

Surface Engineering for Corrosion and Wear Resistance Application
Prof. Indranil Manna
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Kharagpur

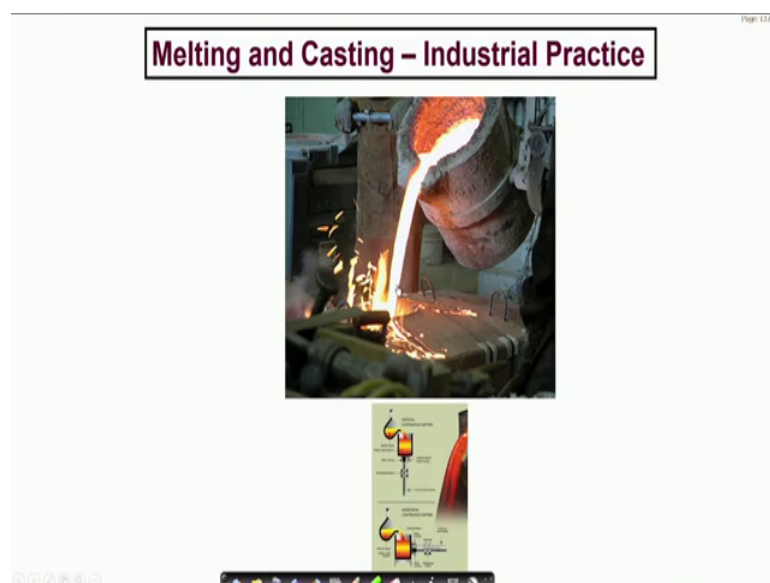
Lecture -02
Microstructure of Solids

Hello welcome to the 2nd lecture of this course Surface Engineering as I said in the very first lecture itself that initially we will be dwelling more upon the structure of solids lay the foundation and we will start talking about surfaces and surface engineering much later. So, for all engineering applications though there are very important applications possible with gases and liquids, but most of our discussion particularly with regard to surface engineering, we will be dealing mostly with solids, how do you form solids?

Obviously if you go into the history of the entire evolution of universe we must realize that everything that, we see today as solid at some point of time all naturally occurring solids, must have been gaseous or liquid depending upon the temperature, pressure and other thermodynamic conditions.

Even for all synthesis all manmade structures, all solids that we deal with we synthesize, we fabricate, we create various devices machines and so on all these actually come initially either from the liquid state or from the vapor state because that is, how it is easier for us to fabricate. So, question is why?

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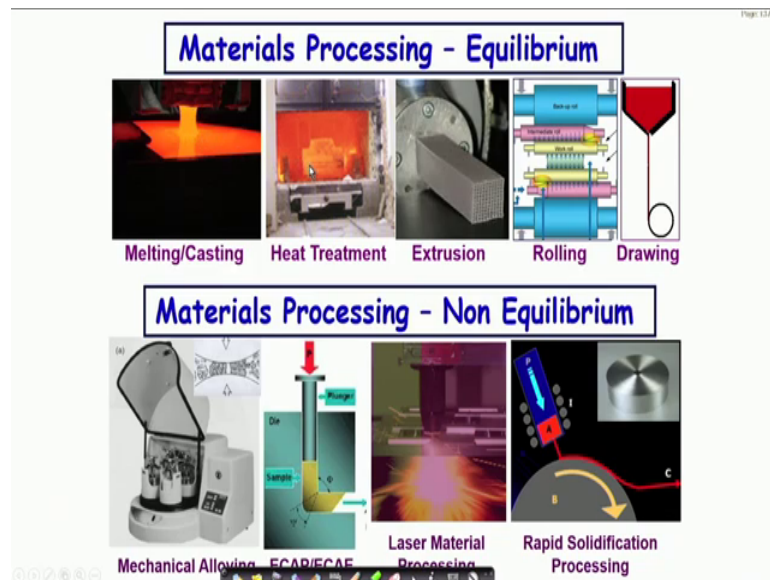
For example, here you are seeing hot metal being poured into our mould and so it is a box in which you have this hot metal which is, so this is the huge container which contains hot metal and this hot metal is being poured into a so called mould box. And when this liquid will solidify you will get a particular solid of a given shape and that shape and size and volume can be fairly complex and not very easy to make in one shot.

