Advanced Materials and Processes
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Lecture - 14
Nano Quasicrystals Part – I

We start today’s class, as we have seen in the last class. We have been talking about the nano quasicrystals. You already know, what are nano crystals? You already know, what are the quasicrystals. And we try to see, under what conditions, you get nano quasicrystals. That means, you have a matrix, in which you get these quasicrystals, precipitated in a fine form. And we have seen already, that some of the mechanical properties can be improved, if you can have that kind of a precipitation of nano quasicrystals.

One of the conditions, which we have talked about, is the oxygen. We showed, before in the last class, that oxygen plays a very important role. And in case of zirconium, based alloys particularly, we showed a particular example. Where, without oxygen or with a very small amount of oxygen, below a certain critical value, you do not get any of this nano quasicrystals precipitated in an amorphous matrix.

But, once you have more than the critical value of the oxygen, you see that, there is a precipitation. This is what; we have shown in the example of zirconium copper aluminum system. We have also shown that, if you take only zirconium copper, such a thing does not happen, because the atomic configuration is such that. Unless, you have all the three elements, zirconium, copper, aluminum.

If you look at the atomic sizes, zirconium is a very big atom, copper is a very small atom and the aluminum is an atom, which is somewhere intermediate between these two. So, if you have a big atom and a small atom and put another atom, which is intermediate size, that this. When, you get the best type of a packing. And what we have seen is icosahedra packing is the densest packing.

So, if in the liquid, if you stabilize the icosahedra packing. That is, where oxygen helps oxygen, goes into the interstitial positions and then improves the packing density. So, that, the overall atomic packing, becomes very dense. And such a dense atomic clusters, which are available in the liquid will have the icosahedra type of arrangement of atoms. And such icosahedra clusters, when you quench them, rapidly by rapid solidification.

They do not get precipitated, during the solidification, because the solidification is very rapid. So, they remain inside the glass, as clusters and we know the clusters are always embryos with sizes less than the nuclei. And unless, the size becomes equivalent to nucleus size, it will not become, the growth will not occur. So, we know that, any size of an embryo, unless it crosses size of the nucleolus, the growth will not occur.

So, when you have these clusters, which are of the size of embryos. That means, very small clusters. During the solidification, the liquid has all these clusters now. They are very fine clusters. And but, when the liquid is being solidified, very fast, there is no sufficient time for this clusters to grow to become nuclei. And finally, grow into bigger crystals and give the nano quasicrystals.

So, as a result, what happens is, they remain inside the liquid and when the liquid is quenched, very rapidly, that liquid becomes a glass. But, inside this glass, you have these clusters remaining. So, you have these nano clusters, I will show you after a little while, some of the high resolution pictures, which shows such clusters. So, these clusters remain inside the glass.

So, the glass, though we say it is a random arrangement of atoms, but it will have some short range order. We say that the liquid always has a short range order. But, in some of these liquids, the short range order will have the type of structure, which is icosahedral type of structure. For example, I told you before also; if you take a pure aluminum and then take the liquid aluminum, bring the liquid, near to the melting point.

That liquid, which is close to the melting point, it will have a large number of these short range clusters, which will have the same unit cell as that of the aluminum, which is going to come out of the liquid. That is the FCC unit cell. Otherwise, how does the liquid know, that it has to become FCC, when you solidify it. So, all this liquid, everywhere you see, there will be small clusters. That is why; we always say liquid has a short range order, whereas a gas does not have any short range order.

So, every liquid has a short range order. And the type of atomic arrangement, within that short range order, depends on the type of crystal. That is going to come out of the liquid and the type of crystal, which has the lowest free energy. So, in case of aluminum, I told you, before that FCC aluminum has a lowest free energy. As a result, the short range clusters in the liquid of aluminum, will always be FCC clusters.

And once, you bring it to the melting point, if you cool it slowly, at the melting point, that short range clusters, will be become equalant into that of the nucleus. And then the nucleus grows and that is how, you get the grains of aluminum, which are FCC structure. Same thing happens here, this we are stabilizing the quasicrystal in clusters, which are icosahedral clusters by putting elements, which densify the whole liquid.

So, you have these clusters, inside this liquid, which are icosahedral clusters and these icosahedral clusters, we are stabilizing them, by putting oxygen into them. If you do not put sufficient amount of oxygen, it cannot densify the clusters to such an extent, to get the icosahedral kind of arrangement of atoms. And once, you put a critical amount of oxygen, you get these clusters, but the problem is, now this clusters are so small. That because, you are cooling it very rapidly. Probably, if you cool it slightly slowly, you may be able to get them, but the growth of these clusters, needs some activation barrier.

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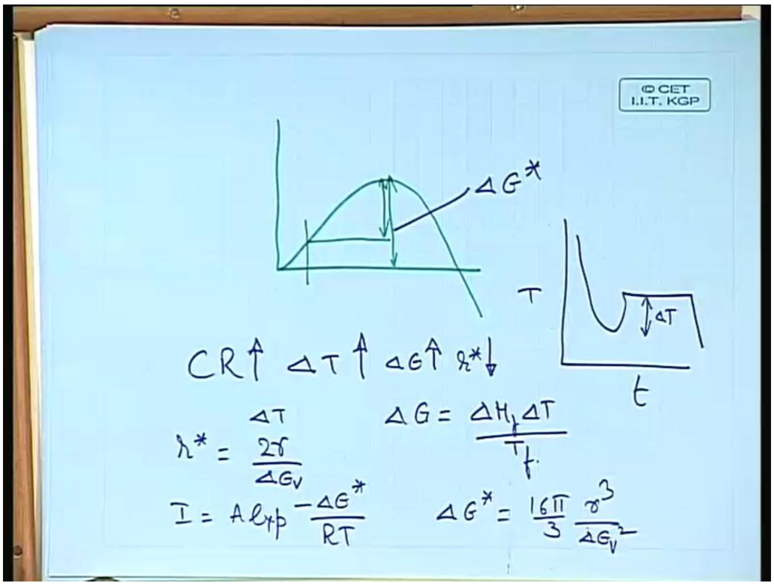

Any cluster, for it to grow, because, we know from our nucleation kinetics, you have this activation barrier always, we say. So, you have this barrier to be crossed for the nucleation to complete. If you are somewhere here, unless you come to this stage, the growth cannot occur. For that, you need to climb this hill, so for doing that, you need to provide certain energy.

When, you are cooling the liquid, you are enabling to provide that much energy for crossing this barrier. And hence, the clusters will remain in the liquid and when, you start heating it in a D S C or during annealing. I have shown you, the examples of zirconium copper aluminum or zirconium palladium kind of alloys. We have seen a number of palladium alloys, containing copper, nickel, aluminum.

So, these are all the cases, where there is no oxygen effect, because palladium stabilizes the quasicrystal. And in the previous case of the zirconium copper aluminum, where we have seen, the oxygen stabilizes these icosahedral clusters. And now, if you are heating this glass, which is obtained on cooling of this liquid, there you are providing the sufficient thermal energy for the clusters to start growing, that you are providing this activation barrier.

And once, you provide this activation barrier and then you start seeing that, they start growing. And that is what, we have seen in case of zirconium palladium alloys and zirconium copper aluminum with some amount of minimum amount of oxygen. But, there are also I told you some systems, where you get these nano quasicrystals, directly by cooling the liquid.

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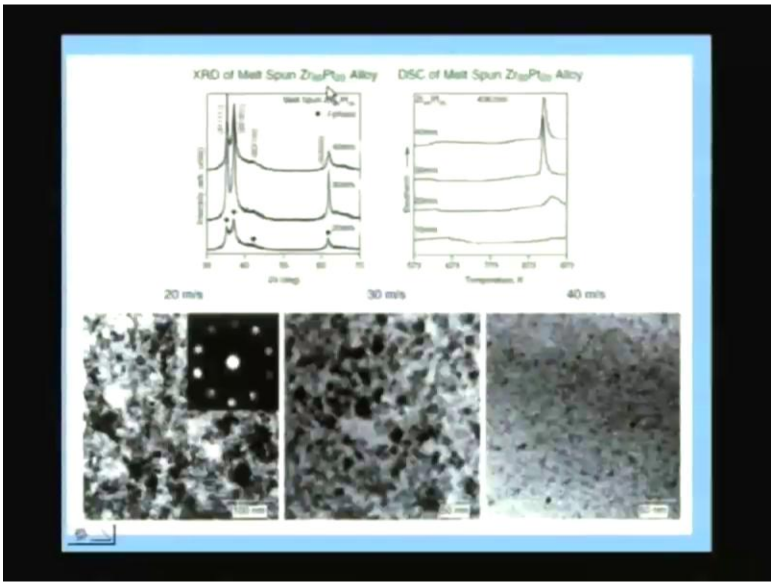

XRD of Melt Spun $Zr_{80}Pt_{20}$ Alloy

DSC of Melt Spun $Zr_{80}Pt_{20}$ Alloy

20 m/s

30 m/s

40 m/s

One such example is zirconium platinum alloy, what you see here is a zirconium 20 percent platinum alloy, 80 percent zirconium and 20 percent platinum alloy. Where, if you take this liquid and start cooling it, at different wheel speeds, this is what we say, melt spinning. We have talked about it; we will talk in more detail, when we talk in the next few classes, about rapid solidification processing.

