Advanced Materials and Processes
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Lecture – 55
Advanced Processess (Contd.)

Welcome to NPTEL. Myself Dr. Jayanta Das from Department of Metallurgical and Materials Engineering IIT, Kharagpur, I will be teaching you Advanced Materials and Processes. Today, we will discuss one of the very major benefit of rapid solidification processing. You may recall from our last discussions that if we quench a liquid through rapid solidification here rapid solidification means the cooling rate is high and this high value means 10 to the power 2 to 10 to the power 6 Kelvin per second.

In that case, we said that if alpha has a maximum solid solubility alpha is a solid solution which has a maximum solid solubility of B in A that solid solubility can be extend if we cool the liquid, quench the liquid very fast. And today, we will go into deeper insight of the thermodynamic aspect of that particular extension of solid solubility concept.

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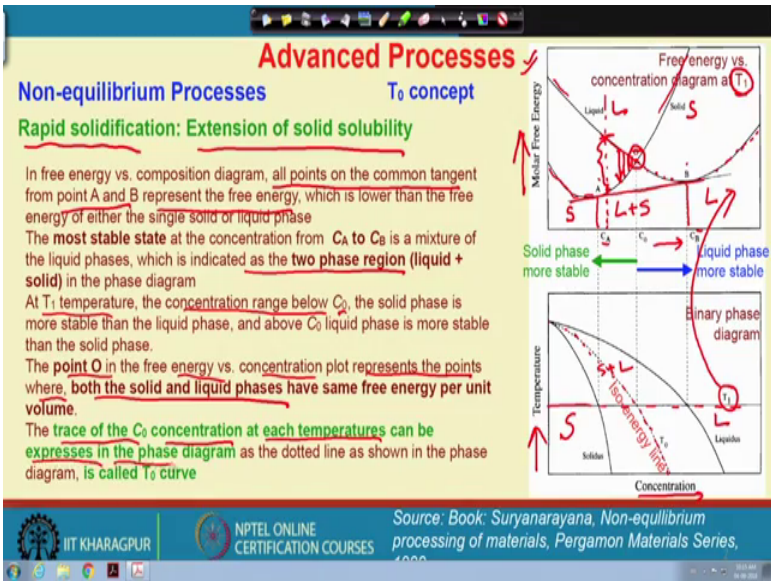

Advanced Processes

Non-equilibrium Processes

T_0 concept

Rapid solidification: Extension of solid solubility

In free energy vs. composition diagram, all points on the common tangent from point A and B represent the free energy, which is lower than the free energy of either the single solid or liquid phase

The **most stable state** at the concentration from **C_A to C_B** is a mixture of the liquid phases, which is indicated as the **two phase region (liquid + solid)** in the phase diagram

At T_1 temperature, the concentration range below C_0, the solid phase is more stable than the liquid phase, and above C_0 liquid phase is more stable than the solid phase.

The **point O** in the free energy vs. concentration plot represents the points where, **both the solid and liquid phases have same free energy per unit volume**.

The trace of the C_0 concentration at each temperatures can be expresses in the phase diagram as the dotted line as shown in the phase diagram, is called T_0 curve

Source: Book: Suryanarayana, Non-equllibrium processing of materials, Pergamon Materials Series,

So, here the point is that during rapid solidification how does the extension of solid solubility occur? Before going to this discussion we first need to understand one of the very important concept that is called T naught concept.

In a free energy versus composition diagram, all the points on the common tangent from point A to B represent the free energy. Please have a look at this diagram carefully. So, at a given temperature, let us say T 1 is a given temperature in a phase diagram this is a free energy versus composition diagram. And I have the free energy curve of solid and I have a free energy curve of liquid. So, this is for liquid, this one is for solid. And let us say if you look at the phase diagram corresponding to this free energy versus composition diagram the free the phase diagram appears to be like temperature versus concentration. And, I have selected this particular temperature T 1 and plotted the free energy versus composition diagram.

So, here we all know that in the left hand side where the free energy of the solid is lower than the liquid. So, here basically I have solid phase which is stable in the right hand side I have liquid which is stable because this is the free energy curve for the liquid. And now, if I draw a common tangent then the common tangent from A to B here liquid plus solid both are stable and that is also represented here. So, in this side I have solid in this side I have liquid in between I have solid plus liquid. So, this is a typical phase diagram explanation that we have learned.

Now, from A to B because a mixture of solid and liquid which has a lower free energy than either solid or the liquid that is why we get a mixture of solid plus liquid in this composition range at a given temperature of T 1. Now, it is basically the most stable state liquid plus solid in this particular composition range between C A to C B, is the most stable state. However, which indeed should have a two phase region.