So, we prefer to usually form solids from the liquid state because of the a major advantage of having the possibility of dissolving all the species into a single solution only in the liquid state. So, in other words liquids usually have unlimited solubility, so no matter what composition of the liquid is we essentially have a single phase liquid and that is easy to deal with because essentially we are dealing with either of fixed melting temperature or a fixed liquid us and solidus temperature or solidification range.

And then that allows us to actually design a particular solid depending upon its volume shape and other geometric factors. So, we pour the liquid into a particular box with a particular shape which we called a mould and then we solidify we get the solid of our particular shape and size desired.

We may also create certain structures, but then when we actually do such pouring we act we do make it we do realize that, they actually take the shape of the mould, but subsequently we need lot of processing because it is not always possible to cast them into a particular shape and size. On the other hand we also can cast liquid metal continuously in the form of in either sheet form or rod form and that also are very useful particularly in the steel industry. So, melting and casting is a very standard industrial practice of forming solids.

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But then that is not the only one say for example, here what we are seeing is casting of pouring of glass. So, this is how glass when made into liquid form brought to liquid state can be gradually cast and structure out of silicate glass or non silicate glass can be formed. This is how we actually can heat and then beat and through such thermo mechanical processing we can create certain solids of very specific shape size and geometry.

This is another mechanical deformation process which allows us to form long structures of a particular diameter or cross sectional geometry we can do rolling, whereby we actually can reduce a thicker section into a thinner one, we can draw either from the liquid or the solid state and draw a solid into very thin wire or rod into very long aspect ratio.

Now, all these processing's are usually done at high temperature or in a condition where which is which allows us to develop equilibrium structure. In other words the time temperature combination for these processes, are fairly conducive to develop a microstructure which is equilibrium nature. On the other hand if you are in a hurry or if we actually want to defy the rules of equilibrium we also adopt or resort to certain processing's which are non equilibrium processing.

For example, we can pack these vials and then mill at a very high RPM and end up converting elemental powders or elemental and compound powders together into a single

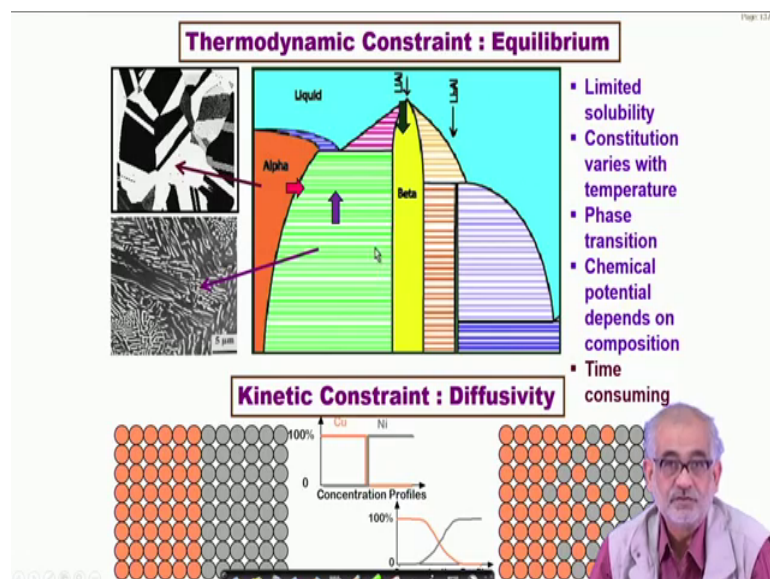
powder mass of different chemistry all together, we can extrude with certain angularity and then end up getting creating microstructure which is ultra fine in nature.

We can do melting of very small volume using a laser beam and under the beam we actually can instantly take a solid in the form of either bulk solid or powders or wires into the liquid state. And then subsequently quench them by self quenching and create certain solid objects from small and gradually built into a bigger one through additive process.

We can solidify a liquid onto a rotating wheel rotating at a certain RPM, but most importantly the wheel is made up of high conducting materials like copper and which allows very fast cooling. So, these processing here we essentially are subjecting the powders to high energy milling, so extremely high rate of mechanical deformation here the deformation rate is low, but yet mechanical and more or less at room temperature or slightly elevated temperature.

Here we are subjecting the material to ultra fast heating and cooling taking it to liquid or even vapour state and the subsequently quenching into solid form and here we are solidifying a liquid melt directly into thin strips or foils of solids. So, either equilibrium or non equilibrium processing allows us to form solids, this solid that we form instantly may not be of the exact shape and size and geometry that we want, but this is the beginning.

