**Advanced Materials and Processes**
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**Lecture - 10**
**Amorphous Materials Part – IV**

Last class we were talking about the glass formation and the various criteria of glass formation. We talked about the thermodynamics of glass formation, we talked about the kinetics of glass formation. As you can see here, what we have is the critical cooling rate which talks about the kinetic constraint. That means, if you can suppress a crystal you can get a glass.

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a) metallic glasses b) bulk metallic glasses
c) fluxed bulk metallic glasses
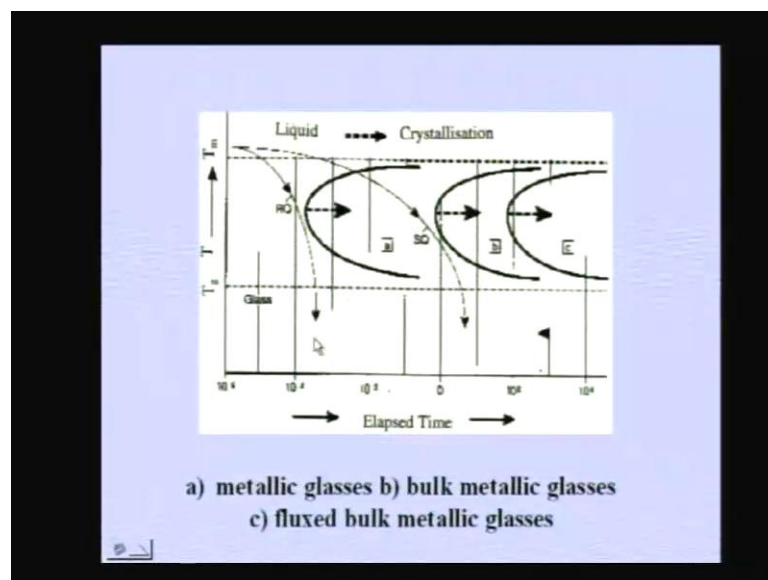
And this is for getting a bulk metallic glass. That one can have, if you can have the crystallization more difficult in some systems. You can have crystallization, I mean glass formation at a very slow cooling rates and that is, what is a bulk metallic glass. Or bulk glasses in silicate systems, that you have seen. We also talked about fluxing the glasses, liquid to get a higher glass forming ability.

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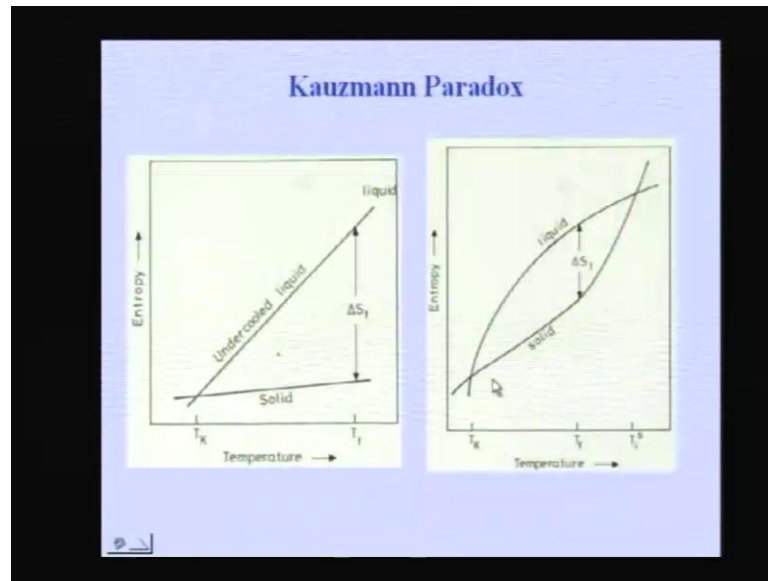


We started talking about the Kauzmann Paradox. You know that if you can take a liquid keep on cooling it below a certain temperature. Once, you come to a certain temperature the entropy of the liquid goes below that of the crystal, which is a paradoxical situation. And at that condition the liquid will undergo a glass transition, this is what is called ideal glass transition temperature T K or the Kauzmann temperatures.

We also talked about the entropy catastrophe. That means, if you take a solid keep on heating it to above the melting point, the entropy of solid keeps on increasing. And once you reach a particular temperature, which is called the TSI or the entropy catastrophe temperature. At that temperature the crystal will have higher entropy, then that of the liquid which is again a paradox.

And as a result crystal will catastrophically melt. And that is a situation which is usually not observed in practical applications. Because, the temperatures that you need to go or much higher than the melting point, which is not usually possible. So, we talked about this.
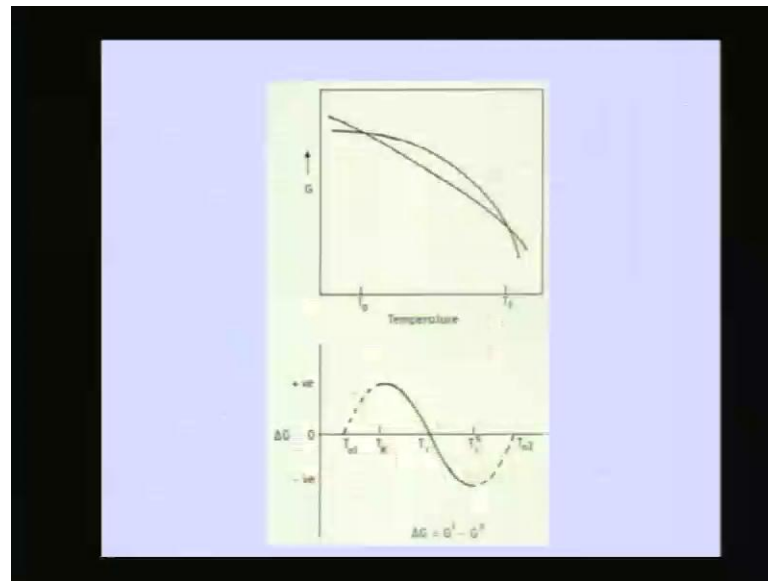
We also talked about the possibility of various temperatures, at various at under different conditions. For example, the observation of you can see here, the melting point which is the T F, and if you keep on going below the melting point at the temperature T K. One thing that you need to see is that, last class there was a kind of confusion among this delta G whether it should be 0 at T K, as we are talking of this delta G, which is the delta G between the liquid and the crystal. We are not taking of the delta G between liquid and the glass. So, what is being plotted here is a liquid and crystal. So, free energy of the liquid and free energy of the crystal.

So, because we are taking of the free energy of the liquid and the crystal in solid., so as a result this free energy of the crystal in solid is always lower below the melting point. As a result, if you talk of G L minus G S, G L minus G S is always positive at temperatures below the melting point. And that is what we are plotting here. And once you come to a temperature below T K it falls down. But, this part is shown doted. Because, once you reach T K already the glass forms. So, there is no question of talking a temperature below the T K, because by that temperature the liquid has already to transform to a glass. So, there is no liquid left out for it to become a crystal.