Now, at T 1 temperature the concentration range below C 0 the solid phase is more stable than the liquid phase. What I am talking about the meta stability of the system. So, if I take a liquid. So, let us say I am talking about such a composition, ok. So, I have a liquid and then I have always a decrease of the free energy up to here. So, this can be also here means I have liquid I pull it down. So, here the solid free energy is always lower than the liquid. So, I can keep on increasing my composition. And then I can reach up to point O where the free energy of the solid and the liquid they are the same.

Now, in the right hand side the liquid is always stable liquid is always stable than the solid phase. So, I can draw a this the locus of point O with respect to different temperature means the free energy composition diagram at different temperature I can draw the locus of this point O and I will get basically this particular curve. And, this point O in the free energy versus composition plot represent the point where both the solid and liquid phase have the same free energy level that already understood by us.

So, the trace of this C 0 concentration at each given temperature can be expressed in a phase diagram and this dotted line is called as a T naught curve, ok. So, this dotted curve is basically the T naught curve. So, there is some other important factor related with this T naught curve. What I want to mean that if I start with liquid let us say I have this is my average composition I start with the liquid I cool it down. And so, in this particular composition range I have always a decrease of the free energy, ok.

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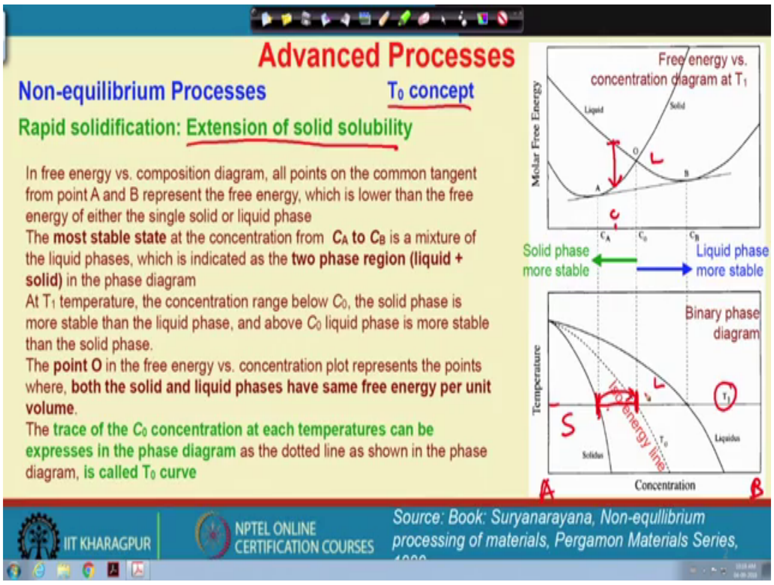

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And, in such a case I do not need the liquid to be partitioned means partitioning means partitioning of the alloying elements I am talking about. So, if I have a liquid composition which is here C, I do not need A and B type of atom to diffuse, so that this liquid can transform into the solid. So, in this particular case the liquid can be directly transformed into solid without any atomic diffusion to occur means long range partitioning I am talking about.

So, it is very clear that in the left hand side of the O, I really do not need any partitioning of the alloying constituent means the enrichment of B and enrichment of A component does not require at all. So, the composition of the liquid and the composition of the solid will be remain same. So, even though at this T 1 temperature the maximum solubility of this solid phase is up to here, but I can extend it up to this composition, ok. So, this is the fundamental aspect of this T naught curve to enhance the extension of the solid solubility.

So, from such a composition of B; let us say this is the B side and this is the A side I can extend the solid solubility up to here, but beyond this it is not possible and here liquid is stable liquid is stable and I need partitioning of the long range partitioning of the atomic species.

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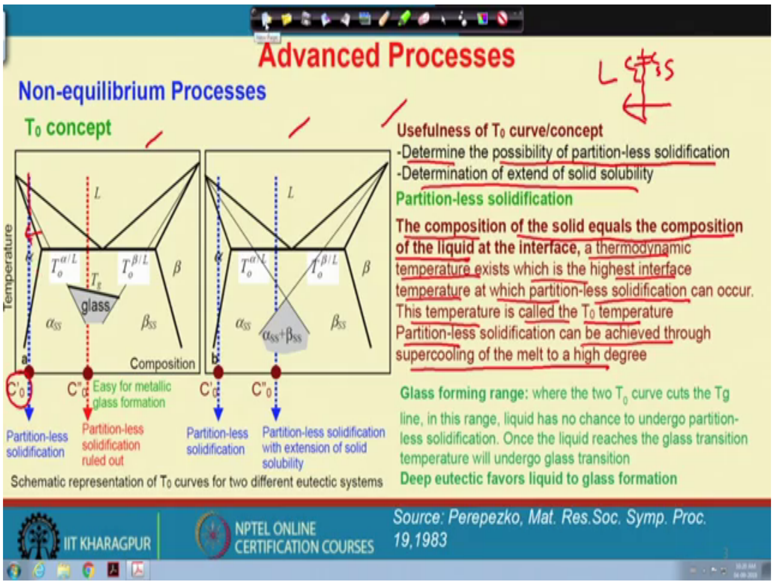

