

Advanced Materials and Processes
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Lecture - 13
Quasicrystals Part – II

In metallic systems, non metallic systems, we have talked about what are the properties of them, we talked about it. Then, we went to glasses, we talked about the glasses, how the glasses are made? Particularly, the metallic glasses, we are more concerned about the metallic glasses. Then, we looked at the various criteria, for making the glasses. What is called the glass forming ability? We talked about glass forming ability. How some kind of systems, some kind of alloys can easily become a glass. Whereas, some alloys will not become a glass.

So, we looked at various conditions under which you can get a glass. Then, we also talked about, what are called bulk metallic glasses. So, how to make these glasses in a bulk form, not just a ribbon, which were the initial materials, which were made. When, 1959, Paul Duwez has discovered this particular technique called rapid solidification processing.

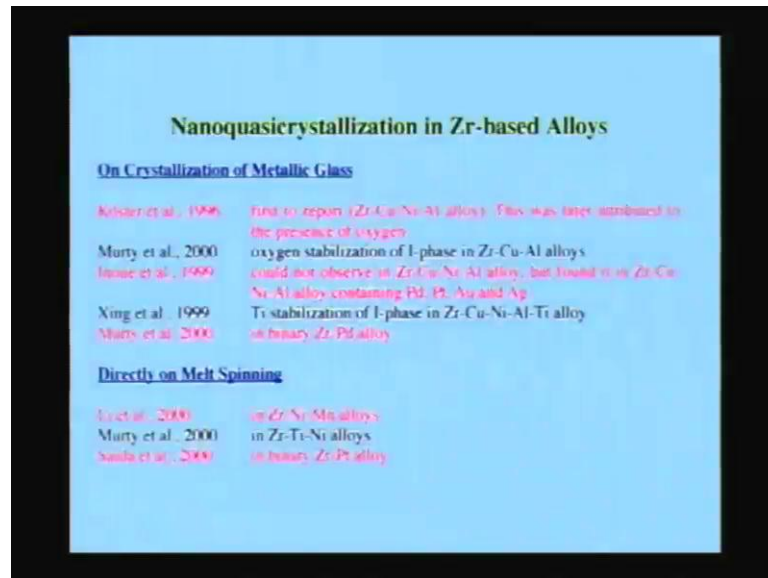
So, we talked about how bulk metallic glasses are made. And under, what conditions an alloy can give you a bulk metallic glass. That also, we talked about various criteria for formation of bulk metallic glasses we talked. Then, we went to into another class of materials called quasicrystals. We talked about, what are quasi crystals, under what conditions; you get quasicrystals and looked at a few examples of quasicrystals.

And today, what we will look at is, what is called nano quasicrystals? How to get quasicrystals in a nano crystalline form? That means, fine quasi crystals dispersed in an amorphous matrix. These are nothing but like composites. So, you have amorphous matrix. We have talked in the last class, that when you take a glass and crystallize it and get nano crystals in it, then the properties can be improved.

We have shown that some the mechanical properties can be further improved by just dispersing nano particles in a matrix of amorphous phase. So, we will try to see, how these nano quasi crystalline particles can be embedded into an amorphous matrix. And under, what conditions we can get such a thing and what are the systems, which can lead

to this kind of nano quasi crystalline materials in an amorphous matrix. So, to go about it, we should first see where this whole field has started.

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Long back in 1996, Kiosker is the person, from Germany, who reported that, when he took a zirconium copper nickel aluminum alloy. And then took that alloy, rapidly solidified that alloy, he got a glass. And when, he started heating this glass, he saw that, it undergoes crystallization in basically two stages. And in the first stage of crystallization, this glass gives you, what are called nano quasicrystalline stages. That means, quasi crystals come out in a very fine form, uniformly, distributed in a matrix.

And but the problem was that in almost similar years, 1999, which is in 3 years, after that. In Japan, another group, which is called Inovase group, professor Inove in the Institute of Materials Research University, he took the same alloy. But, he could not get the same phase. He took the same alloy could make a glass out of it and he tried to crystallize. And when, he crystallized it, he did not see any two stage crystallization, but he could see, only one stage crystallization and the product of that crystallization was a crystalline material, but not a quasicrystalline material.

And also, the crystals that were obtained were big crystals, not even nano crystals. So, the question here was, why this particular alloy, could give a nano quasicrystals. Why the other alloy, with the same composition, could not give. Just, the only difference is one was made in Germany, another was made in Japan. Does it differ, the formation of

various stages, if it should change from country to country, obviously, there is no science in it.

So, then this was the condition at which the Ilaver group took this particular problem and wanted to understand, why this happening. Then, one of the things that people were thinking those days is, probably this whole thing is happening, because of the oxygen. Because, we know zirconium has a strong affinity to oxygen. It can absorb oxygen to a large extent. When, it is melted, because these are all melted, zirconium, copper, nickel, aluminum. You take these elements and then melt them together and form an alloy.

During this alloy is made, may be, if it is possible that, the two laboratories, where it is made. The conditions were such that, in one of the case, probably the amount of oxygen is more, which probably is affecting this. To understand this, what has been done is, to take an alloy and introduce oxygen into it, deliberately in different amounts. And try to see, whether this oxygen, really plays a role.

So, that is, where this whole work has started to understand, what are the conditions for this nano quasi crystallization process? So, this is one part of the work. Then, people have seen that the nano quasicrystal can come in two kinds of possibilities. One is, you can get a glass and crystallize that glass and get a nano quasicrystal or you can take the liquid and cool it rapidly by melt spinning technique, rapid solidification and directly from the liquid, also one can get.

So, there are some systems, such as zirconium nickel manganese, zirconium titanium manganese, zirconium platinum kind of systems, where people could show that, yes, you can directly get a nano quasicrystal by just cooling the liquid. Whereas, in some cases like this kind of alloy, zirconium copper nickel aluminum alloy or zirconium palladium alloy. People could not show that, you can get the nano quasicrystal stage, directly. But, it always forms, as if subsequent step, after the glass has been made.

First, you get the glass and crystallize the glass and this glass undergoes two stages crystallization. And the first stage crystallization has always been the formation of nano crystal. And Inove, has also further showed, that a number of elements, such as palladium, platinum, gold, silver these are the elements, which can stabilize this nano quasicrystal phase. That means, if you do not add these elements, you do not get that phase.

But, if you add them, there is a tendency for the formation of the nano quasi crystalline phase. That means, the alloy composition has an effect. So, we will try to see, why it should affect and what are the conditions under which, you can make this kind of thing. And there is also another group, Xing in 1999, where they also showed that, probably titanium also affects it.

And this is a another case, where they showed that in a zirconium, copper, nickel, aluminum alloy, same alloy has been taken and some titanium has been added to it. And they could show that, if you do not add titanium, you do not get that phase. But, if you add the titanium, you get these nano crystals, nano quasicrystals. So, we will try to see, how these are correlated and what is the ultimate truth, behind this whole story?

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Experimental Details

Alloys :

- ◆ $Zr_{65}Cu_{27.5}Al_{7.5}O_x$ ($x=0.14, 0.43, 0.82$)
- ◆ $Zr_{65}Cu_{27.5}Al_{7.5}Ni_{10}Pd_{10}$, $Zr_{65}Cu_{27.5}Al_{7.5}Pd_{10}$, $Zr_{65}Cu_{15}Ni_{10}Pd_{10}$, $Zr_{65}Cu_{25}Pd_{10}$, $Zr_{70}Cu_{10}Ni_{10}Pd_5$ and $Zr_{70}Cu_{15}Pd_5$
- ◆ $Zr_{100-x}Pd_x$ ($x=35, 30$), $Zr_{50}Pt_{20}$, $Zr_{50}Co_{20}$, $Zr_{50}Ni_{20}$ and $Zr_{50}Cu_{20}$
- ◆ $Zr_{52}Ti_{25}Ni_{23}$ and $Ti_{52}Zr_{25}Ni_{23}$

Alloys Preparation : Arc Melting in Argon atmosphere

Rapid Solidification : Single roller melt spinning (5-40 m/s)

Characterization :

- ◆ X-ray Diffraction (Rigaku)
- ◆ Differential Scanning Calorimetry (Perkin Elmer-Pyris I)
- ◆ Transmission Electron Microscopy (Philips CM200, JEOL 4000CX and Gaton Imaging Filter)
- ◆ 3 Dimensional Atom Probe (CAMECA)

