# Advanced Materials and Processes

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## Lecture - 11
## Amorphous Materials Part – V

Last class we are talking about various class forming criteria. We talked about the criteria based on the phase diagram. And we also talked about the criteria based on, what is called T g and T x.

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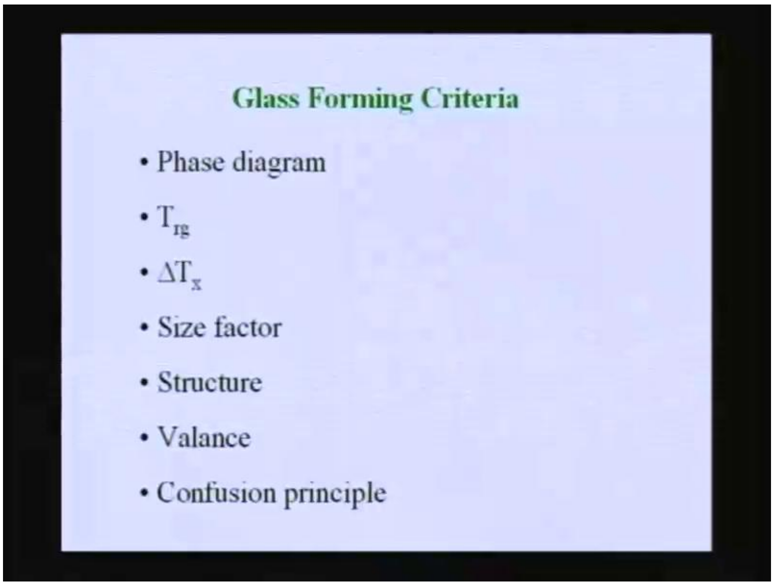

**Glass Forming Criteria**

- Phase diagram
- $T_{rg}$
- $\Delta T_x$
- Size factor
- Structure
- Valance
- Confusion principle

For example, T r g and then delta T x.

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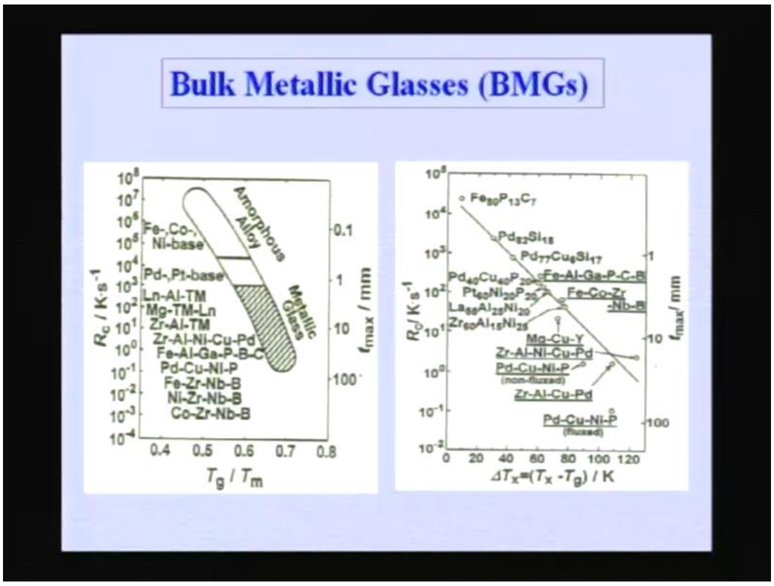

Bulk Metallic Glasses (BMGs)

And we tried to look at how we classify glasses, into bulk glasses and conventional glasses. Based on these two criteria, one is called the T r g, which is T g by T m and another is the delta T x. So, if you look at these two plots. Basically, what you see is that, as the T g by T m increases, beyond a particular value of above 0.6. The R c which is the critical cooling rate becomes so low of the order of around 10 to the power 2 Kelvin per second.

That means, about 100 Kelvin per second, which is something which is easily achievable by conventional casting roots. For example, if you use a normal chill casting, or casting in a water cool copper mold. What you achieve is of the order of around 100 Kelvin per second. So, that is the kind of cooling, which one can easily achieve, without really going into any rapid solidification processing techniques. So, these are conventional casting techniques.

So, just by conventional casting, one can achieve glasses and which is what we define them as bulk glasses. So, all those glasses which can be assured using the conventional casting techniques or those which are bulk glasses, so in this particular aspect the T g by T m, which is called the reduce glass transition temperature T r g. If one can have more than above 0.6, we can say these are bulk metallic glasses.

Similarly, coming to above delta T x again. If have a delta T x beyond about 60 degrees Kelvin or 70 degrees. You can again see, there is inverse relation between the delta T x and the R c. So, as you increase the delta T x, which is nothing but the T x minus T g.

The region where the super cool liquid is stable, we talked about it in the last class, which is call the super cooled liquid regime. So, if the super cool liquid regime is large, we can say the glass formation is more easy or the glass is more stable. So, the glass, whatever glass it has formed, it does not crystallize up to high temperatures.

That means, the glass is more stable. So, such stability of the glass can be correlated to the R c again. And you can see, if you about 60 or more than 60 delta T x, the R c will be less than about 10 to the power 2 Kelvin per second. So, again you can call those things as bulk glasses. So, bulk glasses are those, where the T r g is above beyond 0.6. And delta T x is a about beyond 60, but as I mentioned to you, in the last class. These are the empirical criteria, based on a large number of experiments, on a large number of systems. You can see here itself, about 20 different compositions have been put down here. So, based on various experiments that people have carried out on a number of alloys. They have found out of each alloy, what is the R c. For each alloy, what is the delta T x by measuring the T g and T x. And finally, found out this kind of empirical criteria.

So, these are not really predicative type of criteria. It cannot tell you, before doing a experiment, whether a glass is good bulk metallic glass or not. But, only after doing an experiment, one can find out, whether it is good glass former or not. But, at the same time these are also useful. Because, one need not have to really cast it into the form of way normal casting. And finding out, whether it is a bulk glass former or not.

What one can do is make an alloy, subjected to melt spinning, which is one of the rapid solidification techniques. And once you subjected to melt spinning, you get a ribbon. And take that ribbon and subject it to at DSC. And if heat it an DSC you will get the T g and T x very easily. And from the delta T x or T g by T m, how do you get the T m, you heat the same alloy up to it is melting point, in a DTA or in DSC.

If you can heat it up to the melting point, you can find out the melting point also. And once you know the T g, once you know the melting point T g by T m can be found out. So, from such a thing one can find out, if it is very large, we can say this alloy is a bulk glass former. So, now if I take that composition, and cast it by the normal casting route, I can get a good glass former.

And this plot also gives you an idea of what is relation a between T g by T m. And delta T x with the t max, which is what is the maximum thickness one can achieve, as an amorphous phase. This is what I told you, it has some correlation to what we say, the critical diameter for a hardenability. So, whenever we are saying that, a particular alloy is more hardenable than another alloy. We always talk in terms of the critical diameter. If an alloy has a large critical diameter, we say it is more hardenable.

So, similarly here if the delta T x is very large. Then, you can see the t max is also very large. So, as a result for all those alloys where the, for example you take the case of delta T x being 100. If you take that 100, so the T x is the order of around. This is logarithmic scale. You should see that, this not a linear scale 1, 10, 100. So, you can get above 30 millimeters without any problem.

So, if you go to about 120 or so it would be around 130, 140 like that, above 30, 40 mille meters. So, one can achieve large thicknesses, if you have large delta T x. Similarly, if you have large T r g, again one can achieve large T x. So, this can give you idea, that once I measure the delta T x put that delta T x in a plot, like this. Put that point on that line. And from that line you can measure what is the t max, that can you achieve, for that new alloy.

And take that new alloy now melt it and cast it, and you may able to get. In principle, because these are all empirical relation there can be few exceptions. But, otherwise in general one can say, that if you take that alloy, you will be able to achieve that much t max. That means, up to that thickness, one can easily get amorphous phase without getting any crystalline phase. So, this is something one can do it.

So, though this criteria or not really predictive type of criteria. That means, they cannot predict, whether an alloy is a good glass former or not, without making the alloy first. But, at the same time there are help full to make bulk glasses, whether an alloy can really become a bulk glass or not, we can get an idea from this. And there are also, as I was mentioning in the last class, there also thermal dynamic criteria which are available now.