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T_0 concept

Usefulness of T_0 curve/concept

-Determine the possibility of partition-less solidification

-Determination of extend of solid solubility

Partition-less solidification

The composition of the solid equals the composition of the liquid at the interface, a thermodynamic temperature exists which is the highest interface temperature at which partition-less solidification can occur. This temperature is called the T_0 temperature

Partition-less solidification can be achieved through supercooling of the melt to a high degree

Glass forming range: where the two T_0 curve cuts the Tg line, in this range, liquid has no chance to undergo partition-less solidification. Once the liquid reaches the glass transition temperature will undergo glass transition

Deep eutectic favors liquid to glass formation

Schematic representation of T_0 curves for two different eutectic systems

Source: Perepezko, Mat. Res.Soc. Symp. Proc. 19,1983

So, once again if we think about the usefulness of this TTT curve first it assists basically to determine the possibility of the partition-less solidification. Means, the left hand side of this T naught curve will give us a partition less solidification also it can assist the extension of the solid solubility.

So, we need to think about what is really this partition-less solidification means the composition of the solid is equals to the composition of the liquid at the interface. Means I have liquid and I have a interface where solid so, the solid phase is growing. So, the composition here of the liquid and the composition of the solid they remain the same. So, these are equal. So, a thermodynamic temperature that exists where the highest interface temperature at which the partition-less solidification can occur and this temperature is called as a T naught temperature.

So, the partition-less solidification can be achieved through supercooling or undercooling of the melt to a high degree. So, if undercooling goes much higher we call it as a supercooling. Now, please have a look at these two diagram that I like to show you. So, we understood that if we take a composition that is C dash 0 and cool it very fast or undercool it, then we will get actually a alpha here and alpha here has a is composition that is definitely a composition that is lower than the maximum maximum solubility of beta.

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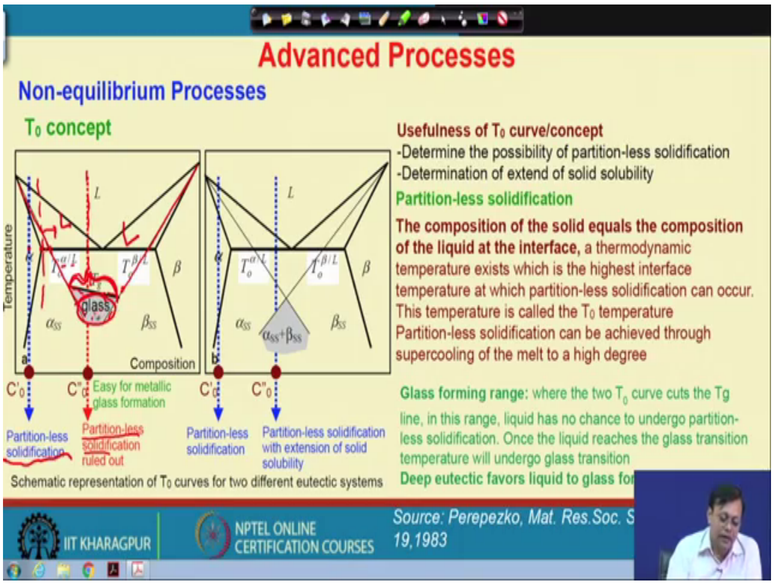

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However, if we can still go further into this side and then I can quench it and still I will get alpha. So, this is actually the partition-less solidification because in this case we do not need any atomic species to be partitioned. But, if we go a little bit away from this T naught point where alpha and liquid a coexist in this case liquid is mostly stable huh. On the right hand side if we come then also here liquid is stable. And if we simply a quench a liquid then we do not get any partition-less solidification. So, here it will be partitional solidification means at the solid liquid interface the atomic species need to be partitioned means long range diffusion of atoms are required.

And, now if the T g is relatively higher, then instead of partitioning to occur we can quench the liquid and transform the liquid into a glassy phase. So, this is the composition range where it is possible, but one thing, please have a look here the T naught line are more steeper at the same time they do not cut each other. So, that is why I get a small window of getting glass in this composition range. So, if the eutectic is more deeper and deeper and this T naught liner are more stiffer then I will get such a possibility to get a glass.