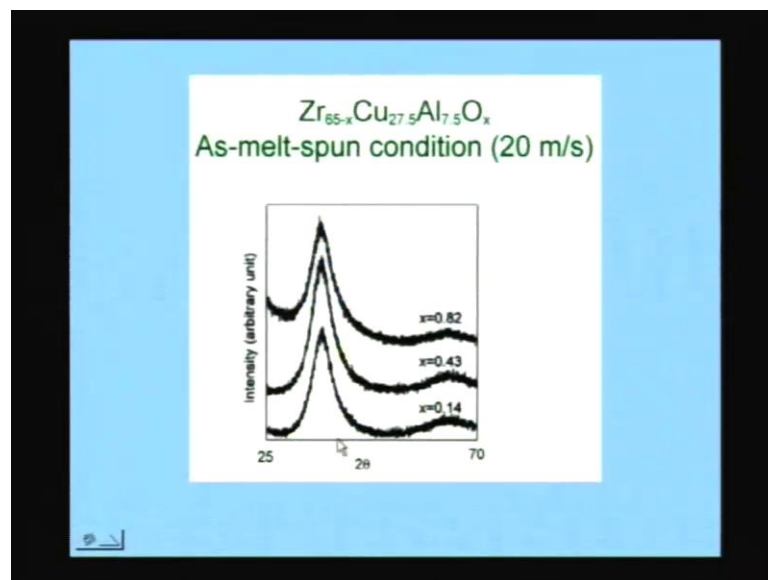
And to understand this, a number of alloys have been taken. One alloy, which has chosen is zirconium copper aluminum, which is a standard glass forming alloy. Zirconium with 65 percent, zirconium 27.5 percent copper and aluminum 7.5 percent is a standard glass forming alloy. And that has been chosen, where definite amount of oxygen has been put in.

How, do we put oxygen into it, how can you introduce an oxygen into an alloy, in a known quantities. If you take liquid metal and melt the liquid metal in an oxygen environment. Then, if you can increase a partial pressure of oxygen; that is one possibility by which you can do it. The technique that has been used in this particular study was to add some copper oxide to this zirconium based alloy.

Copper oxide has a much lower melting point about 1200 degrees. The melting point of a zirconium based alloy is about 1500 degrees. So, when you add this copper oxide, immediately copper oxide melts and then goes into the solution of zirconium. And copper and oxygen, become elemental constituents and they can easily dissolve into zirconium. And one can control ((Refer Time: 09:28)) one can introduce the oxygen.

And a number of other compositions have been chosen, I will show you a little later. Why these have been chosen and then all these alloys have been studied to understand, the basic principles behind the formation of these nano quasicrystals. And they have all been made the alloys have been melted by arc melting in an argon atmosphere. And then they have been melt spun. You all know by now, what is melt spinning and they have been studied by a number of techniques.

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What you see, first of all, is that when you take the three compositions, zirconium copper aluminum alloy with different amounts of oxygen. You see, all of them, show this kind of an x r d pattern, what does that mean? What does this kind of an x r d pattern signify.

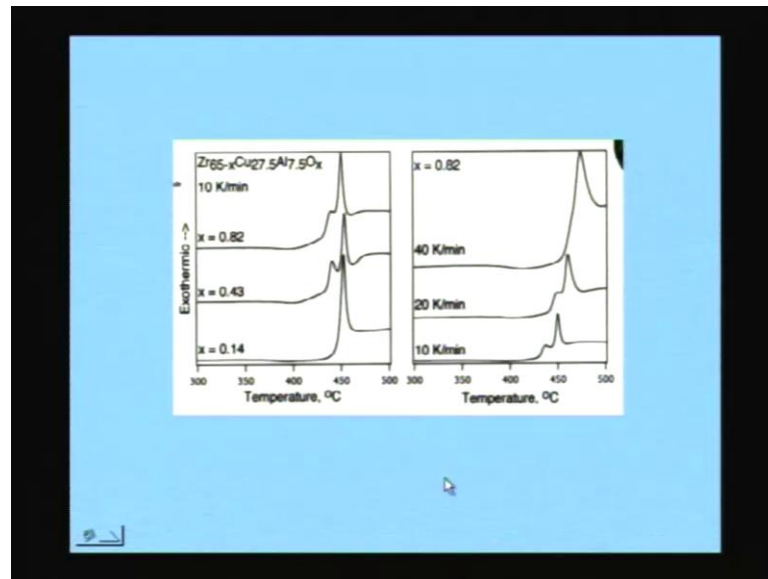
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These are all amorphous alloy. This particular broad peak always signifies an amorphous phase. So, this alloy, which was melt spun is an amorphous alloy in all the three

conditions, that means, it is a glass. So, a glass has been made in all the three alloys. (Refer Slide Time: 10:51)

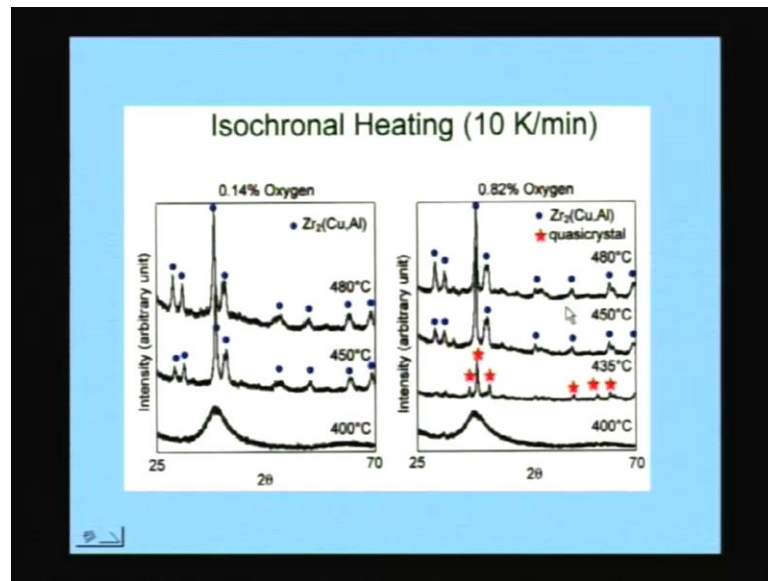


But, when you take these three alloys and heat them in a D s c, what you see is that, the alloy with a very small amount of oxygen, gives you a single stage crystallization peak. But, when you increase the oxygen, beyond about 0.4 percent, you see two stages crystallization. That means, what I have told you before, that possibly a nano quasicrystal phase is coming here. So, that has to be proved now.

That D s c, cannot prove, what phase is coming out. It can only tell you, that something is coming out; otherwise there will be no peak there. The moment, you see, an exothermic peak, means, a glass is crystallizing. So, these two are exothermic peaks. So, suggesting that, there are two stages of crystallization. And what is also interesting is that, if you take a high oxygen alloy and heat it at different rates.

If you go to high heating rates, you see that, the two stage crystallization vanishes into single stage. That means, the phase, that is, forming in this first phase is a very meta stable phase and if you heat it very rapidly, it does not form. So, one has to understand, what is that phase, that is forming.

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So, to understand this, what has been done is, to take this alloy, heat it to various temperatures, and then take this sample and study it by x-ray. So, this alloy has been heated to different temperatures. You take 400 degrees, 450 and 480 degrees. So, these are the temperatures, where the crystal. For example, if you go back, so 400 degrees is somewhere here. That means, where no crystallization has taken place.

And 450 are just between the two crystallization peaks and 480 are after the second stage crystallization. So, that means, if they have been heated in D s c. This is one facility, a D s c gives you that, you can hear it in a D s c. And then immediately at a particular temperature, stop it and quench it. Quench it means, cool it rapidly, there is no possibility of quenching into water or something like that in a D s c, but you can cool it rapidly.