One can calculate, what are called the free energy of an amorphous phase. And if the free energy of the amorphous phase is highly negative, we can say the amorphous phase is more stable. So, in all those systems if you take any binary system or ternary system or a quaternary system. For any given composition, if you can calculate what is the free energy of the liquid at any temperature? Let us say consider any temperature, such as eutectic temperature.

At the eutectic temperature, for that particular system or at the room temperature, if you do not know where is the eutectic for that particular system. You can calculate at room temperature. At the room temperature if you can calculate, and find out that the free energy of the liquid is highly negative. Then, you say that liquid is more stable liquid, when you compare with some other liquid, which are the low negative enthalpy of mixing.

Or even a positive enthalpy of mixing, or a positive free energy of mixing, because it is possible, that in cases where you have immiscible system. The free energy of mixing will be positive, we have talked about it in the thermodynamic class. So, that if you have delta h mixing being highly positive. Even if you add T delta as mixing to it, it will not really make it completely negative. So, usually at some compositions, you see their free energy of mixing will be positive.

So, it is possible in some systems, it is positive. And in all those systems, it is almost next to impossible to get a glass. If you want a glass the liquid should be stable first. Single phase liquid should be stable. And that is possible, only when the delta h mixing is highly negative. So, if you one can calculate the delta x mixing. And intern the delta r, the t delta is mixing to it, and get what is called the delta g mixing. For that particular phase, liquid phase.

And find out the it is highly negative. And one can say that without even making an alloy. That it is easy to predict that, this alloy would probably become a glass. And one can make such an alloy in a system, in a ternary system or a quaternary system. Identify all those compositions, which are highly negative and enthalpy of mixing. And you can make only those few compositions. And then check whether they become a easy glass formers. And in most cases, they would become a easy glass formers.

So, these are some of the predicative kind of criteria. And there are number of peoples in the world, who are trying to make this kind of predicative criteria. Otherwise, the existing criteria are these.

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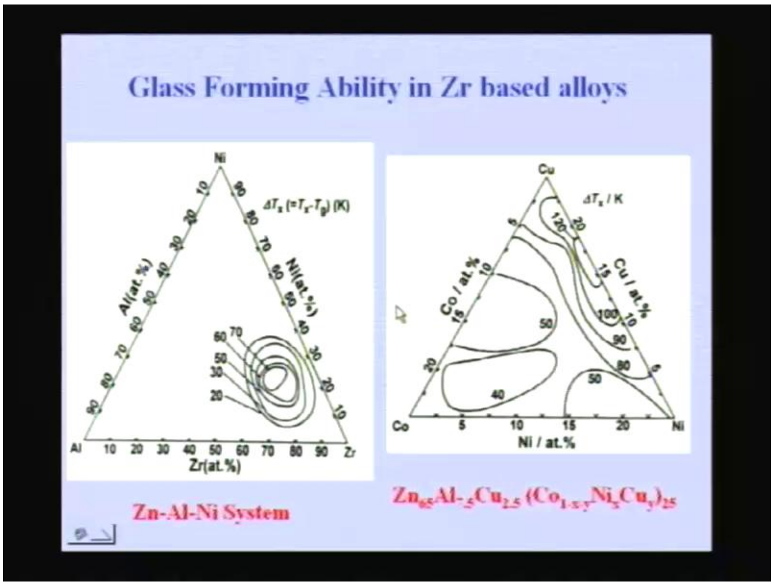

Glass Forming Ability in Zr based alloys

Zn-Al-Ni System

$Zn_{65}Al_{7.5}Cu_{2.5}(Co_{1-x-y}Ni_xCu_y)_{25}$

And we talked about, what is the effect of multi components system on the glass forming ability. We told you that, one of the criterion is what is called confusion principle. That means, you are confusing the liquid. As far as what kind of a crystal it should take, when you add a large number of elements, when you put 5 or 6 elements in to the liquid. Then, all these elements have to rearrange themselves, in to the form of one crystal structure when liquid has to crystallize into a crystal.

And the diffusivity of all these elements have to come into picture. And as a result, you may end up in a amorphous phase, instead of getting a crystal. Whenever, you have a large number of elements. That is what you is shown by this particular two plots. One is simple ternary system, zirconium, aluminum, nickel system. And another is a 6 component system, zirconium, aluminum, copper, cobalt, nickel, copper kind of a system.

And you can see, the delta t the maximum delta T x hear is only 70, whereas as the maximum delta T x hear is 120. What is plotted here is that, iso delta T x plots. All those compositions having the same delta T x are plotted, here as one line. And if you look at all these lines, finally you can come to one small domain, which gives you all those compositions which have a delta T x of 120. And you can compare that with this, which is only about 70.

So, 70 is the highest in this system. And the highest in this 6 components system is about 120. So, from that one can say that, this is a better glass former. These 6 component system is better glass former. And at the same time, one can have a large t max. What is called the maximum thickness for the glass formation, would be much higher in this case when compare to this. So, this is one possible way of finding out, whether you have a easy glass formers or not.

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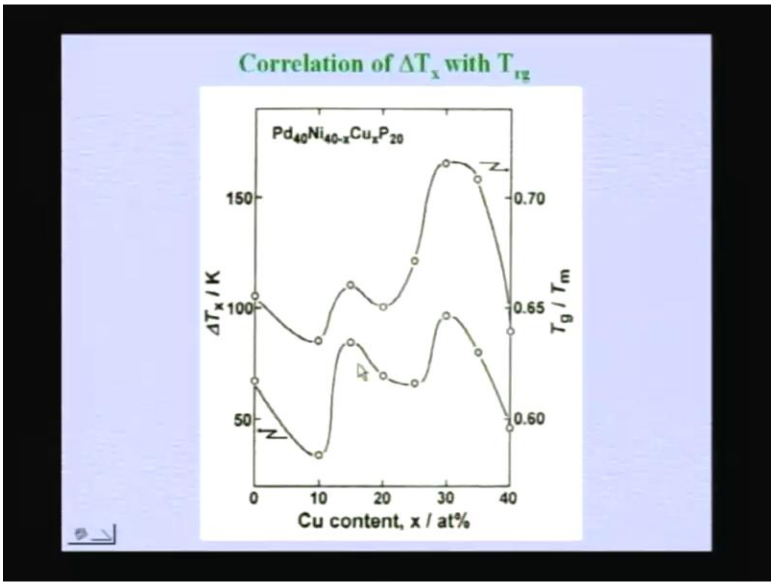

Correlation of $\Delta T_x$ with $T_{rg}$

And one more important point to remember is that, we use two criteria T r g, which is T g by T m and delta T x. What is important note, is that both this criteria are quiet synonymous. You can see from this figure that, this is a particular system palladium nickel copper phosphorous. And what we are plotting is the two parameters, delta T x and T r g, as a function of copper content.

If you keep on varying the copper content, both T r g and delta T x are varying. But, what is interesting to note, is that wherever the T r g goes, this is the bottom curve is for the delta T x, the top curve is for the T r g. Wherever the delta T x goes to a minimum, the T r g also goes to a minimum. Wherever this goes to a maximum, that also goes to a maximum. So, any one of this parameters is more or less a good parameter.

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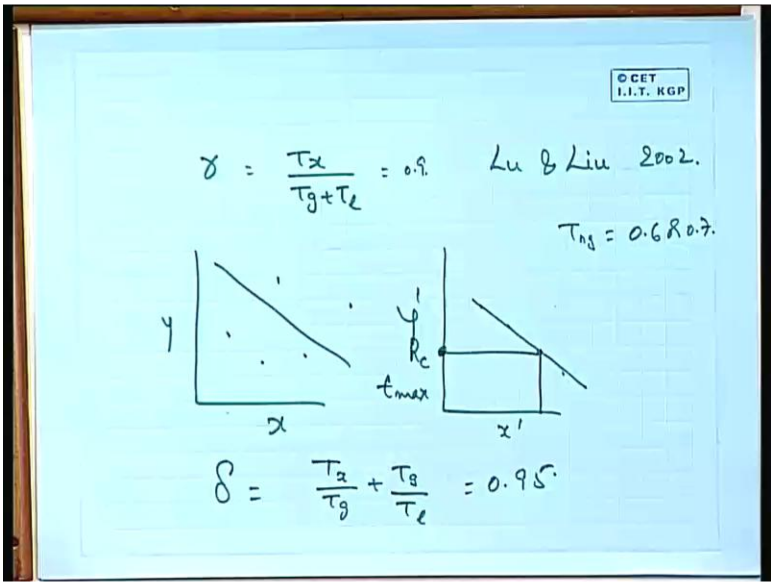

$\gamma = \frac{T_x}{T_g + T_l} = 0.9$ Lu & Liu 2002.

