Theory of Production Processes

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Lecture – 02

Theory of Solidification: Cooling Curves

Welcome to the lecture on theory of solidification. So, in this lecture we are going to discuss about some of the theoretical aspects about solidification, and we will also discuss about the cooling curves of different type of materials what we get. So, first of all we will have the concept about the solidification, why solidification is important? How solidification proceeds? Why it happens? Then in what way it leads to a different kind of structure?

So, basically the solidification is nothing, but when we talk about the solidification in the sense of casting process, and we talk about the solidification term it is nothing, but conversion from liquid state to solid state. So, basically you are changing the phase of the material from liquid state to solid state. So, that is a kind of phase transformation process.

Now, the thing is that why solidification; we need to study in such a detail and why we need to study the solidification as regards to its importance. So, solidification is very important, because as you know that we have the materials available in raw form, and you are converting it to certain form and then ultimately you have to make it in a certain shape. So, you are basically melting it.

Now once you are melting it then all the atoms are in the random state and so, again when it will be cooled all these atoms will try to take its position. So, that is test processes through the solidification process, and it starts with the fixing the position of certain atom and then you know there will be growth of that atoms attaching to that atom which has been fixed at certain point, and then ultimately you have the grain formation and hold to all together whole matrix, you have a fixed structure. So, why solidification is important in the case of casting?

Now, as you know that in solidified products, you have the development of grains. So, now, this development of grains the process through which it goes it is very important what way it should proceed in the case of casting, as you know that the way heat is extracted the interface will grow towards in a side. So, that we will see when we talk about the theory of solidification further in the sense that, we will talk about the formation of cells also. Before that what happens mainly we are we have to see that why it happens.

Now, the thing is that in thermodynamics we have studied about the Gibbs free energy.

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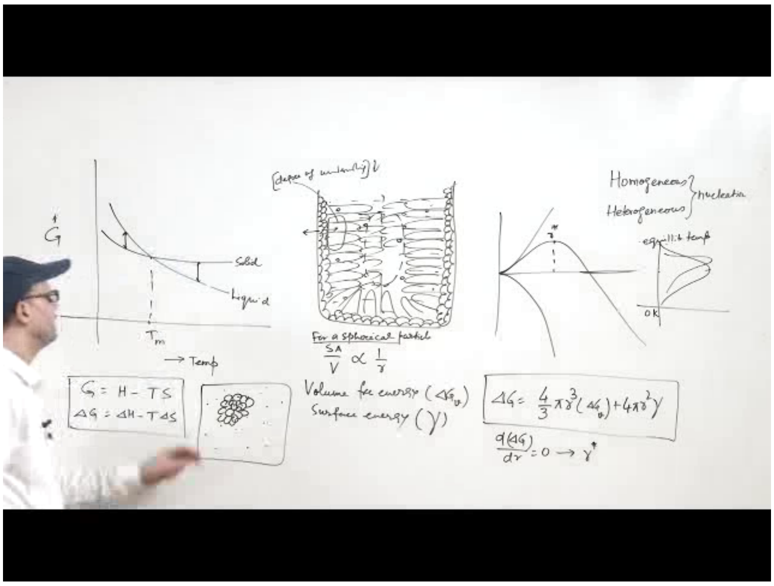

So, normally whenever in whatever state the Gibbs final free energy is less the material will try to have that particular state. So, if you find the value of Gibbs free energy for the solid and liquid state, you have such kind of curve comes, and this is basically the melting temperature. So, this is temperature and this is the Gibbs free energy line and this line is for the liquid, and this is for the solid. Now what we see is that when the temperature is made more than this melting temperature or many a times we also call it as equilibrium temperature, in those cases what happens that the this value g value is smaller for liquid. So, that is why the material is in liquid state. As the temperature comes down from here to this side, in that case what we see is the solid line has the lower value of Gibbs free energy.

So, this is basically so, as we move from here now the change in free energy has to be negative for any transformation to take place. Transformation from one state to another will only take place, when the change in free energy during that transformation is negative the final states Gibbs free energy and initial states Gibbs free energy, if that difference is positive or you know that suppose if you are coming from the this side.

