

**Advanced Materials and Processes**  
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**Lecture - 10**  
**Bulk Metallic Glass, Glassy and Amorphous Materials (Contd.)**

Welcome to NPTEL, myself Jayanta Das from department of Metallurgical and Materials Engineering IIT Kharagpur. I will be teaching you Advanced Materials and Processes. Since last classes we have discussed many different aspects of glassy and amorphous alloys or materials, and today we will go into a little bit deep inside of the glass forming ability.

Let us say we may start with the composition and we found that there is a possibility for a particular cooling rate to obtain a glass during solidification. And now how we can assess different alloys in terms of their ease of glass formation and today we are going to discuss those issues in terms of glass forming ability. It is a very well known fact that many of these glasses are formed by choosing the composition by trial and error.

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**Glass forming ability (GFA)**

Many glasses formed by choosing the composition by trial and error;  
It requires a unified approach/criteria to characterise the glassy alloys  
to understand **ease of glass formation**

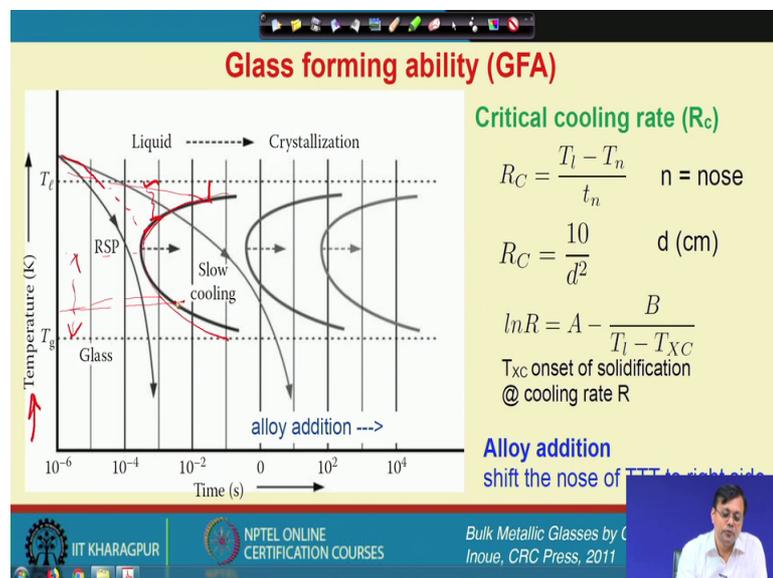
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So, which is very hard to predict that we can design a composition and the glass will be easy to form in those composition and therefore, people had to go for trial and error, mix different elements with different composition atomic percent of weight percent and then solidify it at different cooling rate and try to look at what is the microstructure evolved.

And in this way people find out many different composition since 1993 when the first bulk metallic glass, bulk here means basically greater than 2 millimeter in any of the dimension which was discovered in a Vitreloy system by Professor Johnson at Caltech.

Therefore, since so many different glass forming alloy composition has been developed in different alloys system, we really need a unified approach or to characterize this glassy alloy in order to understand the ease of glass formation, and this is a very important aspect to understand the glass forming ability of an alloy. And therefore, we need to go a little bit step by step and let see how we do we understand this matter.

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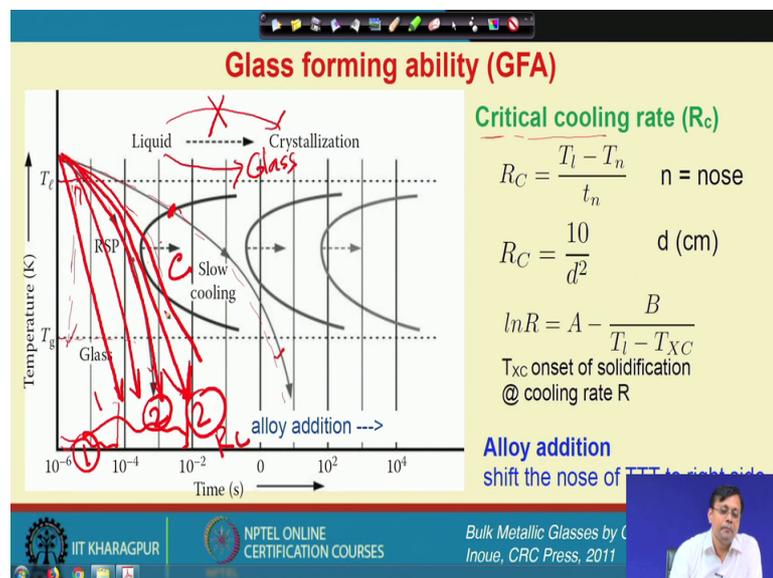
In earlier classes, we have talked about this time temperature transformation diagram and which is also a important diagram for glass forming alloy, in the left hand side you can see, here I have plotted schematically a temperature versus time, time is shown in a log scale. So, let say I may have taken or chosen an alloy and this alloy has a TTT diagram like this. C type of curve. And when we cool it and since if the under cooling is very high then nucleation rate is very high ok.