But, at the moment, you already know, what are melt spinning, where the copper wheel is rotted and the liquid is allowed to fall on that. And if we rotate this wheel at different speeds, 20 meters per second, 30 meter per second, 40 meter per second. What you see is, that this XRD peaks of quasicrystal peaks, you start to see. Whereas, if you remember the previous case of zirconium palladium, when you cool it at these speeds, you never get a quasicrystal during cooling. You always get a glass, you get a broad hump.

Whereas, the same system, basically zirconium base system, but instead of palladium, we are putting platinum. Just, you replace palladium with platinum, instead of 7030 zirconium palladium alloy. Now, what you do is, you take 8020 zirconium platinum alloy. This zirconium platinum alloy is very close to the eutectic composition. So, we are choosing the deep eutectic composition in this zirconium platinum system.

And then cooling it and when you cool it, what you see is that, directly icosahedral phase comes out. And if you want to confirm, that it is really icosahedral phase, what you do is, go to TEM. If you see in the TEM, you see, these fine particles, all these particles are quasicrystal. You have almost 100 percent quasicrystals in particles, in this 20 meter per second.

And you can see that, micro diffraction pattern, taken from one individual particle, which shows you, the tenfold cemetery. To give an idea, yes, these are nano quasicrystal in particles. And if you increase the cooling rate, increasing the wheel speed, means what, increasing the cooling rate. When, you increase the cooling rate, what you see is that, the size of these particles, become very fine. This we already know from our early knowledge in metallurgy. That whenever, I use a higher cooling rate, the grain size decrease, why, how is the grain size is related to cooling rate.

Student: There is no time for growth

There is no time for growth, anything else

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Anything else, one crucial aspects, you are missing it

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Yes, the nucleation rate increases, why it increases, you can see here, if I increase the cooling rate, I increase the under cooling, why, the liquid instead of solidifying at the melting point. It solidifies at a temperate, much below the melting point. Because, of the inertia, there is an inertia in the system. That whenever, I am cooling the liquid, very rapidly, it does not solidified at the melting point and goes below the melting point and starts solidifying and that is what, we call the under cooling.

And this is what, if you plot temperature verse time, you see this kind of under cooling. For a pure metal, we draw this kind of a cooling occurs. We know, this is, what is called under cooling delta T. And this delta T is higher, the higher the cooling rate. And if the delta T is higher, we know the delta T is related to the nucleation rate and also the size of the nucleus.

For example, delta T is related to, what is called delta G? If the delta T is higher, the delta G is higher, why, because, delta G is shown as delta H f into delta T i by delta T f. This formula you all remember I think. In thermodynamics we have talked about it, this is, what is turnbulls formula, for the free energy, change of the liquid to solid. Where, delta H is nothing but, the heat of fusion and T is T f is nothing but, the melting point and delta T is a under cooling.

So, the higher the under cooling, the higher the delta G and this, if you take the r star, which is the critical nucleus. Critical nucleus is 2 gamma by delta G v. The higher the delta G v, what you see, the smaller the r star. So, if the C R, if the cooling rate increases, the delta T increases. If the delta T is increases, delta G increases, if the delta G is increases, the r star decreases.

So, you will get fine nucleate; that is one thing. Second thing is, we also know that nucleation rate is nothing but, I is equal to pre exponential term, multiplied by exponential minus delta G star, which is called the activation barrier for nucleation, divided by R T. This is a delta G star. Here, you see, this is the G delta star for nucleation. Everybody, who knows a little bit about nucleation, we all know about this and this delta G star is directly related.

There is an inverse relation between this and the delta G. You remember that, 16 pi by 3

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Gamma cube by delta G v square; that is a formula, we all know this. From our secondary year metallurgy itself, second year, B tech metallurgy, we teach this. So, you know this formula. So, from here, you know that the delta G star is universally proportional to the delta G v square. And if the delta G star decreases, then I increases. Because, there is a negative term, before this delta G star.

So, if r star decreases, then if the delta G increases, then delta G star also decreases. And if the delta G star decreases, finally, you will see, I increases. That is the nucleation rate. So, you will get high nucleation rate and because of which, you get fine nuclei, large number of fine nucleate, r star is small, I is large. And that is why, you see, this kind of fine size icosahedral precipitates.

But, the question now is, why that is, in this particular system, you get the nano quasicrystal in phase directly, during cooling from the liquid. Why, is that in zirconium palladium case; that you do not get it, but you have to heat it?

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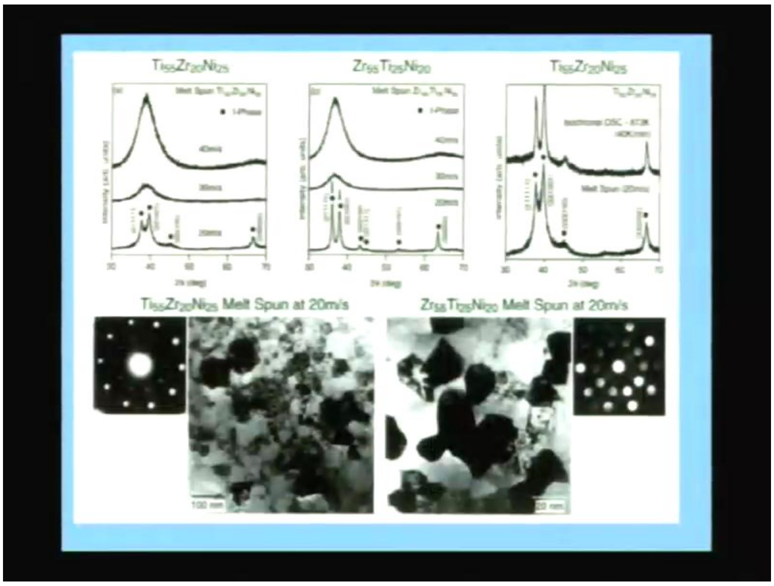

To understand this, we have understood to little bit more. So, to understand this further, we see another system here. This is the zirconium titanium nickel system; it is a ternary system, where you see two compositions. One is the titanium 55, zirconium 20, nickel 25. Another is zirconium 55 titanium 25 nickel 20; these two are two eutectic compositions in the ternary phase diagram.

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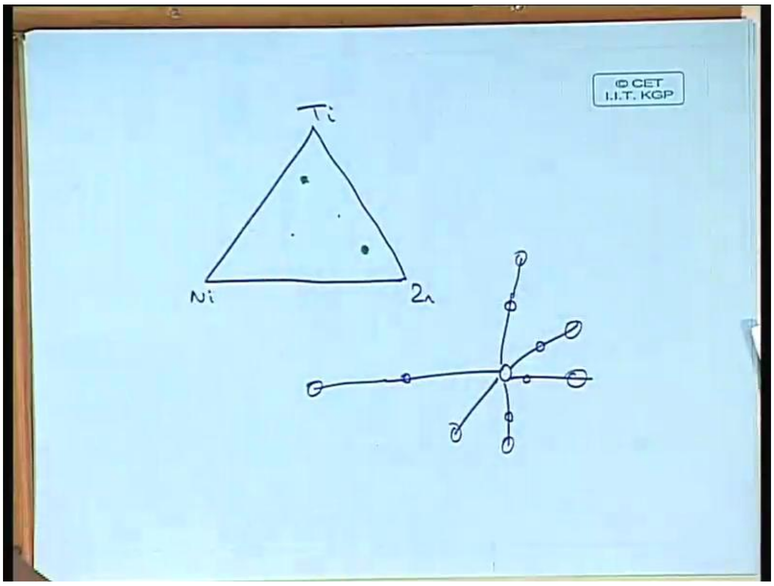

If you look at the ternary, such as titanium, zirconium and nickel, you have two ternaries here. Somewhere, depending on the particular composition, one can find out, one is the titanium rich composition. So, comes close as to the titanium end and zirconium is above 20 percent, so somewhere here, you will get. So, this is the type of composition, you will get, this is one composition, another is a zirconium rich composition and again nickel is very small here. So, you will have some compositions somewhere here.