So, if you go to the left hand side, you have this line as the liquid one. So, this is basically negative this change is negative, this value minus this value. So, any transformation will take place in such as this this way that if there is a liquid and the temperature is made smaller, then this liquid will transform to solid.

The solid cannot transform to liquid in this condition whereas, if you increase the temperature in that case you have again this is the negative. So, once you increase the temperature the solid will basically slowly convert to liquid. So, this is how the this is the concept of transformation and based on this Gibbs free energy and that is how the liquid changes to solid.

Further you know that this G is basically H minus T S. So, delta g will be H delta H minus T delta S. So, this is the basic concept for the change in Gibbs free energy and based on that you have the presence of any you know phase at any particular temperature. As you know that once you provide energy go for higher and higher temperatures, then in that case you have these two terms which basically govern the value of delta G.

So, depending upon the T or delta S because you have the entropy value which will be changing with the change in temperature; so, as, that is basically in the detail analysis you can refer it. So, basically when this condition comes when this favourable condition comes, that there is change in free energy that to negative sense then the transformation will proceed.

Now, what happens in the case of solidification? So, what happens that when you are melting the liquid and you have altogether, because you have once you heat the metal more than its melting temperature then the whole domain is now into the liquid state because in the liquid state you have lower free energy.

Now what happens that in this when you are coming to this line this condition as you are approaching towards this temperature line you are somewhere very close to this temperature. In that case what happens mean sometimes some of the at some localized place it may be so, that you have the nucleation starting or you have the birth of a certain particle. Now that birth may be somewhere starting and then that is may further will go into the melt. So, this way you have at many places these birth starts.

Now, if it is the equilibrium temperature condition, in that case basically once there is birth of any particle, then there are two things which happen. The first thing is that you have the creation of a surface. So, this creation of surface basically it will try to suppress this is not. So, this requires energy for the creation of the surface whereas, once you are having a volume. So, that basically does not require extra energy.

So, basically you have the favourable condition for the volume creation whereas, you will have an unfavourable condition for the surface creation. So, these are the two contrasting requirements, these are the two contrasting conditions now what happens if you look at the surface area by volume for a spherical. So, if you assume that there is spherical kind of particle which is going to be originated.

So, for a spherical particle if you look at, surface area by volume it will be proportional to one by r. So, if you take the spherical particle of radius r in that case this is 1 by r. So, basically as the r is very very small, in that case it tends towards infinity. So, very small particle once it comes out it is not able to sustain and it goes into the melt.

So, as long it will come off certain radius it will go on dissolving, and going into the melt at the equilibrium temperature. So, then slowly if what happens that you have now if the r is becoming more and more, in those cases; now what we discuss is that you have two things one is surface energy another is volume energy. So, you have two terms one is volume free energy, which is denoted by delta G v and then you have the surface energy.

So, this is known as terms this is basically surface energy, I mean term this is per unit area and this is per unit volume. So, what happens that, this value is negative and this is always positive. So, if you look at the energy you will have a surface energy term, which goes in the this direction and you have the volume free energy goes like in this direction one is positive another is negative. Now what happens as we discussed that initially, you have the dominance of the surface energy term. So, this curve goes initially positive and then after some time it comes goes on decreasing.

So, this is the basically the change in free energy will be basically 4 by 3. So, if you have two terms. So, it will 4 by 3 pi r cube, multiplied by delta G v and then you will have 4 pi r square and this is surface energy term. So, this is what the expression comes out. Now what happens that this term talking about this line, which talks about the change in free energy line now what we see that after this point, it starts decreasing because as we know that slowly this term starts dominating when the when it moves further. So, for that what we do is normally we differentiate this with respect to r. So, this is how. So, we will differentiate with this r and this way this way we will get r star. So, this is the r star

Now, what we see in this case that once you this is not as the critical radius. So, this is the concept of nucleation, because you will have the conditions at which the embryo will be developed and then, once it is able to you know stabilize then we tell it that it is nucleated. Further you will have the addition of atoms to it and then that is known as the growth. Our thing is that you will have this nucleation at random positions; we do not know where the nucleation, nucleation will be. Now in normal circumstances if the probability of this nucleation is equal in whole domain then it is a case of homogeneous nucleation.