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Now, when we do this processing we also have to be aware of two important aspects, one is the so called thermodynamic aspect related to the equilibrium which allows for example, this two dimensional pictorial description actually is so called thermodynamic phase diagram, where the x axis describes the composition of a binary system and the y axis refers to the temperature assuming that in a condenser system like this pressure has a very little influence.

So, in a situation like this suffice to say that if this end left end is hundred percent a and the right end is hundred percent b, then if we mix a and b at any proportion from 0 percent to 100 percent and we heat them from anywhere from room temperature all the way up to a temperature where both a and b should be in the liquid state. Then the entire history of evolution of the phase aggregate is captured in this diagram called phase diagram.

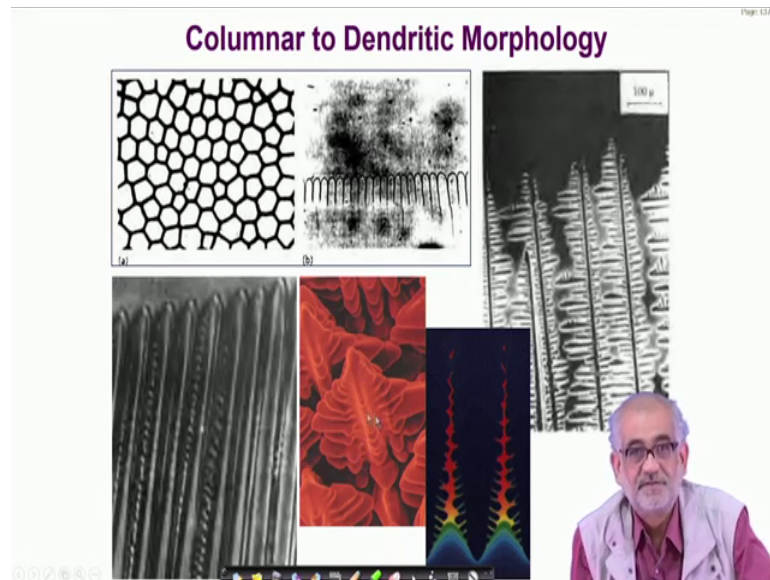
And this diagram tells us for example, that if we want to dissolve b in a, the two components we are we just call them a and b here. So, this is the maximum amount of b that you can expect in solid state in a. So, this is the thermodynamic limit of the solution of b in a and this is an important information because if you want for whatever reasons more amount of b in a, then thermodynamics come in the way.

So, in simple words thermodynamic restrictions impose certain limitations of having phases of or they impose certain compositional restrictions which cannot be defied in equilibrium processing rules. And if you want to defy this equilibrium limits of solubility, then you resort to the so called non equilibrium processing some of which we saw just now.

There is another constraint we have to worry about when we talk of creating solids or obtaining solids of our desired shape and size and that is kinetic constraint based on the rate at which the species move or transport in the solid or may be even in the liquid and that is typically explained in terms of the diffusion coefficient or diffusivity. So, the rate is embodied in the kinetic considerations and is defined by the species diffusion rate or transport rate called diffusivity. And the equilibrium constraint explained in terms of solubility limit coming from the equilibrium considerations are captured in pictorial descriptions as phase diagram.

In simple words when we want to design a solid, we must realize that these two constraints have to be considered and adhere to or followed and if you want to defy, then we must know what is a limit we are dealing with. So, that we can defy them and these two constraints are coming from thermodynamic and kinetic origin.

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So, when we cast these are the kind of fancy structures we see not always, but we may end up actually seeing such growth of columns and at times those columns which are unidirectional in nature of growth can also manifest themselves in a similar tendency of growth in the lateral directions leading to what is known as dendrites, which is essentially borrowed from the Greek word which means essentially far tree like structure.

So, this essentially these either columnar or dendritic structures are typical manifestations of the so called micro or macro structures that we see in solidified or cast masses. When you take a section of these kind of columnar structures, then you see such very nice equiaxial regions.

For solidification processing we have to realize that as soon as the hot metal or hot melt comes in contact with the solid mould heat transfer starts immediately and that is when the transfer rate heat transfer rate is the fastest. So, we first get very ultra fine structures followed by rather gradually rather coarse structure and finally, in the middle we are

likely to see such equiaxed zones where the tendency of growth or the rate of growth of the crystallite in all three directions would be about the same.