$T_{rg} = 0.6$ & $0.7$.

$\delta = \frac{T_x}{T_g} + \frac{T_g}{T_l} = 0.95$

And recently a new parameter has been found out in 2002, which is called gamma parameter which is nothing but T x by T g plus R l. This is by two persons Lu and Liu. In 2002, this has been proposed. And this is when the people try to plot the R c as a function of this gamma parameter. Instead of T r g or delta T x, you get a much better plot. That means, all the points can be fitted into a better list square fit line, rather than the other.

Whenever you fit points in a two dimensional map, what is important, is what is called the co-relation factor. How good is the co-relation, is it 0.9, people say if it is 0.95, 0.99, then you say it is a better fit. If it is much lower value, then we say it is not a better fit. For example, if you are plotting some y with x. And you have points like this. And you draw a state line, obviously it not a good fit. But, if you have some y dash with some other x dash.

And you have all the points like this. And then you draw a line where all points fit onto the line, then we say better fit. So, people have found that, this parameter is much better. And in fact, from our own research, we found out another parameter which we call it as a delta parameter, which is nothing but T x by T g plus T g by T l. Is nothing but just playing with the parameters. And we found that this gives much better fit, than any other parameters that have been reported so far.

And the correlation factor for these is of the order of around 0.95, and whereas for this gamma, you get about 0.9. And for the T r g many times you do not get beyond about 0.6

or 0.7. The r parameter which people usually refer to ask us, which is a correlation factor. So, like that one can, how do we do this, what we do is, we choose a number of data that is available already in the literature. For various alloys and then try to find out what is the R c for all these alloys, 40, 50, 60 alloys whatever is the available.

And plot that R c as a function of this parameter for that particular alloy. And if you try to plot for all these alloys and try to see, which kind of parameter gives you the best fit. And with that parameter, we can say yes, it is better. The advantage of finding out a better parameter is because, in future what you need to know; Is just find out what is that gamma parameter or delta parameter or some x parameter. For that particular new alloy, any new alloy that you are making.

And once, what is that parameter for that new alloy. From that parameter, you can find out, if you know this parameter, you can find out what is this. That whether it is R c or t max, one can find out very easily. And once we know that, this is the R c, this is the t max. One can easily make a bulk metallic glass of that particular thickness, without trying various thicknesses. And trying to look at which thickness will give me glass or which thickness does not give me glass.

So, without going into a number of experiment for that particular alloy, one can just read from such a plot. But, for that you are plot should be reliable plot. That means, the correlation factors, for that particular plot should be as high as possible. So that, that particular parameter which represents a glass for ability of various alloys, can be a reliable parameter.

So, what we need is a reliable glass forming criteria. And people whole of the world, people are struggling for finding out such a reliable parameter. And still lot of research, this is something which we have just found out about 2, 3 months back. And so there is lot of work going on in particular period. The other parameter is what is called?

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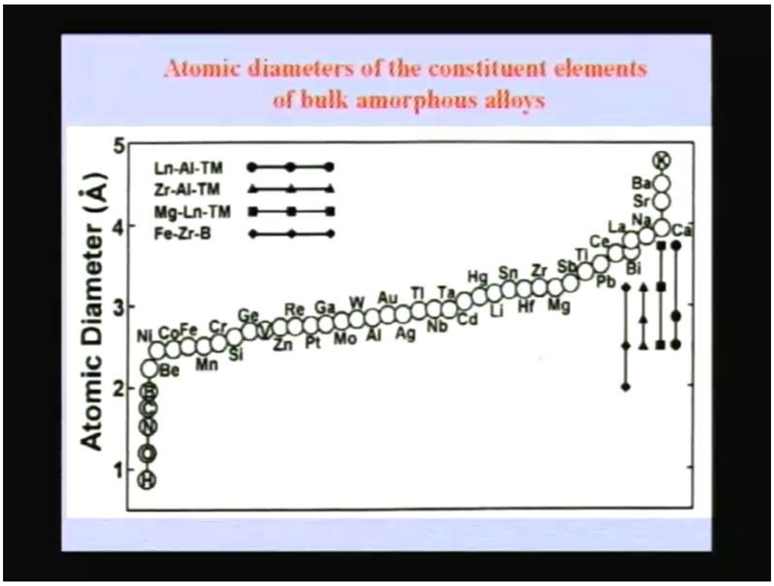

Atomic diameters of the constituent elements of bulk amorphous alloys

The radius, you all know from the Hume-Rothery rules. That if you have the size factor which is very small. What is the size factor tell me?

Student: ((Refer Time: 18:11))

So, atomic size difference between the solute and solvent atom is that the size factor.

Student: ((Refer Time: 18:20))

Yes, so that is what is what we call delta, which is r solvent minus r solute divided by the r solvent, the mode of it.

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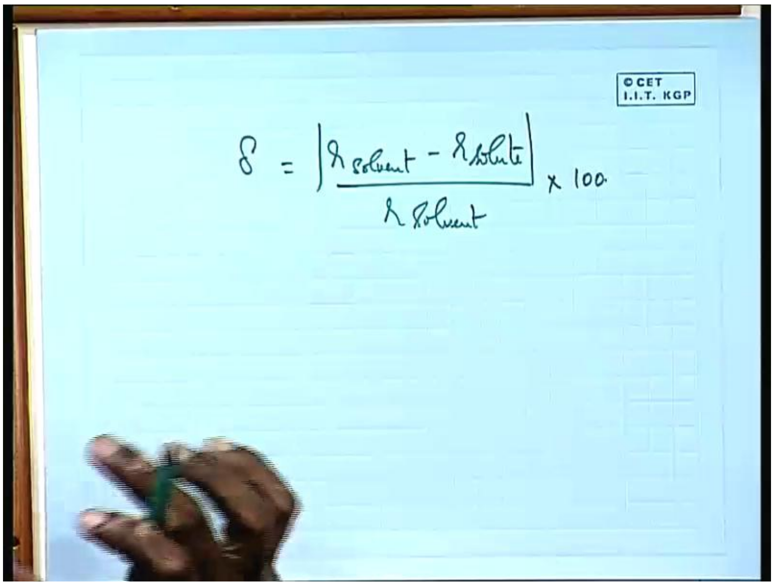

$$\delta = \left|\frac{r_{solvent} - r_{solute}}{r_{solvent}}\right| \times 100$$

Obviously, because solvent can solute, I mean solute can bigger or smaller we do not know. So, always this is expressed in terms of percentage. Multiply it with 100, you will get some percentage. And that is what is we called as size factor delta. So, it is this size factor, if it is much smaller, we get solid solution, that is what we say.

And if this size factor is larger than about 12 percent or 15 percent, this is again I can say is a thumb rule, which is an empirical rule. And people have found, let you one can easily get a glass. And now people differentiates, the conventional glasses which are the binary glasses which people have found long back. Like such as gold silicon, which is the first class that people have found.

And the bulk metallic glasses, which are multi component systems, where people see that you have, you need at least three elements, in a bulk metallic glass. Where one element is much bigger, another element is very small, which is very close to being an interstitial element, in that big atom. On the third element, should be somewhere with is in the middle of these two.

So, that you have big atom lattice, which is a solvent lattice. Into which we are putting very small atoms, which try to occupy the interstitial positions. Or occupy in the substitutional position. But, by that the they create lot of voids. And then were in the medium size atom goes and sits. And then gives you the best packing possible. If you want get a good glass, what people say now days is that, you should make the packing as efficient as possible.

The atomic packing, what is called dense random packing, this is called. So, if you can make the dense random packing as high packing as possible, then one can achieve a good glass. So, that is why what people are doing, is you can see here they various types of glasses people have found. Where one of them is lanthanum based, zirconium base, magnesium base, iron base, if you can look at all of them, which are shown here as bars.

What you are choosing is for example, let us take one of the example, lanthanum aluminum transition metal or any one. For example, zirconium aluminum transition metal, where is zirconium, zirconium is somewhere here, which is you can see triangles; where is the triangles here. So, zirconium is here, the aluminum is here, where is the aluminum, aluminum is in the middle. And then the other transition metal, such as copper nickel, which is much smaller.

So, you have small atom which is nickel, and the big atom which is zirconium and aluminum which is in the middle. So, if you choose such a structure with a small atom, which is about one Armstrong is a atomic size of nickel. Whereas, zirconium is close to about two Armstrong are bigger than that. And then put aluminum which is in the middle of that, you can get a good glass.

