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Lecture - 17 Crystalline vs Amorphous

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Crystalline vs Amorphous

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Hello everyone and welcome back. So, right now we are talking about this atomization process and in past few classes we are on this topic, microstructure control right now.

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And in the previous class we have seen the solids can be categorized into two broad categories as crystalline and amorphous and we have had a discussion on what a crystalline material means and what is the structure of a crystalline material and so on.

So, I hope that was useful for many of you to understand what a crystal structure is and also this amorphous kind of structure that also we have discussed. So, I hope by now you have developed an understanding of crystalline as well as amorphous structures. So, today we are going to talk about this transition between crystalline and amorphous structure in the atomization process and why it is necessary to talk about that and understand it is the fact that amorphous materials especially, in metals if you have a glassy structure that is kind of unique, because metals are generally crystalline. They will fall in this category rather than this one under normal conditions. Amorphous metal are glassy metals. If they can be formed into an amorphous structure, these glassy metals can have unique properties which cannot be achieved by the crystalline materials.

And therefore, if somebody wants to make amorphous powder in the atomization process, it is important to understand how the crystalline or how the formation of the crystalline solid can be avoided. So, that this amorphous structure can be generated and that is what we are going to discuss as I said in today's class.

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Nucleation and Growth Kinetics >Once the embryo exceeds the critical size rt, the growth of the nucleus starts. Nucleation continues simultaneously. >Nucleation and growth rates are function of temp. Nucleation = T_m - T). > High nucleation rate and low growth - Finer grain size. > The over all transformation rate is the product of nucleation and growth rates. G, = AG, AT

You may remember this particular image that we have over here and here you can see this nucleation rate curve which is proportional to the under cooling ΔT .

So, whether the nucleation rate is high or low depending on that, the microstructure can be fine or a coarse kind of microstructure that we have seen before, but this will also have a bearing on the transition between crystalline and amorphous structure. So, let us take this nucleation rate curve separately and try and understand its implication on this crystalline to amorphous transition.

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So, we will take that nucleation rate curve separately, where the nucleation rate is plotted as a function of temperature and undercooling and we have also seen before that the temperature and undercooling, these are two interrelated parameters.

Now, during this liquid to solid transformation, the nucleation rate will be mostly controlled by the undercooling, but if you see it in terms of the temperature or the variation of the nucleation rate with respect to temperature, it is not constant it actually varies as we can see. It increases then goes to a peak and then again comes back.

Now, at this peak at a particular undercooling the nucleation rate is high or highest. So, if the liquid is cooled from this peak or from the conditions which lead to this peak, the undercooling conditions, if it is cooled from that particular condition then the solidification of the crystals can be prevented and it is going to solidify as an amorphous solid and as I said the temperature is interrelated to the undercooling. When you are on the high temperature side the undercooling is low right, because undercooling ΔT is given by this. So, if T is higher then obviously, ΔT or undercooling is going to be lower and similarly, low temperature will have higher undercooling. So, now, we need to understand what is the implication of this on the structure which is going to form in the final solid.

So, as I said before if we cool through this peak, the solidification of crystals is limited or it can be avoided and the liquid is going to transform into a glass or an amorphous structure.

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And the other aspect that we have seen before also is the cooling rate, this is the other parameter which is again interrelated to the thermal gradient and the undercooling.

So, this will have a bearing on this transition between crystalline and amorphous as we have seen before. So, we will come to that, but before that you need to understand as I said what is the bearing of this undercooling on this transition between crystalline and amorphous solids.

So, when the temperature is high in this scenario the undercooling is low and as a result, the driving force for nucleation is also low, because we have seen that the nucleation rate equates proportionately to the undercooling right and as a result of that high temperature conditions which lead to a small undercooling will give rise to a low driving force for the nucleation process.

And when you are on the lower temperature side in this kind of conditions, since the temperature is low, the transportation of atoms or diffusion will be limited, because diffusion is a thermally activated process and as a result if you lower the temperature diffusion is also going to be limited.

So, in one hand we have high temperature and low driving force for nucleation and on the other side we have low temperature where diffusion is limited. Now, you might know that the slower process is the rate controlling and therefore, on the high temperature side; that means, this right hand side here the process will be nucleation control.

The solidification process that we are talking about here that would be nucleation control, because here the nucleation is slower or limited and on the other side when you are on the lower temperature side that is on the left hand side the diffusion is limited. So, this will be diffusion control right. So, that is what you see over here. On the higher temperature side it is nucleation control and on the lower temperature side it is diffusion control on either side of this peak.

And we have understood before that the formation of the solid or the growth process, the growth of the solid is diffusion controlled, because the atoms have to come from the liquid side to the solid and get attached to it for the solid to grow right. So, therefore, we need to see that how this diffusion of atoms is going to be affected by the process parameters particularly the cooling rate.

So, that is what we were discussing here that how the cooling rate is going to affect this transformation between crystalline to amorphous structures. If the cooling rate is high, time for atoms to arrange in a pattern is low. That is obvious, because the heat is extracted fast and the liquid is cooling down quickly and the solid is forming at a faster rate and therefore, there is not enough time for the atoms to get arranged in a particular pattern.

