Advanced Materials and Processes
Prof. Jayanta Das
Department of Metallurgical and Materials Science Engineering
Indian Institute of Technology, Kharagpur

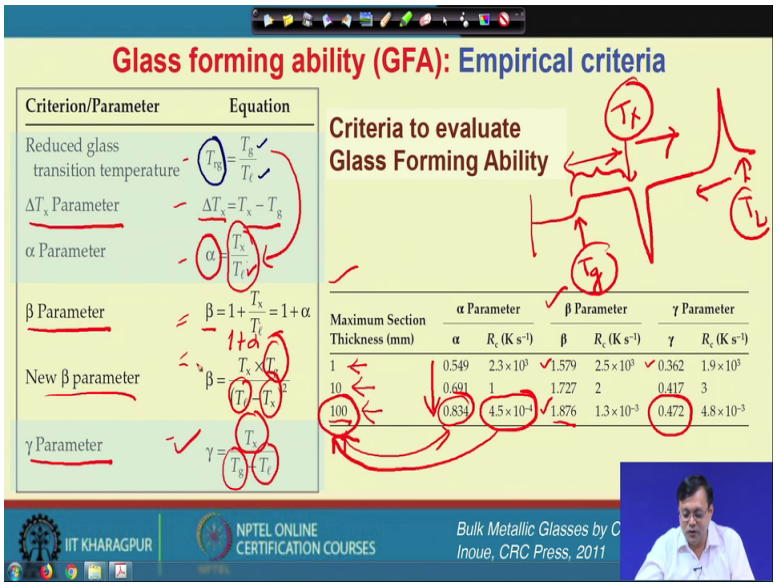
Lecture – 11
Bulk Metallic Glass, Glassy and Amorphous Materials (Contd.)

Hello, welcome to NPTEL; Myself Jayanta Das from Department of Metallurgical and Materials Engineering IIT, Kharagpur. I will be teaching you Advanced Materials and Processes. There are a couple of lectures, we have discussed the relevance of advanced materials, and we were just going through the amorphous or glassy alloys. In that particular topic, we are discussing the ideas of glass forming ability. It means that how we are going to characterize an alloy, which is undergoing vitrification during solidification or let us say rapid solidification.

And, now if someone designs an alloy composition, and how will we compare between other compositions; whether the newly designed composition is a better glass former or a worst glass former. In that direction, we talked that the larger the critical thickness means, the slowest possible cooling rate, so that we can vitrify the whole a melt at a lower cooling rate or critical cooling rate or see the better the glass former ok. Means two composition; one require a very high rate of cooling, another one need very slow rate of cooling for vitrification. So, the alloy which need, slow rate of cooling is a better glass former.

However, we can somehow put the same glassy alloy into a differential scanning calorimeter, and we can measure some characteristics temperatures; and through that we were evaluating the glass forming ability of the alloy. So, today we will continue the discussion and try to look at, what are the different empirical relations we have talked about or people or researchers think about.

(Refer Slide Time: 02:39)



So, so far, I said that, the reduced glass transition temperature, which is a quite important, and $T_{rg} = \frac{T_g}{T_l}$, T_g is a glass transition temperature and T_l is the liquidus temperature, where a crystal melts or let us say a super cooled liquid leads to a very low viscosity value. And similarly, we can talk about the stability of the super-cooled liquid region.

What I want to mean that if we take it easy stress, and which looks like such a way, and here, this is a T_g, and here, this is the T_x. So, the temperature difference of these two characteristics temperature will give you the stability, and the larger the value of ΔT_x is the more stronger the liquid is, and more stability of the glassy or easy glass former is. So, this is the way, we define the ΔT_x or parameter. However, we can also very similar way, like the reduced glass transition temperature, people talk about the α parameter, which is the ratio of the crystallization temperature and liquidus temperature.