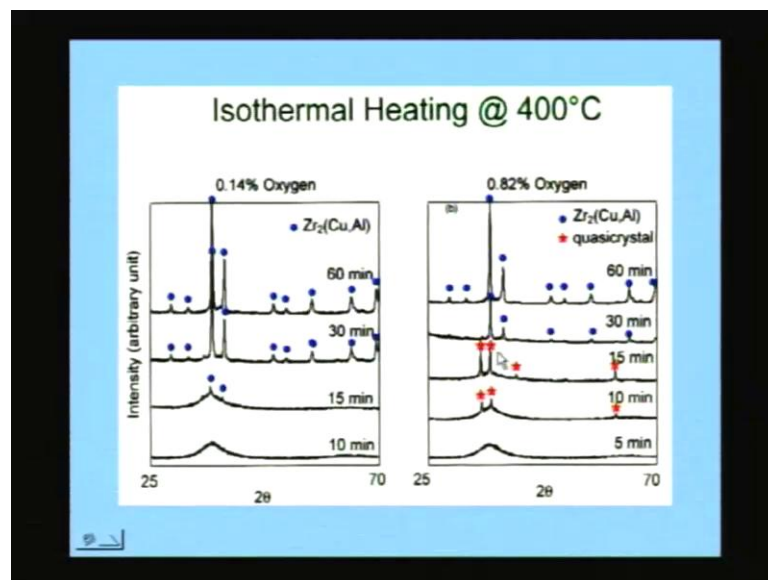
So, that any further transformation can be suppressed and whatever transformation that has taken place in the two, whatever temperature, you have heated, that can be retained. And take that sample, which has come out of the D s c and then study it by any technique; that you want. For example, here in this case, heat d x-ray has been used to study, what phase is forming out.

So, you can see that, x-ray tells you, that this is amorphous at 400, but at 450 some crystals have come out and 480, again exactly the same peak. That means, whatever is coming out in 450 is same as 480. This is, for the low oxygen. In fact, the low oxygen content alloy has shown, only one, crystallization peak. So, this tells that these particular glasses undergo crystallization by forming this phase, which is called $Zr_2, Cu Al$.

Whereas, when you take a high oxygen alloy, it shows something interesting. That it gives you some peak at 435, which is a first stage crystallization. When, you go to 450, within 15 degrees, all those peaks have vanished, you get new peaks. And which are corresponding to the Zr_2CuAl phase and when you go to 480; again the same peaks will remain. That means, this phase, which is forming at 435, it is vanishing after 450 and then the same phase persists, even, if you go to higher temperature.

So, some phase is forming, we do not know, but from x-ray, we could index them, as a quasicrystal. But, x-ray is not a technique to find out, whether something is quasicrystal or not because it just gives you peaks. So, we have to find out, what is the rotational symmetry and rotational symmetry can be obtained, only if you can do the electron diffraction.

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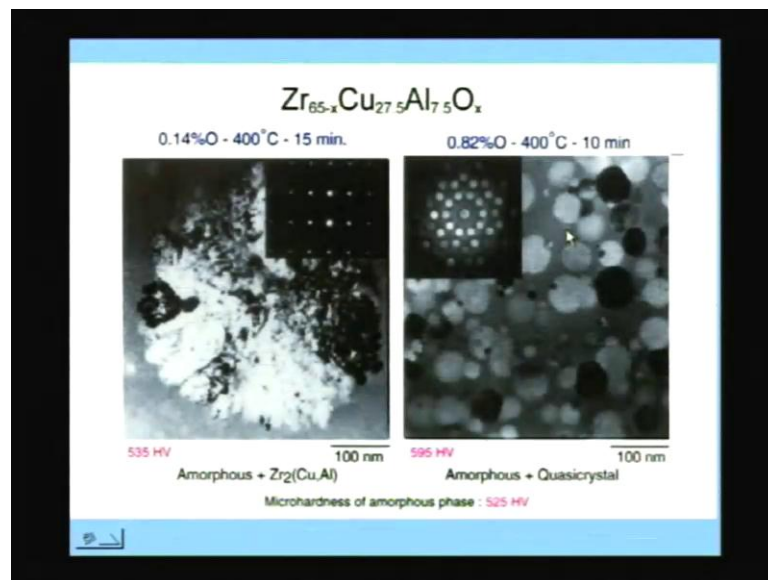
So, to do that, what has been done is the electron diffraction. But, before that, it is also possible to do, what is called the isothermal heating. Taking both the alloys, one alloy has been heated at 400 degree centigrade, for various timings. You start with 10 minutes, nothing happens, it is amorphous. Then, go to 15 minutes, you start getting some crystals and then go to 30 minutes, crystals becomes bigger, you get sharp peak. And then go to 60 minutes, the same peak persists.

So, you can see exactly the same peaks exists there. So, it is again amorphous giving you to Zr_2CuAl . But, if you come here in this case, where high oxygen content alloy, it gives you this peaks, which are nothing but the quasicrystalline peak in 10 minutes and

15 minutes, the same peaks are there. But, when you go to 30 minutes, you do not see those peaks.

Some other peaks, start coming and those peaks remain, when you go to 60 minutes and those peaks, which are coming in the second stage are the Zr_2CuAl . That means, these particular first alloy crystallizes in a single stage by formation of Zr_2CuAl from the liquid or from the glass. Whereas, in this case, the glass gives you first, another phase, which we are at the moment calling it as quasicrystal, only based on the x-ray. And then that undergoes, another stage of crystallization, which gives you, what is called the equilibrium Zr_2CuAl . Zr_2CuAl phase is the equilibrium phase in this particular composition.

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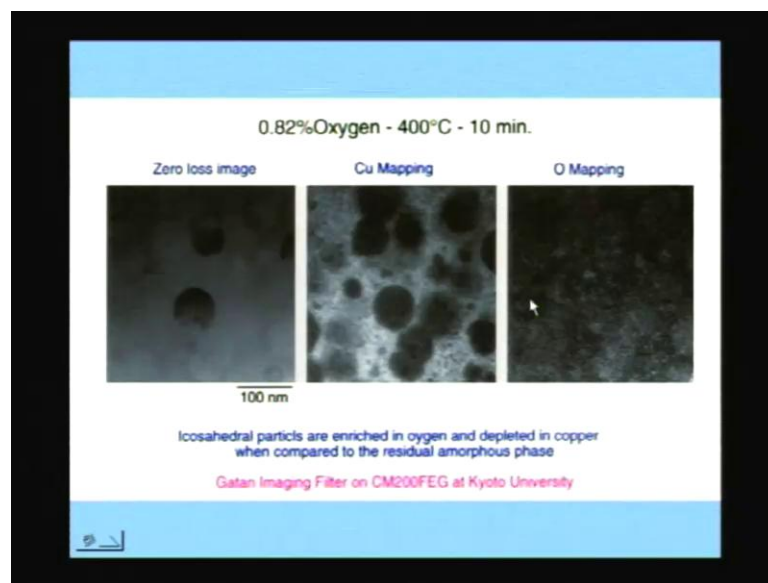
And if you do the TEM, what you see here is that, at low oxygen level. What you see is a formation of big crystals, which are dendritic type of crystals, coming out and they are all Crystalline. How, do you know, they are crystalline, you can see this pattern, the diffraction pattern, obtained from this, which is the periodic arrangement of spots. And periodic arrangement of diffraction spots, means, periodic arrangement of the atoms in a crystal structure. So, that is why, this is the Zr_2CuAl .

And whereas, this particular alloy, gives you the same alloy, which has been crystallize, after putting around 0.82 percent of oxygen and then heated to about 400 degree centigrade. For 10 minutes, it gives you very fine nano particles. You can see this scale is

about 100 nano meter. That means, you have particles, ranging from almost 5 nano meters, very small particles to almost about 50 nano meters.

So, a spherical particles of large size range from 5 to 50 nano meter and all of them have been confirmed to be the quasi crystalline. How, do you know, you count these numbers, they are the tenfold symmetry, you can see. So, that tells you, that this alloy, cannot give you a nano quasicrystals, whereas, this alloy can give you. That means, oxygen is really doing something. But, really, we still do not know at this stage, where this oxygen is really going and what this oxygen is really doing.

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To understand that, we have taken this alloy and then studied by what is called an imaging filter. An imaging filter is similar to something like an ((Refer Time: 18:06)) in an SCM. Most of you, must have heard of energy dispersive x-ray analysis in SCM, we always regularly do it. Where, you can do, what is called elemental mapping. You have a material, two phase material or a single phase material, which has a number of elements.

You can identify, where the element is distributed in that microstructure, what is called is the elemental mapping. If you do this kind of elemental mapping, usually dark regions, indicate the region where that particular element is depleted. That means, it is amount is small, whereas, the bright regions are those regions, where the amount is large. So, like that one can do mapping.