But in between when we have right in the core where we have equiaxed to the surfaces where we have chilled or ultra fine zones, we are likely to see directional solidification. And this directionality comes from the fact that heat transfer is across the mould wall which could be the side walls or the bottom walls and since the heat transfer is maximum across the wall the growth front which is essentially carried out through the solid liquid interface will actually be in the opposite direction exactly in 180 degree.

So, if heat moves out of the wall in this side along this side wall in the direction from right to left, then we expect the solid to grow from left to right in exactly opposite direction. So, in this particular case possibly the mould wall was somewhere at the bottom and that is why the directionally grown solids actually grew to the top.

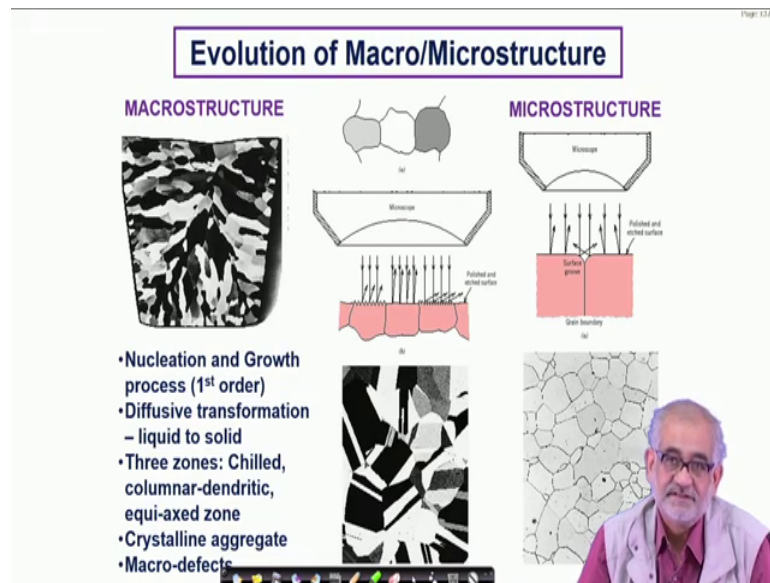
And in a situation where such solid liquid interface can no longer maintain planarity and deviate from planarity and move into the non planar solidification front, then we end up getting such dendritic structures where we see growth not only in one direction, but also in lateral perpendicular direction and even in the tertiary direction.

So, these kind of structures are not desirable, but unavoidable and when the form we are worried because they carry certain signatures of in homogeneity both in terms of length scales of the structures that we develop and also or more importantly in homogeneity in terms of composition.

So, composition from the center to the surface of these kind of columns or dendrites would be fairly non uniform and that is why they are called cold structures, where the center will have the least solute content and the surface will have the maximum solute content. Now, that is a very different subject matter altogether suffice to know that when we form solids essentially which will be useful to us and in particular course where we want to deal with the surfaces of those solids.

We have to realize that whenever we form solids either directly from their cast from the melting to casting procedure, then we may see such macro or micro structures developed in the bulk in the core and certainly also on to the surface. Similar structures one may see also happening when solid is formed directly by condensation of a vapor.

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So, this leads to the concept called microstructure, so as I said to begin with we must say that the first step to understand is a macro structure which by definition is the possibility of seeing the structures with naked eye or with at very low magnification. And that is when you actually see these descriptions called the chilled zone, the columnar dendritic zones or even the equiaxed zone.

But these are possible, so this is the so called macro structure and these are possible when for not for every single solid, but most of the metallic solids, so this is essentially a section of a bulk solid after solidification. Now, the question is the different colors of the entities that we are seeing here essentially are showing different crystallites and their directional and their growth directions.

As you can see that from the sidewalls this is having a certain directionality which is perpendicular to this sidewalls either to the right wall or the left wall and also from the bottom wall we see tendency of growth towards the top. Now, apart from directionality it also tells us another very important feature and that is related to their orientation. This particular melt even if it is of the same composition throughout, it certainly shows that the entire block is not exactly one single entity, it certainly has certain constituents in between which differ from each other at least now what is apparent to us is bicolor.