And then there are some other parameters, like β parameters, people talked about. In this case, here we take basically this α parameter, where 1+α is basically introduced or let us say some new β parameter, which are considering T_g, T_l and T_x. So, a more we have seen a very important and more reliable parameter, which J P Lu has proposed, which is the γ parameter, where we consider all these three characteristics temperature, because if we keep on heating this liquid and ultimately it will go to the reach to the liquidus temperature ok

So, all these three characteristics temperature of a glassy material has been considered in this particular case, and you can see some of the real value, and how is the relevance of these empirical criterions. So, please have a look at this table, where let us say maximum thickness of a glass, if it is 1 millimeter in one case, it is 10 millimeter in another case, it is let us say 100 millimeter. And then, you see the α parameter value is basically increasing ok.

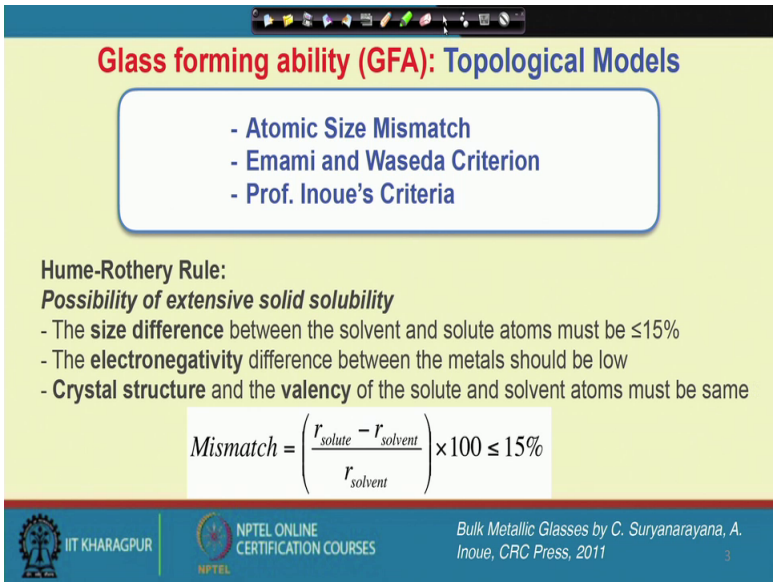
So, α basically means that this T_x, which is the crystallization temperature by the liquidus temperature. So, this means that if the liquidus temperature goes down, and if the Tx goes up, then we can get a larger value ok. And this is a representative of a better glass former and therefore, on the other hand, when somebody try to cool that liquid and then he find out that the maximum section thickness of the glassy alloy is very much high ok. So, these two things, two things are very much well linked.

Very similar way that relatively very slow cooling rate, we can achieve a larger casting thickness, as I said just few minutes ago. And, so, even though there are many different empirical parameters has been proposed so far, but the meaning or the idea behind the discovery of all this empirical formula is basically the same.

Now, if you look at the same glass, and measure these characteristics temperature and measure the value or calculate the value of β; so, here you see that the 1.57 to 1.87, it is increasing, so the larger the section thickness the larger the β parameter. Now, also very similar way let us say the γ parameter, which is also little bit higher. So, from a metallic glass to a bulk metallic glass, and a much larger size glass is possible, when these empirical parameter values keep on higher.

So, this is somewhat, a very interesting and we can we able to characterize all the different glassy alloys, and put a marking on them, which one is a good glass former; and which one is a bad glass former ok. Because ultimately if we really need to vitrify an alloy, we had we need a very important parameter, and these important parameter should characterize a glassy alloy, and tell us the characteristic of the alloy; how easy to form a glass in this alloy during solidification. And since, these are all let us say empirical formula, and the physicist, try to understand in terms of the atomic packing ok. So, a easy glass former, how is the atomic packing or let us say some sort of topology of atomic packing. And in let us say worst glass former, how are they.

(Refer Slide Time: 08:48)



So, along the direction, there are many different approaches or let us say models people have proposed, and tried to satisfy with their criteria. But, I found that this three criteria is somewhat very much relevance; one is the atomic size mismatch ok, means, I have element a, element b, element c, and they these three elements are mixed with different proportions ok.