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Microstructure control Large undercooling does not support the conditions for heat transfer and segregation associated with dendritic solidification. Microstructure shifts to equiaxed. Very high cooling rates > 10⁶ °C/s: Amorphous/Non-crystalline powder. Rapid heat extraction chills the surface giving rise to high temperature gradient (higher undercooling). Atomic difusion is needed to arrange atoms in crystals. At normal equilibrium) cooling rate time is sufficient for atoms to arrange in an order. At high cooling rate not enough time for the atomic sorting process.

So, this if you remember we have seen before also here that high cooling rate does not allow enough time for the atomic sorting process or the atomic arrangement process for a crystalline solid to form. On the other hand, when the cooling rate is low like how you have under equilibrium conditions that will allow sufficient time for the atoms to arrange right.

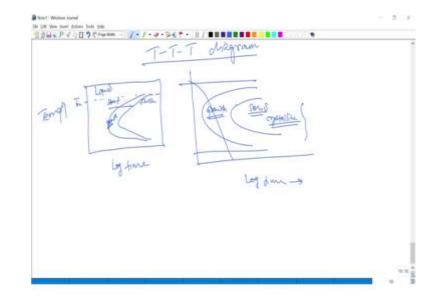
So, in other words we can say that equilibrium cooling rate or low cooling rate will lead to formation of a crystalline solid and if we can achieve a high cooling rate which will prevent this atomic arrangement of the atomic sorting process that would lead to an amorphous solid.

So, it is all about how you control the cooling rate during the process which would dictate whether a crystalline solid or an amorphous solid is going to form right.

So, we need to see that in terms of the cooling rate; that means, at what rate the heat is extracted or the temperature is lowered and how that will affect the transformation between liquid to solid ok. So, in order to understand this effect of cooling rate on this transformation, we will have to take the help of a plot known as time temperature transformation diagram or T-T-T in short.

So, this is a diagram which describes the relation between temperature and time during a particular type of transformation; that means, how you lower the temperature or at what

rate you lower the temperature that would dictate you know, what kind of transformation will take place and lead to what kind of microstructure in the final solid.



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So, if you draw the T-T-T diagram of this liquid to solid transformation then you will have something like this that the y axis is the temperature and x axis is time in log scale. So, if this is the melting point Tm, above this it is liquid as we know and as and when the temperature is lowered below the melting point, the solid is going to form.

So, at a particular temperature what fraction of solid can be formed that can be determined experimentally and when you take those fractions and then you know plot a diagram, you will get a plot like this which looks like a C, like this. So, this tells you that when you come to this curve at a particular temperature the formation of the solid is going to start.

So, this is the start curve. Similarly, there will be a curve for the completion of the process, completion of the transformation. So, this is the finished curve. So, here if you go from here to here, the solidification starts here and is completed here.

So; that means, in between you have the growth phenomena. So, this region between these two C curves is the growth of the solid right, where you have both the solid and liquid together; that means, the solid phase is still growing from the liquid ok. As it proceeds, as you allow more time and it cools down, it will reach this finishing curve and beyond that it is going to be a solid.

So, the question is whether this solid will be crystalline or not. When this transformation is completed, we reach this finishing curve. Whether the solid will be crystalline or not that is the question that we had right. So, let us try and understand how that is going to happen or what role this cooling rate will have on this phenomena right. So, how the cooling rate; that means, how it is cooled from the melting point all the way to room temperature.

How that is done you know that is what is going to dictate, whether it will be a crystalline or amorphous and that is what we will try and understand with the help of this T-T-T diagram, but that has to be discussed in more detail and we can therefore, take it up in the next class. So, for today I will stop here, but before we wind up today's class let us quickly summarize as to what we discussed today and what is today's learning.

We started to discuss this transition between a crystalline and amorphous solid during this liquid to solid transformation as it happens in the atomization process and we were trying to understand as to how one can control the process parameters in a manner that instead of forming a crystalline solid at the end of the process an amorphous solid is generated right, because this kind of amorphous metals can have very unique properties.

And with regard to that we had discussed this particular concept as to how the undercooling dictates the nucleation rate and what role the temperature plays on the nucleation rate and as well as the diffusion process which happens during the solidification.

So, in one case when the temperature is high due to the small undercooling the driving force for the nucleation is low. So, on the higher temperature side the process is nucleation controlled and on the lower temperature side since, the diffusion is limited this solidification process becomes diffusion controlled and the arrangement of atoms for the formation of the crystalline solid will depend on this diffusion process. Since, the atoms have to arrange themselves into a particular order or into a particular pattern.

So, enough time has to be allowed for this atomic diffusion to take place so that this atomic sorting or this atomic arrangement can take place. So, when you talk about the

temperature-time diagram that comes into picture and this kind of diagrams are known as the time-temperature-transformation diagram which will show the interrelation between temperature and time; that means, it will show the effect of cooling rate; that means, how or at what rate the temperature is extracted or lowered right.

So, that will dictate what kind of transport of the atoms will take place or what will be the diffusion of atoms and that in turn we will finally, dictate what kind of structure will be generated in the final solid whether it will be a crystalline structure or it will be an amorphous structure . So, this is the T-T-T diagram that we will be discussing in more detail to understand this particular phenomena, but today this is all I will have.

Thank you for your attention.