So, if you talk of any temperatures below T K for the liquid to be under cool below T K. We cannot under cool liquid below the T K. Because, once you under cool a liquid to T K by that time the entropy of catastrophe comes into a picture or the Kauzmann Paradox

comes into picture. So, liquid cannot remain as liquid and it immediately transform to a glass.

And once, you it has transform to a glass, it is a glass that we have and no more a liquid. So, we cannot still talk about the free energy of the liquid below the T K. So, as a result though thermodynamically one can really calculate that a free energies. And talked about what is called a T naught temperature, that T naught has no meaning. Because, by that time you reach T K all ready a liquid has vanished it has transformed to a glass.

So, there is no liquid left out for it to transform into a crystal. So, as a result we show this part dotted. Similarly, if you are on the other side above the melting point, if at all you can heat a crystal above the melting point, keep on heating the crystal above the melting point. The free energy of the crystal will be higher than that of liquid above the melting point.

And as a result the delta G will be negative. Because, we are showing delta G as G L minus G S you can see here. Because, it is G L minus G S, G L is smaller than G S above the melting point, this part is negative. But, as you keep on increasing the temperature we have as we saw in the previous slide ((Refer Time: 05:53)). The entropy of the solid keeps on increasing.

And once you reach a temperature TSI, at that temperature you will see that the entropy of the solid will become equivalent of the liquid. So, even though the delta G is a negative. That means, free energy of the solid is higher than that of the free energy of the liquid there, at that particular point of time, but because of this entropy paradox coming into picture. The crystal cannot remain as crystal and it has to catastrophically transform into a glass.

That is, what would happen? For example, we have seen a number of cases you can take a crystal, keep on bombarding it with some kind of a irons. And we know that, you keep on increasing the defect concentration unit. And as a result the free energy increases and as the free energy increases, the crystal will have a high free energy.

But, at that same the entropy will be so high in the system, that it can transform to an amorphous phase beyond a certain critical concentration of the defects. So, though ordinary conditions here as you can see. The free energy of the solid is higher than that

of the liquid. But, we reach a condition where the entropy is become 0. And once, this happens the crystal is no more stable.

So, but any way this is a temperature which is only theoretically possible. But, the practically reaching this temperature is very difficult. So, usually in text books you do not come across this a lot of people who are doing research in this area. But, basically you do not talk about this. Whereas, T K is to some extend achievable and in a number of systems we have achieved the liquid under in glass condition, below the T K or T G whatever you want to call it.

Some people refer to it as T G, glass transition temperature some people call it as T K which is Kauzmann temperature. But, the both are basically the same. Only reference is T G is the one, which we usually measure when take a glass and start heating it in a DSC. And it shows you a hump I showed you, a small step and that step is what is called the T G, which is second order transition.

Whereas, here the T K that I am taking is during cooling, the liquid is being cooled and you reach a temperature. Where, the entropies gives you a paradox situation and that is where the liquid transform to a glass. So, one is on the heating side we are talking about it. But, is another on the cooling side, but basically both are the same, the temperatures are more or less the same.

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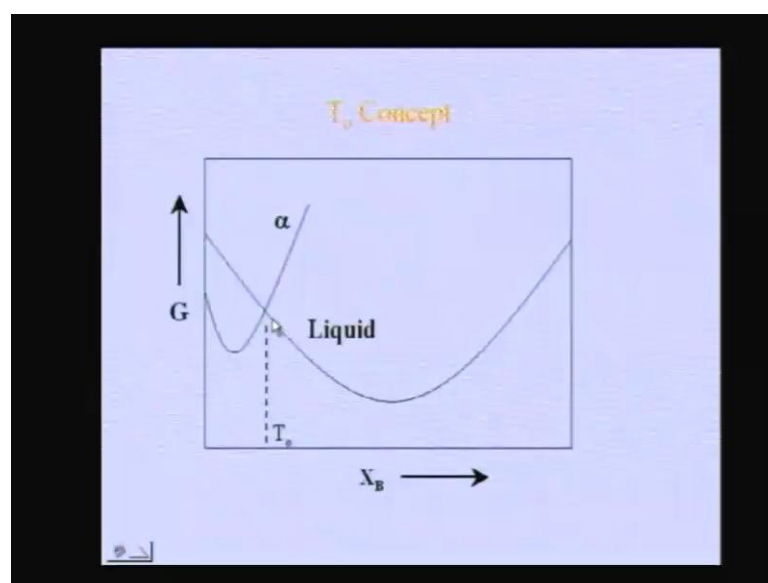
So, we started talking about the T naught concept in the last class. We know that, if we are at any composition which is on the left side of the intersection of the free energy of the liquid and that of the alpha. At those compositions the alpha can come out of the liquid with the same composition, because there is a driving force for the alpha to form for the liquid having the same composition. This is what we call partition less solidification, whereas if the composition is on this side, on the right side of the T naught point. We see that there the alpha cannot come out of the liquid. So, the liquid will remain as liquid. In fact, for people who are interested to produce a partition less solidification to have partition less solidification. Why do you want to have partition less solidification? If you want to have solid solutions with extended solid solubility, we would like to have partition less solidification.

If you have extended solid solubility as I told you, you can have higher solid solution strengthening. At the same time by precipitating a second phase, you can have large volume fraction of the second phase, we talked about it a earlier. So, everybody would like to have a large partition less solidification, large range or which partition less solidification can occur or the solubility to be extended to as high value of possible.

That mean, this T naught to be shifted to the higher concentration of B. But, this is as per as if you want to get a solid solution. But, if somebody is more interested in getting a amorphous phase, he wants this point to be shifted to the left. If this is shifted to a left what does it mean. That means the composition range over which liquid is more stable increases.

If this curve, if this point which is T naught point, if this is shifted to the left. That means, that is a situation, where the liquid is more stable for a large composition range. If the liquid is more stable, what is the advantage? The advantage is if I can keep that liquid stable up to a temperature, which is the T G. Then, that liquid will undergo a glass transition and I will get a glass.

So, if you want to get a glass, the first thing is that liquid should have higher stability. The stability range of liquid should be higher. So, you have to somehow make liquid more stable. If you can make the liquid more stable, then there is a chance for you to get a glass. So, as a result you can see here, this is the domain that you are interested.

That means, the domain which is on the right side of the T naught is of interest to a person who wants to get a glass. The domain, which is on the left side of the T naught is of interest to somebody who wants to get a solid solution.