So, the number of people are trying again empirically with this kind playing, with the atomic radii I as one of the parameter. So, this is another parameter, which people have working on.

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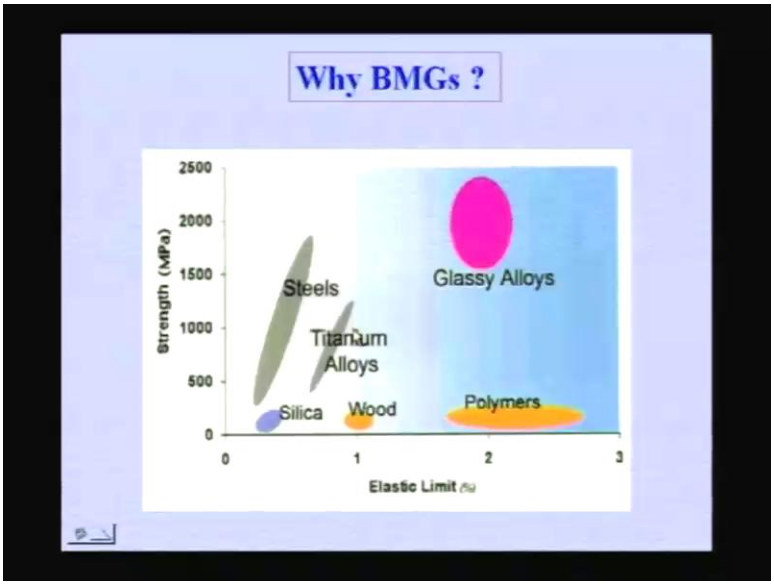

**Why BMGs ?**

Next question is, why do we want go for this glasses, which are particularly the bulk metallic glasses. The major interesting glasses as come now days, only because of these bulk glasses. Otherwise, people have made glasses in 1959, as I told you Pol Duwez has made it. And for few years, people have been very existed. Particular because of some special magnetic glasses, which are iron, silicon, boron type of glasses. Iron, silicon is very important alloy, what for we use iron silicon.

Student: ((Refer Time: 22:23))

Transformer course, all the sheets in the transformer core, they are all made of iron silicon, because it is a soft magnetic material. And it is hesitancies loop is very thin. And when people try to make boron or iron, silicon boron glass, they found this alloy has much smaller hesitancies loop. Or much smaller glasses than the conventional iron silicon alloy. And much higher permeability. That means, the magnetization is much higher and the losses or much lower. So, it is a kind of an ideal, fare magnetic, a soft magnetic glass, soft magnetic material. So, and then people started making these glasses. In fact, there is a company in US called allied signal, which have been making these iron based glasses of the order of around 10 centimeter width. And continuous ribbons like that. You can say strips or ribbons whatever it is, about 10 centimeter width And kilometers of kilometers of just by using at typical melt spinning technique.

So, they take a continuous liquid, which keeps on falling on a rotating copper wheel. And keep on collecting that ribbons. Like a cold rolling mill, you keep wheel at the end and keep on taking this ribbon, which comes out. And then just winding it and on to the wheel. So, like that people have made, a number of compositions like that. And cut that at appropriate position, to whatever appropriate size that you want. And then put in to the transformer.

So, that was the initial studies, I think 70's and 80's people have really work hard on that. But, then realized that beyond that, they cannot really go and use them for structural applications. Basically because the glasses, for magnetic application particularly that particular application, which is a transformer core. You need only sheets, you do not need anything beyond that. You need thin sheets.

And this smelt spinner can easily supplies are sheets. But, if you really want a bulk alloy, for any structural application, we want bulk materials. People try to still compact those sheets and make it bulk. But, still it is very difficult to avoid, any complete bonding between these sheets. So, always see will have some inter phase left out. And that can act as nucleating side for the crack to nucleate. So, people are not really successful to make a bulk alloys from that, but when these new compositions have come up. Particularly with this confusion principle, when people started putting in so many alloying elements. And then started making bulk glasses. That is when people are able to measure the tensile properties. There if you have ribbon, you cannot really measure in tensile property. You can still take the ribbon, put it in a UTM, but unfortunately most of the conventional UTM's, they cannot take a ribbon.

Melts per ribbon of the order of around 20 to 30 micron thickness, it is very difficult to test it by tensile test. In fact, we are struggling recently, we purchased an equipment called a horns will tensometer. You must have heard of this, we say small portable kind of tensometer, which is horizontal tensometer, whereas typical UTM is always a vertical tensometer.

And here, we can vary various grips to hold the sample. And we are just about to get holder, which can hold this ribbons, that you make melts per ribbons. Particularly we are interested to go for the shape memory alloys, where we want to make these ribbons, shape memory ribbons. And then study their mechanical properties. So, people are unable to really make a tensile properties of that. One can do hardness and get a hardness of these ribbons.

But, nothing beyond that, one cannot do any compressive testing. One cannot do tensile testing, one cannot do reffetic, unless you have bulk samples. So, the moment people started getting bulk samples. They were able to measure the strengths, they were able to measure the elastic moduli.

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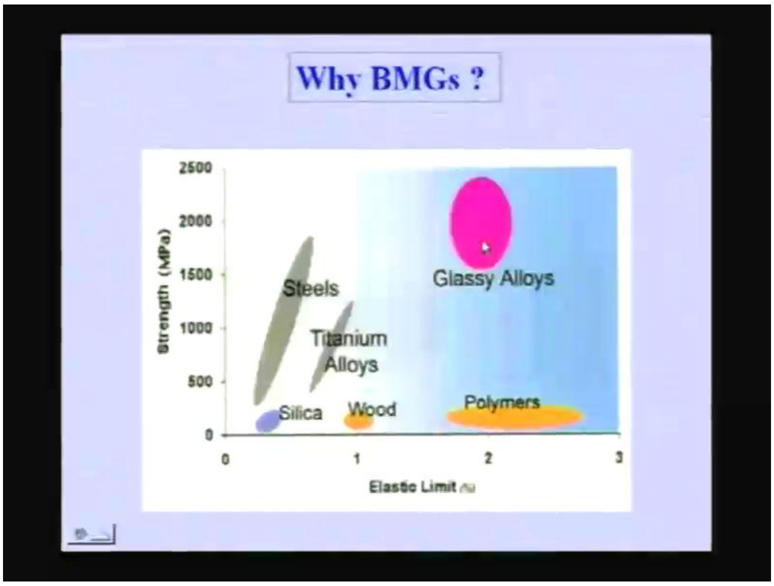

Why BMGs ?

And now they know from this, that many of the glassy alloys have much better advantage. When compare to conventional alloys or conventional materials, such as polymers. If you look at polymers their strength levels are very low. They have very high elastic limit, but their strength is much lower. And you take a silica, it is elastic limit as also low. Their strength is also low, they are brittle.

And you look at steels, they are wide range of steels available from low carbons to high carbon steels. But, still their elastic limit is much lower their ((Refer Time: 27:08)) is not too high. Though people are trying to put as much as alloying elements into it. And new type of alloy design criteria. Nowadays, we talk of interstitial free steels, automobile steel with high strengths HSLA, high strength low alloy steels.

So, all kinds of studies are going on in this, how to increase the strength of them. At the same time, increase the elastic modulus of them. Whereas, in the glassy alloys, if you look at them, you can have a good combination of both strengths and ((Refer Time: 27:36)). So, because of which one can really go for these bulk glasses. Look at another property, one is what is called resilience, which is nothing but the area under the elastic limit.

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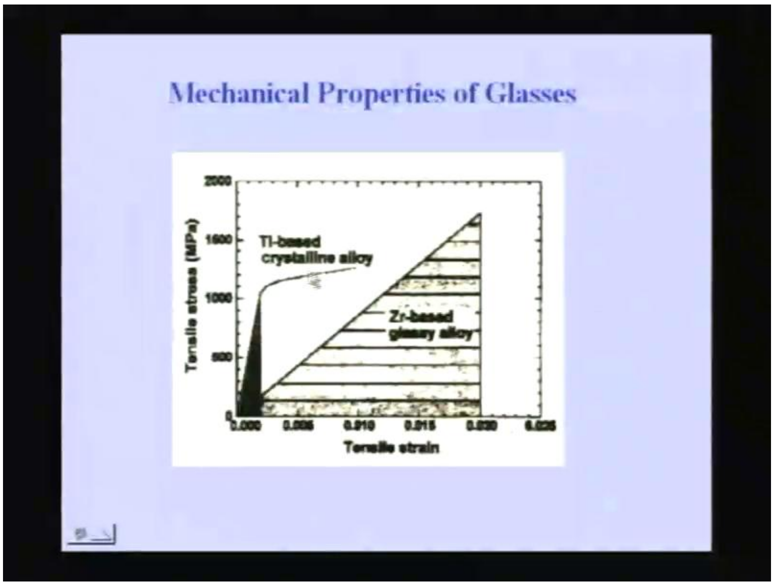

Mechanical Properties of Glasses

So, you look at titanium based crystalline alloy, which has some amount of ductility. And but under the elastic domain, if you look at the resilience, it is very small. Whereas, the zirconium based glassy alloy, though it does not have high ductility. The plastic zone does not exist much, but it is resilience is very large. And because of which people have started using them already, in golf club. The goal stick the head of the goal stick, it needs a lot of what is called damping capacity.