And the differences of their atomic sizes must be a crucial parameter on dictating the glass forming ability of such an alloy. Now, professor Emami and Waseda also have proposed some criteria based on this kind of topology of atomic packing. Professor Inoue from a professor Akihisa Inoue from Tohoku university, who is also a pioneer of these of these glassy field; he also has proposed some rules, and we will be discussing those things in a minute.

However, before discussing all these three model, I would I would request you to listen to and recapitulate some of our old idea in physical metallurgy. So, in physical metallurgy, we know about the solid solution ok, and we know about substitutional solid solution; we know about interstitial solid solution, order phases and so on. And in that particular subject we learn about Hume-Rothery's rule, because Hume-Rothery's rule said, a lot about formation of a solid solution, and how to get a extensive solid solubility, when we mix B in A.

And there are basically four different aspects of that William Hume-Rothery's rule. And those are let us say the size difference of the alloying elements. Let us say electronegativity, crystal structure, and the valance configuration. So, the first one was he said that, the size difference between the solvent and the solute atom must be less than 15 percent.

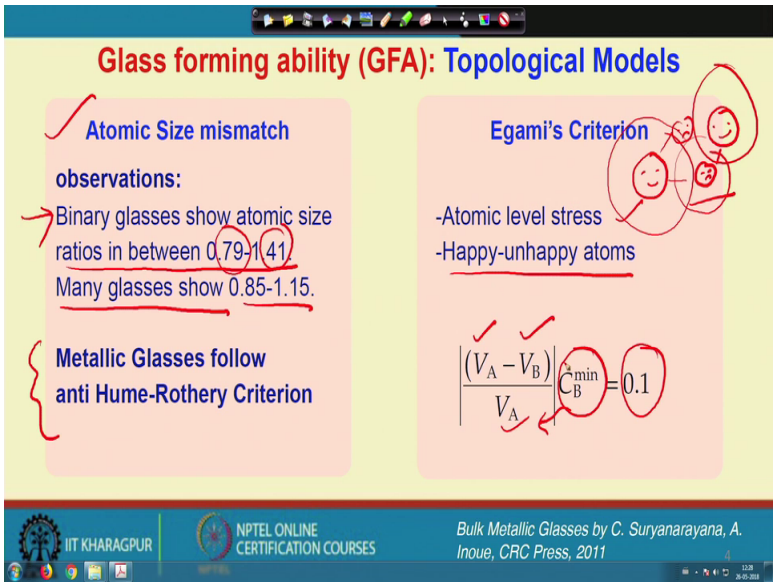
So, we can it is only possible to produce that kind of substitutional solid solution, when there is some correlation between the size of the atom ok. So, if the size is very very large, and another side the solute atom is too small, then it is not really possible to get a solid solution. And in case of glassy alloy, why it is relevance, because you see a glassy alloy, where there is no crystal structure and all the elements, which are present they are dissolved in a in a and they have created a solid solution right.

And, so Hume-Rothery's rule even though it is valid for crystalline alloys, but we can think about and we try to understand by learning Hume-Rothery's rule, and how we can put it in different topological models, people have proposed. Now, the second one is the electronegativity ok. So, electronegativity differences between the two different metals should be low otherwise, they will make some other kind of bonds, and it will be a large ordered phases. And, so it is not recommended to make a solid solution with a large electronegativity difference.

Now, it is also expected that the crystal structure of the solute and solvent atom a must be very similar, like if you like to make a solid solution of gold and copper right, both are FCC crystal structure yes. And they also form let us say the FCC solid solution or let us say nickel and copper and so on. So, it is really possible, also the valency of the solute and solvent atom must be in the same order ok. So, these four important aspects of a formation of the extensive solid solution, in solute and solvent atom by mixing them using this Hume-Rothery's rule is very much important.