The question is where is this color coming from? This color is because of differences in orientation. Orientation of what? Orientation of the crystallites which are growing from

the walls and if the orientations differ they also carry certain because of their crystalline nature, they carry different densities of atom as manifested onto the cross sectional plane to which they are coinciding with.

And since the atomic densities are different they actually have different abilities or degrees of reflectivity and because of that nature we are seeing different colors or different lustrous of these crystallites. This actually is a macro structure which is possible to be seen even by naked eye, but when we actually want to go deeper and understand even more, then we go into the realm of microstructure.

Now, this microstructure is a very composite concept and something which the metallurgist and the materials engineers always take pride in saying, that this is one notion which differentiates materials engineering from the rest of the branches of engineering. And may not be totally off the track to mention that all solids that we deal with to various branches of engineering are characterized by numbers for example, yield strength, for example, hardness, for example, elastic modulus or all these so called mechanical properties even functional properties.

For example, conductivity, for example, magnetic permeability. So, all these properties most of the engineers would tend to believe that they are one and the same for the solids; so long a composition is the same. But the metallurgist and the materials engineers understand the worth of microstructure which actually is as I said is a composite or complex body of knowledge comprising the shape, size, identity, volume fraction, an orientation of orientation and distribution of the various phases that make up the solid.

Now, at this moment we have to understand that if this is the vessel in which we have poured the hot metal that we that we saw right in the beginning. Say for example, if you are pouring the hot metal into a some solid box in which the liquid has to solidify and they go through certain processes of solidification. And eventually when they solidify and they cool down to room temperature, we take a cross section and if we tend to see such a solid here.

So, immediately what we realize is that no matter what the composition was we certainly have entities which are not exactly the same. And that they are not the same tells us that they must have started their journey from different sites, may be at same or different point of time, but certainly following a different history and paths.

And because of these variations in the path and the kinetics that they follow they actually can nucleate and grow independently at different sites compete with each other. And eventually end up being a poly crystalline may be single phase, but also a poly crystalline and a multi phase aggregate.

So, that actually requires us to define a few important thermodynamic terms here if you imagine the universe, so as much or as far as you can think of the entire universe is not of use to us when we are talking about a particular engineering solid. When we are talking about a particular solid, we know it is boundary and that is the thermodynamic boundary of a thermodynamic system.

So, beyond what happens is of no consequence to us all we are aware of that here is a finite size of a solid which is bounded by certain surfaces, so that is the volume we are interested in. And now inside this solid, I may have a single end phase and that phase we define in terms of the compositional and structural homogeneity bounded by a definite boundary.

So, universe reduced to thermodynamic system; thermodynamic system comprising phase or phases and the phase or phases may have differences in orientation leading to formation of various crystallites. And the phases are made up of components, I am not saying elements or compounds, I am saying components they can be either element or compound.

And these hierarchy tells us that a given system like this, may comprise a single or multiple phases and also may comprise a single crystal in very; very rare cases where we create an artificial condition which allows only one single nucleus to grow and consume the entire liquid and end up being a single entity for the entire bulk of the solid that we are seeing.

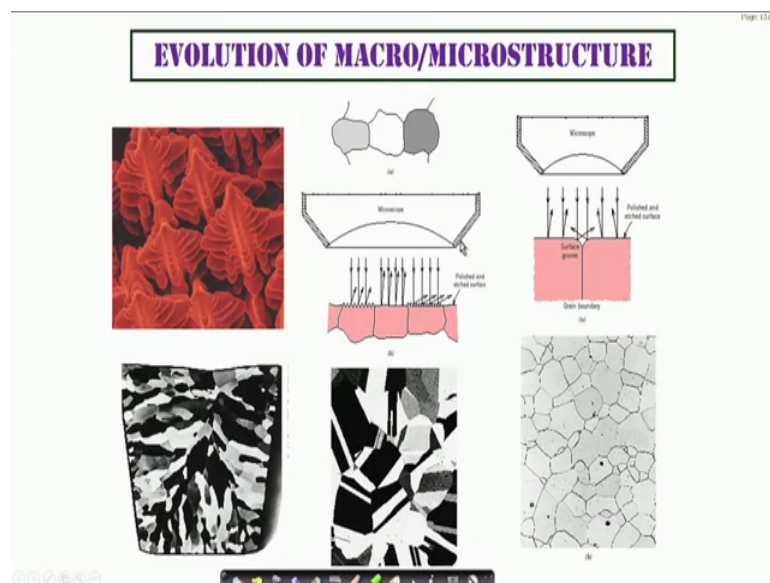
That is a very rare consequence very rare situation in all other practical cases we end up seeing may be the same composition, may be the same phase, but and the same composition, but differing in orientation. And as a result we end up getting a situation where it may be a single phase, but having different crystallites of different orientations.