So, you have two kinds of nucleation one is homogeneous nucleation and another is heterogeneous. So, you have homogeneous nucleation as well as heterogeneous nucleation. In homogeneous nucleation the probability of this nucleation in the domain at any point will be same whereas, in case of heterogeneous nucleation, you will have the probability at preferred sites will be more. As we discussed that for the nucleation to occur you will have you have two conditions.

One is the favourable condition is that because of the volume free energy term and because of the creation of the extra surface you have the condition which is basically detracting. Now if you have any particle foreign particle available, which gives extra surface in that case nucleation is basically you know I mean it gets some help or some you know support from where the nucleation starts. So, in that case all these if the walls have the some rough surfaces or if you have some foreign elements inside, they are acting as those sites which are the preferred locations from here the nucleation can start.

So, basically what we see is that in the case of heterogeneous nucleation, this under cooling requirement is less under cooling means how much you are increasing deeg by what degree you are decreasing the temperature. So, basically what happens once you have you know this any particle has nucleated, then you find the rate of nucleation. So, how many particles are available, and how many are turning into nucleus, how many have already nucleated what happens that once you have the zone.

So, you have different atoms they have to jump and they have to go into it and this way they have to go there. So, all these are basically controlled by certain approximations and that you can read by read from the books and so, but here the main purpose is to tell you, that you have this way once it. So, this occurs when the temperature is basically reduced comes at the equilibrium temperature goes below that.

So, slowly you are that different points this nucleation starts, and then once your nucleation starts. So, in this what will happen normally; normally the nucleation suppose starts here it will start here. So, in the case of casting if suppose it is not a surface where the. So, in the practical cases in and when you are putting a liquid metal into it, slowly the temperature comes down.

So, if the surface is rough here, most likely the first nucleation will start at the surfaces. Now in the case of solidification what happens that as you know it will be loosing the amount of latent heat. So, that heat lost will be going through this side, and heat lost will also go from this direction; so into this direction. So, heat goes into both the directions.

So, what happens once the heat which is going in this direction, it goes into the surroundings, but the heat which goes into this direction basically it will decrease the degree of superheat in the nearby region. So, here in this region the degree of under cooling is decreased. So, it is basically decreased. Now what happens if you look at the nucleation rate you have such curve which occurs.

So, here you have the melting temperature or equilibrium temperature and this is the 0 kelvin line. So, this is a rate of nucleation nucleation starts from here and it will be 0 even at 0 kelvin, and it is maximum at somewhere here. So, what happens that if the under cooling is reduced then in that case also rate of nucleation decreases.

But then there is another graph of the growth also which is similar, but the growth maximum is somewhere here, in the higher side the growth probe predominates. So, what happens in those reasons because nucleation stops and then the growth proceeds. So, initial after few initial layers you have the growth of the layers starts growth of the atom starts.

So, similarly you will have initial very fine grains because of very large under cooling and then slowly it will grow like that. So, basically what happens that you will have the initial. So, this is known as you equate type of grain formation, and then you will have the growth of these kind of grains. So, what is there, what is solidification that, we discussed that solidification is nothing, but it is a transformation from liquid state to solid state. So, that the casting solidifies in certain time.