And therefore, what we learn out of these that the mismatch between solute and solvent are basically the differences in the radii and multiply by 100, which should be less than equal to 15 percent. And if we remember this idea then we look at that what is really happen in case of a glassy alloy, whether there is atomic size mismatch is preferred or not preferred ok.

(Refer Slide Time: 13:57)



So, let us look at that. Now, if we look at many different glasses, whatever has been discussed, whatever has been discovered so far, you will see there are very general observation, let us say there are many binary glasses. Binary means basically two different element is present in that glass, where the atomic size ratio lie in the range of 0.79 to 1.41, means you see that 41 or let us say here, this is a huge percentage. And it does not follow, it seems it does not follow Hume-Rothery's rule, even though they are solid solution.

Now, there are a many glasses or let us say most of the glasses, which has some values like that. And therefore, these atomic size mismatch or more mismatch is preferred to form a glassy alloy ok. And then only probably we can make a cluster; and those cluster will be more close packed cluster, which will give you give us the stability of those glassy clusters, instead of some crystalline clusters.

And therefore, we often call that this metallic glasses follow an anti Hume-Rothery rule ok. In case of crystalline alloy to form a solid solution, Hume-Rothery rule is important. However, in case of glassy alloy, these anti Hume-Rothery's rule or let us say the glassy alloys follow an anti Hume-Rothery type of criterion. Now, Egami and Waseda, they were thinking about, why do not we consider the atomic level stresses that are generated, when we mix a, b or c or d a different type of atoms.

What I want to mean that let us say I may have a two different size of atoms, and I mix another third atoms. And let us say this atom, which was a previously there, and they are somewhat like a like an unhappy; and let us say somebody is occupying more space, they are somewhat like happy ok. So, so happy and unhappy type of situation, and the smaller atoms are a bit more stress ok.

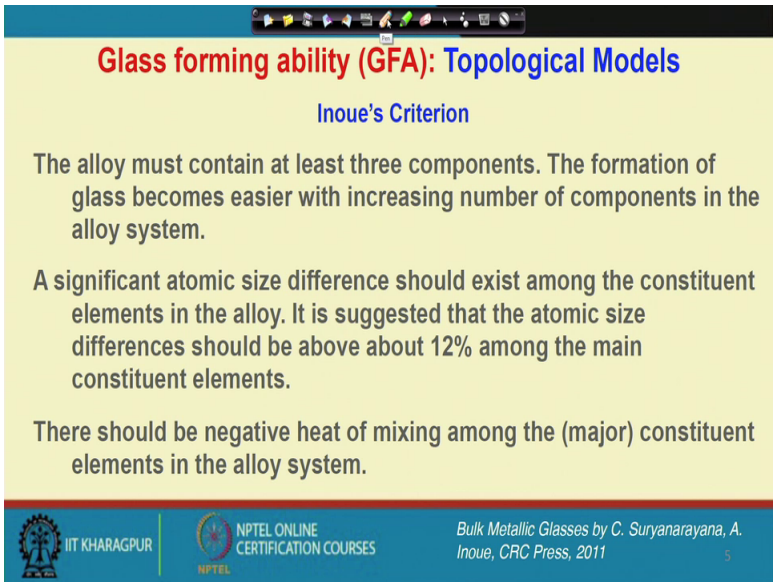
So, in that way, we try to make those clusters, due to happy and unhappy by mixing happy and unhappy atoms. And there are some critical concentration, which is favored to form a glassy phase. And therefore, we can think about this kind of atomic level stresses, and definitely when you think about atomic level stresses, an atom there must be some space around it, and there are some spaces around it.

And that volume or atomic volume must be considered, as an example I can I can tell you, let us say, if there are 15 chairs in a class, and let us say there are 15 students very thin students, who are sitting in the class right. And then I bring another 20 students, who are very very large size, and then asking them to accommodate in those classes, in the in the in the same positions. So, definitely the thinner people will be more stressed, and they will be rather more unhappy right. And, so the situation is like that kind of funny.