So, again microstructure is a composite body of knowledge which talks about the phase, shape, size, identity, orientation, volume fraction of the phase or the phases that are

present in a given system and the total aggregate the manifestation determinates both structural and functional properties that this solid essentially would show.

We will of course, learn more about microstructure as we go down the particular course here and would be in a position to realize that how important, it is to understand the details of the microstructure.

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And this is what I was saying that now in previous one and as well as this one you are seeing certain sketches here which essentially is little cartoon to show that why we see different kinds of lustrous or colors of the of the different grains, when we take a section of a solid and we certainly. For example, this particular solid we certainly see certain regions, which are crystalline and certain boundaries in between the boundaries of course, a very thin line.

So, when we see a boundary like this when we develop such a microstructure through a very well established practice called metallographic practice by which you can reveal the grains and the boundaries and various orientations and shapes and sizes. So, when we go through such metallographic preparation, then we adopt a process called technique called etching which is a selective chemical dissolution of the phases depending upon their electrochemical potential. And since the electrochemical potential of these boundary regions are higher than that of the grain body, so they dissolve faster and now when you expose such a structure under the microscope which also has a source of illumination.

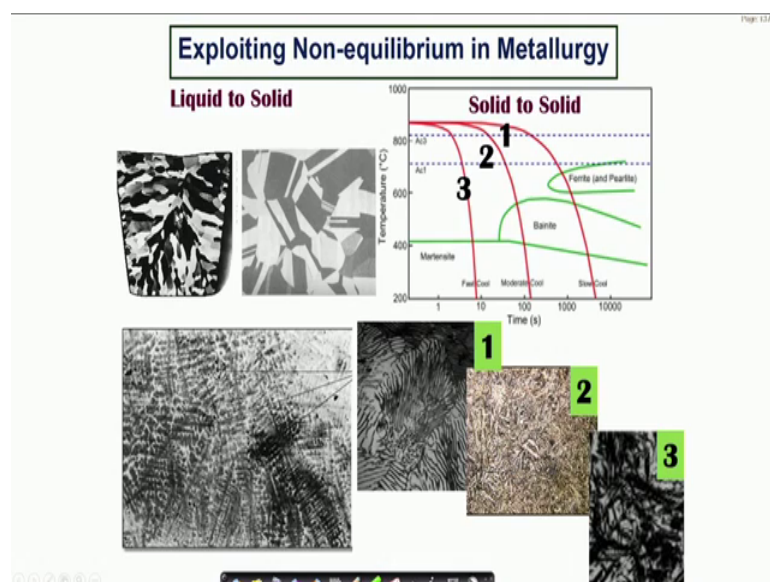
So, the light falling on this object or the surface will get uniformly reflected from the region which is less affected or less chemically attacked and hence there will be more lustrous and bright.

Whereas, the region which is in between which is nothing, but the boundary region will actually would have suffered more amount of chemical dissolution and hence will be uneven and because of unevenness will scatter more light. And as a result the situation is such that the surface will deflect more light and the boundaries will deflect reflect less. So, the boundaries will appear as dark lines whereas, the surfaces will appear as brighter regions.

So, we see a bright and dark contrast and this bright and dark contrast can extend even to the grain bodies in cases where certain grains are offered a particular orientation because of which they etch or chemically corrode more than the neighbors. So, the neighbors which corrode less or etch less will appear as bright and once which corrode more will appear as dark because they scattered more light than the neighbors.

So, this is how we actually see that bright and dark contrast and realize that, this may be a single phase entity solid, but having different orientations and different crystallites.