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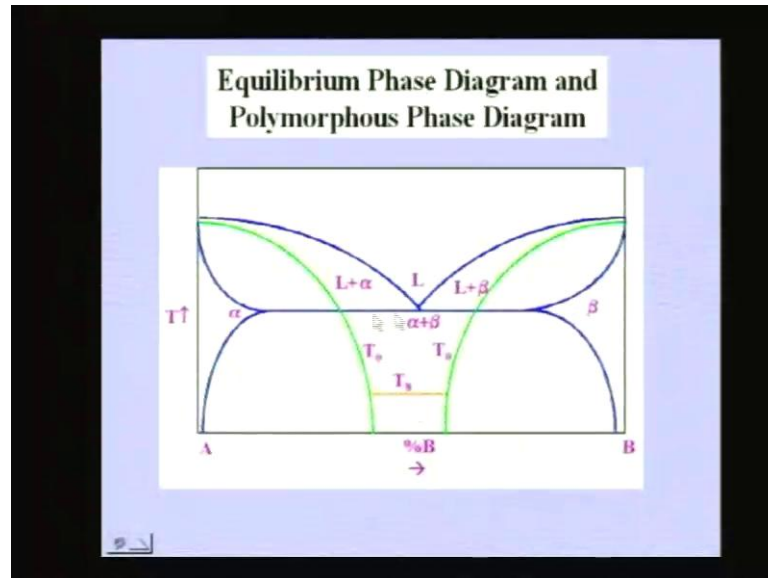


So, if you go to a enlarged portion of the phase of diagram. And talk of the two T naught curves, one which is corresponding to the alpha, the green curve here. This is nothing the, but T naught alpha. And here on the right side, you have another T naught another green curve, which is the T naught beta we call it. That means, the T naught of the liquid with respect to the beta.

That means, the compositions and temperatures, where the free energy of the liquid is equivalent into the of the beta. What is T naught, T naught is a nothing but, the trace of all those temperatures and compositions. Where, the free energy of the liquid is equal to some solid, whether it is alpha or beta or gamma or whatever it is you understand.

So and that T naughts, if you plot both the T naughts. The region which is between these two T naughts is the region, which is of importants to somebody who want to get a glass, because as I told you before it is on the right side of the T naught, where the liquid is more stable. That means, this is the domain, where the liquid is more stable.

And to the left side of the T naught for this T naught alpha and to the right side the T naught for the T naught beta, it is the alpha and beta that are more stable. So, for getting

glass it is this region which is important. And in within this region, if you can somehow under cool the liquid. Let us take a eutectic liquid, bring the eutectic liquid below the T G and if you can bring it below the T G. Then, you can get a glass you understand.

So, this is the very crucial domain for glass forming. And so if I can say, what is the glass forming range for this particular phase diagram. The glass forming range is, starting from this point to this point to this point. So that means, the domain between the two green curves is the glass forming range. The composition range between the two green curves is the glass forming composition range. That is what we have talked in the last class also.

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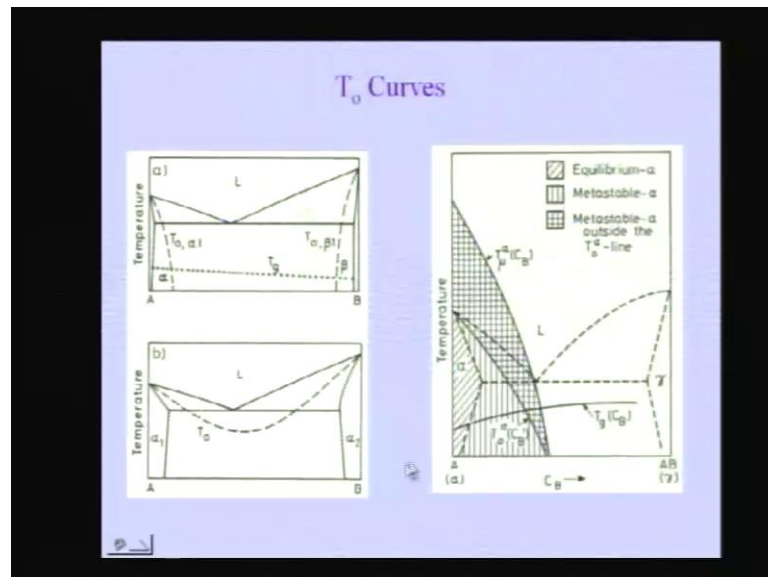


And try to see some other examples of such a thing. Here is what we talk about deep eutectics and shallow eutectics. Take another free energy a phase diagram, this is one example of a phase diagram. Where eutectic phase diagram T naught alpha is drawn here, T naught beta is drawn here the dotted lines.

Or the dashed line I should say, the dashed line here and the dished line here. These are the T naught curves. And the distance between the two T naught curves will give you the glass forming composition range. So, if the liquid us is very sharp. Then, the T naught will also be very sharp. And as a result you will get a very a large glass forming composition range.

But, if you have a situation where the liquid us is very shallow. Then, the T naught will be shallow and the T naught of beta will also be shallow. And both of them mite intersect are in this particular case you are seeing only one T naught, why do you see only one T naught? Because, the structure on this side and structure on this side is the same. Is an example of for example, we talked in the last class about a system do you remember a system where the you get a eutectic.

Student: Silver.

Silver copper correct silver copper is an example, where you have silver of the FCC structure copper of the FCC structure. So, if I draw the T naught, the T will not basically merge. Because, there is only one free energy curve there are no two free energy curves it is not that alpha curve beta curve you have. So, you have one free energy curve for alpha and one free energy curve for liquid.

And because of which you will get basically one T naught, continuous T naught. And in such a case, then there is a no composition range, where glass can be stable. So, the glass forming range in this case would be almost 0. So, there is no glass formation possible, because for glass to form you have to bring the liquid below the glass transition temperature.

And glass transition temperature usually is somewhere below here. And the T naught curve is above, if the glass transition temperature is below the T naught curve, you cannot have any glass. Whereas, if T naught curve goes below the T G then you can get a glass. So, glass transition is possible or glass formation is possible, in any phase diagram.

Where the T naught curve will intersect the T G, if the T naught curve does not intersect the T G. If the T naught curve is above that of the T G, if the both the T naughts are intersecting above the T G, then you will never get a glass. If the both the T naughts are intersecting below the T G. That is when you will get a glass; that means, you will have a situation like this.
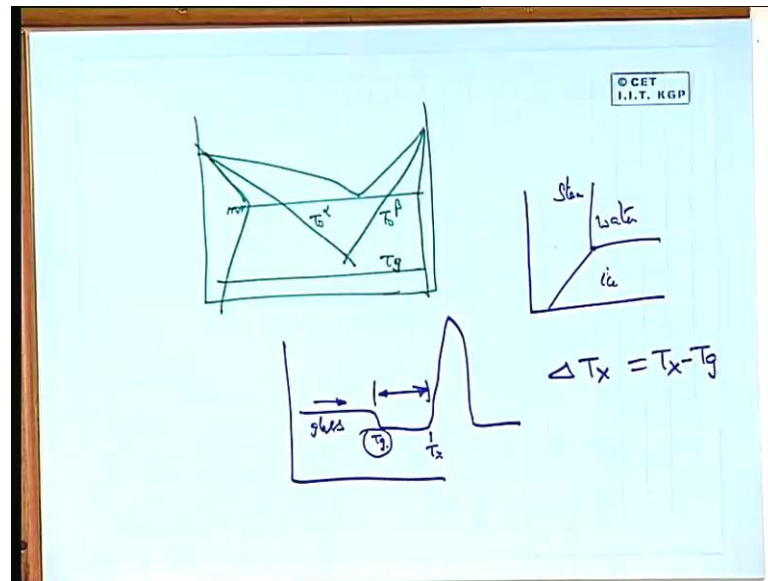
If I draw if this is the T naught and this is the another T naught. If these two are intersecting above the T G, this is T naught alpha this is T naught beta let us say. This part is not there. So, if that is what is happening, then you will never get a glass. But, you can still say yes sir in principle every liquid should become a glass, that is the kinetic part of it.