And, so here, let us say the volume of a type of atom, and volume of B type of atomic volume, and the difference if we put, and then let us say the critical concentration or the minimum concentration of B required, and if we multiply it, it should be somewhat like 0.1 ok. And then only this kind of topology will be created, so that the glassy phase become more stable.

And, so you see that, whatever these ideas, at these ideas are talking about a formation of a cluster, and the stability of a glass cluster. Here, cluster means the atomic level clusters I am talking about, and not only a cluster, but we learned about the free volume also ok. And the free volume means, the excess volume that a glass have than compared to a crystalline alloys. And even though there are some free volume, however, how do we packed different atoms with different sizes, and then put them together to find out a metastability in that cluster.

(Refer Slide Time: 18:56)



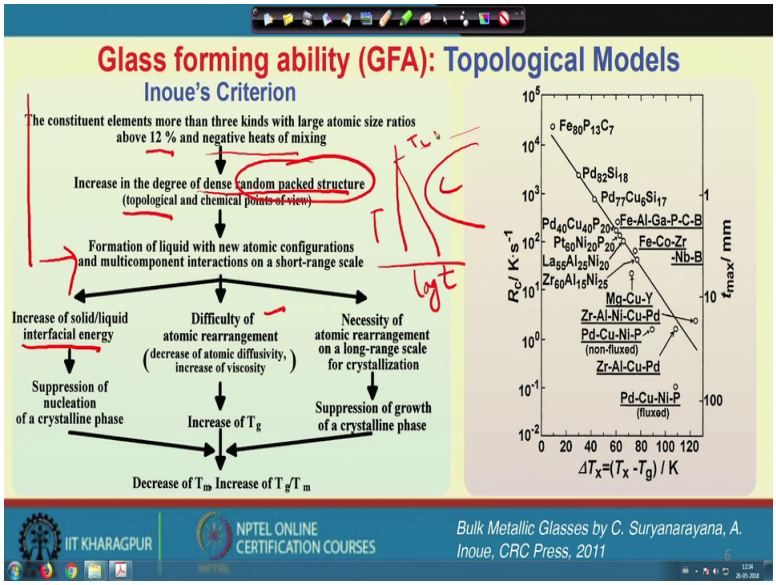
Now, let us have a look at some other model like Prof. Inoue's model, what did he talked about. Prof. Inoue's said that the glassy alloy must contain must contain at least three different components three different elements. The formation of glass become easier with increasing the number of components in an alloy system. This is a very very simplified approach that definitely if we increase the number of elements, then it is expected that the glass forming ability will increase, but it is not true for all the cases, because there are binary glasses developed, yes instead of three minimum component. So, this is a rather I would say a general approach.

And, now he also said that a significant atomic size different should exist, which means basically said that it is it should be like an anti Hume-Rothery type of criteria. And the constituent elements in the alloy, and it is suggested that the atomic size differences should be greater than 12 percent. So, definitely if we really like to make a glass, we must choose elements, which has a size difference a greater than 12 percent than the main constituent element. So, these are the ideas that goal goes along with the direction of Egami as well as the atomic size mismatch, and an anti Hume-Rothery type of criterion.

So, there should be a negative heat of mixing, and this is very very important. So, when we mix different element, there should be a negative heat of mixing then only they will be able to form a solid solution right. And this is very very important, so among the

major constituent elements of the system. So, we must try to understand these three very important criteria even though it appears to be very general. However, these are the important criteria to form a solution and so that we can give a stability of the glass. But, if these kind of criteria's or these criteria particularly Prof. Inoue's criteria is satisfied then what are the consequences in a glassy melt so that must be we discussed.

(Refer Slide Time: 21:20)



And let us have a look, what Prof. Inoue tried to explain with that. He definitely said that the size differences of atomic different larger or a smaller diameter atoms must be greater than 12 percent, and there must be a negative heats for mixing. If such situation arises actually we favor a dense random packed structure, what I was talking so far in terms of atomic clusters.