Now so, this is my glass forming range. On the other hand in this case you can see T naught lines are not so steep and they cut with each other. And in this case here we can again get a partition less solidification with extension of both the phases. How? We quench it and since this is just below the T naught line. So, if we reach here then I have a possible to get a super saturated that alpha and super saturated beta and here if T g is somewhat here then we do not get actually the T g I mean the glass transition here.

So, the glass forming range where the two T naught curve cuts the T g line in this range this is I am talking about the liquid has no chance to undergo a partition-less solidification, once the liquid reaches to glass transition temperature then basically it will undergo a glass transition and the liquid transform into a glass. So, the deeper the eutectic then the steeper the T naught line; and we will get a better glass forming range and this is one of the very important aspect that you should remember to understand the glass formation in any of the near eutectic composition. We will discuss more detail today.

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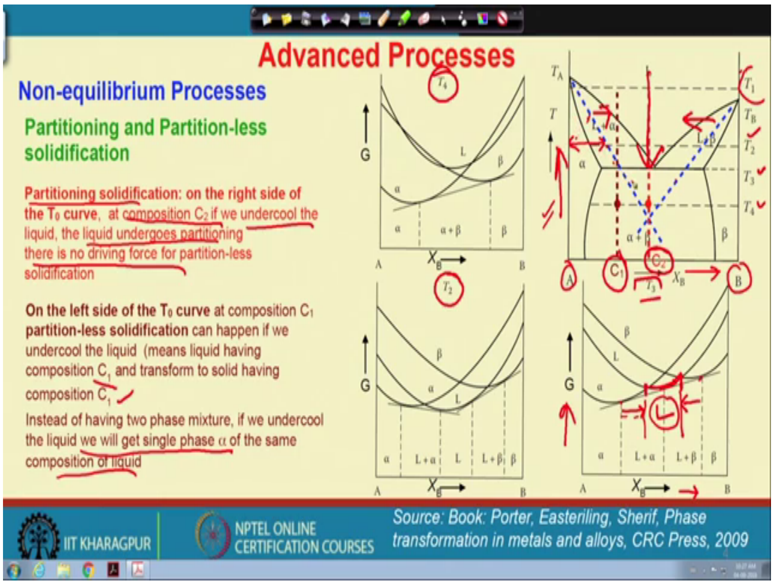

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Partitioning and Partition-less solidification

Partitioning solidification: on the right side of the T_0 curve, at composition C_2 if we undercool the liquid, the liquid undergoes partitioning there is no driving force for partition-less solidification

On the left side of the T_0 curve at composition C_1 **partition-less solidification** can happen if we undercool the liquid (means liquid having composition C_1 and transform to solid having composition C_1

Instead of having two phase mixture, if we undercool the liquid we will get single phase α of the same composition of liquid

Source: Book: Porter, Easterling, Sherif, Phase transformation in metals and alloys, CRC Press, 2009

So, far we were talking about this partitional and partition-less solidification. So, once again let us try to recapitulate with a binary very simple phase diagram here this is the composition of the B and here two species or atomic species one is A and B and this is the temperature axis of Y. So, below T naught below T naught line these are the two different T naught line one is for the liquid beta and another one is for liquid alpha. So, in that case actually we get a super saturated solid solution of alpha up to this range let us say if I think about this temperature. And now, I have selected T 1 T 1 you understand which is at a very high temperature and then interesting will be T 2, T 3 and T 4.

So, the free energy versus composition diagrams are shown here this is for T 3 this is 4 T 2 and this one is for T 4. So, here in case of T 2; we can see that up to here I can extend the solid solubility of the alpha phase here I can get the maximum solid solubility of beta which can be extended up to here alpha can be extended up to here and in between it will be liquid which is stable.

So, in this case the partition-less solidification range for alpha is up to here, partitional solidification require within this particular composition range. So, so, they let us say the partitioning solidification on the right hand side of the T naught curve. So, right hand side means in this side and here for T naught curve this is in the left hand side. So, the composition C 2 if we undercooling it. Let us say we have taken a composition C 2 and then we are undercooling it, or supercooling, it the liquid undergo a partitioning and there is no driving force for partition-less solidification that we already understood because liquid has the highest the lowest a free energy, ok.

So, I do not get any driving force to produce. Let us say super saturated alpha or beta because this is the lowest one, definitely from the stability or point of view alpha beta mixture should be the most stable one, but when we are talking about meta stability then the liquid has the has the lowest free energy here. So, on the left hand side of the T naught curve at composition C 1 partition-less solidification can happen if we undercool the liquid means liquid having composition C 1 and transformed to a solid having a composition C 1, that is already understood by us and instead of having two phase mixture if we undercool the liquid. Then we will get a single phase alpha of the same composition of the liquid in this side.