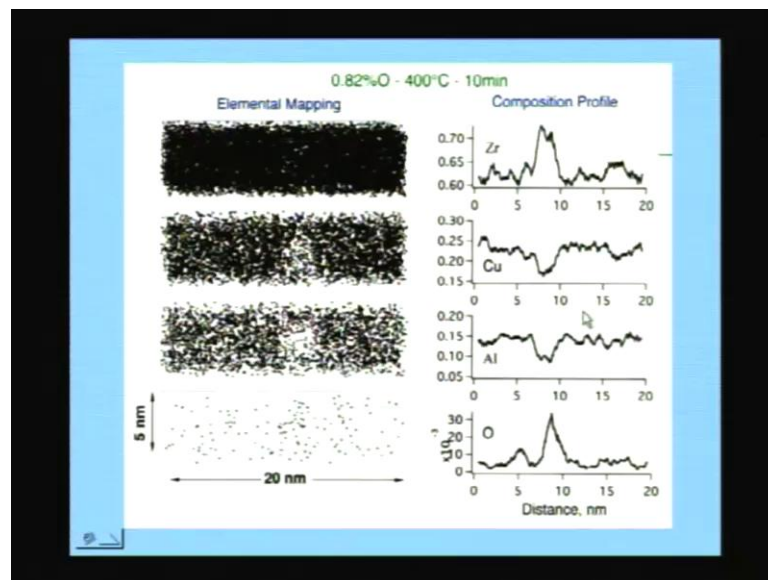
This is, what is called a copper mapping, from an alloy, containing high oxygen content and this is an oxygen mapping. Oxygen mapping, basically shows you in some region,

some oxygen concentration. But, unfortunately oxygen atomic number is very small. So, whenever you have atomic number very small, it is very difficult to find out this kind of mapping. Particularly in SCM, we know that any element less than boron cannot be seen at all.

So, small atomic number elements cannot be seen, because these elements, basically the principle behind detecting these elements is by the electrons, which are scattered by these atoms. Absorbed by knocking out, the electrons from the K shell or a N shell and then electrons from a higher shell, fall onto that lower shell and some energy is released. The extent of the energy, that is released will depend on, what is the atomic number.

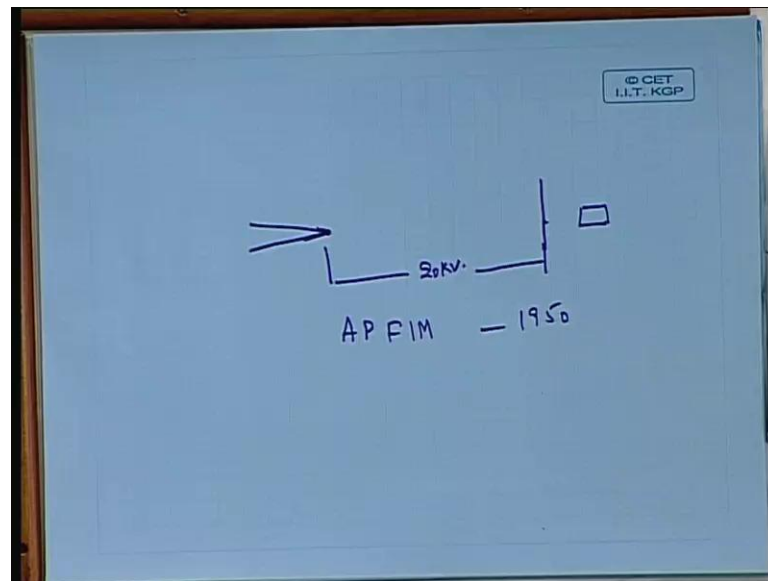
The higher, the atomic number and then you will see the bond energies are stronger. And if the bond energies are stronger, the energy of the x-ray; that is released is higher. If the energy of the x-ray released is higher, the intensity will be higher. So, you can see very bright regions. Whereas, if the atomic number is very small, the energy is very small, you will not be able to see it. So, that is why, what we did was, we went to another technique called atom probe.

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An atom probe is basically nothing but a field ion microscope in a microscope.

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In a field ion microscope, what you see is that, you take a sample in the form of tip and then subject this particular tip to a high energy. That means, high voltage drop with respect to a screen here. When, you apply a high voltage, from here to here. Let us say 20 k v or so. There is, what is called emission, this is called field emission. When, you evacuate this whole chamber, containing the sample and the screen. And then apply a high voltage, the atoms are emitted out of this and then go towards a positive charge.

Because, you make this whole chamber filled with certain gas and that gas gets ionized and the image of this particular tip can be seen here, when these atoms get reflected on to that. So, we can see the image of atomic arrangements on this particular photosensitive plate, which is kept there and this is, what is called Field Ion Microscopy, FIM. And this is a technique, which has come in about 1950's.

People have done a lot of work, on try to see these dislocations in various atomic arrangements. And also, people try to see, how stacking faults are present in various materials. So, one can directly see atoms, that is one of the advantage of this Field Ion Microscope, whereas, in transmission electron microscope. Unless, you go to high resolution microscopy, one cannot really see atoms. So, that is one of the advantages of this.

And later a new technique has come, which is basically a modification of this, which is called Atom Probe Field Ion Microscope. APFIM, what they do in this technique, is that, they remove this plate there and put a detector there. Whenever, you want see the image

of this tip, you put this plate back, you can see the image. And whenever, you want to find out, what how the atoms are distributed what is the quantity of a particular element in a particular material.

What you do is, just remove this plate and allow these atoms to go and fall on to a detector, which can detect various elements. How, does it detect various elements, because, various elements have a different atomic numbers. If you have different atomic numbers, whenever, these atoms are moving from here to here, a particular distance. There is a fixed distance between the tip and the detector.

The time required for the atom to come from here to here is a function of the atomic number. The higher the atomic number, the heavier the atom is, the heavier the atom, longer the time, that it takes for reaching this. So, from this time of flight, what is called time of flight? One can detect, what element is coming and one can find out, all those elements, which are coming at a fixed time. And from that, one can find out, how many such atoms are coming of a particular element.

For example, if your material has aluminum and copper, one can find out, how many copper atoms are coming and reaching that detector at a particular time. And similarly, how many aluminum atoms are coming, like that, one can find out different atoms. And as you keep on sputtering away atoms, this is nothing but sputtering. You are putting high field and when you are putting high field, the atoms are sputtered away. So, atoms are sputtered away, layer by layer.

When, layer by layer, atoms are coming and joining this detector and if you can adjust the sensitivity or and the time required, for the analysis of this detector, such that, each layer once it comes detector immediately recognizes it. And then stores it in to a computer. And the next layer of atoms comes and immediately it detects. What you can do is, you can reconstruct the whole of the data, that has been collected into the form of a three dimensional map.

So, layer by layer, atomic arrangement can be obtained by a three dimensional mapping of all the data, that has been obtained and you get these kind of these kind of blocks. This is nothing but a three dimensional block, one can rotate it in a computer and see, how the atoms are distributed. May be, at some point of time, unfortunately, this particular course is not about characterization of materials.

But, at some point of time, if you are interested, I can give you more images and pictures about, how to use atom probe microscope to understand various phase transformations, which occur. For example, let us say, if you want to know that g p zone formation in an aluminum copper alloy. What is this really, what is the composition of the g p zone is one of a very, you know, astounding questions. People; really do not know, because the precipitates are so small, that they cannot be observed by edax's in an SCM.

So, if you go to TEM also the only way you can image them is only by, what is called the strain field, which is around that precipitate. Because, the g p zones are so small, that they cannot, they are very coherent. So, contrast comes only because of the strain contrast. So, it is very difficult to see them. But, if they this g p zone is nothing but a copper precipitates in an aluminum matrix, with a very fine scale of the order of let us say, 1 nano meter or 2 nano meter size or even 5 nano meter size.

Here, you can really see, what you see here is, each dot is an atom. So, we are able to resolve atom by atom. So, one can see the moment, there is the cluster, you find of a few atoms, immediately you can identify, what is this cluster, what elements are present in that cluster. For example, what you are seeing is this is an amorphous alloy, with a small particle inside that. And you can see, this is the zirconium mapping.

These are all what called elemental mapping. So, a box containing only a zirconium atoms and this is only copper atoms, because one can separate out in a computer, each element. And then can see clearly, how these elements are distributed and this is aluminum and this is oxygen. And if you look at it there is a small particle there, where the oxygen atoms are concentrated to a large extent. And then the aluminum is less there, copper is less there.

So, and if you try to draw a line there and then find out, what is called compositional profile and you can see that, here oxygen is enriched in that particular region. Aluminum is depleted and copper is depleted, again zirconium is enriched. So, one can really see and from the amount of it, one can find out, what is the amount of this various elements. So, one can really do a quantitative study of small particles, very small particles, at the atomic level.