So, therefore, the nose of the top part of the TTT curve will have such a shape. So, lower under cooling will give you larger incubation period for nucleation whereas, a larger under cooling will give you more number of nucleation in the melt and now below certain temperature which is usually the nose of a TTT, below here the diffusion becomes sluggish and therefore, since the atom need to make a cluster to make a nuclei

and that basically decreases. So, diffusion in the melt also decreases ok, and therefore, we can get a larger incubation time. So, this is the explanation why the shape is like a C ok.

Now once again, this is the liquids temperature, and let us say this is a glass transition temperature, and this is the region when we will get a super cool liquid. Usually when the cooling rate is greater than  $10^6$  K/s, we call it as a rapid solidification ok. So, the cooling rate is very very high. Now, if we can apply or adopt such rapid solidification and bypass the nose of the TTT curve; then, instead of going towards this crystalline region ok.

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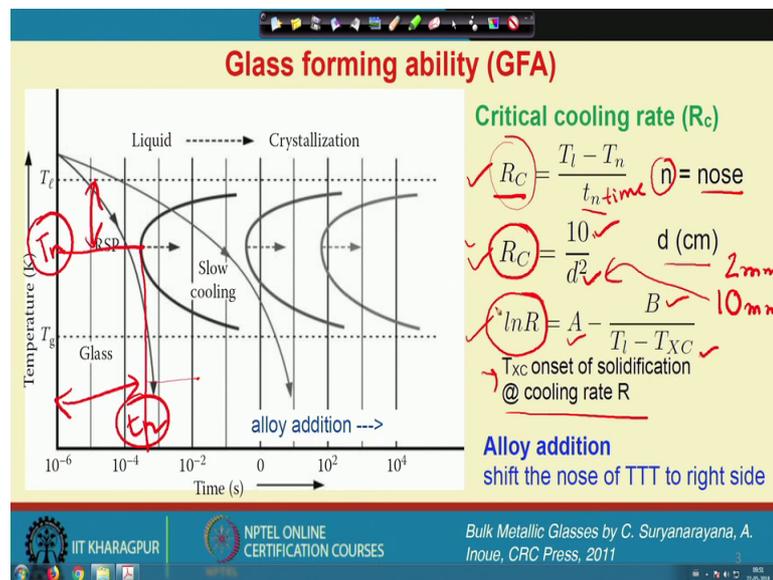
So, we can bypass this and we can transform a super cooled liquid into a glass. However, if we cool it slower than the cooling rate adopted for rapid solidification then we will enter into the crystalline region and definitely there is no chance to get any glass at all in such a situation. So, if this is the general understanding of the solidification process from liquid to crystallization and bypassing liquid to crystallization to in order to form a glass ok.

So, in that case, definitely we have to think about the cooling rate adopted in order to bypass this nose of the TTT curve, and that is very much important. And so, we try to understand that even if we cool more faster you will get a glass little bit slower, we will get a glass again a little bit slower will get a glass, and if we somehow just bypass the

nose of the TTT curve will also get a glass and, but you can see the time required for this solidification is different than this solidification time ok.

So, this is case 1 this is let say case 2. In case 2, the cooling rate is much slower than 1, but in both case it is possible to get the glass. So, we can think about a critical cooling rate in case 2, let us say a critical cooling rate in order to obtain glass, because a slower cooling rate than the critical cooling rate will definitely encounter these nose of the TTT curve and some part some part of the melt will transform into crystal sure surely ok. So, therefore, the idea of critical cooling rate actually comes and now here scientist try to explain  $\frac{T_l - T_n}{t_n}$  here t is the time and n basically means the nose.

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So, the window for this particular time  $t_n$  and this is the temperature  $T_n$  is important. So, small  $t_n$  stands for the time and capital  $T_n$  stands for the temperature of the nose. So, if these difference actually become lower and lower, and the time, if this become higher and higher in that case the critical cooling rate required will be less and then we can tell that yes this is a composition which is easily glass formable ok.

So, this is a good idea and now then there are some other empirical relation that this is a second relation that I am showing you that is  $R_C = \frac{10}{d^2}$  here d is a centimeter. Let us assume I have taken a composition and this composition, I find out the critical diameter,

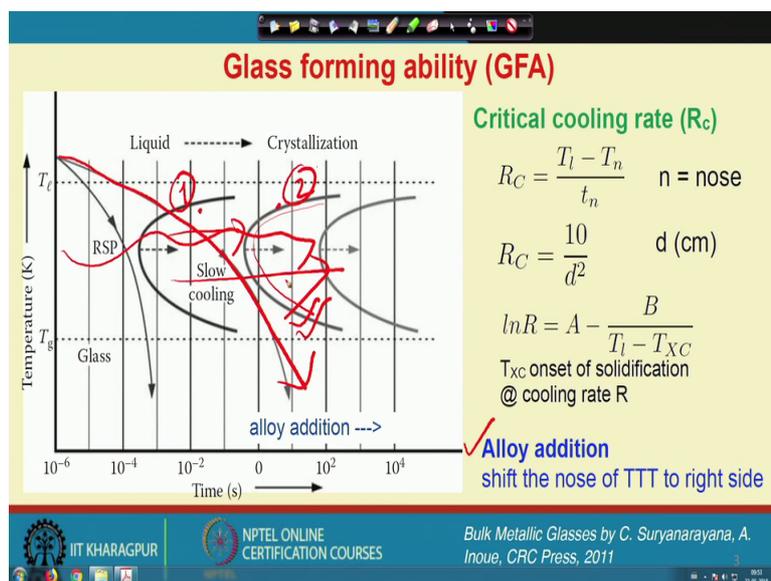
let us say 2 millimeter ok. I have taken another composition where it is 10 millimeter we can form glass.