So, these two compositions, which are the eutectic compositions, when you take them and cool them by, melt spinning technique. What, you see is that, if you cool it slowly, you get the quasi crystal. This is the titanium rich composition and if you cool it fast, 30 meter per second and 40 meter per second, you get a glass. Similarly, here in the zirconium base also, if you cool it slowly, you again get a quasicrystal and again cool it fast, you get a glass.

And interestingly, in case of zirconium titanium base system and zirconium base system, these are melts spun at 20 meter per second, where you directly get a quasicrystal. If you take them, you see, very fine size nano quasicrystal, something like about 50 to 100 nano meters size. And the diffraction pattern confirms that and similarly here also, you see very fine, this bar is 20 nano meters, you can see here. That means, each particle 20 nano meters are so 20 to 30 nano meters.

Such fine particles, you get and the micro diffraction pattern again confirms that these are quasicrystals. And another interesting thing also, is that, you can take this glass and heat this glass in a D S C, you again get quasicrystals. So, that means here, these are the two compositions, where if you cool it slowly, you get a quasicrystal. That means, if you are cooling it slowly, you are providing sufficient time for these clusters, which are available in this liquid.

The icosahedral clusters, which are available in the liquid, to start growing and give you quasicrystal, but if you cool it fast; you are not providing sufficient time. So, the clusters will remain inside the liquid and that liquid will freeze and give you a glass and this glass, if you start heating it; that will get converted to nano quasicrystal. So, here is an interesting situation, where you see both happening, depending on the cooling rate.

If you do it is very slowly, the icosahedral phase comes out, if do it fast, glass comes out, because there is no time available. Because you know even for icosahedral phase to come out, there has to be a nucleation growth. For the nucleation growth, there is always what is called an incubation period. You have to provide that incubation period, if you do not provide that nucleation period, there is no nucleation.

So, as a result, if you are cooling it very fast, 30 meters per second or 40 meters per second, that kind of cooling rate, which is equalant to around 10 to power 6 or 10 power 5 cooling rate, Kelvin per second. At such high cooling rates, the liquid is enable to give you, the icosahedral nano crystals. What happens is that liquid will freeze configurationally into a glass. But, as I told you before, glass structure is same as that of the liquid structure.

So, if there are icosahedral clusters inside the liquid, they will be there inside the glass also. And now, this glass containing the icosahedral cluster inside this has a short range order. If you start heating this glass, it will give you these quasicrystal, nano quasicrystals.

So

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Correct

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It will be nano, only when you have large number of these clusters. Whenever, you take a system, particularly zirconium based and titanium based systems, there is high driving force for the quasicrystal to come out. If the driving force is very high, you can see from here.

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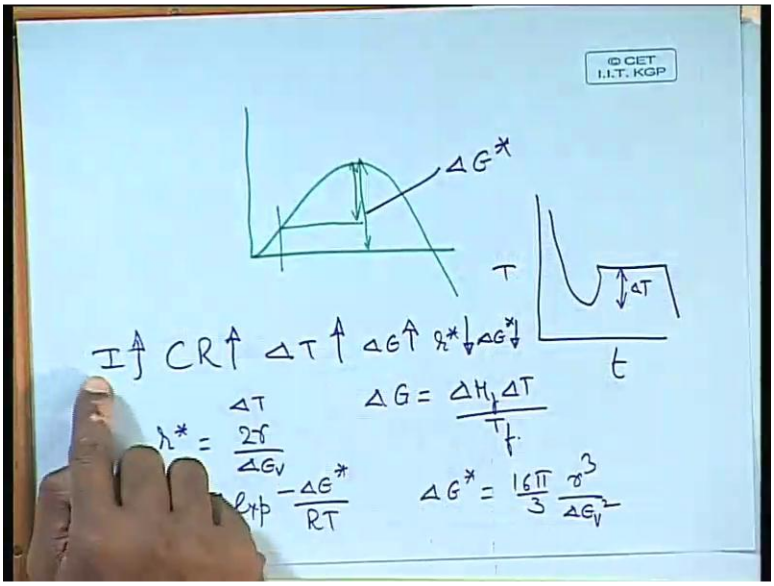

If the driving force delta G is very high, then the I is very high. Because, driving force is related to delta G star and the delta G star controls the I. And delta and delta G also controls the r star. So, as a result, wherever there is a high driving force for the quasicrystal to come out, there will be the fine crystals large number of them.

Student: ((Refer Time: 21:52))

Yes.

Student: ((Refer Time: 21:58))

You can get it, that is what, we are demonstrating, but not in all system this happens. So, the question is, why not in all systems this happens. So, that is what, the question that we should answer. To understand this further, what we have also done is, taken this particular liquid like glass and studied it to, what is called radial distribution functions. I do not know, if have heard off.

Radial distributions functions, basically tell you about, how the atomic arrangement is in a very short range. That means, if you have an atom, how are the nearest neighbor atoms, around that atom are located. What kind of atomic arrangement it has? This is, what you get, from the redial distribution functions.

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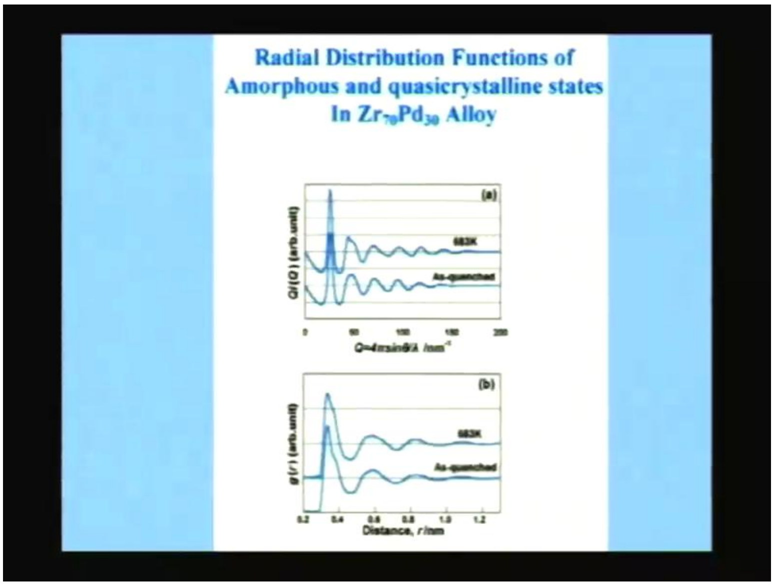

Radial Distribution Functions of Amorphous and quasicrystalline states In $Zr_{70}Pd_{30}$ Alloy

It is a similar to an x-ray diffraction, but a slightly a more advance type of a diffraction technique, where you can see this kind of peaks. And peaks give you, for example, the first peak tells you, what is the fast inter atomic distance. That means, if you chose any atom anywhere and then there are number of atoms around it. Identify, what is the nearest neighbors distance? That means, you draw lines in all directions, take an atom here and then draw lines in all directions.

If you start writing in all directions lines, for example, when this line goes in that direction, may be you find atom there. In this particular direction, you may find an atom here, in this direction, you may find an atom here, in this direction you may find an atom here and here, you may find an atom here, because this is a glass. In a glass, it is randomly arranged atoms.

So, the distance will vary in each direction and if you take the average of all these first nearest neighbors, what you get is the average first nearest neighbor distance. And this first peak, gives you the idea of the average first nearest neighbor distance. And in the same direction, as you keep on going further. You may find, another atoms somewhere and again another atoms somewhere here and another atom somewhere here, another atom and another atom somewhere here.

And take another average of all those second nearest neighbors, what you get is a second peak, which corresponds to the second nearest neighbor. And interestingly, the intensity of these peaks keeps on decreasing, as you go more and more away from that atom Obviously, because as you go from one atom to a far distance, the diffraction intensity will be lower.

So, as a result, you slowly see that particular peak, keeps on oscillating and the finally, the intensity comes down. What is interesting here is, if you take the amorphous alloy, this is a type of atomic arrangement that you get. And the same alloy, if you try to take and then heat it to a temperature, where nano quasi crystal comes out. And take that nano crystalline sample and that do, again radial distribution function, you exactly get the same thing.

That means what it means the atomic arrangement in the glass in a short range is exactly same as that of the atomic arrangement in a nano quasi crystalline phase in a short range. That means, there are defiantly some short range clusters, which are icosahedral cluster. There is no way directly to see them, one way to see them is to look at this kind of high resolution pictures.