It should have lot of shock observing. So, that is what you can achieve with this kind of thing. So, already people started using this zirconium base bulk glasses into that. So, you can really make a bulk glass and put it there. So, this is one application.

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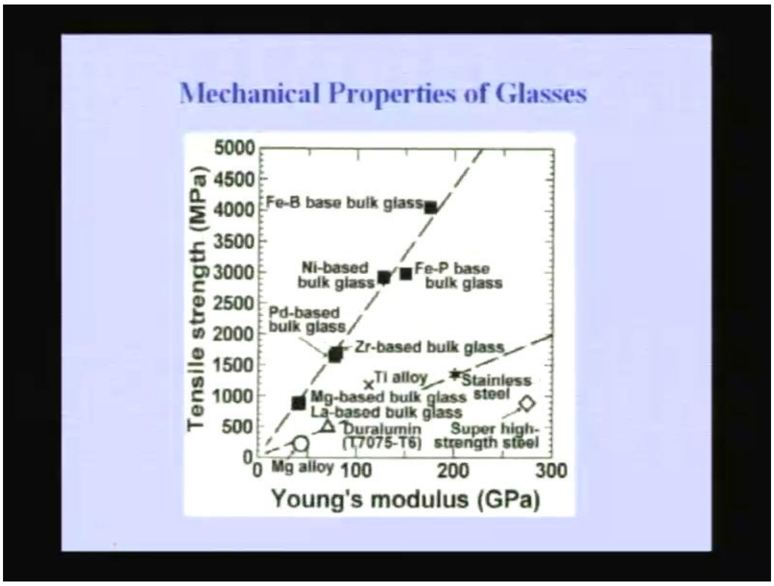
Mechanical Properties of Glasses

Another thing is again, you look at the strength and the modulus. And if you look at the conventional alloys. Conventional alloys if you put, all those alloys including super high strength steels, stainless steels. And duralumin, titanium base alloys all of them. If you plot strength versus modulus, they all have a low slope, they all fit into a straight line. But, that straight line will have a much lower slope, when compared to any of the glasses.

Here all kinds of glasses have been put, magnesium base bulk glasses, palladium base bulk glasses. Zirconium based bulk glasses, nickel based, iron based and iron boron base bulk glasses. All kind of bulk glasses have been put. And you can have much steeper slope. That means, you can have good combination of strength and Young’s modulus in this cases. So, that is one of the reason, while people want to go for all this glasses.

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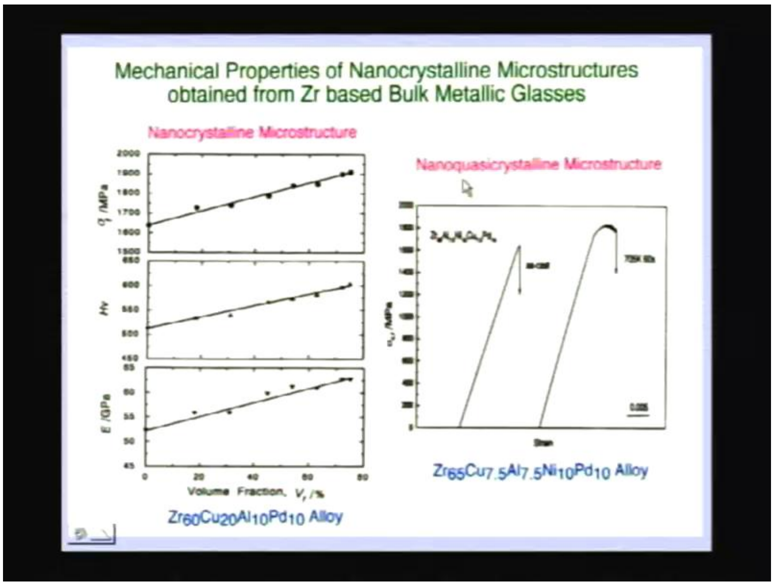

Mechanical Properties of Nanocrystalline Microstructures obtained from Zr based Bulk Metallic Glasses

Nanocrystalline Microstructure

Nanoquasicrystalline Microstructure

$Zr_{60}Cu_{20}Al_{10}Pd_{10}$ Alloy

$Zr_{65}Cu_{7.5}Al_{7.5}Ni_{10}Pd_{10}$ Alloy

And finally, one more point I should say is that, not only that you can make a good bulk metallic glass, that you can also crystallize this glass into nano crystals. That is the basic direction in which the whole world is moving. Now, that people do not want to just make a glass, because glass has its own disadvantages. As I would showed you in zirconium base glass, it does not have good ductility.

People want to have some ductility in any alloy. If I alloy is brittle, however strength it has ceramics. For example, they are all very strong, but they are brittle, we do not use a ceramic for any typical structural application. Any structural application should have good formability. So, as a result how to introduce some amount of formability into it. That is where people have realized, that if you can introduce some nano crystallite into it. That means, take a glass crystallize it under certain conditions.

So, that you can induce nano crystals into them, and such an alloy you can compare here. For example, this is an glass, zirconium based glass and as cast glass is just brittle. It has high strength, about you can see 1.6 Giga Pascal's is the strength of it, which is much higher than a steel. Steel is about 500 mega Pascal, 600 mega Pascal nothing more than that. Aluminum alloy is about hardly 300 mega Pascal's.

So, one can achieve much higher strength 1.6, but it is ductility is pour. There is no plastic deformation. But, by introducing some nano crystals by heat treatment, one can introduce some ductility into this. At least 3 percent, 4 percent like that. And people are still trying more and more how to increase this. And one more thing is that by introducing such nano crystals, by increasing the volume fraction of those nano crystals. One can increase the Young's Modulus, one can increase the hardness, one increase the fracture strength. And also finally the ductility also. So, there are advantages of introducing such nano crystals. So, this is another direction in which people are going...

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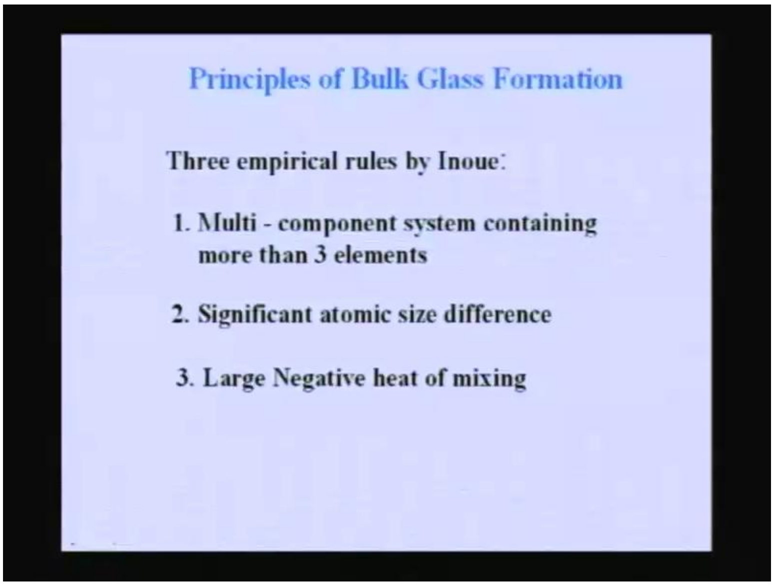

Principles of Bulk Glass Formation

Three empirical rules by Inoue:

1. Multi - component system containing more than 3 elements
2. Significant atomic size difference
3. Large Negative heat of mixing

How is it done simply you make a bulk glass and heat it. That glass you can do in a DSC, find out what is the T g, what is the T x. You know the T g, you know the T x. And if that if you go beyond T x it will crystallize. But, then the rate of crystallization depends on the temperature and the time, particularly the temperature. So, as a result, if you can control the temperature of your heat treatment or the annealing.