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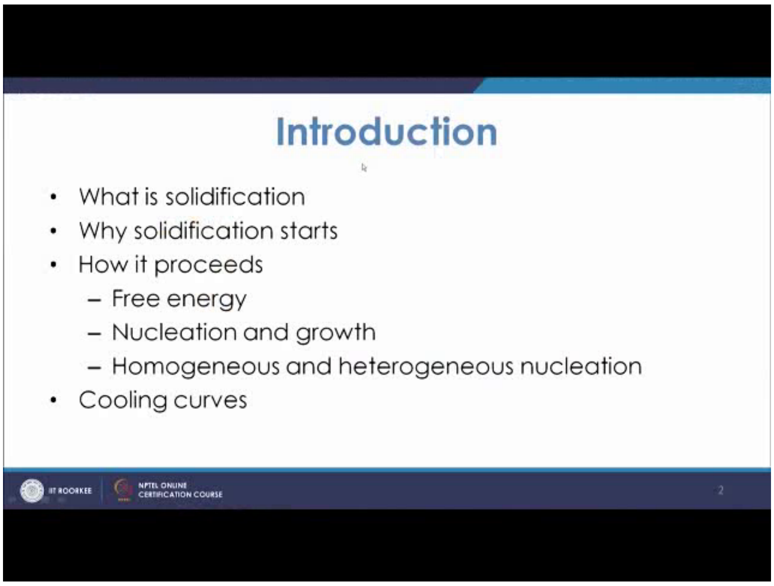

Introduction

- What is solidification
- Why solidification starts
- How it proceeds
  - Free energy
  - Nucleation and growth
  - Homogeneous and heterogeneous nucleation
- Cooling curves

Why it starts because as we know that once we heat after certain temperature, you will have the conversion from liquid to solid to liquid state and then once you cool the liquid state again has to convert back to the solid state. So, solidification starts from there. We discussed about the free energy curve, but what we have seen from that free energy curve is, that you have the values at I mean for liquid it is smaller and for solid it is higher when the temperature is higher. So, that is why it is like this.

Now, what we discussed that in the case of casting. So, it means in the region now the this growth which is going on in this direction, this growth basically is opposite to the direction of heat flow. Now what we see is this will be the last portion to solidify Because ultimately the all the heat is released in this as well as in this direction.

So, in this portion will be the last one to solidify and typically what in in case of metals we get this kind of a structure if you have a large column you will see that you have this way a columnar structure which is coming till the end of the center. So, this is in typically in metals you get it.

Now, what happens that if you control this nucleation by I mean if you increase this nucleation rate, now how can you increase this nucleation rate you may have the extra preferred nucleation sites. Now if you have the preferred nucleation sites, then in that case you can have the nucleation at different places. So, you can have the nucleation at many sites.

So, that is basically achieved by adding basically certain nucleating agents. So, in that case if you have nucleation starting from different places, in those cases you may have the structure like you have acquiesced grains coming up all together like this. So, rather than having the acquiesced system only on the sides, you will have halt all together the acquiesced structure in those cases. So, this happens whenever you use the nucleating agents into it.

Now, this happens. So, in the case of metals as we know, the in the case of metals you have the nucleation occurring and then at that place you have once it has nucleated. So, you will have an interface created. So, on one side and if the growth starts taking place so, on one side you have liquid another side you have solid. So, there is a demarcation there is a front and that basically tells that from here onwards there is liquid and and before that it was solid; however, when we talk about.

So, you have a clear demarcating line or a front that is known as solidification front. However, what happens in the case of alloys in the case of alloys you do not have that demarcation in in that alloy is available because alloys do not solidify at a constant temperature. In the case of metals they solidify at a constant temperature.

So, once the temperature comes at that temperature the temperature is stand still till there will be the transformation finished. Now in the case of alloys this does not happen now what happens in the case of alloys. So, for that we need to know the cooling curve. Now if we look at the cooling curves for metals and alloys.

