 2 that is within certain limits both temperature and composition can be varied independent were the degrees of freedom . Now temperature and composition this can vary independently within a certain limit according to Gibbs phase rule.

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In the case of a single component in system n is equal to 1 which is what the H2o.We get now the Gibbs rule of f plus p is equal to n plus 2, become f plus p is equal to 3 for one phase f is equal 2, that is a T is equal to 1, f is equal to 2 that is both temperature and pressure can vary. So, if you are looking at only ice within the limits of ice existing as such both temperature and pressure can vary similarly for water and for water vapor the liquid and gaseous phases respectively, but if we want two phase to coexist that is equal to 2, then f becomes one right; if b is equal to 2, then f becomes one that is only one of the 2 degrees of freedom can be changed , that is only temperature or pleasure can vary independent.

The other will be a function of the variable that this changing that is if you change temperature for the two phases to coexist. They can be only a certain pressure that goes along with that temperature for three phases to coexist that is p is equal to three s becomes zero that is you cannot change anything there is only one point were all the three phases can coexist that is what we saw earlier and call the triple point.

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So the phase diagram for H20 that is the ice water vapor system is shown here, where you have now pressure on the y-axis, temperature on the x-axis and the different colored regions showing us the different phases; that can the light blue is the ice phase, so this is where ice can exist, the dark blue is the water or the liquid phase and this is the water vapor or the gaseous phase. So, within this you can change both pressure and temperature were only one phases exist that is f is equal 2, both temperature and pressure can be changed same within the liquid and within the solid, but if you want to look at when two phases can coexist we find that it is a line, so at every point if we change the temperature there is only a corresponding pressure over which both the phases can exist.

So for ice and water to exist you have to be along this line there is only one degree of freedom. Similarly for water and water vapor to coexist, you have to be along this line and then you change the temperature there is only a corresponding pressure for which you will be along this line. So f is equal to 1 there is only one degree of freedom for all the phases to coexist there is only one point where this can occur there is no degree of freedom, f is equal to zero, because this is a constant this can only occur at 0.006 atmospheric pressure and zero point one degrees Celsius temperature, so this gives us how water changes from one state to another how ice changes to water to gas and so on.

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Similarly we can have a phase diagram for carbon dioxide. Now again we have this phase diagram were, we have pressure on the y-axis, temperature on the x-axis all of it is CO2, carbon dioxide this part is now the solid carbon dioxide than carbon dioxide can exist as a solid, this is the liquid region and this is the CO2 gaseous vapor and as, we saw before within this region both temperature and pressure can change carbon dioxide will continue to exist as a solid within this region also that is you have only one phase, so f is equal two we have two degrees of freedom you can change both temperature and pressure the liquid.

C02 will continue to exist, but when you will have both two phases occurring you have to be along this line. In the case of liquid and CO2 gas solid and liquid along this line, and for all that three phases to coexist, it can only occur at this triple point degree of freedom zero, because it's well-defined at 5.11 atmospheric pressure and two hundred and sixteen degrees Kelvin, what is also interesting from this phase diagram is that there is a range of temperature and pressure were solid carbon dioxide can convert to gaseous form which includes the normal pressure that is one atmosphere, so at normal pressure one atmosphere carbon dioxide can go from solid form that is that dry ice form to directly to gaseous form, that is why it's called dry ice does not go from solid to liquid to gas but directly at normal pressure can go from solid to vapor.

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Another single component system which is of interest to us is the system of iron on the right here, you see the phase diagram iron at very high temperatures, you have iron in the gaseous form when the temperature at atmospheric pressure is more than three thousand degrees, you have the gaseous form as temperature decreases the gas will become a liquid. The liquid will exist at atmospheric pressure up to a temperature of thousand five hundred and thirty five degrees Celsius. These lines give now the boundaries in terms of temperature and pressure when two different phases can coexist that is along this line gas and liquid can coexist and along this line now liquid and a gamma phase of iron can coexist.

The temperature decreases different phases of solid iron form this is the gamma phase which is an FCC structure the alpha phase which is a BCC structure and in some cases when you have a very high pressures, you have and epsilon phase which is HCP structure, so we find that in equilibrium at normal temperature, we have alpha in the BCC form that is at normal temperatures and pressure up to 910 degree, you have iron existing in alpha form that is a BCC structure when we heat further, when we cross 910 degrees Celsius, we have iron going into the gamma structure which is an FCC structure further heating there is a small region were a delta structure is formed which is a BCC structure and after that the iron completely melts and as a liquid structure. we saw that there is a case were very high pressures more than 15 GP, we have HCP phase and epsilon phase form, so in this part of lecture five; we've looked at how different microstructures form. We looked at solidification from melts starting from nucleation to the dendrite structure and grains forming and then are gone on to see, how we can describe phase changes to phase diagrams until now we've looked at single components system. We looked at the case of H20 or ice water vapor system, the CO2 system and the iron system and we saw what defines are determinants when the phases change in the case of water and CO2, when this solid will become liquid will become gas and so on and in the case of iron.

We saw that there are several solid phase which can occur, which could be the FCC are the HCP structure and we also saw in which case is different phases can coexist, we looked at Gibbs phase rule which defines, when the different phases can coexist, and we look at examples of the same. Now in the next part of this lecture we look at binary systems and will see, how we can have binary phase diagrams which again explain to us, how there is the interaction between temperature and the composition to define their different phases that can coexist and the types of phases that occur.

Thank you.