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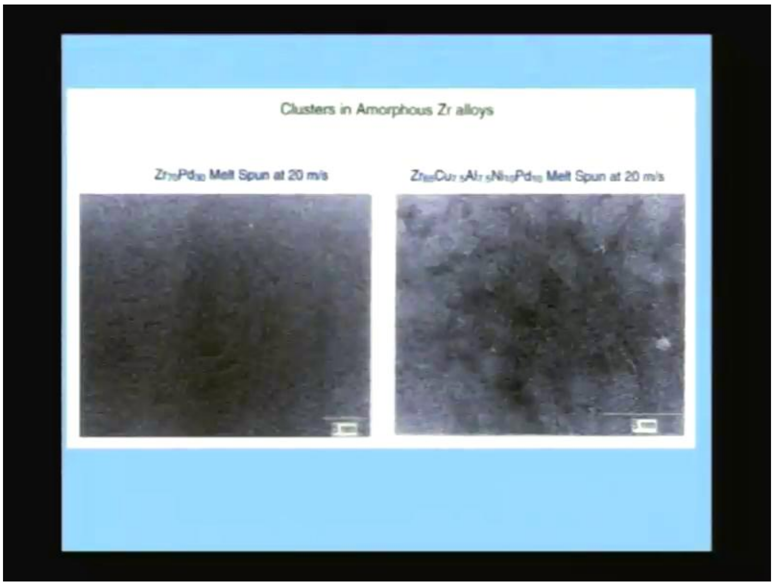

Clusters in Amorphous Zr alloys

$Zr_{70}Pd_{30}$ Melt Spun at 20 m/s

$Zr_{65}Cu_{7.5}Al_{7.5}Ni_{10}Pd_{10}$ Melt Spun at 20 m/s

If you look at high resolution picture, which is basically of a glass, this is a binary glass, this is a 5 component glass and both are glasses. But, what you see carefully is that, there is random arrangement of atom in this. But, you look at small regions like this, look at small region, there are fringes there, can you see those fringes there, atomic fringes. For example here, you see some atomic fringes there.

The atoms arranged as spots like lattice fringes. That gives you an idea, that there is some kind of lattice there. And if there is a way to really to find out diffraction from there, unfortunately, the size is very small, you can see, what is this bar is 5 nano meters. That means, the small cluster you talking of 2 to 3 nano meters clusters, such fine clusters and you just come here you will more here. Here, you see this is a cluster again, which is shows you the individual atomic planes, each line means at atomic plane.

So, there is a small short range order, there similarly you go here, you see another, you see another some somewhere here, yes, you see another here, like that. So, the whole glass is composed of these small short range clusters. And these short range clusters, as you can see, from the previous radial distributions functions; that these are nothing but, icosahedral clusters.

Because, there no way, directly to know, because one cannot do micro diffraction from there. They are so small, that you cannot really do diffraction from there to get a tenfold symmetry pattern. But, from this kind of in direct evidence one can get an idea. So, it is clear, that in these liquids, there are icosahedral clusters. But, the question still remains is that, if this clusters are there in both zirconium palladium and both and zirconium platinum, why is the zirconium platinum is able to give you directly. When you cool it from liquid, why is that zirconium palladium is unable to give, you to understand this, we should try to compare to these two.

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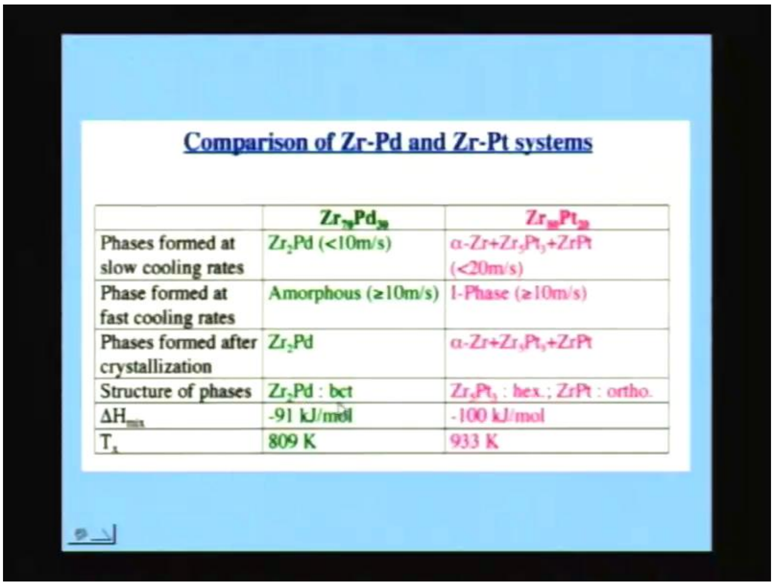

Comparison of Zr-Pd and Zr-Pt systems

	$Zr_{70}Pd_{30}$	$Zr_{80}Pt_{20}$
Phases formed at slow cooling rates	Zr_2Pd (<10m/s)	α-Zr+Zr_5Pt_3+ZrPt (<20m/s)
Phase formed at fast cooling rates	Amorphous (≥10m/s)	I-Phase (≥10m/s)
Phases formed after crystallization	Zr_2Pd	α-Zr+Zr_5Pt_3+ZrPt
Structure of phases	Zr_2Pd : bct	Zr_5Pt_3 : hex.; ZrPt : ortho.
ΔH_{mix}	-91 kJ/mol	-100 kJ/mol
T_x	809 K	933 K

And what you see is that, various parameters, which are compared here. One is, what are the phases, which form on a slow cooling condition. When, you cool it very slowly, under equilibrium conditions, here you get a Z r to P d, single phase; here you get a three phase mixture. So, obviously, there is no real correlation between these two. Here, you get one single phase, here you get three phases. So, obviously, there is no correlation.

And if you cool it slightly faster, here you get only amorphous phase, here you get a icosahedral phase, nano quasicrystal. And if you heat it to a higher temperature, the glass the phase that you get is Z r to P d, whereas, here you get a three phase mixture. So, again there is no correlation there. The only way to check, we see a correlation is that, the delta h mixing, which is tells you, what is a driving force for the liquid.

Heat of mixing is a is a direct correlation to free energy of mixing and free energy of mixing, gives you an idea of how stable a particular phases is. The delta g, which we are talking about so far, the delta g is correlated to this delta h. So, here, you have a high delta h, whereas, here it is slightly lower. So, that means what, it means that, there is greater driving force for the quasi crystalline phase to form, here there is lower driving force.

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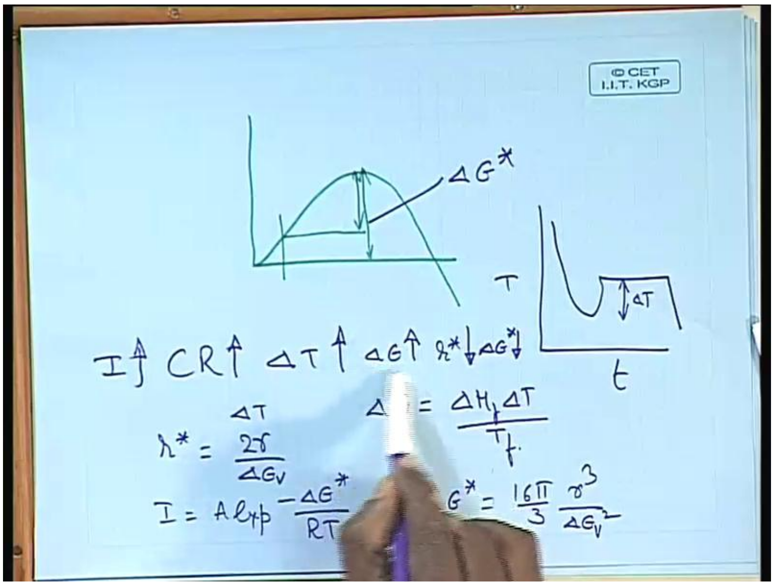

If the driving force is higher, then what you see, go back to your pervious calculation, if the driving force is higher than the activation barrier is smaller, for the nucleations. So, as a result, the icosahedral nuclei can easily form, even during cooling the liquid, when the driving force is very large, whereas, here the driving force is not large enough, for the nuclei to form. But, they remain inside the glass. And when you start heating this liquid, this glass, it will form the quasi crystal. And another important factor for their formation is also, what is called the size factor.