This is the only technique, which can do this and with this is called three dimensional atom probe, because you are probing atoms and in a three dimensional manner. So, in a three dimensional structure, one can really see. In fact, people have seen, whenever a

precipitate comes out and if you can look at the cross section of this precipitate and if you, 1 to 500. For example, particularly, nowadays, people talk about, aluminum silicon carbide composites.

The moment, you put silicon carbide, whoever have studied aluminum silicon carbide, you know that, there is a possibility of some kind of a reaction, between silicon carbide and aluminum and formation of some Al₄C₃. So, there is a possibility of a compound called Al₄C₃. And sometimes this Al₄C₃ is such a thin thing layer; you may not be able to see it by any microscope such as SCM.

And the only way is possibly by TEM. But, in TEM also, you will not be able to see, really the presence of, how much carbon it is, because the carbon, cannot be detected. So, easily by the edax's; whereas, here is technique, where, you can really see a layer of carbon atoms and aluminum atoms, distributed on a silicon carbide particle, between the silicon carbide particle and the aluminum matrix.

And any such precipitates, for example, when in an aluminum magnesium silicon alloy, when Mg₂Si comes out, on the silicon particles, one can really see that. And similarly, if you add the magnesium to the aluminum alloy, where silicon carbide is there. Everybody, says, whenever, you add magnesium, the weight ability of silicon carbide to aluminum gets enhanced.

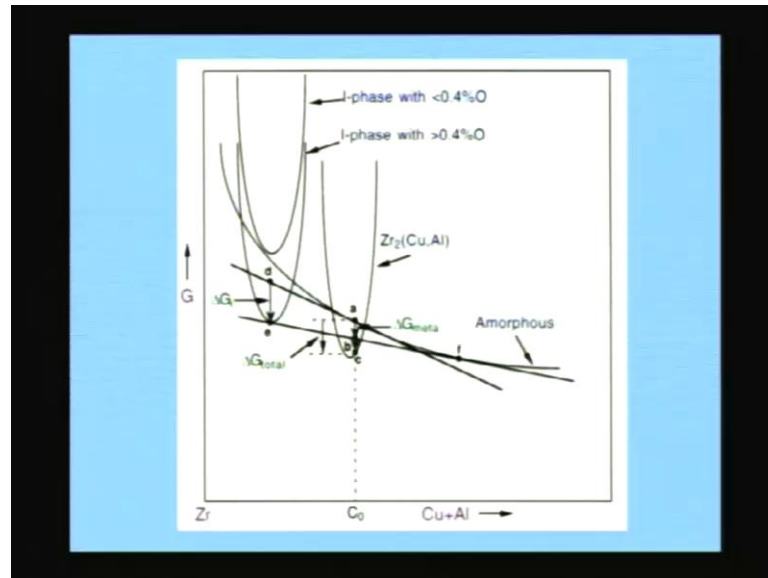
How does it get enhanced, people says it is because of formation of some spinel. Everybody, who works in composites, knows about it. But, the presence of such a thin layer of spinel, the only way to find out is, by such kind of techniques, where you can really see the presence of these atoms. And one can quantify and find out, how much of elements in that are there.

And this is one technique by which we could show, that all the oxygen goes in to that quasi crystalline particle and how do you know that this is quasi crystalline, immediately you can take that sample, put it in a TEM and locate that particle there. And see that, yes, this is particle, that we are talking of is that quasi crystalline particle and get a diffraction pattern from the particle. So, that is why, it is very crucial, that one technique is not sufficient for everything.

One has to use various techniques, as complementary tools, to understand the whole thing. So, that is why, if you have atom probe in conjunction with a TEM, one can

really do a lot of work. And we could show, that all the oxygen goes in to the particle and then stabilizes the quasi crystalline particle, whereas, there is no oxygen in the glass. This has been shown in a number of cases.

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And from thermodynamics also, one can say this, what happens if oxygen goes in to the quasi crystalline phase. Usually, we know, oxygen is an interstitial element. Whenever, oxygen goes in to a structure, what it does is it densifies the structure. Icosahedral, packing is the densest packing. That is feasible. That is why; carbon buckyballs are called the densest molecules in the universe.

So, if oxygen goes in to the liquid, which is nothing but the glass and the moment oxygen goes to a critical amount, it goes and occupies all the interstitial positions. And once, it occupies all the interstitial positions, then that liquid becomes dense. And because of that, the icosahedral particles can easily nucleate. And if you look this free energy, what you see is that, without the presence of oxygen, if the oxygen content is less than a critical amount, such as 0.4 percent or so.

The free energy of it is much higher than that of the amorphous phase. If I take an amorphous alloy, which is nothing but a glass, having a certain composition c_0 and draw a tangent for that. Usually, we know from our thermodynamics, that any phase that intersects that tangent can come out of that parent phase, which is nothing but the glass here.

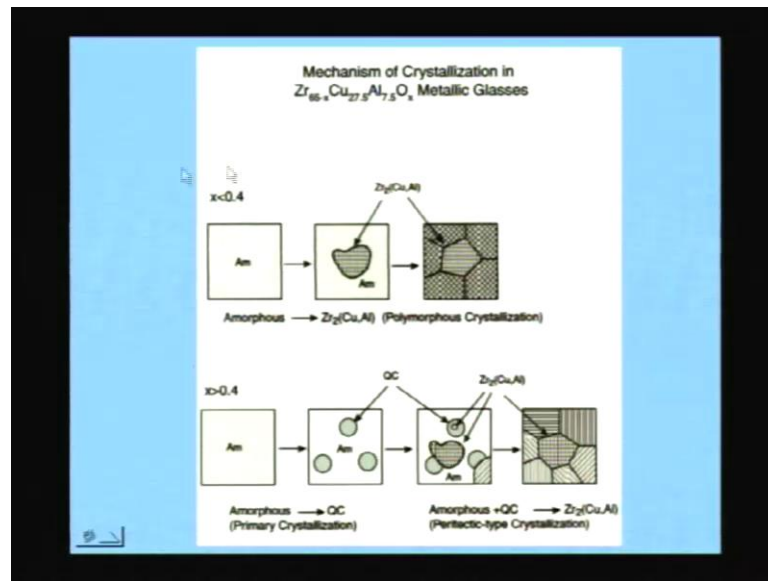
But, if the phase free energy is, above that of the tangent. Then, it cannot nucleate, because there is no driving force for that phase to form. For example, if you look at the the icosahedral phase or the quasi crystal, with carbon oxygen content less than 0.4. Its free energy is such that, it is above this tangent. If it is above this tangent, that phase cannot nucleate.

But, the moment you put certain amount of oxygen greater than a critical amount, its free energy comes down and the moment it comes down, it intersects this particular tangent. And then immediately, there is a certain driving force, which is shown by ΔG . And that driving force, drives the formation of the quasi crystalline phase. And the moment quasi crystal forms, then there is an equilibrium between the quasi crystalline phase and the amorphous phase.

But, if you carefully look at this tangent, which is the tangent between the icosahedral phase and the amorphous phase, this tangent intersects this. Equilibrium compound, which is nothing but Zr_2CuAl and the free energy of the Zr_2CuAl is lower than that of the two phase mixture, which is nothing but the quasi crystal and amorphous. So, as a result, two phase mixture of quasi crystal and amorphous has still a higher free energy than the Zr_2CuAl .

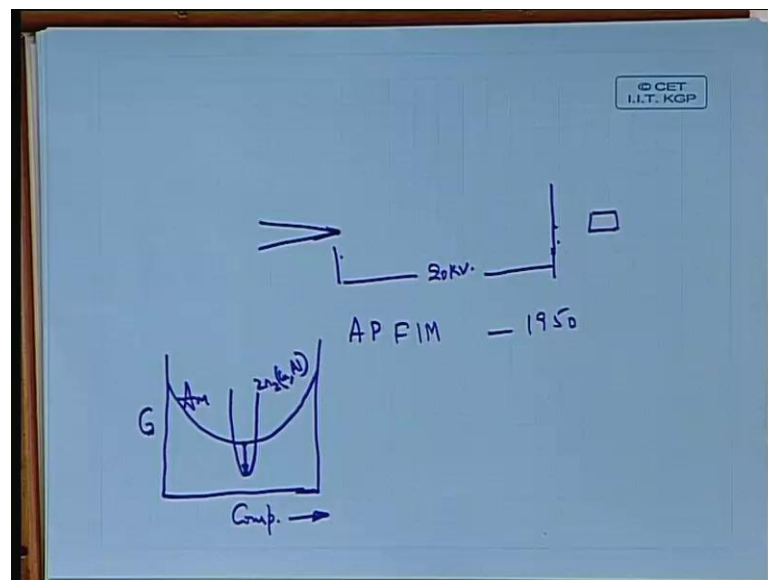
So, that means, ultimately, if you hold it for a long period or heat it to a higher temperature, what happens is that this two phase mixture of amorphous phase plus icosahedral phase will ultimately transform to the equilibrium Zr_2CuAl . And this is what exactly happens, when you look at the mechanism of its formation.