However, if we take a C 2 composition if we take a C 2 composition in this particular case then we need a partitional solidification to occur in this range and if glass transition temperature is little bit higher, then we will get a glass. Otherwise let us say at T 4 also what we have that here. So, liquid is present and almost let us say we can they are alpha and beta they have basically the alpha and beta they have the lowest free energy.

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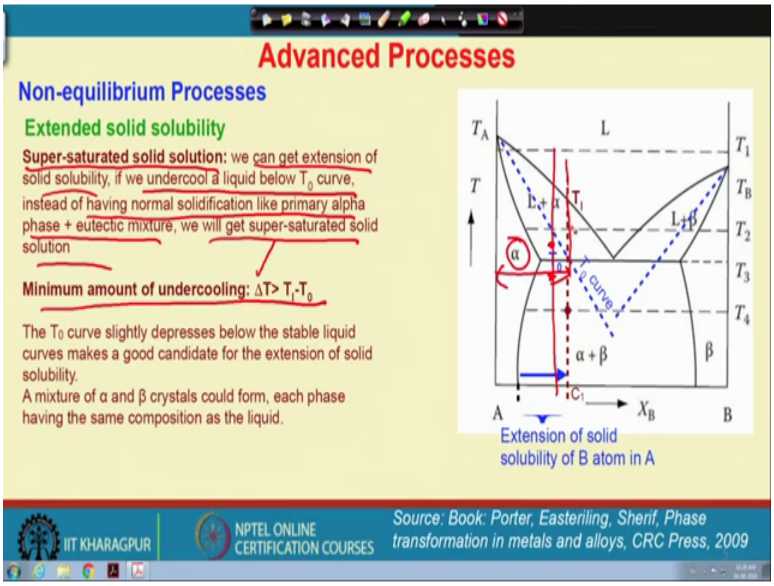

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Extended solid solubility

Super-saturated solid solution: we can get extension of solid solubility, if we undercool a liquid below T_0 curve, instead of having normal solidification like primary alpha phase + eutectic mixture, we will get super-saturated solid solution

Minimum amount of undercooling: $\Delta T > T_l - T_0$

The T_0 curve slightly depresses below the stable liquid curves makes a good candidate for the extension of solid solubility.

A mixture of α and β crystals could form, each phase having the same composition as the liquid.

Extension of solid solubility of B atom in A

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Source: Book: Porter, Easteriling, Sherif, Phase transformation in metals and alloys, CRC Press, 2009

Now, with the same concept if we if we continue so, the extension of solid solubility means we can create a super saturated solid solution. So, in this particular range not only we get a extension of the solid solubility, but also we can create a super saturated solid solution, because we can get extension of the solid solubility and we undercool a liquid below T naught curve instead of having a normal solidification with a primary alpha phase plus eutectic mixture, we will get a super saturated solid solution. What I want to mean if I simply think about such a composition range or a composition in the left hand side then here I should get a primary alpha and below this I should get alpha plus eutectic mixture of alpha plus beta that is expected here, but if we quench very fast, then I will get a single phase alpha.

So, instead of getting a eutectic microstructure and primary alpha phase we can simply get a single phase alpha, ok. So, this is the benefit of the rapid solidification. However, one should keep it in mind that the minimum undercooling delta T should be T l minus T naught. So, let us say for a this particular composition of C 1 we need this minimum amount of undercooling so that we can overcome this T naught curve and come to below the T naught line.

So, the T naught curve slightly depresses below the stable liquid curve makes a good candidate for the extension of the solid solubility. A mixture of alpha and beta crystal will form each phase having the same composition of the liquid that we already talked about in my earlier slide.

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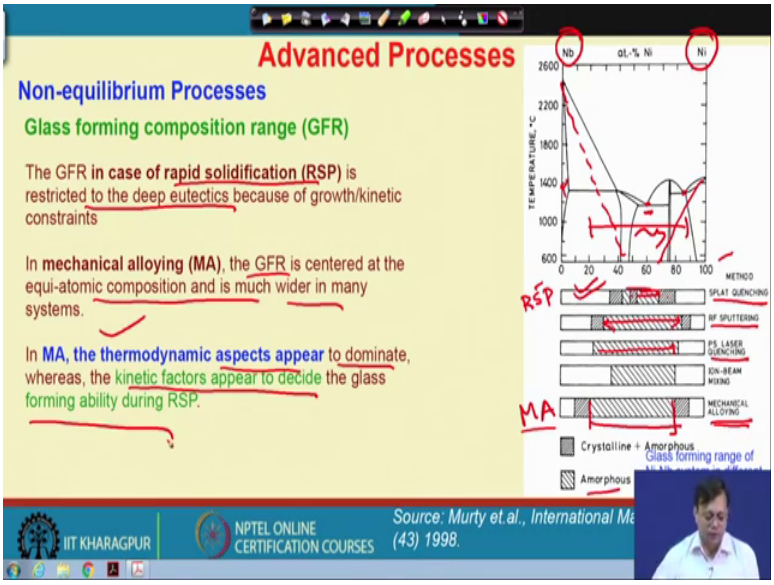