For example, we know cold working an annealing, we do it to control the grain size. One can control the grain size, by just proper choice of the temperature. So, if you play around the recrystallization temperature, do not heat much beyond the recrystallization temperature. You can produce fine grain material. Similarly, here you do not go to much higher temperature, where the crystals grow to much bigger size. And then one they grow you lose a lot of advantage of having a nano crystal material.

So, you can control

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Yes, this again depends on the type of a nucleation kinetics. If the nucleation kinetics are very high. Then what you achieve is the whole alloy, whole glass would have a large numbers of nucleate, five nucleate form and they grow. And more or less it is possible, that the whole glass would convert into a nano crystal. But, it all again depends on a number of parameters. For example, whether what is called a primary crystallization or Polymorphous crystallization.

What is the primary crystallization, what is the polymorphous crystallization. For example, if you take a glass, let us take this is the free energy of a glass. If you have a inter metallic compound in that system, which has a much lower free energy. And if this is the alloy composition with which you are starting, if you hold this alloy glass at high temperature.

The glass has a tendency to form a crystal, is it not? There is a driving force. And because of this driving force, the glass would tend to become the crystal. And if the driving force is much larger, then the activation barrier will be lower. The nucleation rate will be higher. So, there is a possibility that the glass having this composition, can transform to the crystal having the same composition.

This is similar to polymorphous crystallization of a liquid, is it not. We talked about polymorphous solidification, liquid having a certain composition, transforming to solid of the same composition. If this is happening, then what you see is that. If you take a glass and this glass can undergo nucleation. And the number of nuclei of this particular inter metallic compound, having the same composition has that of the amorphous phase.

Can nucleate everywhere in this. And then they start growing and when they meet each other they stop. So, you will get a fine nucleate of this. So, complete conversion of the amorphous phase to a complete nano crystalline alloy. To give you what is called a bulk nano crystalline alloy. Bulk metallic glass giving you a bulk nano crystalline alloy is possible, if you have a polymorphous solidification, polymorphous crystallization.

But instead, if there is no inter metallic compound in that system, which can form easily are whose activation barrier per formation is low. Instead what would happen is, the glass of this composition would try to transform to a solid solution first, having an alpha solid solution. So, if you start this alloy, for example if I draw a common tangent. If I am starting from an alloy composition of this, that glass composition of this; instead of this composition number 1.

I am starting let us say from number 2. Now, the glass of this composition number 2. Can either form this alpha or form this what is called the inter metallic, by if you draw a tangent between the glass. And the inter metallic, this is the tangent.

Student: ((Refer Time: 36:22))

By chance let say, even if it is their at it is activation barrier for it is formation is high. Then, in such a case even though there is a driving force for the glass, to transform to a inter metallic. But, if it is composition, the glass composition is not same as that of the inter metallic. If the composition of the glass is not same as that of the inter metallic composition, what will happen? What you will see is that, after the nucleation of the inter metallic, if it all inter metallic nucleates or the alpha nucleates.

If this is the liquid or glass whatever you want to call it. An inter metallic has form, you have to have some amorphous phase left out. In order to maintain what is call the mass balance. Let us say the inter metallic compound. Let us say A B kind of a system, you have the inter metallic is a A 50, B 50 kind of a composition. And you are starting, you are alloy composition glass composition is A 80, B 20 from this A 80, B 20. It is impossible to get 100 percent of inter metallic compound having A 50, B 50, is it not.

So, as a result you will always have some fraction of the inter metallic. And multiplied by it is composition of the inter metallic. Plus some fraction of the amorphous phase will be left out multiplied by it is composition. Given by the equilibrium composition given by the common tangent. Once an inter metallic comes out, you will see that the composition of the amorphous phase shifts. Because, they has to be common tangent between the amorphous and the inter metallic.

So, the composition of the amorphous phase shifts to this point now. And now, that is the composition of the amorphous phase. This should be equivalent to what from the mass balance, should be equivalent to the glass composition, composition of the glass. Original composition of the glass, which is nothing but A 80, B 20. That is what is lever rule, that is what is mass balance.

So, the composition of the inter metallic multiply the volume fraction of the inter metallic. Let us say, if I am talking interns B atoms. Some B atoms are there in the inter metallic. Some B atoms are there in the amorphous phase. So, the fraction of the inter metallic multiplied by the number of B atoms, for mol of that inter metallic. Plus the fraction of the amorphous phase multiplied by the number of B atoms form of the amorphous phase.

If you add this, that should give you the total number of B atoms, which are there from the starting glass. Otherwise, you are creating some atoms, you cannot create it. There has to be the law of conservation of mass has to be maintained. The first law of the thermodynamics has to be maintained. So, if you do that way, you can see you will always get, what is called a mixture of amorphous place plus inter metallic compound. This is what is called primary crystallization.

Not a polymorphous crystallization. If polymorphous crystallization means what? That glass composition is same as the inter metallic composition Or the product phase that is coming out. So, the composition of the product phase, if it is same as that of the starting phase. Then, we can say it is a polymorphous. And then you may end up in a 100 percent, otherwise you will always have a composite. This is what we call it a nano composites, that you have an amorphous nano crystal composite. And you can have a better properties of both, that of the nano crystals, and that of the amorphous phase. And you can have the advantage of both, that is why we make composites. You want to have the advantage of the ductile material. And also the advantage of the brittle material. So that, you can have a good combination and the...

Student: ((Refer Time: 40:22))

Yes, but here this is another thing. Whenever you make them in the nano crystalline form. Then the brittleness, which is coming is basically because of the inter granular cracking. So, here you have nano particles embedded in an amorphous matrix. So, as a result, you do not have brittle complete grain boundaries in that, it is not a poly crystalline material. So, as a result the crack does not go through the grain boundaries. So, as a result you can have some kind of a rest of these cracks. So, the crack do not propagate.

So, that is one of the advantage of making these nano particles, in a embedded in an amorphous matrix. So, one can have additional advantage of good fracture toughness, in this materials. People have shown in a number of materials, that even by putting these inter metallic’s in a nano form. For example, we have seen ourselves, that you have an aluminum matrix with a inter metallic’s of A l 3 T i.

You can have much better fracture toughness. Provided their morphology is controlled, when we talk about titanium based alloys. It all depends on the morphology of the second phase particles. And one can control the fracture toughness just by changing the morphology of the second phase particles, will talk about it. So, this is basically about the formation of the composites, from the bulk metallic glasses.

But, coming to the bulk metallic glasses itself. Under what condition a bulk metallic glass can form. People have thought of basically three criteria, one is a multi component system.

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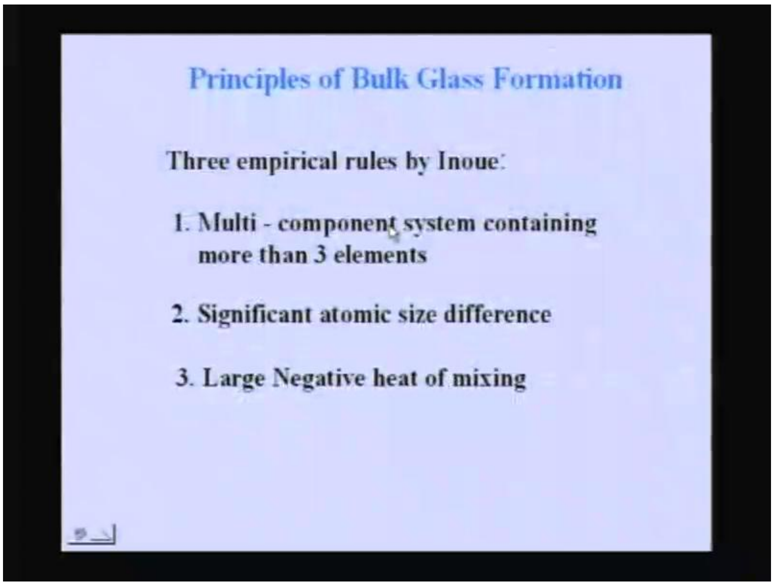

Principles of Bulk Glass Formation

Three empirical rules by Inoue:

1. Multi - component system containing more than 3 elements
2. Significant atomic size difference
3. Large Negative heat of mixing

That it should be a multi component system. Otherwise, you will not get a bulk glass. Second is that it should have significant of atomic size difference, the size factor should be large. And third it should have a large negative heat of mixing. This is what I told you from the beginning itself. That if the liquid has a large negative enthalpy of mixing, then it is more stable. And if it is stable, then the glasses stable, if the liquid is stable glass is stable glass is nothing but liquid.