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If the all oxygen content is below the certain value, what you see is that amorphous phase, gives you Zr_2CuAl and this Zr_2CuAl grows. And finally, you get a simple Zr_2CuAl and this is what called polymorphous crystallization. What is polymorphous crystallization? I think, we talked about it, in the last class.

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Basically, if you look at the free energy composition diagram and look at an amorphous phase, which is having a free energy like this. This is the free energy versus composition and if you look at an intermetallic compound, which has something like that a Zr_2CuAl ,

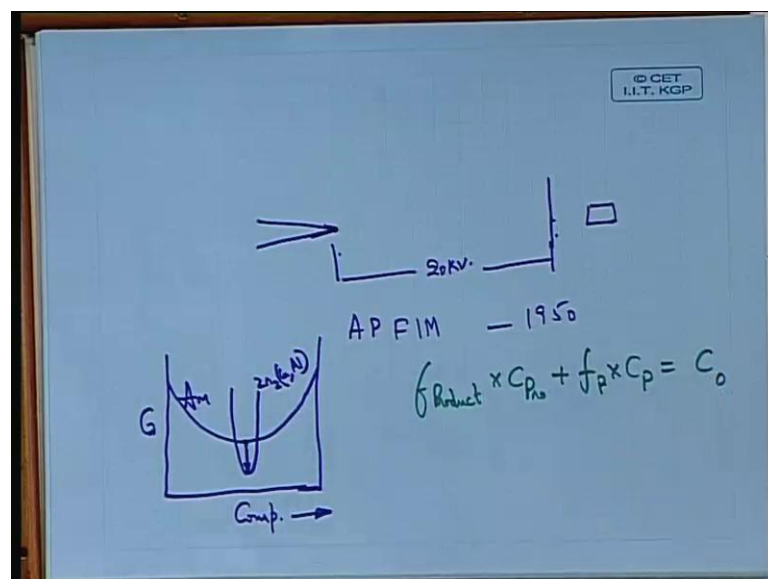
a l. Amorphous phase having certain composition, if it transforms to the crystal, having the same composition, which is nothing but a z r 2, c u, a l.

In this particular case, we call this as, what polymorphic transformation, because, the one phase, parent phase, which is nothing but a glass here is transforming in to another phase, having the same composition, but a different crystal structure. The only difference is the crystal structure, but the composition is same. And this is what is called polymorphous crystallization or polymorphic transformation.

And that is what is happening, if the oxygen content is less than certain amount. Otherwise, if the oxygen content is more than certain value, critical value what you see is a first stage of crystallization, gives you quasi crystal. Whose composition is different from that of the amorphous phase? This has been proved by atom probe. We have shown that the composition of the quasi crystal is different from that of the background matrix. And we have also shown from the thermodynamics earlier.

This is the composition of the amorphous, which we are starting with c naught. And the composition of icosahedral phase is this, which is different from the c naught. So, when a phase having a different composition, comes out from parent phase, we call this as primary crystallization. And in such a case, you will always having the mass balance; you will have some volume fraction of the product phase and some volume fraction of the parent phase. We talked about in the last class, that unless, you have both the phase coexisting. It is not possible to have the mass balance.

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If the two phases have the different composition and that is what, we talked in the last class. Where, we said volume fraction of the product phase, multiplied by the composition of the product phase. Plus, the volume fraction of the parent phase, after the formation of the product phase, multiplied by the composition of the parent phase, after the formation of the product phase is equal to the starting composition c not.

What is the composition of the product phase here, the composition of the product phase is this, the point e ; that you are seeing. And what is the composition of an amorphous phase, after the product has form, it is this f . The starting composition is c naught, but once the icosahedral phase forms. Immediately, there is equilibrium between the icosahedral phase and the amorphous phase and the equilibrium composition of that amorphous phase.

In equilibrium with the icosahedral phase is nothing but this f and not, the starting c naught. So, that f is this composition of the parent phase; that we are talking here. And that, if you multiply by the volume fraction, then you can see the total number of atoms can be balanced. Otherwise, you cannot balance the atoms. So, and we know that, one cannot create the new atoms and one cannot destroy, already existing atoms. So, there one can only do is, one can distribute the atoms, between two phases.

So, some of the, an atoms go in to one phase and some of the atoms will go in to other phase. So, that overall number of an atom is same as the starting material. And that what happens here, that you get a quasi crystalline phase, with a different composition. And after sometime, what you see is that some zr_2cu phase forms. At the interface, between this quasi crystal and the amorphous phase and then start growing by something like a paratactic type of reactions.

That means, the amorphous phase plus quasi crystal gives you zr_2cu . This is similar to a peritectic type of reaction. Only, difference is, what is a peritectic reaction? Can somebody tell me, what is peritectic reaction?

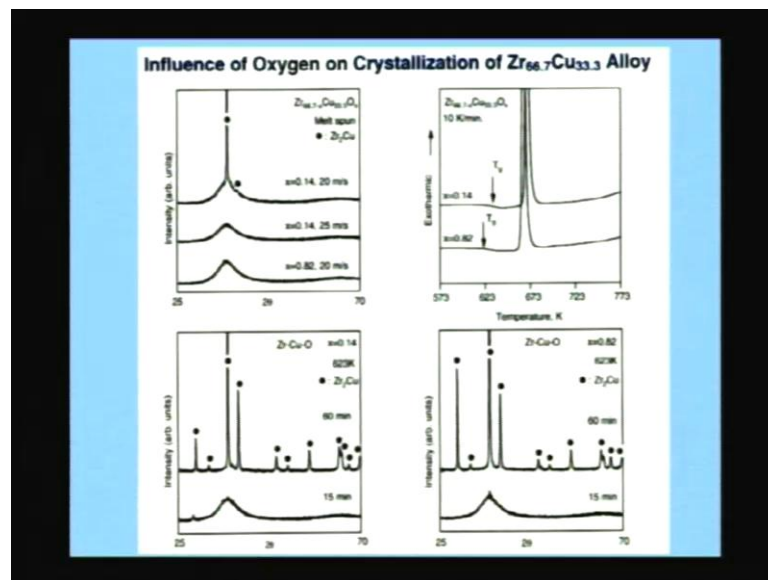
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Liquid plus solid gives another solid. But, here we are not talking of liquid plus quasi crystal giving another solid, but amorphous plus quasi crystal giving another solid. So, this is actually to be called as a peritectoid type of a reaction, where you have a solid plus

another solid, giving you a new solid. All the three of them, have a different compositions.

And finally, you get the z r 2, c u, a l and so if you look at the final microstructure, both of them have similar microstructure, you have grains of z r 2, c u, a l. But, this particular alloy goes through a second stage, whereas, this whole thing undergoes one stage crystallization. So, this is, how we see the formation of nano quasi crystal. So, we clearly now, know that it is oxygen, which stabilizes this nano quasi crystals stage. But, at the same time, one more important point; that one has to know is oxygen is not sufficient, how do you, know that.

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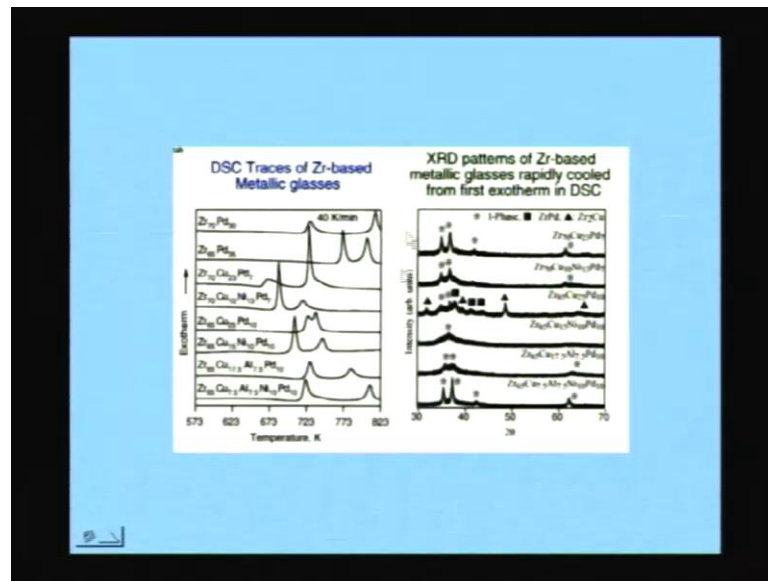


So, this is another study, which has shown that. That oxygen is not sufficient, what does it say. So, here what has been done is, we have taken zirconium copper alloy, without any aluminum in it. And put again, same amounts of oxygen, you keep on increasing the amount of oxygen and see what kind of phases form and you see amorphous phase can be obtained at high oxygen levels and take that and then do D s c. You again see here, instead of two crystallization peaks, you see only one crystallization peak.