This is, what thermodynamics tells us. That if the T naughts are intersecting above the T G, you should not get a glass in principle. But, if I take that liquid and cool it so rapidly. That no alpha or beta can nucleate at cooling rates. Such as what we have experience in laser, in a such a case the liquid has to remain as liquid. Till you come to very low temperatures and then you get a glass.

So, in principle every liquid can be made a glass if you consider the kinetic aspect and this is what thermodynamic tells. So, thermodynamics basically is useful when you are comparing two systems, when I am comparing two systems I can say. This alloy is easily glass formable, it can easily form a glass then these alloys are this particular system is easily amenable for glass formation then this.

So, which has a higher glass forming ability, this is what for comparing the two systems, one can use a thermodynamics approach to. For example, shallow eutectic, deep eutectic, we can say easily if a liquid if a particular phase diagram is a deep eutectic kind of a phase diagram. We will come to them a little later, we can say easily you can get a glass.

Whereas, if you it is shallow eutectic will say, it is more difficult for you get a glass. But, at the same time I will never rule out that you can never get a glass. So, keep this in mind. Then, this is a another example ((Refer Time: 19:18)), where all kinds of curves are shown here, the T naught curve which you have on the T G. And here if you see various domains are shown.

What is this domain on this side? This where alpha is written, can you tell me what is that domain? This domain which is a enclosed within that alpha region. That is the stable alpha region, where the alpha is stable. That means, on the left side the terminal solid solution alpha is stable and if you look at the T naught curve. And you have another hazed portion there, the vertical lines are drawn there. And that portion if you consider what is that portion?

Student: ((Refer Time: 20:04))

It is meta stable alpha, there also alpha is possible. If you can under cool the liquid from above the melting point from above the liquid us stain. And come to a temperature below the T naught yes alpha is possible. And that is a super saturated alpha, which is not a equilibrium alpha. You will get that only under fast cooling, whereas this alpha which is the terminals solid solution is equilibrium alpha.

So, alpha is possible even beyond the equilibrium solubility range. And that is what is called meta stable alpha. And above the T naught curve what you have is the liquid, which is meta stable liquid. And once you come below the T G, that meta stable liquid will undergo a glass transition and that is a glass.

And you also see another curve here, which is called T mu. That is a T mu is related to the shear modules. For any given composition, one can calculate what is a temperature at which the shear modules goes to 0. From that concept of you, this is the particular temperature, where the shear modules goes to 0. So, this is a mechanical definition of the melting point. So, how the melting point changes as a function of composition, one can talk about when he considers not form the thermodynamic point of you. But from the shear modules point of you, because we know that shear modules goes to 0 above a particular temperature. But, usually you do not come across is this.

Because, before that the thermodynamics melting points comes into picture and then immediately liquid melts there. In principle if the liquid does not melt here, if you keep on heating the solid. A once you reach this particular temperature. That is, where the solid will be melt. But, then there are number of a melting points that can be possible people talk about a hierarchy of melting point now a day's.

For example, the entropy catastrophe is another melting point. If you keep on increasing the temperature. First melting point that you will come across is thermodynamic melting point. The second melting point that would come across, if at all you can suppress melting at that particular thermodynamic melting point. And keep on increasing the crystal to higher and higher temperature.

Once, you reach a what is called T s i which is somewhere between the T naught and T mu. It will always like between the T naught and T mew. And that is a temperature where the entropy catastrophe comes into picture and the crystal will undergo a glass I mean liquid, it will catastrophically become a liquid, if you somehow suppress that, which is impossible.

Then, you can still a go ahead, them you come across the shear modules go into 0. And that is what is the other catastrophe comes into picture. So, now a day's the people these are all you know theoretical concepts. But, practically reaching those temperatures are very difficult. But, physics work on all this kinds of a possibilities and in principle these are possible. And this is another situation, where we can combine the glass formation both from the liquid and from the crystal. That means, solid states amorphization and amorphization form the liquid can be combined one diagram.
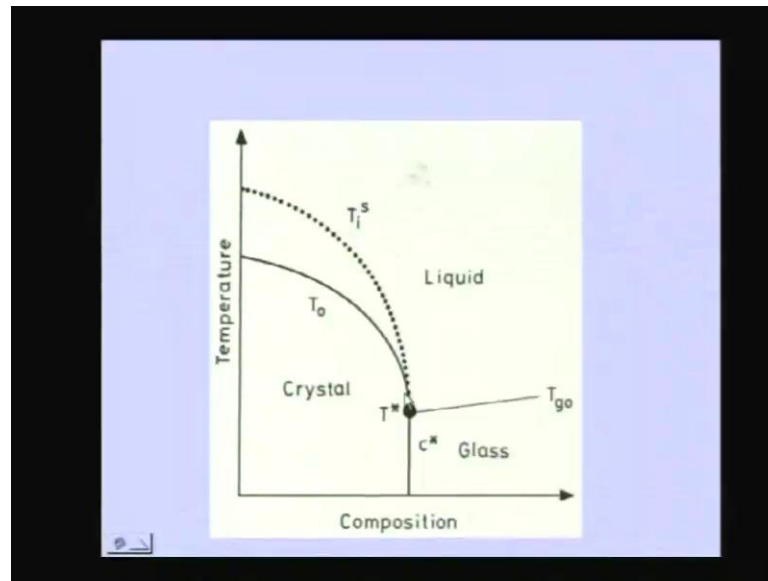
What you can see here is, one what you are seeing T naught curve. And the T s i curve which is the entropy catastrophe curve. And the T G, what we see is that, if you take a liquid come below the T G, you come to a glass. This is similar to you know when we talk about. For example, you remember ((Refer Time: 23:49)) we draw the free the phase diagram for the water.

This kind of a phase diagram, that you have the solid which is the ice and water and steam, there is a triple point we talk about. Similarly, here you have a triple point, the liquid the crystal ((Refer Time: 24:13)) and the glass. This is the triple point, what we basically mean here is, if you take the liquid come below the T G, you get glass.

If you take crystal and keep on increase it is concentration, in a rapid fashion. Then, that crystal can become a glass, this is what we see in a solid straight amorphization. That means, you take a crystal allow one of the element to diffuse very rapidly into the other. In such a case, then the solute element rapidly diffuses is into the solvent element, I told you anomalous diffusion of one element in other.

An in such a case, then the concentration rapidly increases. And once, it crosses a certain critical concentration, the crystal is no more stable. Because of the large number of defects that are introduce, because of this rapid moment of one of the element into the other. Then, the crystal will become a glass.