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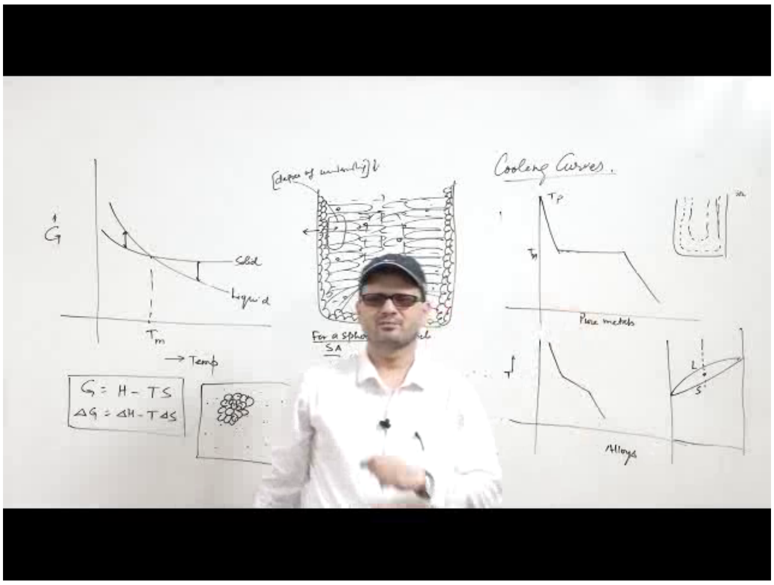

So, let us see how the cooling curves are drawn. So, cooling curves are basically the variation of the temperature as you cool the material. So, how this temperature comes down while solidifying. So, in the case of metals pure metals, the as we know that you have the here you have the this is the melting temperature, this is the cooling temperature, and this is the degree of superheat. So, this is your pouring temperature somewhere, and this is your T P this is your T M and then this comes out and goes to the room temperature.

So, this is for the case of pure metals; now what we see in the case of pure metals now in actual condition you have some under cooling which occurs at this point, and that under cooling basically promotes or starts the nucleation. Now in the case of solid as we see I mean pure metals as we see you have this temperature as a constant temperature.

So, once the temperature comes here of the entire mass, then there will be basically transformation starting there will be nucleation starting. Now as we discussed that once there is nucleation started, once their conversion from liquid to solid state some heat will be liberated. So, that basically neutralized here now as at this process the heat is also extracted. So, heat extraction is going on and at the same time the heat is also liberated.

So, it goes and also into the melt it is basically even making the temperature even further, further your the nucleation starts at different positions nucleation and growth is going on.

So, it will go and in this case you will have a plane front ready. So, you will have suppose this is the container. So, at some point of time you will have this as the front which is coming after some time. Then after when it has reached here may be that your this is reached at this like that. So, this way you can see that you have a thickness of solidified cell proceeding in certain direction and which time. So, this way it goes now in the case of alloys what happens that in the case of alloys when we have the solidification starting, as you see the free I mean phase diagram for the alloys in typical alloys you have such is the alloys.

So, what we see is in this case you have this is as the liquidus temperature and this are liquidus line and this is the solidus line. So, what we see is in this case, when the temperature comes down and solidification starts, at every point you will have certain solid and certain liquid part, and temperature is constantly decreasing.

So, it means when the solidification is proceeding there is no change. I mean there is change in temperature as there was no change in temperature in the case of pure metal here that temp change is there. So, you will have going on like this. So, this is for alloys this is for pure metals. So, what happens that in the case of alloys this is your temperature in the case of alloys the temperature goes on decreasing even during the solidification process. So, in this case this happens because of the concentration gradient you have the solute concentration difference that we will discuss in our next lectures.

So, in this case the temperature goes down. So, this cooling curve tells that event during the solidification, the temperature was going down. While in the case of pure metals the temperature was not going down during the solidification process. Now the same type of curve applies even for the eutectic materials. So, in eutectic materials you have typically you get this way, and this kind of cooling curve where the solidification is starting at a particular temperature, and finishing also at that particular temperature. In this case solidification starts here, but finish as here.

So, that temperature is different. So, this way the cooling curves talk about the solidification mechanism. Now in the case of alloys what happens here the you cannot predict that you will have such because you will have you will have no you know interface, which is clear defined. Because of the concentration gradient you will have many places where you will have the pre like structures, you will be getting that is known as generating structure. So, this is the difference between the mode of solidification for pure metals and alloys, and this is the about the cooling curve of pure metals and cooling curve for the alloys.

Thank you very much.