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Glass forming composition range (GFR)

The GFR **in case of rapid solidification (RSP)** is restricted to the deep eutectics because of growth/kinetic constraints

In **mechanical alloying (MA)**, the GFR is centered at the equi-atomic composition and is much wider in many systems.

In **MA, the thermodynamic aspects appear** to dominate, whereas, the kinetic factors appear to decide the glass forming ability during RSP.

Glass forming range of

Source: Murty et.al., International Ma (43) 1998.

Now, we have discussed that during mechanical alloying we can produce amorphous phase, during rapid solidification processing also we will get some glass forming range. However, the question comes to our mind whether this glass forming range is the same for all the different non-equilibrium processing or not.

So, people have investigated that particular aspect and find out that in case let us say of such a phase diagram where you have multiple different reactions. So, like here you have another one eutectic here is another eutectic here you have a primary phase which is alpha and so on. So, in that case let us say this is a just a case in case of nickel niobium system. So, if we go for this splat quenching method then amorphous phase is possible a near eutectic range. So, this is the range, where you will get amorphous phase, but beyond this range you may get a mixture of the crystalline plus amorphous phase nearby region or let us say in this case.

Whereas, let us say for sputtering you will get a larger range; means a sputtering phenomena you already know and let us say the laser quenching you will get a larger. However, in case of mechanical alloying actually you will get a much larger amorphous range than a splat quenching or melt spinning. So, this is let us say a RSP rapid solidification processing and this is the comparison with the mechanical alloying and mechanical alloying gives us a relatively wider range of the glass forming ability. And, in case of rapid solidification processing we need a deep eutectic, because the T naught line that should not cut each other even you decrease the temperature. And if glass transition temperature is higher than you will get.

So, in this case let us say I can simply extend the T naught curve and in this case let us say T naught curve. And then I may get a composition range where this glass formation is possible, whereas such mechanism or thermodynamic understanding does not require in case of mechanical alloying, where the crystal which is undergoing excessive alloying or super saturation then the crystal free energy become higher than the liquid, or the amorphous phase. And therefore, the crystal transform into a into a glassy phase actually.

So, the glass forming range a at the center equi atomic composition is much more wider in many of the system. So, in case of mechanical alloying the thermodynamic aspect appeared to be dominate where the kinetic factor appears to decide the glass forming during the rapid solidification processing.

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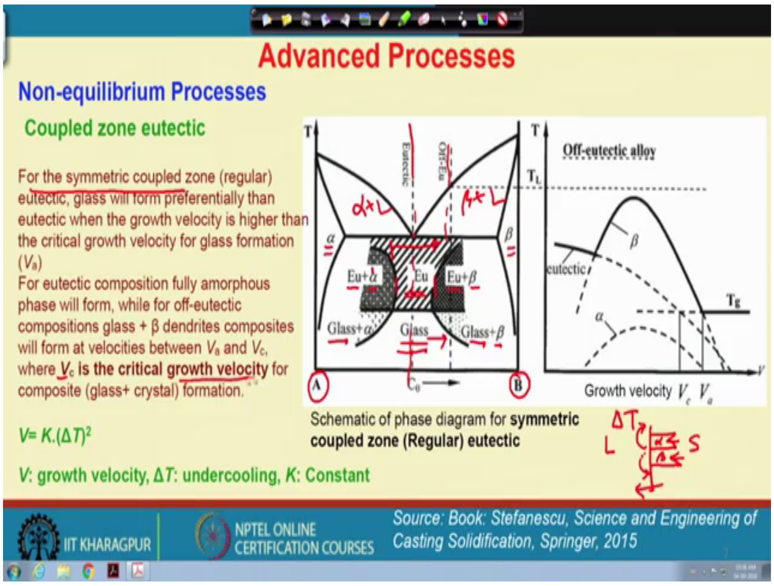

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Non-equilibrium Processes

Coupled zone eutectic

For the symmetric coupled zone (regular) eutectic, glass will form preferentially than eutectic when the growth velocity is higher than the critical growth velocity for glass formation (V_a)
For eutectic composition fully amorphous phase will form, while for off-eutectic compositions glass + β dendrites composites will form at velocities between V_a and V_c, where V_c is the critical growth velocity for composite (glass+ crystal) formation.