One crystallization peak tells you, that it transforms in one stage. And what does it transforms to, it transforms to z r 2, c u. There is no aluminum here; it forms only z r 2, c u phase. So, whether it is a high oxygen or low oxygen, this is a low oxygen, this is a high oxygen. So, an amorphous phase goes to a z r 2, c u, a l without any intermediate step of any icosahedral phase.

So, this clearly tells you, that for oxygen to stabilize an icosahedral phase, one needs to have a certain environment. So, if you have zirconium copper aluminum kind of a combination, where the sizes of the interstices will be bigger, where oxygen can easily go and then make the icosahedral phase stabilize. Whereas, if you do not have aluminum there, then you will not have such a thing happening. So, one can talk in terms of, what are the criteria for such formation, this is one study.

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The other study to show, what the conditions are, for the formation of this icosahedral phase, nano icosahedral phase, is lot of people have shown, for example, inovase group. That palladium, platinum, some kind of elements like that, can stabilize a formation of a nano quasi crystalline phase. So, what has been done here is that, this is a standard composition, which people have been studying for quite sometimes.

With, where you have about 65 percent zirconium and copper about 7.5 and aluminum about 7.5, nickel 10 percent and palladium 10 percent. And the understanding at that time is that, this nano icosahedral phase will come out, nano quasi crystal will come out, only when you have a multi component system. And unless, you have a large number of elements, you will not get this kind of a phase is some myth, I would say was existing those days.

So, we again have wanted to look at it, more closely and what we did was, we try to eliminate various elements, systematically from this base alloy by eliminating. For example, here you can see in this nickel has been removed. In this, aluminum has been

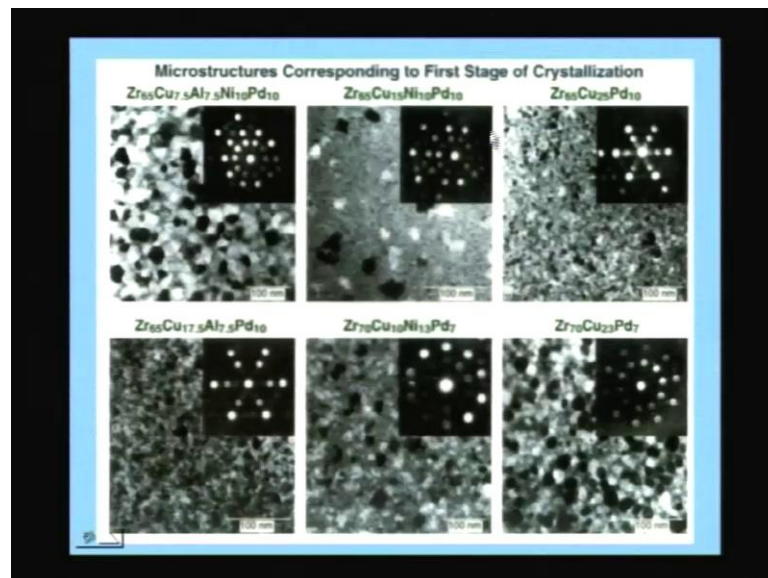
removed and in this, both nickel and aluminum have been removed. Again, over all composition has been maintained the same. Palladium is again 10 percent, you can see in all of them. Zirconium is again 65 percent in all of them, only thing is you have removed certain elements and maintaining the composition the same.

And similarly, you remove aluminum here and again remove aluminum and nickel here. And see that in various cases, what kind of D s c; that you get. All these alloys, if you look at the x-ray, they are all amorphous, when you make the alloy. And when you do D s c, you always get two stages crystallization; always you get two peaks, always. And that means probably, there is an icosahedral phase.

And if you do, take this alloy to the first stage and quench it, you see, that in all the cases you get an icosahedral phase. Excepting, in one case, which is zirconium 65, copper 25, palladium 10, where you get another crystalline phases. Basically, because in this alloy, the two peaks are very close to each other, you can see here, this is the alloy for which this is the XRD pattern after the first stage.

So, because these two are overlapping with each other, when you heat it to this temperature, already the second stage crystallization starts. So, you cannot really suppress the second stage crystallization. That is why, some crystals come out. Otherwise, in all the cases, you get an icosahedral phase.

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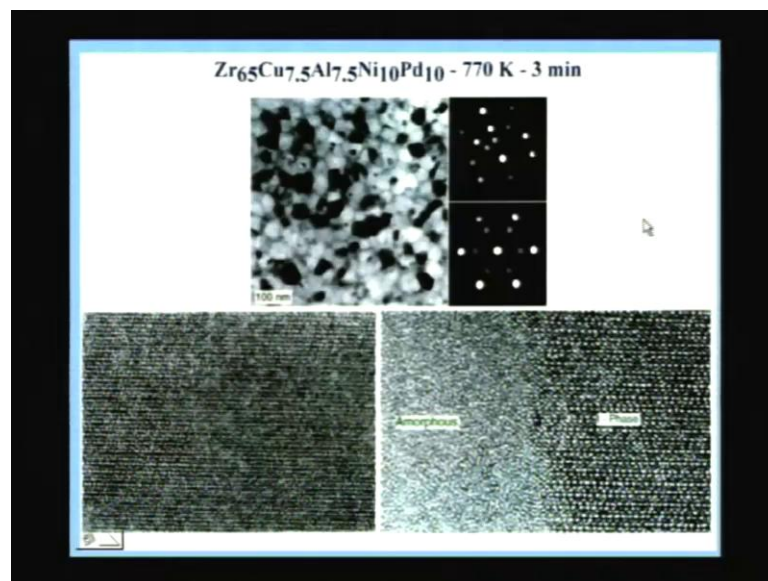


And to confirm that, what we can do is that, we can heat it to the first stage and put it in TEM. And you can see, all these fine nano crystals, these are all nano quasi crystals.

How, do you know, that in all the case, you have either the tenfold or the threefold, showing the quasi periodicity. You can look at this threefold and see the distances, they are not equal, in any direction, look at any direction and they are not equal.

And similarly here also, you see this distance and this distance, they are not the same. And that is what is an indication of this is icosahedral phase. So, you can get nano quasi crystalline phase here again. In all the compositions, including a binary, this is from 5 components, 4 components, 3 components and even a binary also has been done.

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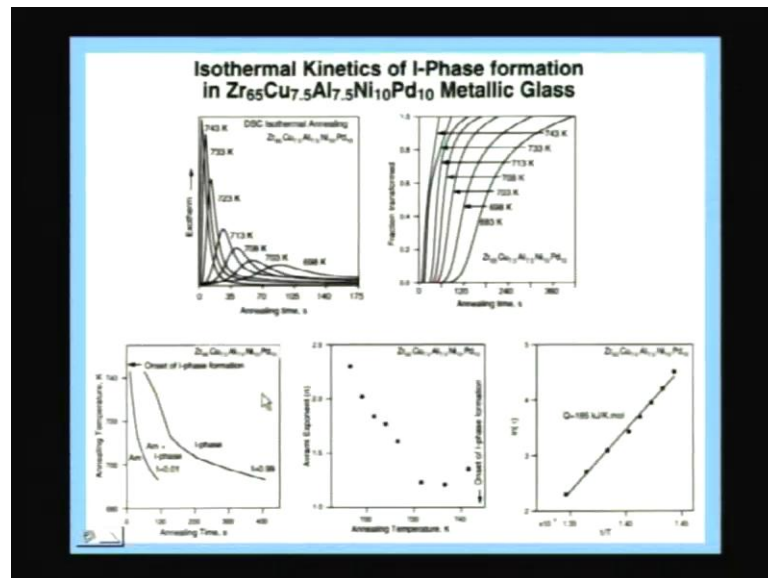
I will show you a little later, that even, when you go to binary also, one can get it. So, this is one proof that, yes, you do not need any multicomponent system. Then, in such a cases, what is that, that is making these alloys to become nano quasi crystalline. So, that is something, which one has to understand. To understand this, people have done much more work in our group and you can see this is one such a detailed work, showing the formation of the icosahedral phase.