You can also have liquid becoming crystal, if you come below the T naught. Either, you bring that liquid below the T naught you get a crystal. And the take crystal again above T naught or T s i you get a liquid. T naught is the thermodynamic I so free energy T s i is I so entropy. That means, here is the catastrophic melting taking places, the here is the thermodynamic melting place.

So, if you take crystal keep on heating it come T naught, you will get a normal thermodynamic melting. But, instead of that if you somehow suppress melting at that point. And keep on increasing to a higher temperature. Once, you come across T s i for any given composition you will see that crystal will undergo a catastrophe melting and will be become a liquid.

So, you can see all transformations here, liquid giving a crystal, crystal giving a liquid and crystal giving a glass. And the liquid giving a glass and glass again giving you liquid, this what we see when we take a glass keep on heating it I told you before ((Refer Time: 26:19)). If you take a glass and heat it in a DSC, what you see is bee on the T g below the T x, you have a region this region. What is there in this region can somebody tell me.

What you have there is a liquid? What is this glass transition? Glass transition is where, the liquid transforms to glass, glass transforms to liquid, it is a transition between liquid and glass. So, it is not a no crystal is forming at this temperature as I am heating a glass, I am taking a glass here. Heating this glass, the moment I reach the T g at that T g glass will undergo a transformation.

And gives you what is called a super cool liquid are under cool liquid. Because, liquid is not stable there. So, it is under cool, because we are still below the melting point. So, it is a super cooled liquid. And once I come to a T x at that T x this super cool liquid will undergo a crystallization, because at that temperature liquid is not stable.

So, liquid is above the T g, if it was below the T g it would have transform to glass. Already we are starting with a glass and heated it above the T g. So, liquid has form and this liquid is a meta stable liquid, it is not a stable liquid. So, this liquid has to undergo a crystallization and that is what you see here.

And this particular range is called delta T x which is a very crucial parameter, which is called T x minus T g, which is a parameter which can measure how easily a glass can form how stable is a glass. For example, if this delta T x is very large, what does it mean, it means that if it all I form a glass. This to crystallize I need to heat it to very high temperatures.

Unless I heat it to a very high temperatures, it will not crystallize. That means, the glass is a stable glass. When, people are talking about bulk metallic glasses. What is important is how easily a glass can form and at the same time, how stable is that glass both are important. I make a glass I have to keep that glass, as a glass without it transforming into crystal for a long period.

So, that is why stability of the glass is also very important. And this is a indicator it is a parameter which indicates, the stability of the glass delta T x, which is called super cooled liquid regime. That means that temperature regime or temperature range in which the liquid super cooled liquid can exist before it crystallizes.

So, glass transforms to a super cooled liquid and this super cool liquid will take some time for it to transform to a crystal. What is that period, in terms of that delta T is what is crucial here. So, that is what we are talking about. So, you can talk about a glass going to a super cool liquid. Now, let us come to what are the criteria of glass formation. There are number of criteria people have proposed starting from criteria based on phase diagrams.

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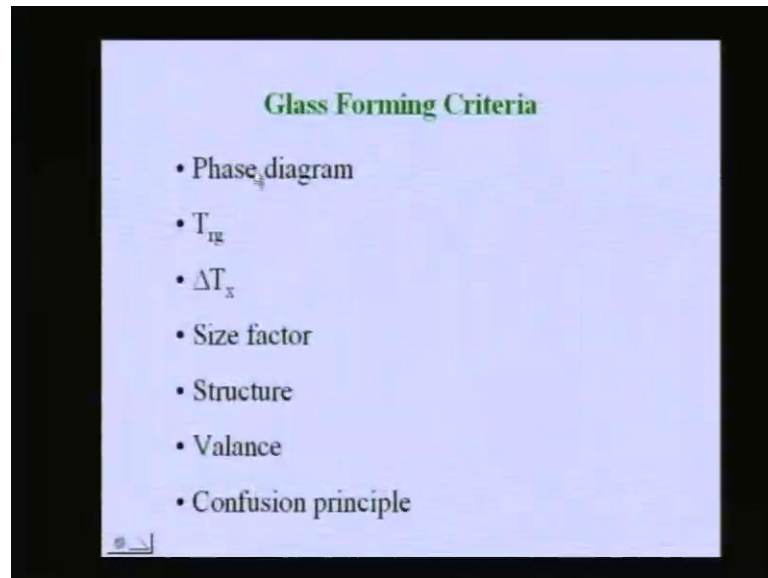


And we will come to one by one.

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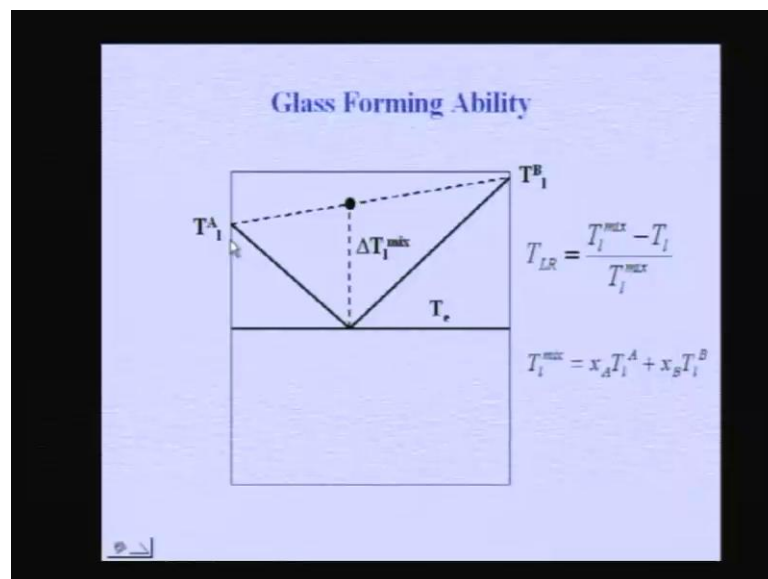


For example, for the phase diagram criteria, let us look at it. This is what tells you deep eutectics, whether a you eutectic is deep or shallow is what is decided by this criterion, which called the phase diagram criterion what does it tell you. For example, choose a eutectic phase diagram. It is important to know one thing, that you get glass only when you have eutectics in a system.

If you have isomorphs, then it is very difficult to get a glass please listen carefully. I still say, it is very difficult to get a glass I have never said it is impossible to get a glass. So, if you want to a have a glass very easily, you have to have eutectic in the system. If you have peritectics no it is not easy. Peritectics usually are situations, where the liquid stability range is very limited.

If you have look at a peritectic phase diagram and compare it with a eutectic phase diagram you will see. In a eutectic phase diagram the liquid as comes slow. When, you add b to a or a to b the liquid has decreases that is a meaning of eutectic. What is the meaning of eutectic? Eutectic means low melting. So; that means, the melting point decreases, when you add a to b or b to a.