If we make 11 millimeter diameter then there is no possible to make a glass, let us assume at this moment. And then if we put this 10 here, then we can estimate the value of the  $R_c$  ok, and this  $R_c$ , the critical cooling rate, which has a lower value tells that a glass is easily formable ok, very similar way here is also  $\ln R = A - \frac{B}{T_l - T_{xc}}$ , A and B are the constant,  $x_c$  is basically stands for the onset of the solidification.

So, this 3 relation explain that a lower value of  $R_c$  defines the ease of the glass formation, and which is expected. So, let us say if I have to develop a glass easy glass forming alloys. So, I have to go for a lower  $R_c$ , then I can make much bigger and bigger size glasses. Now, on the other hand the question may come to our mind that, how we are going to explain the increase of the glass forming ability, yes and that is why people have tried to make different alloy composition or changing little composition.

So that we can make a larger diameter or we can cast a larger diameter and how to do that? Yes there is a good option that is called alloy addition. So, let us say I have 3 elements in a glass forming composition and I am adding another fourth element into that composition and in this way what we are trying we are moving this CCT or TTT curve to the right hand side actually.

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So, from let us say composition 1 and composition 2. So, in case of composition 2 there is shift of this nose of the TTT curve and in that case actually much slower cooling rate we can get a glass and therefore, the glass forming ability of glass 2 is more than glass 1 and this is what we learn by alloy addition or we can do by alloy addition.

So, theoretically the more and more shift or more and more incubation time of crystallization will allow you to form a glass more and more easily because our intention is to bypass the crystallization or avoid crystallization. So, that we can reach to  $T_g$  and there will be a phase transformation in the super cool liquid in order to transform a under cool liquid into a glass.

So, this is what we learn from here now let us have a look at a different alloy system and different alloy composition I just need summery to show you what are their critical cooling rate values, because there we can learn which one is much easy to form a glass and which one is more difficult to form a glass, since I told you that rapid solidification processing means like melt spinning.

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| Critical cooling rate ( $R_c$ ) |   |
|---------------------------------|---|
| $R_c$ K/s                       | Alloys  |
| $3 \times 10^6$                 | $Au_{77.4}Ge_{13.5}Si_{8.4}$                        |
| 24                              | $Ca_{40}Mg_{25}Ni_{15}$                             |
| <20                             | $Ca_{45}Mg_{15}Zn_{20}$                             |
| 250                             | $Cu_{50}Zr_{50}$                                    |
| <40                             | $Cu_{48}Zr_{48}Al_4$                                |
| 4.4                             | $Cu_{42}Zr_{12}Ag_5Al_5$                            |
| 100                             | $Fe_{15}Cr_{15}Mo_{10}C_{10}B_3P_{10}$              |
| $4.4 \times 10^7$               | $Fe_{50}Ni_{40}P_{10}B_5$ (Metglas 2826)            |
| 124                             | $Hf_{70}Pd_{30}Ni_{10}$                             |
| 58                              | $La_{35}Al_{25}Cu_{20}$                             |
| 69                              | $La_{35}Al_{25}Ni_{20}$                             |
| 1                               | $Mg_{65}Cu_{25}Gd_{10}$                             |
| 100                             | $Mg_{65}Cu_{25}Y_{10}$                              |
| 0.7                             | $Mg_{65}Cu_{14}Ag_5Pd_5Gd_{10}$                     |
| 20                              | $Mg_{65}Cu_{7.5}Ni_{7.5}Ag_5Zn_5Gd_5Y_5$            |
| 4                               | $Nd_{40}Co_{30}Al_{10}$                             |
| $R_c$ K/s                       | Alloys  |
| 57                              | $Ni_{62}Nb_{38}$                                    |
| 10 <sup>6</sup>                 | $Ni_{65}Pd_{15}P_{20}$                              |
| 550                             | $Pd_{75}Cu_{25}Si_{16}$                             |
| 128                             | $Pd_{40}Ni_{40}P_{20}$                              |
| 0.067                           | $Pd_{42.5}Cu_{30}Ni_{17.5}P_{20}$                   |
| 0.150                           | $Pd_{40}Cu_{25}Ni_{15}P_{20}$                       |
| 1.58                            | $Pd_{40}Cu_{30}Ni_{10}P_{20}$ (without fluxing)     |
| 0.1                             | $Pd_{40}Cu_{30}Ni_{10}P_{20}$ (with flux treatment) |
| 0.067                           | $Pd_{30}Pt_{17.5}Cu_{12.5}P_{20}$                   |
| $1.8 \times 10^6$               | $Pd_{82}Si_{18}$                                    |
| 800                             | $Pd_{52}Si_{18}$                                    |
| 6                               | $Pd_{41}Si_{19}$ (with flux treatment)              |
| 1.5                             | $Zr_{65}Al_{17.5}Ni_{10}Cu_{17.5}$                  |
| 1.4                             | $Zr_{41.2}Ti_{13.8}Cu_{12.3}Ni_{10.0}Be_{22.5}$     |
| 28                              | $Zr_{46.25}Ti_{8.25}Cu_{17.5}Ni_{10.0}Be_{27.5}$    |
| 10                              | $Zr_{59}Cu_{15}Ni_{12.5}Al_{10}Nb_5$                |