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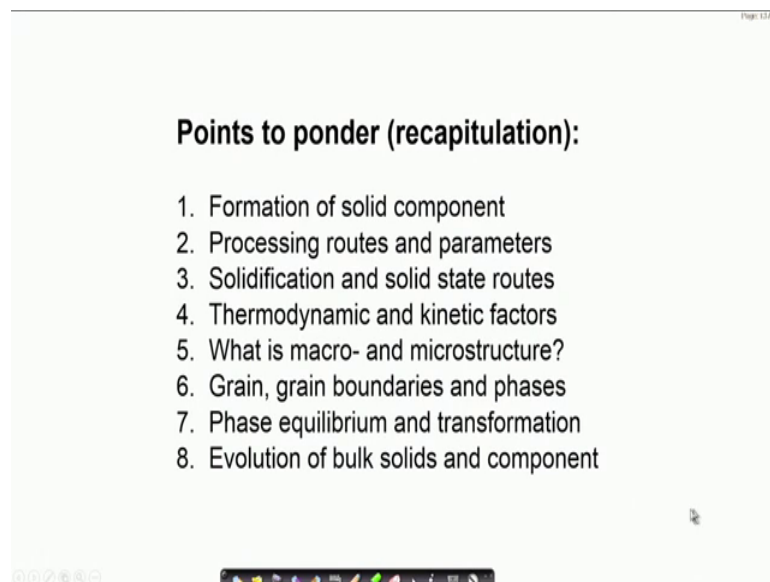


We actually in the solid state by the way this is another view of seeing the dendrites on the surface. In fact, when you melt a surface not nestled the bulk you are likely to see such very fine dendritic structures onto the surface.

So, one can see the cross section of a solid as this macro or a micro structure and onto the surface such fine dendritic patterns developed because of solidification processing. In the solid state also depending upon the way you cool through single to double phase or vice versa you actually can develop various kinds of micro structures.

And this is a typical example borrowed from steel which shows that the same steel same composition depending on the cooling rate of 1, 2 and 3 can give you microstructure which is lamellar pearlitic which can be bainite which is another aggregate and finally, also something which is martensitic. And simply going by the mechanical property one easily can understand that mechanical property would significantly differ from 1 to 2, 2 to 3 just because of differences in microstructure from the same composition of the same alloy.

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So, what is important is that we must appreciate the value of pre understanding microstructure. So, why microstructure is important? Because we are dealing with solid components and solid components or the properties of solid components would greatly depend upon not only the composition, but the evolution of the microstructure. In order to understand the evolution of microstructure we must understand the processing routes

that we followed and the process parameters that actually affected the various thermal and mechanical conditions during the processing we can actually form the solids either coming from the melt which we call stratification I did not mention, but we certainly can form solids we do form solids in various important cases from the vapor and we call them condensation processing.

We can also form solids from solid itself and; that means, that we actually can allow the solid by way of either thermal or thermo mechanical treatment to change its phase from one to another and during such transformation of phases we actually can bring in very major changes in the microstructure. And such micro structural changes or evolution will be vastly governed by the thermodynamic and kinetic principles namely the solubility limits the the diffusion coefficients and so on.

We understand that in order to approach the understanding of microstructure we go initially at lower magnification, so called macro structure and then higher magnification which is able to give us further details. And what I have not mentioned, but eventually we will have to understand in the future course is that this, so called micro structure actually is dependent upon various length scales or the description of the micro structure is length scale differ dependent.

So, when we use an optical microscope or optical illumination by optical rays, we can reveal up to a certain length scale and in that case we see that the resolution is up to a certain limit and not beyond. And if you want to reveal finer details, then we have to use electromagnetic radiation of shorter wavelength for example, electron beam and in such situation we actually can see details which are not possible to be seen under optical microscope.

So, but what we reveal in terms of microstructure comprises grains the boundaries and various shape, size, morphology and volume fraction of the phases and the the these phases or the phase aggregates basically is embodied in the concept called a phase equilibrium and phase transformation which is primarily governed by the stability index called Gibbs free energy or to be more precise the chemical potential of a particular species or component in a given phase or in a given phase aggregate.

And when the chemical potential is of a particular component is same for all the phases present in an aggregate, Then we say the microstructure or the aggregate is in

equilibrium and when we see differences between them between phases, then we see the possibility of a transformation. So, all these body of knowledge is very important for us to understand the overall manifestation of properties of both the bulk properties or bulk solids and components and also their surfaces.

So, this was our scope of discussion today wherein we understood try to made an attempt to understand the evolution of solids, either from the liquid state or from the vapor state leading to formation of various shape, size and morphologies of the phases and what we call the composite knowledge of that we call as microstructure.

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Thank you very much.