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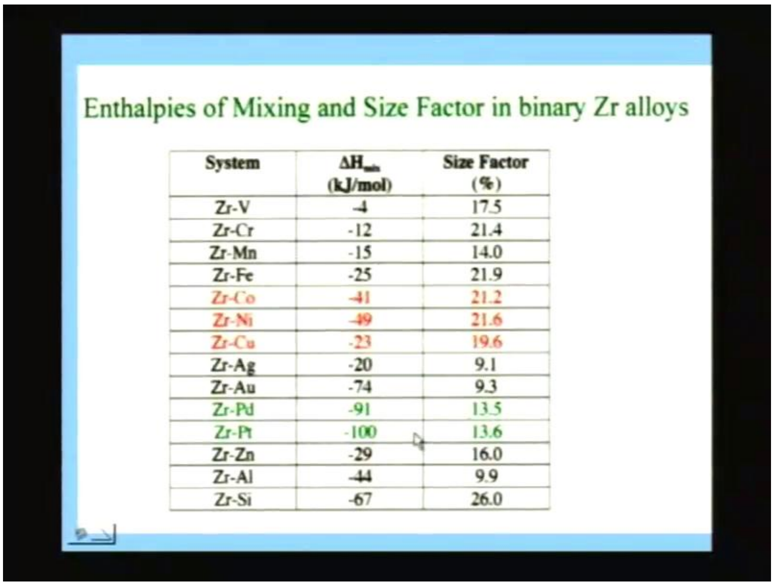

Enthalpies of Mixing and Size Factor in binary Zr alloys

System	ΔH_{mix} (kJ/mol)	Size Factor (%)
Zr-V	-4	17.5
Zr-Cr	-12	21.4
Zr-Mn	-15	14.0
Zr-Fe	-25	21.9
Zr-Co	-41	21.2
Zr-Ni	-49	21.6
Zr-Cu	-23	19.6
Zr-Ag	-20	9.1
Zr-Au	-74	9.3
Zr-Pd	-91	13.5
Zr-Pt	-100	13.6
Zr-Zn	-29	16.0
Zr-Al	-44	9.9
Zr-Si	-67	26.0

If you look at the size factor and delta the h mixing, compare both of them. Look at all the binary systems of zirconium, among all the binary system; these are the only two systems, with the large negative heat of mixing. All others are very small less than about 70 or so. So, none of them give this kind of nano quasi crystalline phase, either during cooling or after crystallization of the glass. For example, the red color picture system, that you see, zirconium cobalt, zirconium nickel, zirconium copper, which is are very small delta h mixing. They have been cooled rapidly.

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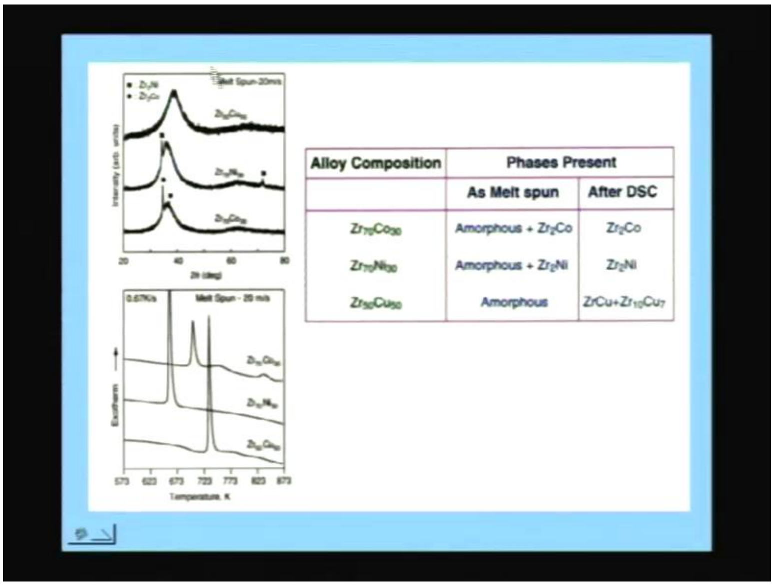

Alloy Composition	Phases Present	
	As Melt spun	After DSC
$Zr_{70}Co_{30}$	Amorphous + Zr_2Co	Zr_2Co
$Zr_{70}Ni_{30}$	Amorphous + Zr_2Ni	Zr_2Ni
$Zr_{50}Cu_{50}$	Amorphous	$ZrCu+Zr_{10}Cu_7$

And we try to see, what happens to them, they give a glass. For example, zirconium copper gives you a glass, zirconium nickel and zirconium cobalt, give you glass, but some amount of crystals is there. And when you heat these things, you always get a only one single peak. That means, there is no nano quasicrystals and if you look at, what are the phases, that are forming, both after melt spinning and after D S C heating, you will never get an any nano quasi crystalline phase, that means, what is crucial is this.

And if you look at zirconium titanium copper, zirconium titanium nickel, which is this system. In this system, the delta h mixing is not really is very large, not really highly negative. But, what you see here is that, there is a crystalline phase in this system, which has the crystal structure very close to that of the quasi crystal. These are, what are called Frank Casper phases. Frank Casper are the two people, who have discovered this phases, they have called Frank Casper phases.

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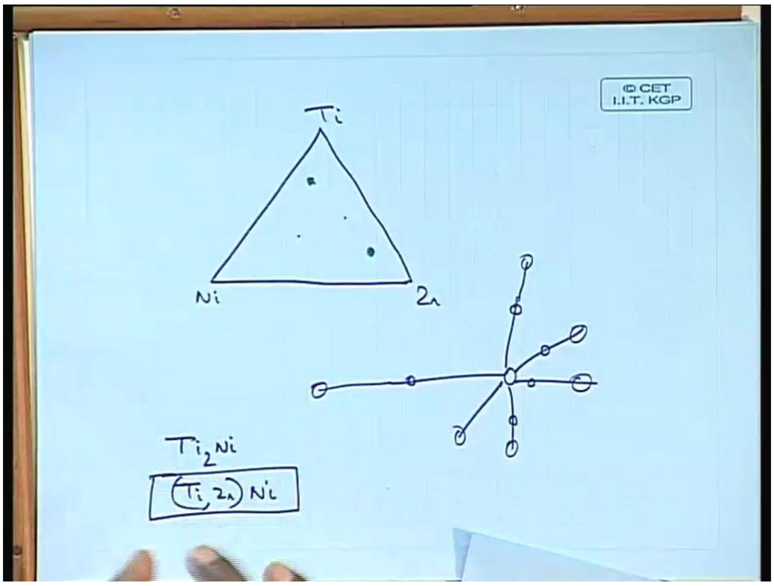

And the phase in this system T i 2 N i and if you replace some titanium with zirconium you get T i, Z r, N i. So, these two phases, which are called the Lavaca phases, they have a crystalline structure, which is very similar to that of quasi crystal. So, it appears that, there are two conditions, under which you get a nano quasi crystalline phase. If there is no oxygen, if there is oxygen, oxygen is stabilizes, you already know it.

In case, there is no oxygen, either you should have a large negative enthalpy of mixing, which you stabilize the liquid. Because, whenever there is large negative enthalpy of mixing, you get deep eutectics. We have talked about it earlier, wherever, there is a high driving force for the liquid to form, there is a deep eutectic. So, wherever there is deep eutectic, the liquid is stable, if the liquid is stable. Then, the icosahedral clusters inside them are also stable and so they can easily give you nano quasicrystal.

And in those cases, where the delta h mixing is high, it is not highly negative, but less negative, that means, are closer to 0.. In such cases, you need to have a Frank Casper phase. And that is what, we try see in this system. We try to revisit the zirconium, palladium and this time, what we did was, we chose the composition, which is real deep eutectic composition, that composition is 75, 25 composition. And when, you take that composition and start cooling it.

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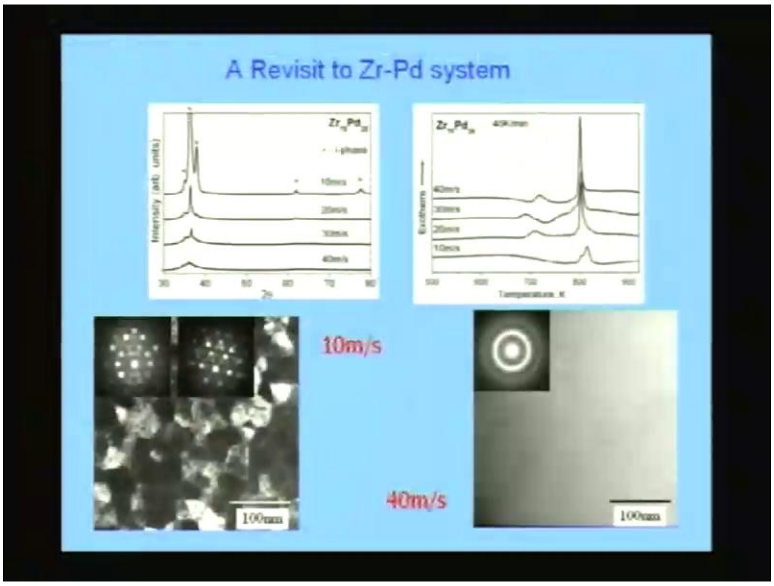

A Revisit to Zr-Pd system

Here, you see interestingly, that if you cool it at even it 10 meter per second, you get a quasicrystal 20 minute per second, 30 minute per second, at all conditions, you get a quasicrystal. And if you cool it, very rapidly, you get a glass and that glass, if you crystallize it, you get a quasi crystal. And you can see from here, this is a cooled 10 meters per second. You get very fine nano quasicrystals, above 20 to 30 nano meter size and you can see, the tenfold pattern here, you can see the three fold quasi crystalline pattern.