So, where there is a liquid which is injected on a copper wheel and the wheel is rotated at a very high speed and then we can make a 60 micrometer or 100 micrometer thin film, out of this melt spun which are called as a ribbon and those ribbon we can really as a very high cooling rate and we can form a glass. And therefore, here you can see that

there are some glasses which has a  $R_c$  or critical cooling rate value of  $10^7$  K/s and this is a very famous glass forming composition called as Metglas

Because it is a soft magnetic glass which is used in many transformer core with zero core loss. There is no hysteresis almost like that and here also some gold germanium glass, so here also the cooling rate require is very high. So, we can directly say by looking at the  $R_c$  value that these are poor glass forming alloys or the glass forming ability of this alloy is low. Now let us have a look at let us say a magnesium based glass forming composition, yes here it is 1.

So, compare to a metglass this is a better glass forming alloy, so this 1 is better and now let us go to this quinary alloy here magnesium copper, silver, palladium, and gallium is there and here some extra alloy addition has been made in order to form the glass at a lower cooling rate, because the cooling rate required is 0.7, which is lower or slower than 1. Now let us have a look at the right hand side this is very much interesting here mostly nickel niobium or nickel palladium phosphorus.

So, if somebody ask me then I will definitely say that nickel niobium is a better glass forming alloy then the nickel palladium, because here the value is much higher I need much cooling rate to bypass the crystallization. Now, that is another interesting thing what we can do during glass, glass formation that we can use some flux because in order to avoid crystallization the melt should be more and more pure.

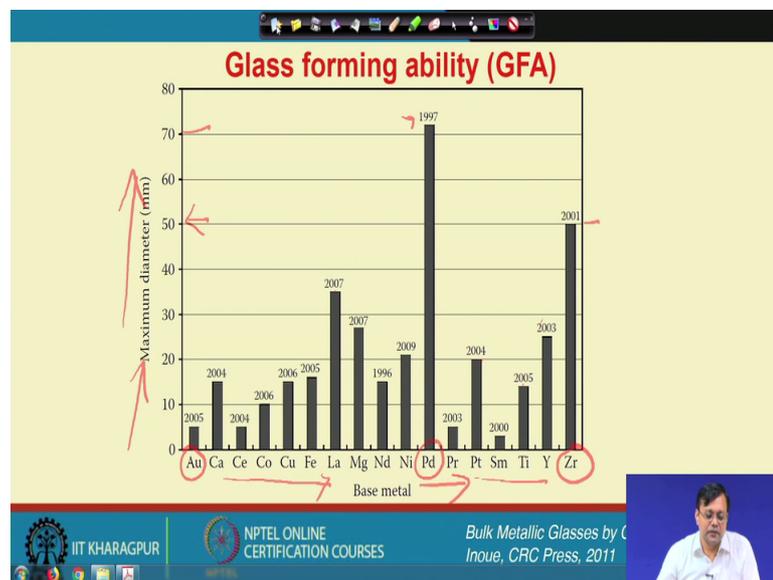
So, here purity means there will be no dissolved glasses, there will be no oxygen content ok. So, in that case we can avoid in homogeneous nucleation and to avoid inhomogeneous nucleation the liquid melt should be more pure and therefore, fluxing technique is a good idea or a good approach to adopt. And therefore, even you can see that without fluxing here you need 1.58 Kelvin per second cooling rate whereas, with flux treatment we need 0.1.

So, we learnt that this is a better even though the compositions are same ok, so by using flux treatment we can improve the glass forming ability. So, how we can improve glass forming ability if somebody ask you then there is a alloy addition by which we can shift the nose of the TTT curve also we can improve the glass forming ability by fluxing technique. Now let us have a look with some palladium silicon and here with flux treatment the cooling rate is much slower. So, we improve again.

Now, if you compare this, the palladium based glasses. The one here with this one, let us see and compare here. So, here also palladium, copper, nickel, phosphorus, here palladium silicon. So, by quinary system by adding some multiple element we have enhanced the glass forming ability compared to palladium silicon binary alloy. So, you can see that the adding another two element improve the glass forming ability.

However this may not be true in all cases. What I want to mean that you can keep on adding different element and you will make a better glass. It is not like that. There are many different calculation I should do and also there are many different trials and error one has to look at those things we will discuss in detail.