Nothing but liquid its only in a solid form. Configurationally frozen liquid, this what we say. So, based on this people have given a some kind of a route map, of how to get a glass. How to get a bulk glass?

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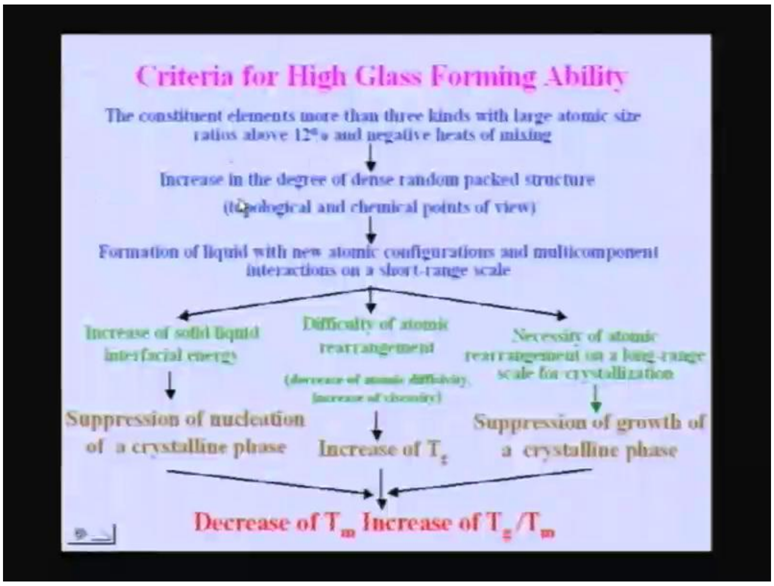

## Criteria for High Glass Forming Ability

The constituent elements more than three kinds with large atomic size ratios above 12% and negative heats of mixing

↓

Increase in the degree of dense random packed structure (topological and chemical points of view)

↓

Formation of liquid with new atomic configurations and multicomponent interactions on a short-range scale

Increase of solid liquid interfacial energy → Suppression of nucleation of a crystalline phase

Difficulty of atomic rearrangement (decrease of atomic diffusivity, increase of viscosity) → Increase of $T_g$

Necessity of atomic rearrangement on a long-range scale for crystallization → Suppression of growth of a crystalline phase

Decrease of $T_m$ Increase of $T_g/T_m$

And this route map is something like this. If you take constitutive elements, that means if you have more than three type of elements, with atomic size differences more than about 12 percent. And you have a large negative enthalpy of mixing. If you choose such system, what you do basically is that, you increase the degree of dense random packing. So, if you increase the dense random packing, you will have a good topological packing. And at the same time chemically also the bonds will be stronger.

Because the delta h mixing is highly negative. And as a result what you end up is that, new types of liquid. The liquids with dense random packing. The liquids with good short range order. And such liquids which are multi component liquids with good short range orders, in such a liquid. And those liquids will result in, increase in the solid liquid interfacial energy. And if the solid interfacial energy is high, then the formation of crystal in phases is more difficult, when a liquid is giving you a crystal. What is that, that gives you activation barrier for a crystal to form. It is only the interfacial energy, if the interfacial energy is very low. Then, the crystal formation is very easy. If we can somehow increase the interfacial energy, or the surface energy, then the crystal formation is more difficult. That is why we always say the liquid to crystal formation is more difficult, than the crystal to liquid formation.

Any set a liquid crystal and start heating it. I always see, a crystal always melts at the melting point. But, when I take a liquid and start cooling it, it never solidifies at the melting point. I always have to cool it below the melting point to or it to solidify. Why does it happen like that, because from a liquid a solid has to nucleate. If a solid has to nucleate a new surface has to be created. If you want to create a new surface, you need to have certain energy, to overcome the surface energy. And how do you get that energy by under cooling.

If you under cool it, you have certain free energy which is available, because we know that free energy, which is the driving force is directly proportional to the under cooling. So, if you have some under cooling, some driving force is there. And that driving force can be used for creating the surface. And that is how you create a surface. And if you do not give that driving force, you cannot create a surface. That is why you keep your liquid at the melting point forever. Crystal cannot form, unless is a condition under which it can still formed.

Student: ((Refer Time: 45:38))

We are some heterogeneous nucleating sites. If you really add heterogeneous nucleating sites, which can provide that surface. You can still have solidification occurring at the melting point, without any under cooling. And that is what is heterogeneous nucleation. Whereas, if you are doing the reverse process, crystal being heated, you do not need anything. Because, already heterogeneous nucleating sites are there, which is nothing but the surface of the solid.

And that is why I told you before, also when you take a ice cube always melting starts at the corners, because those are the regions of high surface energy. And that is why the number of bonds broken are high there. So, the broken bonds is what do you see the high energy, this is what I do not know, if you have ever thought of with this. Whenever you take a poly crystalline material, that is a simple aluminum.

Pure aluminum, poly crystalline aluminum, you cut it, polish it, an put it in a etching and put it under a optical micro scope. What do you see, you see grains. And you see grain boundaries. But, at the same time if carefully observe each grain, each grain will have a different grain level. Some grains looks bright, some grain look dark, why is that? We say this is orientation difference. Why should orientation difference really give you this kind different shades, have you ever thought about it.

Student: ((Refer Time: 47:18))

Do you think that optical light is interacting with bonds there, nothing…

Student: ((Refer Time: 47:29))

It is the etching, which is different in different grains why the etching is different in different grains?

Student: ((Refer Time: 47:37))

Different plains.

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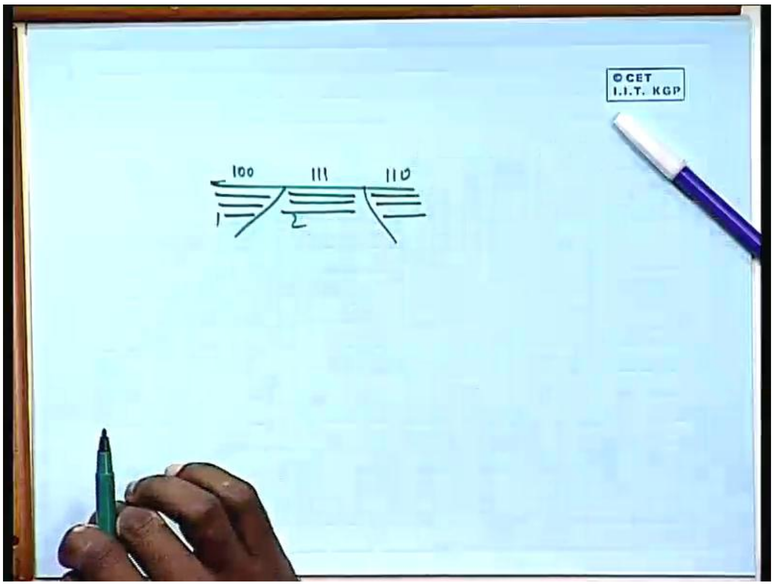

If you think of at material with two grains, here grain 1, grain 2 and grain 3, let us say. You imagine look at what are the plains, which are parallel to this surface. If you look at here may be 1 0 0 planes are parallel to this surface. And may be in this particular region 1 1 1 planes are parallel to this surface may be here 1 1 0 planes are parallel to this surface. If you look at three different grains with each one of them, because you are polishing it.

You are cutting a surface and polishing it and putting an enchant there. And look at any plane which is parallel to that surface. And if you look at each grain, each grain will have a different plain which is parallel to the surface. If they are the same plains, then you do not call it as a different grain. So, we say each grain should have a orientation difference. So, if there is a orientation difference, then the orientation is different. So, the same plane cannot be parallel in grain one and grain two for the top surface.

Each grain should have a different plain, which is parallel to the top surface. If that is the case, now if you put an enchant on this uniformly. And the amount of attack that you have is going to be different in different regions, because each of this regions will have a different energy. And that energy depends on the surface energy of that particular region. And that surface energy is different for different planes. For 1 1 1 plane the surface energy will be different.

For 1 1 0, it will be different, for 1 0 0 it will be different for a given crystal. Let us say it is an FCC crystal like aluminum. In an aluminum, which particular plain will have the highest energy, 1 1 1 why?