$V = K.(\Delta T)^2$

V: growth velocity, ΔT: undercooling, K: Constant

Schematic of phase diagram for **symmetric coupled zone (Regular) eutectic**

Source: Book: Stefanescu, Science and Engineering of Casting Solidification, Springer, 2015

Now, there are two other important aspect we must try to understand. These are called as coupled growth. What I want to mean if I have a liquid and solid interface and I have a solid interface then this interface is growing inside the liquid. And let us say for a given delta T; delta T here is the undercooling and in that case I may need some atomic species to diffuse to the localized region or may not need if it is in case of a of a super saturated solid solution. But, we cannot generalize the situation in case of a eutectic; means, if I take such a composition is it necessary to get a hundred percent eutectic microstructure only when the only when the composition just lie at the eutectic point? So, probably it is not because we have two phase that is growing together. So, I have alpha phase, I have beta phase. So, here it is alpha I have beta.

Now, these two phase are growing and at the inter phase the partitioning is occurring partitioning of the alloying element means B type of atoms are enriching B beta and A type of atom are enriching alpha. Now, if we think about the individual growth rate of alpha and beta they may or may not be similar. Even though if I take a off eutectic composition and cool very very slowly then if this growth rate is almost equal then we will get a wider window for getting a coupled growth. Here coupled growth means the growth of alpha and beta will occur together. So, one will not dominate with other, ok.

So, in that case I will get such a eutectic microstructure for a wider range, but this can happen only when the coupled growth zone or coupled zone off eutectic is symmetric. In this case you can see that the eutectic plus alpha; this alpha basically means the primary alpha where alpha plus liquid exists here beta plus liquid exists here in this right hand side it is eutectic plus beta ok.

So, if such two different coupled growth zone exists and eutectic has a quite wider and symmetric type of coupled zone and if we cool a liquid of such a composition it is much easier to get a glass,. And, in this particular case if we go to right hand side of the composition will glass plus beta in the left hand side we will get glass plus alpha, but the question comes here how this explanation is valid. Means; what I said if the undercooling is very slow what does it mean undercooling is very slow means the growth rate is also very slow. Here the growth rate is linked with the velocity growth rate I am talking about the growth velocity of the solid phases.

So, V c let V is let us say the growth velocity. So, this growth velocity scales with the undercooling that we produce that is by delta T square. So, if 2 degree undercooling is more than the velocity will increase 4 times, ok. So, it multiplied by a constant. So, V is a growth velocity and delta T is the undercooling and K is a constant. For a very slow growth velocity within such composition range we will get a eutectic.

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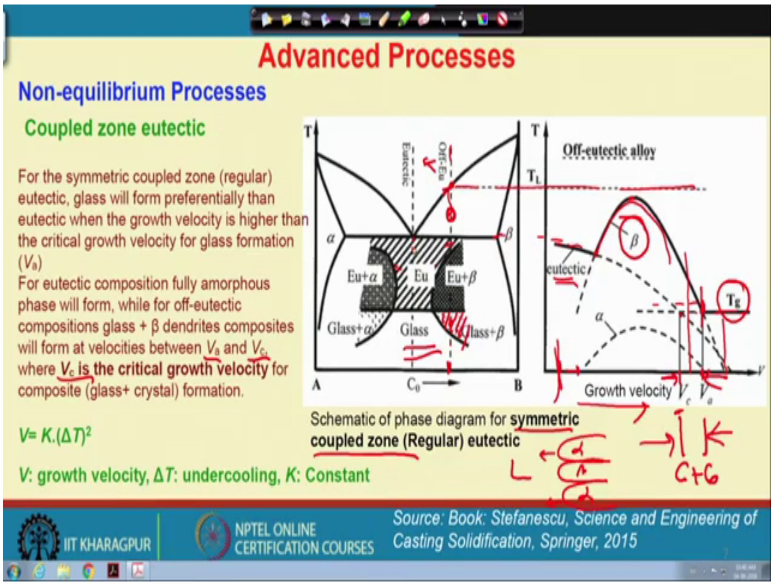

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Schematic of phase diagram for **symmetric coupled zone (Regular) eutectic**

Source: Book: Stefanescu, Science and Engineering of Casting Solidification, Springer, 2015

But, let us say I have taken a off eutectic alloy let us imagine at this moment that I have taken a composition that is off eutectic alloy and I am showing it here. So, a in this very slow growth velocity we will get a eutectic. Now, if I keep on increasing the growth velocity I will get actually I will get actually beta basically means that the pro eutectic beta I am talking about and so, the solid liquid interfacial temperature and the temperature of the interface will also increase actually because the heat will recalescence will occur and so on.