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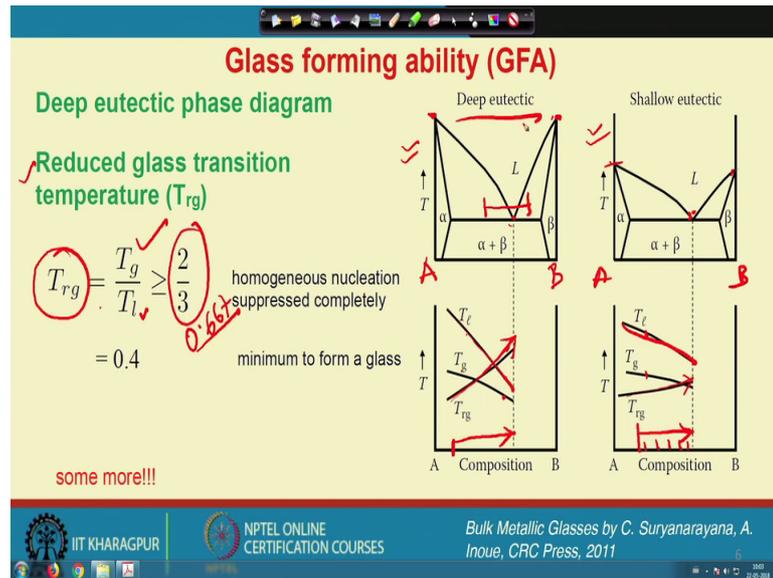


So, let us have a look at a different alloy system and the maximum diameter has been reported so far. So, in the x axis I have plotted here the base metal and here this is the maximum diameter. So, as the cooling rate is important, if somebody tell you or proves that 10 millimeter diameter has been made as a fully glass ok. So, the 10 millimeter diameter that composition is better than 1 millimeter diameter.

So, glass forming ability of 10 millimeter diameter rod forming composition is better and therefore, the maximum diameter is also a measure of a good glass forming ability. Now, this is reported in 1997 something like 7 centimeter ok. So, this is the palladium based glass, so palladium based glasses shows a better glass forming ability then the gold ok, so these zirconium based alloys like Vitreloy alloys ok.

So, the maximum diameter so far it has been made something like 5 centimeter ok, so you can have a look at different base alloying element and how the maximum diameter is reported at what time and day by day this data is updated and one can look at different review literature and so on. Now, again to understand this glass forming ability we have discussed about the Critical cooling rate and maximum diameter.

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However, by looking at the phase diagram we can also learn something. It is told that it deeper the eutectic phase diagram will enhance your glass forming ability because what you need to deal with basically the liquidus temperature in case of eutectic alloy the liquidus temperature is low ok, and if the glass transition temperature is sufficiently high then we can also make a composition and transform it to a liquid transform to a glass. Like here please have a look this is a deeper eutectic and this is a shallower eutectic how you will prove that ok.

These are the melting temperature of 2 different element let us say A and B and here is also A and B; however, the eutectic temperature compare to their individual melting temperature is relatively high ok, so the ratio of this one and the eutectic temperature is high here and. So, the liquidus temperature very sharply falls and here it is less sharply falls ok.

So, in that case the deeper eutectic, people find out that there are more easier to form the glass. The reason is here because there is a parameter scientist have told that is reduced

glass transition temperature, what is reduced glass transition temperature? Which is defined by  $T_{rg} = \frac{T_g}{T_l}$ ,  $T_g$  is glass transition temperature,  $T_l$  is liquidus temperature which should be always greater than 0.667 ok.

So, if you can get a glass or if you simply make a glass and measure its glass transition temperature and liquidus temperature and make a ratio you can say a good glass forming will always have a greater than 0.67 value, that it says. Now, if you have a look at this deeper eutectic this also explain how these reduce glass transition help in estimating the glass forming ability, yes here this is the liquidus temperature and this is the glass transition temperature.

So, the reduce glass transition temperature increases by taking the ratio. So, if you go from this composition to the right hand side you see the glass forming ability in terms of reduced glass transition temperature increases whereas, in this case since it is not a deeper eutectic. So, if you start from this composition and go towards here means you make different composition and measure its liquidus temperature and measure its glass transition temperature and make the ratio.

And then you will see and then you will see the  $T_{rg}$  is not increasing too much and therefore, we learn that a deeper eutectic is always beneficial a in a phase diagram in order to give you a better glass forming composition. Now, let us have a look at different glass forming ability and reduce glass transition temperature of different systems so far reported.

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**Glass forming ability (GFA)**