Student: ((Refer Time: 49:32))

Close pack, what is the meaning of close pack, because the number of broken bonds are more per unit area. The number of broken bonds are more, if the number of broken bonds per unit area, then it has more surface energy. If the more surface energy, then more attack. Why is the grain boundary get attack, more easily then the grain. It is just because of the higher surface energy. So that is why, you can see that interfacial energy is crucial to separates crystal ((Refer Time: 50:00)).

Second, similarly difficulty of atomic arrangement, when you have large number of atoms, all these atoms have to come together to form a unit cell, which is much more difficult. Again you are making it difficult for the atomics atoms to diffuse. Diffusivity gets restricted. And because of the diffusivity getting restricted, you an having higher viscosity when you put large number of atoms. The viscosity is increasing, because of which you can see there is an increase in the T g.

Glass forms more easily, that means when you are cooling the liquid. The glass can easily form, because viscosity is much higher, I have shown you a viscosity plot. Viscosity versus temperature plot once in the beginning, and you can see if the T g is, if the viscosity of a liquid is much higher than the glass formation is achieved, much easily. So, as a result that is one.

And similarly in case of crystallization, you have a necessity for atomic rearrangement on a long scale. You need long range atomic arrangement for a crystallization. And that is more difficult with the diffusivity. And because of which you can suppress the growth of a crystal. Not only crystal nucleation is difficult, crystal nucleation is difficult because of the atomic rearrangement is difficult. And because you need a long range at a arrangement for making the crystal to grow.

And that is again difficult, because of the again diffusivity being low. All these things will lead to a decrease in the melting point. And then increase in the T g by T m. And that is what will give you a ((Refer Time: 51:42)) class.

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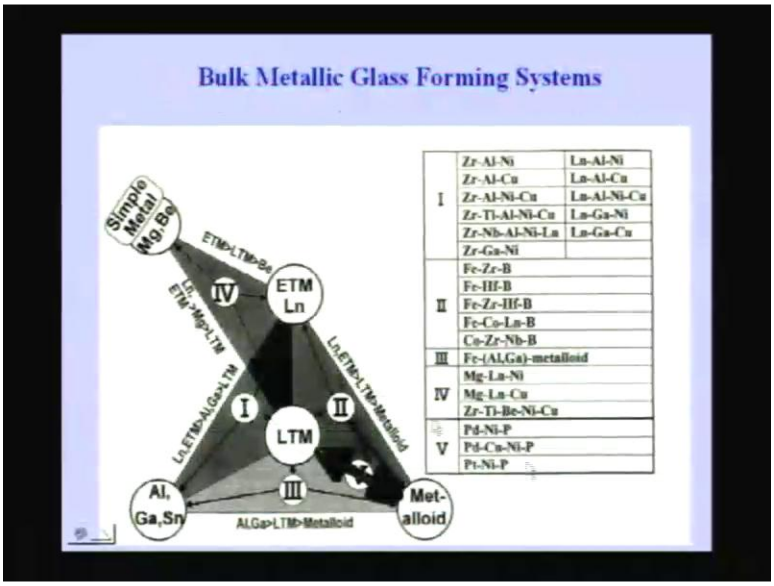

## Bulk Metallic Glass Forming Systems

| | | |
|---|---|---|
| I | Zr-Al-Ni | Ln-Al-Ni |
| | Zr-Al-Cu | Ln-Al-Cu |
| | Zr-Al-Ni-Cu | Ln-Al-Ni-Cu |
| | Zr-Ti-Al-Ni-Cu | Ln-Ga-Ni |
| | Zr-Nb-Al-Ni-Ln | Ln-Ga-Cu |
| | Zr-Ga-Ni | |
| II | Fe-Zr-B | |
| | Fe-Hf-B | |
| | Fe-Zr-Hf-B | |
| | Fe-Co-Ln-B | |
| | Co-Zr-Nb-B | |
| III | Fe-(Al,Ga)-metalloid | |
| IV | Mg-Ln-Ni | |
| | Mg-Ln-Cu | |
| | Zr-Ti-Be-Ni-Cu | |
| V | Pd-Ni-P | |
| | Pd-Cu-Ni-P | |
| | Pt-Ni-P | |

And so this the based on this, people have seen, there are number system where people have got these glasses. And I just quickly give you some classification of these glasses. They are basically are classified into five groups. One is a early transition metal, lead transition metal and aluminum type of group, group number 1. And the group number 2 is early transition metal lead transition metal metalloid. For example, zirconium aluminum copper nickel, zirconium aluminum copper, this is an examples of group 1.

Iron zirconium boron, theses iron is a lead transition metal, zirconium is early transition metal, boron is a metalloid. So, that is the group 2. And group three is lead transition metal, aluminum metalloid type of thing, iron aluminum metalloid kind of example. group 4 is another, which is early transition metal, lead transition metal magnesium type of alloys. And group 5 is the lead transition metal and metalloid, which is the simple palladium nickel, phosphorous palladium copper nickel phosphorous. So, a number of such alloys have been made. And people have found good glass forms in all these.

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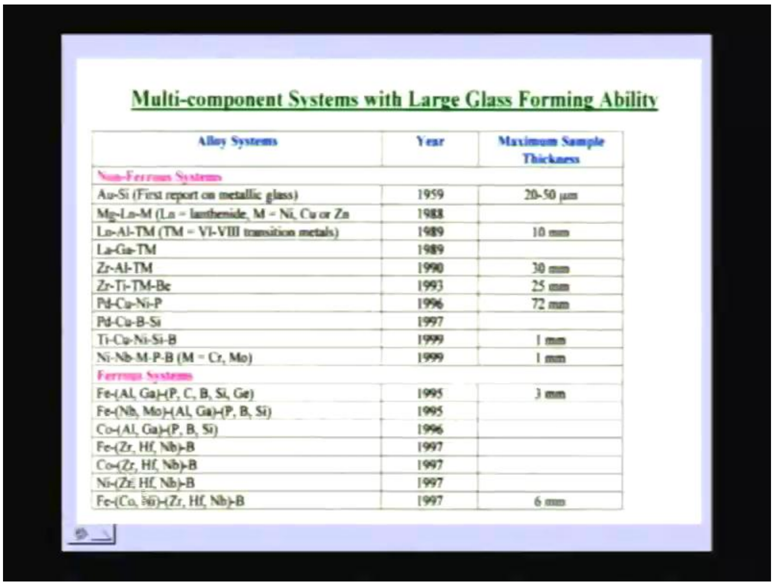

## Multi-component Systems with Large Glass Forming Ability

| Alloy Systems | Year | Maximum Sample Thickness |
|---|---|---|
| Non-Ferrous Systems | | |
| Au-Si (First report on metallic glass) | 1959 | 20-50 μm |
| Mg-Ln-M (Ln = lanthenide, M = Ni, Cu or Zn | 1988 | |
| Ln-Al-TM (TM = VI-VIII transition metals) | 1989 | 10 mm |
| La-Ga-TM | 1989 | |
| Zr-Al-TM | 1990 | 30 mm |
| Zr-Ti-TM-Be | 1993 | 25 mm |
| Pd-Cu-Ni-P | 1996 | 72 mm |
| Pd-Cu-B-Si | 1997 | |
| Ti-Cu-Ni-Si-B | 1999 | 1 mm |
| Ni-Nb-M-P-B (M = Cr, Mo) | 1999 | 1 mm |
| Ferrous Systems | | |
| Fe-(Al, Ga)-(P, C, B, Si, Ge) | 1995 | 3 mm |
| Fe-(Nb, Mo)-(Al, Ga)-(P, B, Si) | 1995 | |
| Co-(Al, Ga)-(P, B, Si) | 1996 | |
| Fe-(Zr, Hf, Nb)-B | 1997 | |
| Co-(Zr, Hf, Nb)-B | 1997 | |
| Ni-(Zr, Hf, Nb)-B | 1997 | |
| Fe-(Co, Ni)-(Zr, Hf, Nb)-B | 1997 | 6 mm |

And if you look at how the whole field is evolved, starting from the simple gold silicon system in 1959, with 20 to 50 microns, and now we see we have palladium nickel copper phosphorous, with about 72 millimeters. This is about a one, I think a slightly old news. Now, very recently people even found out about 100 millimeters. And so you can see that a number of nonferrous systems, ferrous systems, it is not this is restricted to one type of systems only. All kinds of systems, wherever all those criteria, which have mentioned before are satisfied one can get a glass, will stop here. And in the next class, we talk about quasi crystal.

Thank you.