So, if we have atoms with very different sizes greater than 12 percent, and if they have a negative heat of mixing where free energy is favored, then we can produce a very very dense cluster or very dense random packed structure. And this is not only in terms of topology, because topology talk about only the size. However, the chemical point of view is also important.

Here chemistry means that the affinity of different atoms or let say a type of atoms and b type of atom, so they are difference in their chemistry. And if such a thing happened, then we can have many different configuration, and out of let us say n number of

configuration, one configuration will have the lower free energy, and which will stabilize in the melt or in the super cooled liquid in order to form the glass, so that was the idea.

So, formation of a liquid with a new atomic configuration; so, we have a under cool liquid, and I have already created some dense random packed structure, where viscosity is very very high. And in case of that kind of multi component interaction in a short range scale, where short range means, basically two nanometer or less than two nanometer in size, then it will be more and more favored.

Now, if such these three important things appear in a melt, then what are the other consequences are happening. See these are very much interesting that we basically increase the solid liquid interfacial energy. And definitely, difficulty will be in the atomic arrangement, because we have already created a very random packed structure.

A random packed structure means that the viscosity level goes very very high; a viscosity is high; that means that the diffusivity is low; and diffusivity is low; it means that the crystallization in the melt is very difficult. So, crystallization become difficult means, we can easily avoid or bypass crystallization, and if we think about a TTT curve ok, and then let us say this is the time, log of time, and this is the temperature, then we bypass the crystallization. So, this is the crystallization phase, and this is let us say the liquidus temperature ok.

So, this was already discussed earlier. And, so we increase the viscosity; decrease the diffusivity; and the necessity of long range arrangement, it means basically to form a crystal, we need a long-range order. A long range order basically means that we need atomic diffusivity, in order to form that long range order. But, we are suppressing that ordering in the super cooled liquid.

And once that kind of situation appear, we automatically suppress the growth of the crystalline phase, also first is the nucleation of the crystalline phase is suppressed. And once, these two things happen, we automatically increases the glass transition temperature, and there is a decrease of the T m and increase of the T g by T m, which basically means that a reduce glass transition temperature, can be increased and we can easily form a glass.

So, Prof. Inoue's criteria even though it looks very simple, but it tells almost or it summarizes all the criteria, whatever has been discussed by several peoples And, so ultimately as I said earlier that delta T_x, which gives us a idea of a of a of a stability of the super cooled liquid, which means the T_x minus T_g ok. As it increases, the stability of the glass is also increases means that the composition is a better glass former ok.

And, now you please have a look at the Y-axis in two different size. Here, this is the t_{max} means, maximum thickness of the of the cast glass; and here this is the minimum cooling rate require to form the glass. So, as the T_x delta T_x increases, then as the delta T_x increases ok, so from here to here, the required cooling rate is low ok. So, here this is 10^3 K/s and here it is 1 K/s ok. So, this is a better glass former palladium copper nickel phosphorus or the same time the maximum thickness from a 1 millimeter, we can reach let say something like 20 millimeter. So, by looking at this plot, we realize that these are very important parameter.

And, so if we produce a glass, we need not to measure its cooling rate. However, by looking at the microstructure and confirming that it is only a glassy phase, then we can surely say by measuring T_g, T_x and T_l, We have developed many different empirical formula that says that the glass is a better glass former or a worst glass former. However, before designing a new glass, we can consider Prof. Inoue's criteria, or atomic size mismatch, or Prof. Egami's criteria, and look at different elements, and calculate their heat of mixing, and then by some computational approach, we can design new glasses.

So, there are many different glasses, which has shown that it is really possible to design some new glass or a better glass by considering both thermodynamics as well as some of this topological models. So, these models are definitely important; however there are many and many different criteria or let us say physical parameters are also important in order to describe the good glass forming ability. And those parameters even though we will we will discuss in the next class.

Thank you.