$$T_{rg} = \frac{T_g}{T_l} \geq \frac{2}{3}$$

**Reduced glass transition temperature ( $T_{rg}$ )**

| Alloy Composition  | $T_{rg}$ |
|--|----------|
| Ca <sub>65</sub> Al <sub>35</sub>  | 0.69     |
| Ca <sub>67</sub> Mg <sub>19</sub> Cu <sub>14</sub>   | 0.60     |
| Ca <sub>57</sub> Mg <sub>19</sub> Cu <sub>24</sub>   | 0.64     |
| Cu <sub>65</sub> Hf <sub>35</sub>  | 0.62     |
| Cu <sub>49</sub> Hf <sub>42</sub> Al <sub>9</sub>  | 0.62     |
| Cu <sub>64</sub> Zr <sub>36</sub>  | 0.64     |
| La <sub>55</sub> Al <sub>25</sub> Ni <sub>20</sub>   | 0.71     |
| La <sub>62</sub> Al <sub>15.5</sub> (Cu,Ni) <sub>22.3</sub>                                  | 0.58     |
| La <sub>50.2</sub> Al <sub>20.5</sub> (Cu,Ni) <sub>29.3</sub>                                | 0.47     |
| Ni <sub>62</sub> Nb <sub>38</sub>  | 0.60     |
| Ni <sub>61</sub> Nb <sub>33</sub> Zr <sub>6</sub>  | 0.49     |
| Pd <sub>40</sub> Ni <sub>40</sub> P <sub>20</sub>  | 0.67     |
| Pd <sub>40</sub> Cu <sub>30</sub> Ni <sub>10</sub> P <sub>20</sub>                           | 0.67     |
| Zr <sub>41.2</sub> Ti <sub>13.8</sub> Cu <sub>12.5</sub> Ni <sub>10</sub> Be <sub>22.5</sub> | 0.624    |

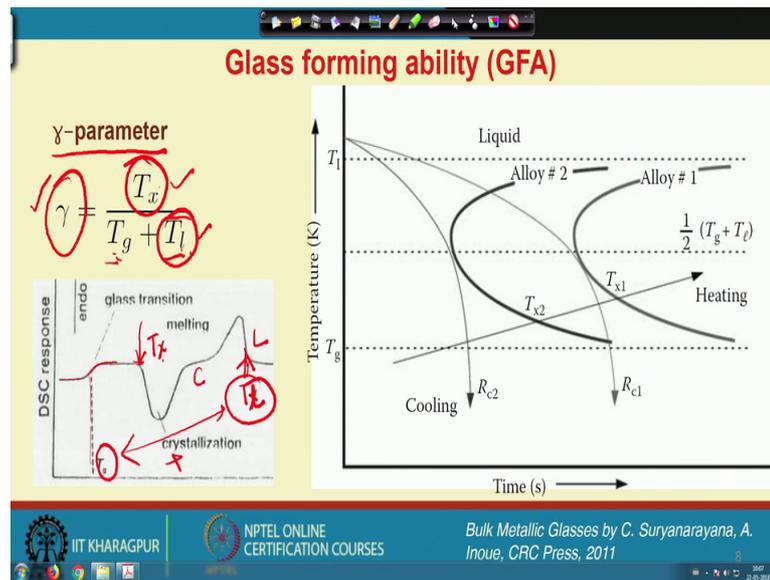


*Bulk Metallic Glasses by C. Suryanarayana, A. Inoue, CRC Press, 2011*

So, the definition of reduce glass transition temperature is here and you see these are calcium and some copper base glasses and where these values are 0.69, 0.60, 0.64, 0.62, 0.64 and so on, where some lanthanum based alloys shows little bit higher and this composition are much poor which is not really very good whereas, nickel niobium is little bit better or palladium which is a very good glass former has a value which is greater than 0.67.

So, out of this whole list we can easily say that palladium base these composition are better glass formers, and that we have already looked in the plot that we can make a much bigger size in terms of glass forming ability. Now, there are other parameters which has been explained by Z. P. Lu and he proposed that we can again consider this gamma parameter and it will help to explain the glass forming ability ok. How we do that? This gamma he introduced a parameter, which is a ratio of  $T_x$  by  $T_g$  and  $T_l$ .

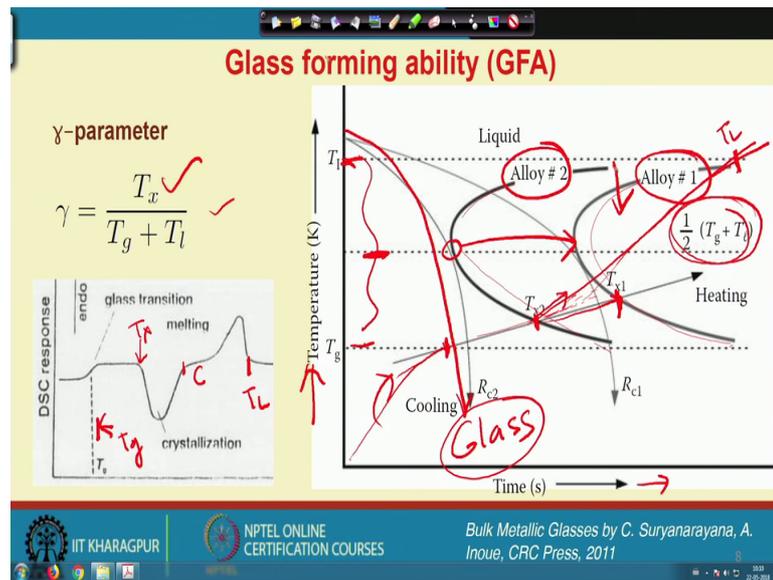
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Now we need to look at what is  $T_g$ , yes if we see that DSC response of a glass did the onset of glass transition is a  $T_g$  ok, and here this is the onset of crystallization which is called as  $T_x$  and here it form the liquid, here it is liquid and this is basically crystal and here this is called as a  $T_x$ . So, this is the temperature  $T_l$ , so this is the liquidus temperature ok. So, now, we simply see a response, the DSC response of a glass and then we simply take this ratio  $\gamma = \frac{T_x}{T_g + T_l}$  And now we can make a higher value of gamma by increasing the  $T_x$  and by decreasing the  $T_g$  plus  $T_l$  ok.  $T_g$  plus  $T_l$  and maybe initially it may looks a little bit complicated, but you realize that the lower the  $T_l$  will be beneficial for a better glass former there is no doubt or higher the  $T_x$  will have a beneficial effect on ease of the glass forming ability and let us have a look how we explain this feature using a TTT diagram.