And so; that means, the stability range of liquid is higher in a eutectic when campier to a peritectics. So, that is why eutectic are the systems, where the glass is easy. But, among eutectics how do we say which eutectic can easily forma a glass, which eutectic cannot form a glass, are which eutectic is more difficult to form a glass is depends on this parameter.

For example, if you take the two pure metal melting point T l A and T l B. And use the rule of mixtures and calculate what is that called T l mixing. That means, the melting point of a mechanical mixture of a and b of a certain composition, which is shown by this point. There, the melting point of such a mixture is given by any point on this straight line dotted straight line. That will give you the mechanical mixture melting point is not it.

So, I am choosing the composition which is the eutectic composition. At the eutectic composition, if want to know what is T L mix. I find out what is the eutectic composition in terms of x a and x b put it there I get the T L mix. And from that deduct the T e here instead of T L, we should T e actually. T L is here is the eutectic temperature.

But, why we are putting T L means, this is applicable not for the eutectic composition, but for any composition. If I choose some other composition, either hypoeutectic or hypereutectic. Then, for that composition I choose that particular T L mix minus the T L corresponding to that composition. And that difference is what is called delta T L mix.

That divided by the T L mix for that composition will give you a parameter called T L R, and if this parameter is larger than a certain number.

That number is here given 0.2 which is given by Donald and Davies long back. And if T L R can be higher than 0.2, then you will get a easy glass former. So, easy glass formers are those, where the T L R is grater then 0.2. And where ever the T L R is less then 0.2 we can say that difficult glass formers. That means, if you want to get a glass there.

The critical cooling rate is higher for a such a glasses. That means, if you use higher cooling rate, you may get a glass in those systems. Whereas, in these composition are in these systems, where T L R is grater then 0.2, the critical cooling rate is low. Then, let us go to the other criteria what is it, one is the T r g criteria. What is the T r g? T r g is nothing but, T g by T l the glass transition temperature divided by the liquid us.

And if this value is grater then about 0.6 Turnbull in 1969. He was the first to postulate a glass forming criterion. And he said, if the T r g is grater then 0.6 T r g is called reduced the glass transition temperature. That is why the term letter R comes there, reduce glass transition. That means, we are normalizing the glass transition temperature with respect to the melting point ((Refer Time: 34:42)).

For example, come to this phase diagram I choose any composition here. And the glass transition somewhere here below the eutectic. And I take the glass transition temperature
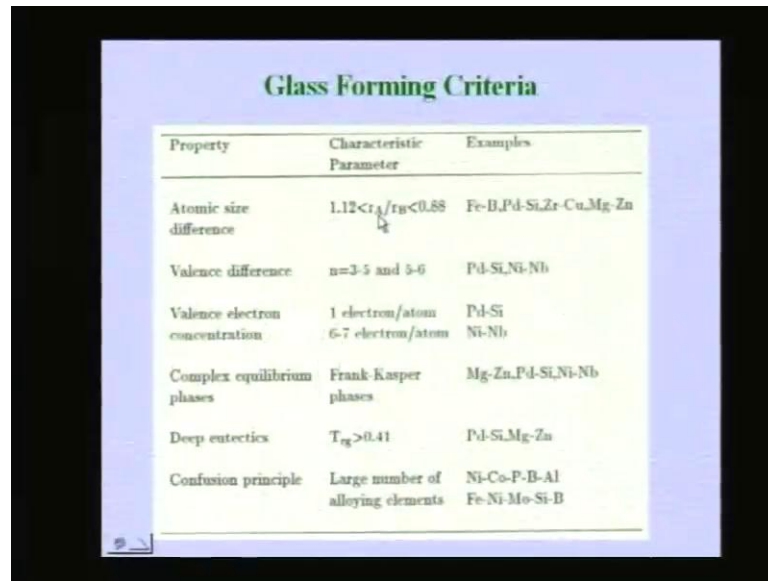
divided with the liquid us temperature. That fraction is what the T r g. And if I can campier for various compositions, I can easily see that T r g will be the highest for what composition? For the eutectic composition, because for the eutectic composition T l is lowest. So, in a T r g the denominator is a lowest. T g is more or less constant, T g is does not depend on the composition much. T g is more or less constant in phase diagram. Whereas, T l can vary T l is a lowest at the eutectic. So, because T l is lowest, so if the denominator is the lowest the fraction will be the highest.

So, at that eutectic temperature the T r g is maximum. That is way eutectic composition are the easy glass forming compositions. If you want to get a glass, you look for the eutectic in phase diagram. So, find out all the phase diagram identify, where is the eutectic composition. And among the two eutectic phase diagrams compare the T l r.

And choose that particular system, which has higher T l r you have a greater chances of getting a glass in that system. That is the second criterion. The third criterion is delta T x ((Refer Time: 36:12)) as I told you. So, that larger the delta T x, the easy the glass former, the higher of stability of the glass. And also you have the four Hume Rothery rules which also form part of this glass forming criteria.

One is the size factor, we know that if a solid solution has to form. The size factor has to be very small, if it is less then above 15 percent we say glass easily form. I mean solid solution can easily form. But, if it is higher than 15 percent, that is when you can form easily glass. In fact, here we have put down all these criteria in the form of a table.

And you can see that atomic size difference is one of the first and four most criterion. which show that if the r A by r B atomic radii of A and B are greater than 12 percent or less then 0.88. That means, if the ratio is grater then 1.2 are less then point or less than 0.88. That means, if the difference is grater then 12 percent. Then, you can easily get a glass.

And there are number of a examples, where such a situation exist. And you can get glasses very easily, iron, boron is one of the crucial examples for the Palladium silicon, gold silicon is another. And then the next thing is the structure ((Refer Time: 37:43)) we know if the two elements have a the same critical structure, then you never get a glass.

It is almost very difficult to get a glass, it is very difficult to get a glass. Because, it is isomorphous system, if A and B have the same crystal structure you end up in a isomorphous system. So, it is a very difficult to get a glass if A and B have different crystal structure if I have the same crystal structure. But, if they have different crystal structure, then it is more easy for the formation of the a glass, because for the crystal to form in a solid solution or in the form in alloy, it is more difficult. And the more complicated the crystal structure is, the more easy to glass transformation. That is, why we have see that silicate glasses it is very easy for glass to form. Whereas, in pure metals it is more difficult for a glass to form.

Then, the Valance factor and this is what you can see here, if the valance difference is grater then about 4. Then, you can easily get a glass and the reverse is what we taking of solid solution. When the valance of A and B are similar very close to each other, then we can get easily solid solution.

When the valance a difference between the two is large, then you get a you do not get a solid solution and there is a chance for getting a the amorphous phase or the glass. So, wherever the criteria are not favorable for a solid solution formation, then you have the criteria which are favorable for the glass formation. Because, if at all a solid solution can easily form, then glass would not form.

Then the liquid would tend to become a solid solution, rather than the becoming a glass. So, where ever the solid solution is more difficult to form, then the liquid would undergo a glass transition more easily ((Refer Time: 39:45)). So, this is an and the final thing is the confusion principle we say, which is one of the very common phenomena or common feature now a day's in most of the new glasses that a form which are called the bulk metallic glasses.