On the other hand if I keep on increasing the growth velocity and then very fast cooling. iIf we apply I will get a glass because if the temperature the temperature reaches below glass transition temperature which is definitely lower than that. So, I will always get a T g here and so, eutectic temperature is here and the temperature for beta is lying somewhere here, right. So, this is the liquidus temperature I am talking about. So, this is the case of the temperature we are talking about with the growth velocity. However, I if the cooling rate is somewhat in between this region then I will get a mixture of beta plus g the glass.

So, V a and V c these are the two the velocity range within which we expect that if V c is the critical growth velocity beyond which we can forget a composite microstructure;

means if the velocity growth velocity lie in this range then I will get a crystal plus glass. And, this is the understanding we need that if in such a region we can reach when the growth velocity is just above the critical velocity we can form to a glass, what if we shift the composition to left hand side then we have a wider window in order to form a glass.

So, this is the explanation came due to the symmetric nature of the coupled zone or a regular eutectic which is explained through that I have two phases which is growing in a liquid here I have alpha, I have beta and I have alpha. So, they are growing together and the growth rate are very much close to each other and they are quite symmetric in nature in terms of the growth coupled growth. And so, if the undercooling is very slow very very slow velocity will be achieved in that case we will get a eutectic even though the composition is not really at the eutectic point.

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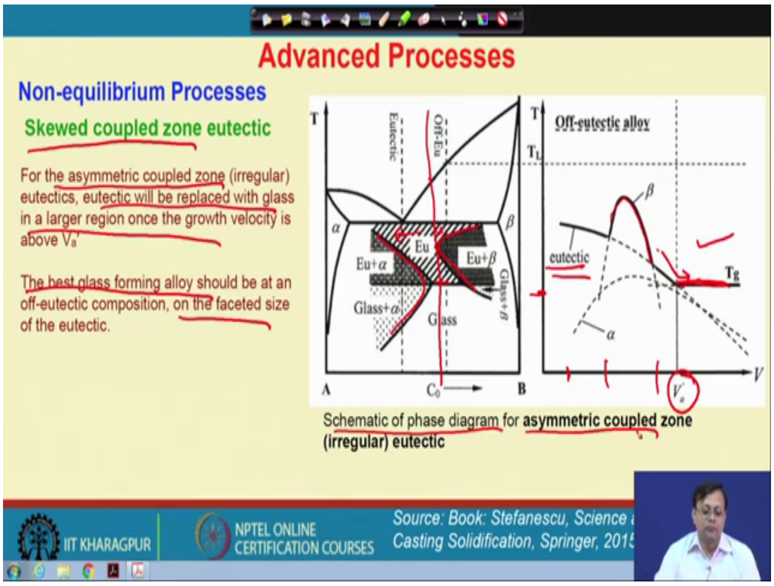

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Skewed coupled zone eutectic

For the asymmetric coupled zone (irregular) eutectics, eutectic will be replaced with glass in a larger region once the growth velocity is above V_a'

The best glass forming alloy should be at an off-eutectic composition, on the faceted size of the eutectic.

Schematic of phase diagram for asymmetric coupled zone (irregular) eutectic

Source: Book: Stefanescu, Science
Casting Solidification, Springer, 2015

Now, on the other hand these coupled zone may not be symmetric and it could be asymmetric. So, what does happen if the zone is asymmetric in nature? You can see here, so, this is asymmetric zone when eutectic formation probability is within this composition range and this is called as a skewed coupled zone eutectic. For a asymmetric coupled zone eutectic or a irregular eutectic will be replaced with the glass with a larger region of the growth velocity if it is applied.

So, I need a much larger velocity. So, the glass formation will may not be so easier like the other one actually. So, the best glass forming composition should be always an off eutectic composition where the faceted size with a faceted size of the eutectic is pronounced. And that is why it has been shown. Instead of getting such kind of composite we can always get a and it has been observed this off eutectic composition are always better, and we can produce such a undercooling and we can bypass the formation of the eutectic and overcoming by formation of a glass.

So, let us say if the velocity is very slow here also again we will get a eutectic. And let us say if I have a chance to increase the velocity then we will get a beta, but here T g is lines in this temperature range. So I will get if I can cross this velocity and go above this velocity V a I will get a glass in this range. So, this is just a schematic of the phase diagram of a asymmetric coupled zone. So, usually when designing a composition for formation of a glass or rapid solidification processing to achieve a glass we must consider all these coupled zone below the eutectic exist and the growth velocity of the individual phases, and also the concept of T naught should be considered.

So, with this we complete the discussion on the advanced processes this week. And we will continue with new topic in the next class.

Thank you very much.