So, here in the right hand side I show you a TTT diagram with temperature versus time, so, here, let us say this is alloy 2 and this 1 is the alloy 1 ok. Now, when we start with liquid melt and under cool it and then super cool it then we may get a glass, let us say the case is like this ok. So, here we already get a glass. We start with this glass and then put it inside a differential scanning calorimeter, then we are heating it.

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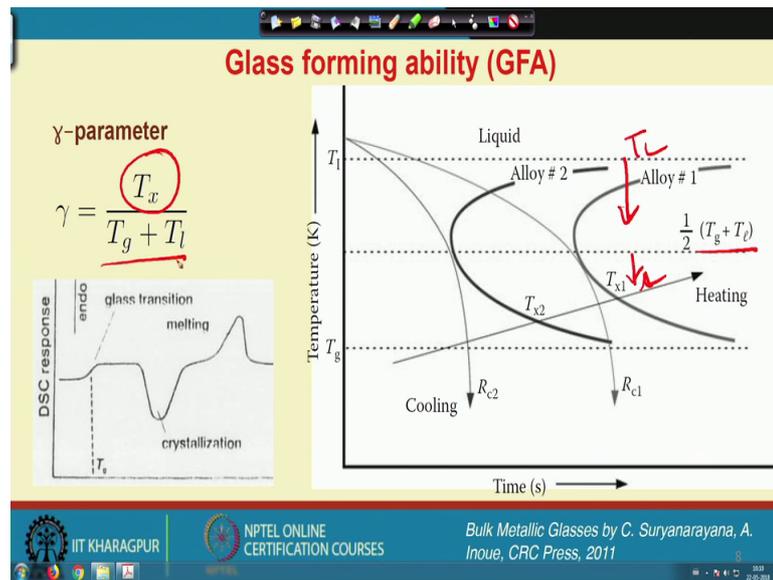


So, during heating means we are going from this side we are heating it, so first we will encounter this phase transition that is called  $T_g$ , here this will first encounter and now what we will see? We will again encounter here the we will touch the TTT curve and crystallization will begin and after sometime, it will be fully crystallize which is happened here and here the transformation finish completed and here it is basically crystal and then will go further and then will ultimately reach to  $T_l$  ok. So, here we already reach to  $T_l$  and this is  $T_x$  and this is  $T_g$ . So now you understand how the events goes on ok.

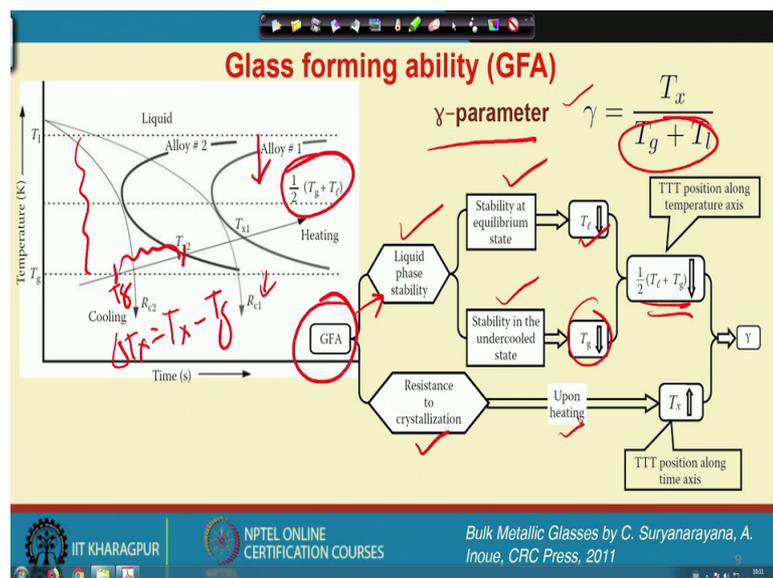
Now let us think about only alloy 2 and try to explain the gamma parameter here, so what we are telling that  $T_x$  should be should be higher and higher. Yes that is a good idea. So, it means if we have alloy 1, then alloy 1 where TTT curve is shifted to right hand side then we will have a higher  $T_{x1}$  value and this will increase the gamma parameter yes that we can also prove using the TTT curve because the nose of the TTT curve has been shifted from here to here.