Bulk metallic glasses are those, where the glass can be obtained in the bulk form, we talked about it in a last two classes. And such glasses are possible only when you put large number of elements into a system into a alloy. For example, there are a bulk metallic glasses, which have 5, 6, 7 number of components in them. If you introduce so many elements into the alloy. Then, formation of a crystal structure becomes very difficultly, because all these have to sit somewhere in the unit cell. So, that becomes very difficult. So, there is a kind of confusion in the liquid of what kind of crystal structure it should choose, when you have so many elements in it.

And in such a circumstances under those circumstances liquid would easily become a glass, rather than becoming a crystal. And that is what is called a confusion principle. And so this is possible, when you increase a number of components. That is why, multi component alloys are easy glass formers, will come it a little later when we talk about bulk metallic glasses.

So, this is one of the important criteria, which people considered now day's when ever, they want bulk metallic glasses. It is almost next to impossible to make a bulk metallic

glass in a two component system. In a binary system nobody could so for achieve a bulk metallic glass it is very difficult.

Even, if all other criteria are satisfied. If you want to really make a glass in a thick form, then you need a large number of elements. So, that you make the liquid very viscous, once you make liquid very viscous, diffusivity is very much restricted and that is when the crystal cannot form. So, liquid become a glass, why is that silicate liquid is becoming glass very easily?

Because, liquid is viscous and the crystal is more complicated. So, both of them are making it easy glass former. That is what people are now a day's using it in the metallic systems also making the liquid more viscous by introducing large number of elements, which make the liquid very viscous ((Refer Time: 42:15)).

So and the other criterion which turn bulling 1976 postulated is what is called T naught L minus T l criterion, where T naught is given by this expression, where delta H f is the is what delta H f is?

Student: Enthalpy of fusion.

Enthalpy fusion or latent heat of fusion for the A, A is the solvent item. Here, we are talking respect to a solvent item A. If A is the solvent item and B is the solute item, we take the delta H of A and the melting point of A divided with delta H of minus R, which is the glass constant multiplied by l n 1 minus x. Where, x is the solute concentration x b into T f. So, 1 minus x is nothing but x a.

So, this parameter minus the liquid us temperature divided by the parameter once again, if the this fraction is grater then 0.09. These are all again mostly empirical rules, they have found that a number of system these things are valid. So, they say that yes, if you find out the this is valid then can you get a glass very easily. So, this is another criterion which people use very regularly ((Refer Time: 43:37)).

Then, valence electron concentration we talked about valance difference. With the valance electron consternation is very large. You can get a easily glass formation, complex is equilibrium phases, if the structure is complicated such as Frank Kasper

phases. You can easy glass formation, the examples are given here deep eutectics where the T r g is greater than about 0.4.

Then, you can get a easily glass formation palladium silicon is a example, there iron boron is also example, gold silicon is another example there. Confusion principle when you have large number of a alloying elements. For example, you have a five component two five component examples are given here, all these are various glass forming criteria.

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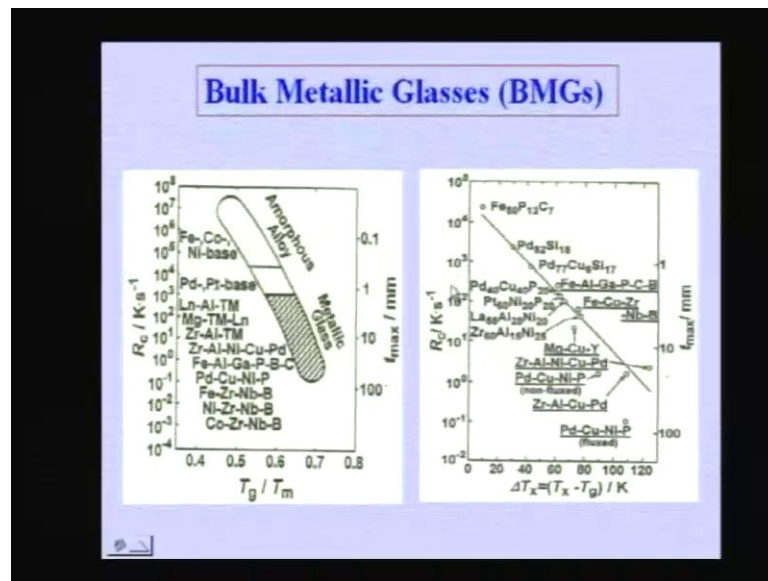


Recently, there have been a lot of interest on bulk metallic glasses. And people started looking at this glass forming a criteria very closely, and looking at the correlation between various criteria with the experimental parameters. R c is what is it, it is a critical cooling rate for the glass to form. And this t max is the maximum thickness, that you can achieve, which is a glass.

This is similar to in a marten site formation, we talk of critical diameter. Whenever, we talk about harden ability, we give harden ability in terms of a critical diameter. That means, what is the minimum diameter, where you can get a glass, you can get a marten site throughout the section. In fact, the way best way to define is 50 percent marten site at the centre, that is how people definite.

Because, it is impossible to look identify which is the region 100 percent is the marten site is... So, the critical diameter there is an indicator of the harden ability. If the critical

diameter is lager for a particular composition, then we say it has a harden ability. If it is very small, then we say it is not really hard enable. Similarly, if the t max which is the maximum thickness over which you can get a glass very easily. How people find out of this, there is a very easy way to find out.

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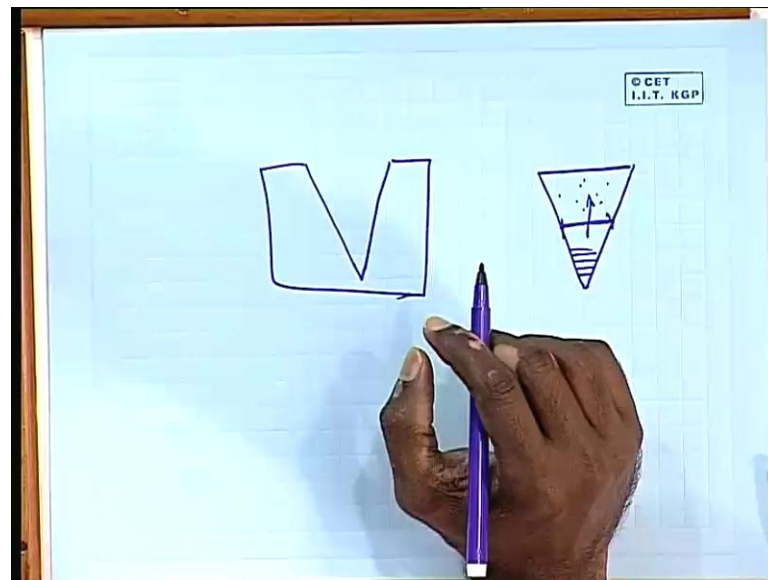


Now, a day's what people do is take a liquid and pour it into a tapered mould like this, tapered copper mould. And once you pour the liquid, once it is solidifies, you take that casting which is of this shape. And then section it vertically. And then look at the structure from the tip up words. And see, what is that distance up to which it is completely amorphous.