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No, it is a wheel speed, wheel speed can be directly co related. When, we come to rapid solidification process, I tell you, how to correlate the cooling rate to it. Then, is direct correlation, the higher the wheel speed, the higher the cooling rate. So, we can indirectly say lower wheel speed means lower cooling rate. So, you can see, high cooling rate, gives you a glass and this glass if you crystallize it, you get a quasicrystal.

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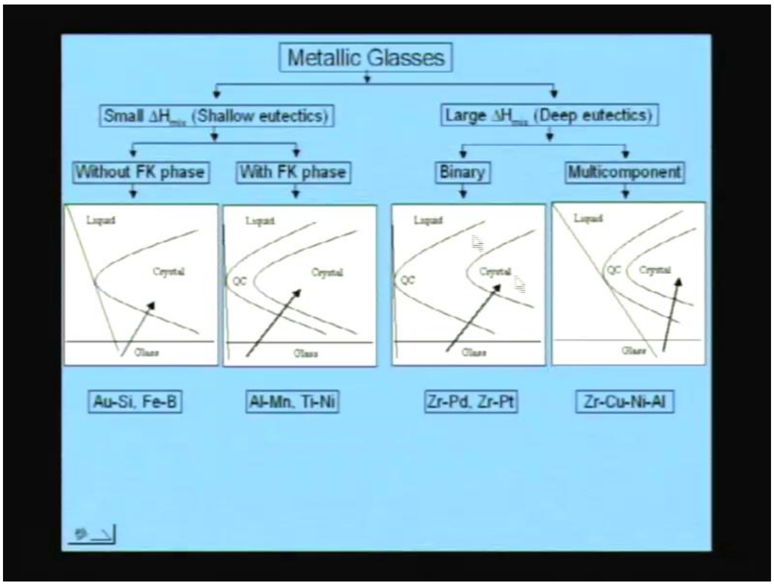

Metallic Glasses

Small ΔH_{mix} (Shallow eutectics)

Large ΔH_{mix} (Deep eutectics)

Without FK phase

With FK phase

Binary

Multicomponent

Au-Si, Fe-B

Al-Mn, Ti-Ni

Zr-Pd, Zr-Pt

Zr-Cu-Ni-Al

So, we can summarize the whole thing, like this. Glasses can be divided in to two categories. One is a glass, which has small delta h mixing, another is a glass, which has large delta H mixing. This means deep eutectic liquids, this means shallow eutectic, in the case of phase diagram. So, both of them can give you glass, but in systems, where you have a deep eutectic; that means, higher negative enthalpy of mixing.

Even, if you cool it slowly, you can get a glass, like bulk metallic glasses, you all know. If the eutectic is shallow eutectic, where the delta H mixing is small, you need to cool it very rapidly, for the glass to form. So, these are the two types of liquids, you can say, one is an easy glass former and which a high delta H is mixing. Negative, delta H mixing which is a deep eutectic liquid, deep eutectic liquids are easy glass formers. And shallow eutectic liquids are poor glass formers.

But, I will never say, they are not glass formers. Every liquid will become glass, that is what is Turnbull had said, long back in 1950, itself. Every liquid will become glass, unless the crystallization intervenes. This was the standard statement made very bold statement, long back about, 50 years back. That means, unless crystallization comes into pictures, every liquid wants to become a glass.

Because, the liquid structure is same as that of the glass structure, so there is no problem for the liquid become a glass, only problem is crystallization comes into in between. So, if you suppress the crystallization, every liquid become a glass. And it is easy for the liquid to become a glass in deep eutectic; it is more difficult in shallow eutectic. And in shallow eutectics, also we can divide in to two groups, one without Frank Casper phases, and one with Frank Casper Phases.

That means, those systems, where Frank Casper phases do exist and those systems, where Frank Casper type of phases do not exist. Not every system will have this kind of phases, for example, if I take a copper nickel phase diagram, it is a solid solution. There are no inter metallic there at all, but if I take aluminum nickel, there are inter metallic’s. So, every system is not the same, some system show inter metallic, some system show solid solution, some system show complete immiscibility.

So, like that, some systems have a tendency to show Frank Casper phases. What are those, the examples are aluminum manganese and titanium nickel, which show Frank Casper phase. So, if you take that kind of a system and look at the T T, type of a diagram, here you take a liquid, cool it rapidly, you get a glass. And that glass, if you start heating it, that glass will give you a quasicrystal first and then finally a crystal.

Because, there is a Frank Casper phase in that system, whose crystal structure is similar to that the quasicrystal. So, there is a greater tendency for the quasicrystal to form. And the same liquid, if you cool it slowly, instead of cooling is very fast, that liquid will give you quasicrystal, if you cool it relatively slowly. If you cool it very slowly, you get a crystal. That means, if you cool at an inter mediate cooling rate, you get a quasicrystal.

And if you take the systems, where there is no Frank Casper’s, these is no another T T curve for quasi crystalline phase. There is no Frank Casper phase, if there is no Frank Casper phase, there is no quasicrystal. So, the liquid, if it is cooled rapidly, it gives a glass. And that if you start heating it, you will get a crystal, you do not get a quasi crystal in that.

So, these are the two systems, where in one system, you get a quasicrystal, either by slow cooling process, inter mediate cooling rate, not very slow. If it is equilibrium cooling, ultimately get a only crystal, equilibrium cooling always gives you a crystal, because quasi crystal is always in a metastable phase. You know that is, always metastable phase, expecting in a few systems, such as aluminum, copper, iron, were we get a stable quasi crystals. Otherwise, in most of the system it is a metastable phase.

So, you can see these are the two types of systems, under the shallow eutectics and if you look at these particular, wherever frank Casper phase there, the cooling rate. That is required, for getting a glass is higher, you can see the critical cooling rate, which is indicated by the steepness of this tangent is higher here, when compared to here. So, wherever, there is the frank Casper phase, if you cool it is slowly, the tendency to get a quasi crystal. If you want to get a glass, you have cooled it, very rapidly.

Then, come to here, here also, there are two possibilities, one is binary deep eutectics and multi component deep eutectics. That means, if you chose a binary system, with high negative delta H mixing, such as in zirconium palladium and zirconium platinum. If you cool it very slowly, ultimately you get a crystal that we know. If you cool at an intermediate rate, you get a quasi crystal, nano quasi crystal and zirconium platinum; we have seen it, already.

Whereas, in zirconium palladium, the driving forces is not so high to give you a quasi crystal phase. So, when you cool it, you get a glass first and that glass, when you start heating it, if gives you quasi crystal and finally, a crystal. But, if it is a multi components system, the problem is in a multi component system, there are so many elements. And because of these so many elements, the diffusivity is very slow.

And because of diffusivity is very slow, for the nano quasicrystal phase to form, during the solidification, it is very difficult. Because, the atoms have to come together, form the nucleus and the nucleus has to grow. For this to happen, it is very difficult, during cooling. So, as a result, it is very difficult to get the nano quasi crystalline phase in a multi components system by cooling.

So, always you get a glass, because the TTT diagram shifted to right, why is it shifted to right, because incubation period is very large. Whenever, there is a large incubation period, the TTT curve shifted to right. That is why in multi components system, the TTT curve is much to the right, when compared to the binary system. You can see, the binary quasi crystalline this one is to the left, when compared the multiple components to quasi crystalline.

And so it is easy to get a glass, so if you look at the slope of this critical cooling rate, that critical cooling rate is much smaller for multi component system, when compared to binary system. So, can very easy glass forming. So, these are all very easy glass formers. That is why, you call them of bulk metallic glass. And such bulk metallic glasses, if you take, you start heating them, all these bulk metallic glasses have these nano quasi crystalline clusters inside them.

Because, as I told you, whenever, stabilize a liquid, you are stabilizing the icosahedrons clusters. There are number of peoples, who have shown that, there are icosahedral cluster inside the liquid, all glass forming liquids. Particularly, strong glass forming liquids, wherever, high glass forming ability is there, there you have these icosahedral clusters inside them. And when, you start heating them, for example, one example as I showed you, zirconium copper nickel aluminum.