Now, let us have a look at what is this half of  $T_g$  plus  $T_l$  value, so half of this  $T_g$  plus  $T_l$  value will give you the  $T_l$  here and this is  $T_g$ . So, half means basically the position of the nose of the TTT curve and which need to be lower and lower. So,  $T_l$  should come down so  $T_l$  should come down this is a  $T_l$  should come down and therefore, half of  $T_g$  plus  $T_l$  will also come down.

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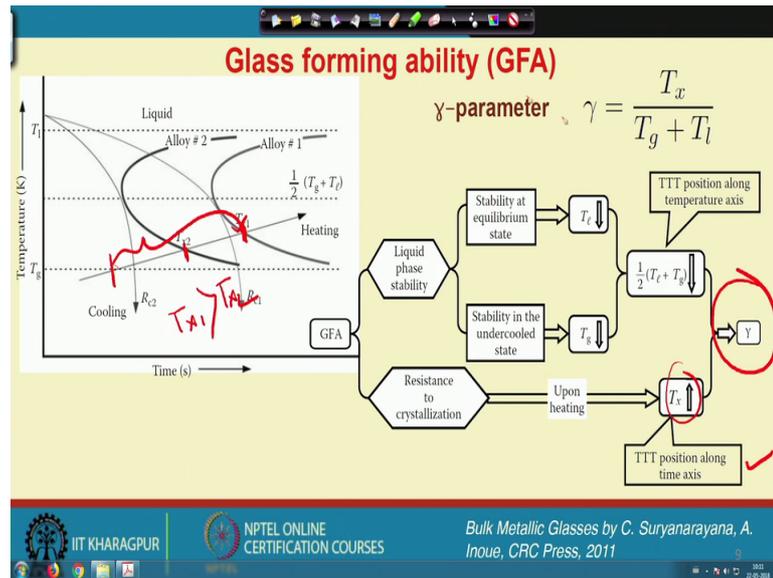
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So, basically it says that we need a higher value of  $T_x$  and lower value of  $T_g$  plus  $T_l$ . And therefore, this gamma parameter actually explained that the glass forming ability has 2 different aspects, the first one is the liquid phase stability. So, liquid phase stability means this is a super cool liquid stage or during heating this is a super cool liquid stage ok. So, the difference between  $T_x$  minus  $T_g$ . So, here is the  $T_g$  ok,  $\Delta T_x$  we call it so this stability we need higher.

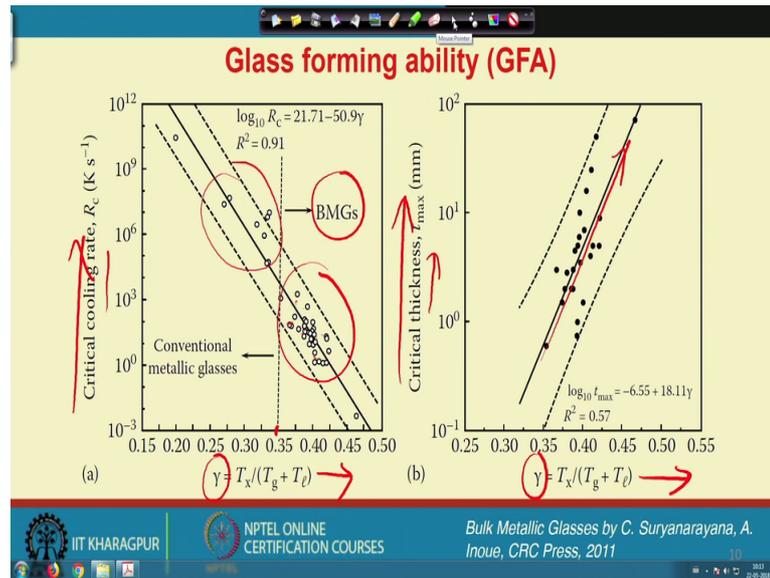
So, stability at the equilibrium state means basically  $T_l$  should go down and  $T_g$  should also go down and therefore, this value will go down, which will increase the gamma value. So, stability of the under cool liquid state will give you also the same. So, this is a parameter where you get. On the other hand we need a high resistance to crystallization and during heating. So, how we get that? Yes the resistance is here.

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So, this is the resistance upon heating and therefore, we need a higher value of  $T_x$ , so this is the higher value of  $T_x$  then  $T_x 2$ . So,  $T_x 1$  is better than  $T_x 2$  than  $T_x 2$  and therefore, the TTT position along the time axis will increase which will increase the gamma parameter and this is the beneficial effect of this gamma parameter to explain the ease of glass formation.

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And therefore, people had a look at the critical cooling rate and casting thickness and so on and they have plotted the gamma parameter in this way and they have a look at what is the critical cooling rate or casting thickness one can achieve, you can see these are the real glass forming composition their gamma values are shown here and their cooling rate is shown or the casting thickness is shown here. You can see that almost a value of greater than 3.5 we can form bulk metallic glass a bulk means basically greater than greater than 2 mm in thickness ok.

So, here these are rapidly solidified glass, which are like ribbon, which are conventional metallic glasses. So, the casting thickness also increases as the gamma parameter value increases and therefore, we understood that gamma parameter, good value in order to explain the glass forming ability. In the next classes we will continue the discussion on the glass forming ability.

Thank you.