What is the diameter up to which it is completely amorphous. Beyond which some crystal start forming. This is similar to what is a we use in harden ability, a testing method. What is the testing method?

Student: Jominy.

Jominy end quench test exactly, similar to jominy end quench test this is a similar test. So, one pour this liquid and then section it and look at the structure, even in an optical microscope many times, you can see crystals forming here. Otherwise, you can go to a T e m kind of situation or do an X-ray section, various sections small things slices each slice subjected to an X-ray diffraction.

That means, horizontally keep on sectioning them a number of section. Each section can be all subject to an X-ray and find out or vertically section it look at it in a optical microscope are in a c m and identify if there are crystals. So, where ever there are crystals you I that particular diameter is the limit of the glass formation. So, we can define what is called critical diameter and that is nothing but, the T max.

So, for a each composition one can find out this. And this if you correlate with to T r g, you can see ((Refer Time: 48:05)) that there is a inverse correlation between R c and T r g. As T r g increases for particular system, then the R c will decrease. That means, that if the T r g for alloy is very large, they critical cooling rate is very small.

That means, it can become a glass very easily, all those bulk metallic glasses are those, which have the T r g greater than 0.6. That means, this domain if you put 0.6 go vertically up and find out. And this hatched region is the region, which is the region for the bulk metallic glasses. And the what is the cooling rate corresponding to that, it is less then to about 10 to the power 3 Kelvin per second.

In fact, all those bulk metallic glasses are those, where the cooling rates of the order of 100 Kelvin per second are lower than that. If the cooling rate more than that, then we do not really call it as a bulk metallic glass. So, bulk metallic glass, if you want to crudely define is a glass which can be obtained at a cooling rate less than about 100 Kelvin per second.

So, if there is composition where you can get a glass. At that low cooling rate, then you can call it as a bulk metallic glass. And correspondingly the thickness would keep on increasing, if you increase the T g, T g by T m. If the T r g increases, then you can see the T max increases. And there are a number of systems which have been shown here, which are examples here.

The Cobalt base, nickel base, iron base, palladium base the best alloy is the palladium copper nickel prospers alloy, which has a value of T max of the order of 100 now 100 millimeters ((Refer Time: 50:00)) obtain very easily. The other criterion is delta T x, again this also has an inverse relation between R c and delta T x.

If the delta T x is very large, then R c is very small. So, for a system where the delta T x is very large. Then, you can say then the R c is very small. So, one can have a glass

formation very easily. And again all these glasses can be clubbed here and one can identify what kind of a plot it is, these are the bulk metallic glasses.

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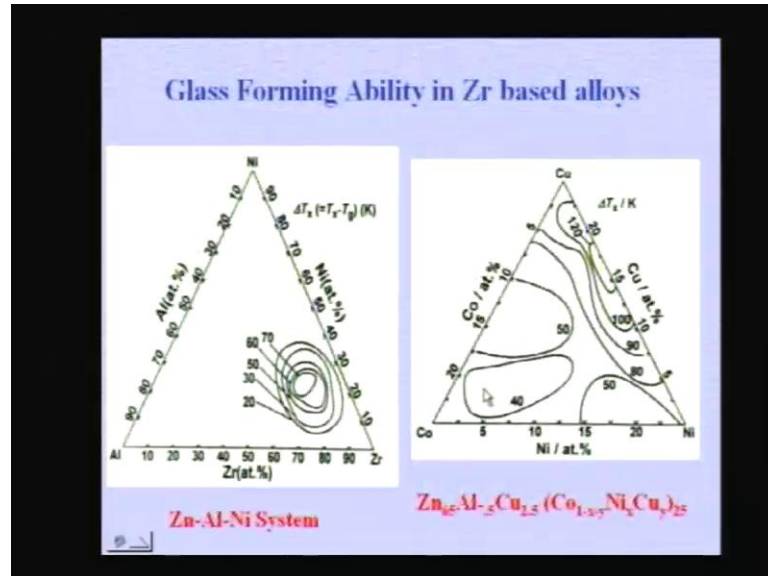


And there are number of such criteria. And these are some examples, one can find out the delta T x for the various compositions. And plot what are call isodelta T x plots. That means, identify all those composition, where the delta T x is the same. And connect them with alloying. And so each line here, each circle there you are seeing an elongated circles there all ellipses.

And each of them corresponds to one particular delta T x. And you can see, as you keep on going to the interior circles, the delta T x is keeps on increasing. And one can identify of a particular composition, where the delta T x is the maximum. So, that is the particular composition, in this phase diagram which has the highest glass forming ability.

So, one can do this kind of things, either in terms of delta T x are in terms of T r g. This is another such, where the delta T x is plotted this is for 40 K, this is for 50 K, this for 80, 90, 100 and 120 this small domain is for 120 K. That means that those are the compositions which are there within this small domain, which has highest glass forming ability.

So, one can identify the compositions. But, the only restriction here is for identifying which is the best compositions? What we have to do is, first you make a glass, you have

to make alloy, make it into a glass. Then, it this glass get the T g and the T x identify the what is the delta T x and then plot it. So, that mean this is we are doing a kind of postmortem, we are already made the glass.

And the finding out among all this composition which as the highest glass forming ability. That means, this is not a real predictive type of a way of finding out, which is the best glass former. But, the advantage with a to some extent with this system is, one can make lot of compositions. And rapidly solidify them by using melt spinning and get ribbons.

And each of this ribbon they can do easily the DSC. And find out this, in fact there is a group in Japan, one professor Innove he has students, each one of the student takes he has about 50 to 60 students research callers us. Each one of them looks at one turnery, they make 100s of alloys. And within a few day's it is very easy to make this alloys, if you have an arc melter, you can just make very easily.

And if you have melt spinner I have made 16 alloys is one day. And did X-ray of all 16 of alloys, identified whether they are amorphous are not. And then did DSC all of them and could find out what is the delta T x. This is all just starting from weighting the sample to making an alloy and doing melt spinning. And then finally, finding out the delta T x, all this I could do just within 24 hours 16 alloys this is possible.

They are number of people who do all this. And then identify, but then what is the advantage that you get. That advantage that you get is you can identify the composition which is the best composition. And take that composition and make this kind of a bulk glass. You can pour it into a mould of cylinder of a particular diameter and then get a easy glass formation.

So, before doing that you can do melt spinning. But, now a day's we are taking of predictive type of models. How to predict which is the best glass, without doing a experiment. So, that is where lot of people we our self are work on that doing thermodynamic calculations. Finding out where is the delta H mixing is a maximum highly negative.

Because, we know that heat of mixing are enthalpy of the liquid highly negative. That means, liquid is more stable. So, if you can stabiles the liquid you can make a glass. So,

identify that composition, where the enthalpy is highly negative, which is one can easily calculate it using thermodynamics. Once, you calculate that, that particular composition one can take it and make a glass. And show that yes this is a easy glass former. Will stop here and continue in the next class.