There is innumerable number of examples here, you put a palladium here, you put silver there, you put a platinum there and you put titanium there, in this multi component system, all of them give you, nano quasi crystal. So, there are so many such multi component systems, which on cooling, they always give you a glass, because there are easy glass formers.

You can never get nano quasi crystalline phase, during cooling, you always get a glass, because, even if you caste it by in to a normal metallic mold, you get a glass in such as an alloys. As a told you, get almost 30 millimeter rods in such zirconium base systems. That means, 3 centimeters dia rods, so very high glass formability. So, this is, what is the way, we can really summaries this whole thing and show, what for the real condition, for the formation of these glasses.

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We will stop here.

Student: ((Refer Time: 45:05))

If it is less than the critical cooling rate, you will defiantly end up in this, what is called the nano quasi crystalline phase. But, the critical cooling rate it iself is so small. For example, if the critical cooling rate is equivalent to that of sand casting. Then, it is very difficult to have cooling rate, even still smaller than that. So, as a result, you rarely see a formation of a nano quasi crystalline.

Always, the liquid will give you a glass and that glass, if you start heating it. It will first give you nano quasicrystal phase. And then finally, it gives you the crystal and when, if you then control that temperature and time, such that, you get a large fraction of these nano crystal quasi crystalline phase, you have now, what is called a composite. You have an amorphous matrix and a nano quasi crystalline phase, disperse in this amorphous matrix, exactly similar to an aluminum silicon carbide kind of a composite.

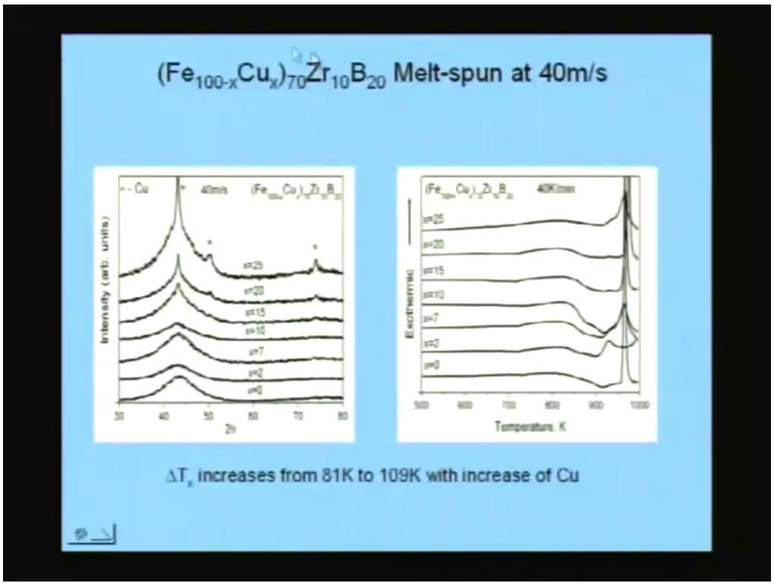
So, that kind of composites have much better mechanical properties and that is why everybody, want to go for such things. Franker's prefaces are basically, you know, we know very inter metallic compound is a complicated inter metallic compound. I have shown you, for example earlier, phase aluminum zinc magnesium kind of phase, which has almost 91 atoms.

You remember, it has an aluminum shell on that magnesium shell, again magnesium zinc shell, another aluminum shell and if you carefully look at those crystal structure and they are all icosahedral structures. So, these are some complicated, there are many simple inter metallic's also, for example, Ni, Al. Ni, Al is just a BCC inter metallic compound, ordered BCC, Fe 3 c, we know Fe 3 c is an orthorhombic structure.

But, not every inter metallic compound is so simple. For example we also know cu 3, au or au 3, cu these are very simple cubic structures. But, there are certain inter metallic compounds, where one unit cell, there are many number of atoms, some time even 1000 atoms. Such crystal structures are very complicated and such crystal structures, have a tendency to have a very large close packing and get into this kind of structures, which are called the Frank Casper phases.

There I told you structures, which are called ((Refer Time: 47:55))) of structures or Frank Casper type of structure. Depending on the person, who have discovered, different names have been given. When, you have discussing about various crystal structures, we talk about that. Anything else, we will also shortly see some nano crystals, which are obtained by a glass.

As I told you, one way to everybody nowadays wants to get composites, not just the glass, not just the quasicrystal or not just the nano crystal, but the composite of all this. We are talking of one type of composite, where you have a amorphous matrix and nano quasicrystals. You can also have a amorphous matrix and nano crystals inside then. (Refer Slide Time: 48:43)



$(Fe_{100-x}Cu_x)_{70}Zr_{10}B_{20}$ Melt-spun at 40m/s

ΔT_x increases from 81K to 109K with increase of Cu

One example is this, iron copper zirconium alloy, which is a glass, iron zirconium boron on alloy, which a glass and put some copper into it. Iron and copper is a system, where they do not attract each other, there is repulsion between iron and copper. So, as a result, there is the tendency for the copper to come out to precipitate, why, for example, in steels, we add copper, have you heard of any steels where people add copper.

Where, copper comes out as precipitate and gives you a very high strength. Even, nowadays people are calling of IF steels, interstitial free steel, where people adding copper. We also know that in steels, we use add led, have you heard of these steels, these are called free machine steels are free cutting steels. Why do, we add, because of led, do not dissolve in iron. So, it precipitates as fine particles of soft particles and so you can easily machine, when it is uniformly distributed.

Similarly, if you can distribute copper, so what we have done is, take a glass having an iron zirconium boron kind of a glass, put difference amounts of copper, this all different amounts of copper. Zero percent copper, gives you a glass and as keep on increasing the amount of copper, you start getting the x r d peaks of copper.

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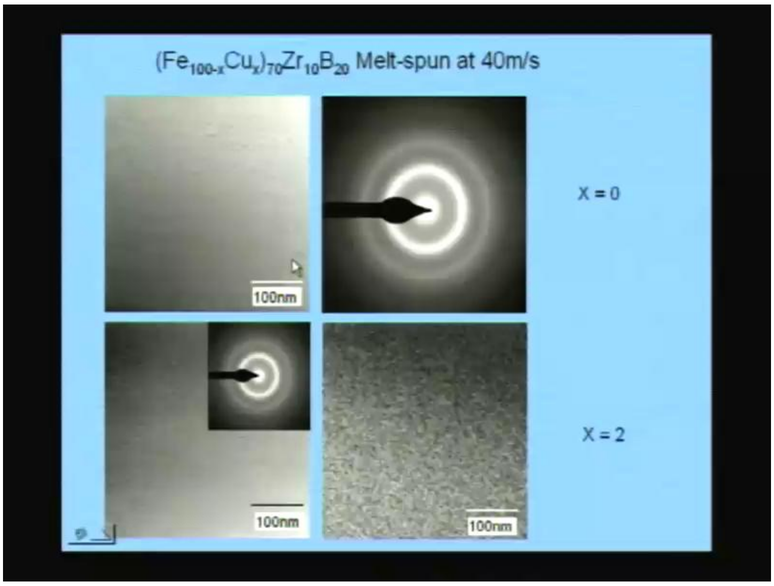

$(Fe_{100-x}Cu_x)_{70}Zr_{10}B_{20}$ Melt-spun at 40m/s

And if you start looking at the TEM, with no copper, it is all amorphous. You see the diffraction pattern, when you start adding some copper, there is very fine precipitate, you can see, this is 100 nano meters. What you have around 5 nano meters are 2 to 5 nano meters particles.

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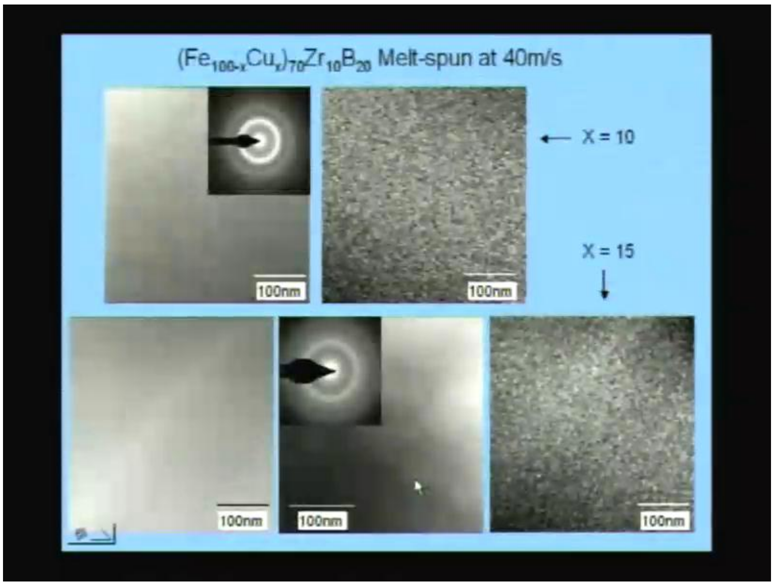

$(Fe_{100-x}Cu_x)_{70}Zr_{10}B_{20}$ Melt-spun at 40m/s

And then you go to higher, the start seeing bigger and bigger particles coming out. And you go still higher, you start seeing big particles. And now at this stage, one can get rings corresponding to this copper particles and one can put diffraction the electron beam on individual particle. And get, what is called micro diffraction patterns and to show, what is zone axis and what kind of particle it is, whether it is copper are not.