This is, what called high resolution micro structure, showing each wide spot here again is an atom. So, you can see really atomic images in a high resolution electron microscopy. And clearly find out, what is the difference between the amorphous phase and an icosahedral phase. You can see amorphous all the atoms are randomly arranged. And so this is basically trying to take a region like this. And then looking at a region, where there is an interface between the amorphous and the quasi crystalline particle.

So, such a region, if you look at it, this is a particle, which you are looking at and this is an amorphous matrix. So, you have a matrix of amorphous in which these nano quasi crystalline particles are embedded and you are looking at them. And this is one individual nano quasi crystalline particle and here also, again in any particular direction.

If you carefully look at it in a line, you can see, you will never see periodic arrangement of atoms. You will see, only quasi periodic arrangement of atoms. This is another way to confirm that, this is a quasi crystal.

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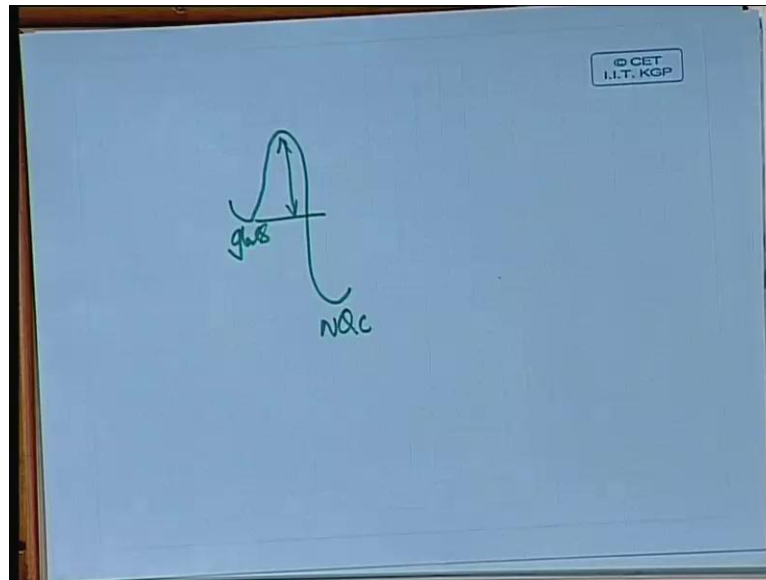
And the one can study, what is called the kinetics of such formation of these nano quasi crystalline phase, what one can do is, what is called isothermal heating in a D S C. What we know is that, we know that in D S C, which I have shown you earlier. That one gets two stages crystallization. If you are getting a two stage, crystallization, what you can do is, you heat it to a particular temperature, hold it at that temperature for a long time.

As you keep on holding the amorphous phase, heated to a particular temperature, hold it for a long time, this amorphous phase, if it is unstable or a metastable there, it should transform to a phase, whichever phase it is. In this particular case, the first stage is nano quasi crystalline phase. So, it will transform to that. So, when it is transforming, you can get a peak, exothermic peak.

As a function of time and you see here, this is the exotherm as a function of time, at various temperatures. As you at very low temperatures less than about 698 or so the temperature is so low. That the activation barrier for the formation of that phase is so

high, that you do not get any exotherm. That means, there is no formation of nano quasi crystalline phase. But, as you keep on increasing the temperature the temperature is high enough to overcome the activation barrier.

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Because, we know that, whenever a quasi crystalline, whenever a glass, if this is a glass has to transform to a nano quasi crystalline phase, you have an activation barrier. If you keep on increasing the temperature, you are able to provide more and more energy to overcome that activation barrier. And one can easily get the formation of the nano quasi crystalline phase.

And how do you know that, it has formed, you can know from the peak. If there is a peak, exothermic peak, that will give you an idea of that the phase has formed. And from the area under the peak, one can find out, how much of this phase transformation has taken place. And that is what, one can plot, what is called fraction transform as a function of time.

That, the amount of phase, that has formed, from the glass; this is just, one particular case of glass to a quasi crystal, but this is a technique, which is known for ages, which people call Johnson- Mehl-Averami equation. If you have done any kinetics, you will come across this particular kinetics, which is called Jhonson-mehl-averami expression. Where, we know that any transformation as a function of a time at a given temperature is like an s curve. This is called a sigmoid curve.

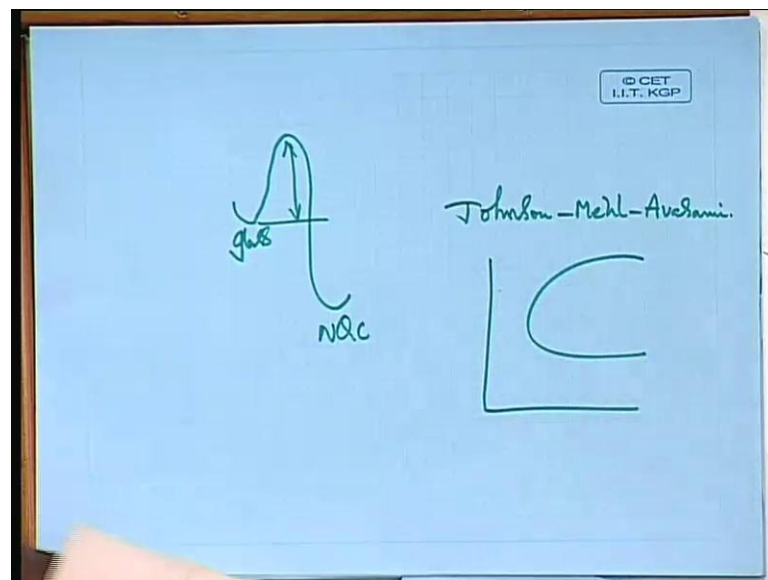
What is the significance of that, it says that, there is always an incubation period, up to certain period, there is no transformation. And after that transformation starts, that is a indication of a nucleation has taken place. And then now growth is taking place and it keeps on increasing and finally, becomes 1, 1 means 100 transformed.

After, certain time; that means, this is a start of transmission this end of transmission. And as you keep on increasing the temperature, the start and end of transmission occur at a shorter period. That means, the kinetics have been enhanced the same transmission occurs in a shorter period and you get the total transformation complete in a very short period.

And this is what is, one can do and one can take, all these start and end of transmission at various temperatures and plot what is called a TTT type of a diagram. And from that, one can see what is a region, metastable amorphous, amorphous icosahedral and nano icosahedral phase. This is what, similar to, what is our TTT diagram for austenite to paralite. How, do you get austenite to paralite TTT diagram, exactly by these techniques?

You take austenite, quench it to certain temperature, hold it for over a period and find out how paralite is forming. And from that, you identify, what is start of paralite formation and end of paralite formation, under various temperatures.

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You do this ultimately, you get this c curve. Exactly, here one can do and one can do, what is called Avrami experiment, which is called, with gives you, what is called the growth condition. What is the rate of growth and from this Avrami experiment; one can

talk about, what kind of transformation it is. Usually, the Averami experiment is about 2 or 2.5; we can say, it is always a primary crystallization.

If it is more than that, then if the Averami experiment, if it is equal to around 4; we can say, it is polymorphous crystallization. So, there is lot of, when you come to probably teaches kinetics, you all this. From Averami experiment, one can find out, what kind of transformation it is. From this, we can prove that, this is a primary crystallization kind of process and not a polymorphous kind of process, which is another controversy that was existing in this particular case.

And similar thing has been proved, also in binary case, what you have earlier is a 5 component alloy here. And now you can see a small simple binary case; that you can get an icosahedral phase, like this. And all these studies can be repeated and again, show that even in a binary case, it is a primary crystallization. From this, one can prove that a multi component alloy is not essential for the formation of a nano quasi crystallization case.

So, this is one of the studies to show that, what are the conditions for the formation of nano quasi crystal phase, we will stop here and continue and look at, what are the other conditions, which are required for the formation of this particular nano quasi crystalline phase in a metallic matrix. To get these kind of composites, which have much higher strength than the either the amorphous phase or the quasi crystalline phase and we will look at it in the next class.

Thank you.