We can also put electron beam on this and also do what is called EDAX to find out that, these are copper particles. So, like that, one can depending, these are all, if you look at, they are all cooled at the same speed.

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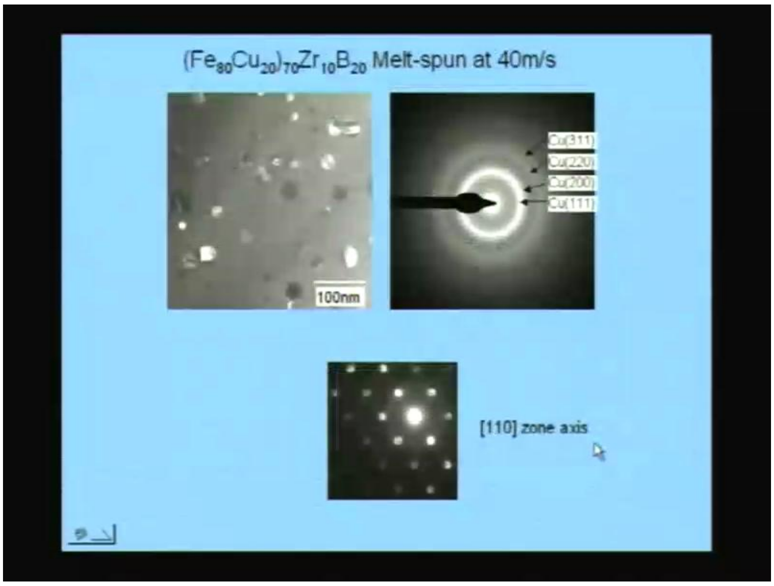

$(Fe_{80}Cu_{20})_{70}Zr_{10}B_{20}$ Melt-spun at 40m/s

40 meters per second, 0 percent copper, 2 percent, 10 percent, 15 percent and this is 20 percent is not really percentage copper in fact. It is out of this, if you have to find, if you want to know, exactly what the amount of copper in this is, you have to multiply 0.2 into 70. So, you will get about 14 percent. So, what you have done here is, we have varied copper and iron in such a way, that the total is 100 is here. So, that is how, because they the copper gets substituted in to iron here. So, that is, we have varied copper here.

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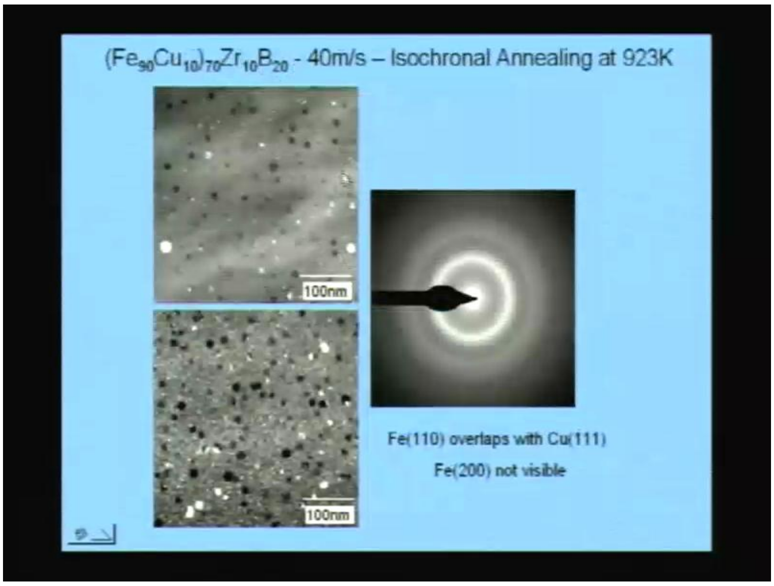

$(Fe_{90}Cu_{10})_{70}Zr_{10}B_{20}$ - 40m/s – Isochronal Annealing at 923K

Fe(110) overlaps with Cu(111)

Fe(200) not visible

And so we can also get a glass, take a 10 percent copper alloy, you see 10 percent copper alloy this, which every fine particles. You cannot really see, you see the diffraction pattern, diffraction pattern does not show any copper peaks, copper rings, it is steel amorphous. There are so fine, that the diffraction pattern is enable to show any rings corresponding to the copper.

And take such a 1 and then start annealing it at some temperature and start getting the fine particles. And when you look at the mechanical properties of this, gives you almost 2 giga Pascal strength a very high strength these alloys.

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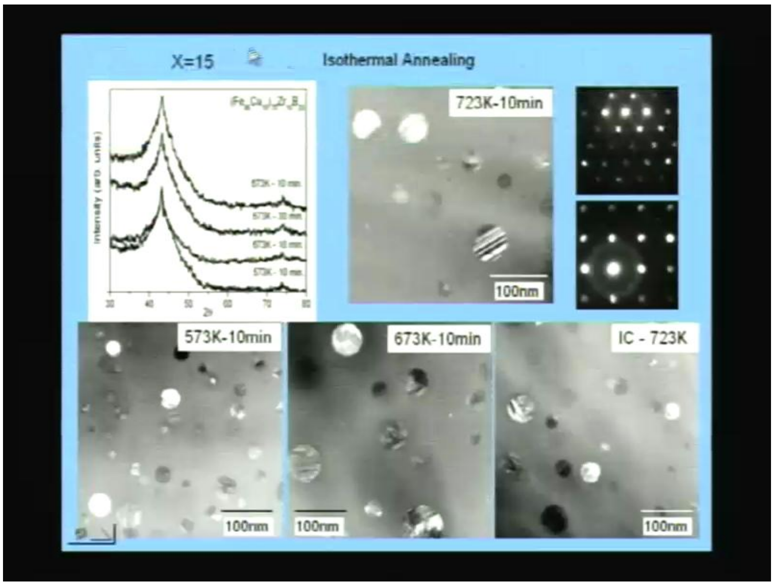
X=15 Isothermal Annealing

And one can do different compositions can be taken isothermal annealing can be done, different temperature and timing, this is 573 and 673 and 773, all 10 minutes. You can see, the particles are very fine at low temperature, particles start becoming bigger, when you go to much bigger. And you can see, all the twining, inside the growth, twins we say, whenever particles, which are embedded in a amorphous matrix.

The matrix is amorphous, mind it, if you carefully observe this diffraction pattern, which is the micro diffraction pattern taken from the one of the particle. But, you can still see the ring, amorphous ring, which is coming from the matrix. So, these are basically, the matrix is amorphous. If I put and the electron beam on the matrix, I will get a only amorphous ring pattern and this is corresponding to the individual particles.

So, that is how, one can find out various particles and see that, one can get such nano crystals in an amorphous matrix, nano quasicrystals in a amorphous matrix. One can control the size and the distribution of these particles, by controlling the temperature and time of heat treatment. And finally, control the mechanical properties. For example, we know in age hardening also, it is the temperature and time is crucial to get the best property.

Because, we know age hardening, always a peck in the hardening, what we call, the peak aging. If you do less then that, the aging time is less than that, you get less hardness, if the aging time is more than that, you lose the hardness. So, like that, there is always a particular temperature and time, where you get the best distribution of these particles. For each alloy, people have started optimizing these conditions. So, that, one can gets the best properties.

As metallurgist, we are more concerned about the mechanical properties, these are the some of the new advance materials, where one can achieve much higher strength. Because, if you have a normal composite, aluminum silicon carbohydrate composite, you can reach strengths beyond 500 Mega Pascal’s, 500, 600 Mega Pascal’s is a kind of upper limit.

But, here are the opportunities, even in a typical aluminum base alloy; one can reach almost 1.5 giga Pascal’s. So, these are some of the real exiting materials, I should say as per as metallurgist and mechanical engineers are concerned. Because, one can thing of only thing is, how to make them in large quantities and then how to control the process parameters. So, that we can make them to large quantities and then compact and then bring them to any particular shapes of our interest. So, and during these processes of compaction and sintering, we should be able to control in such a way, they do not really grow. So, that is another area, where lots of people are working just stops here.