Advanced Materials and Processes

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Lecture - 15
Nano Quasi crystals Part – II

So far we talked about various advanced materials. We talked about nano crystals, we talked about glasses, we talked about quasi crystals, we also talked about nano composites. For example, nano quasi crystals in amorphous matrix or nano crystals in an amorphous matrix. So, all kinds of nano composites we talked about.

So, from today for few lectures we will talk about the processes, which are used to make this advanced materials or what we call them as novel materials, because many of these have much different properties, than the conventional materials. So, we start with one of such process called rapid solidification processing. As a name suggests, this is a nothing but, solidifying it rapidly.

We know solidification in metallurgy very well. So, we take a liquid and allow the liquid to solidify very rapidly. And try to see what kind of new microstructures, new type of materials. That, we can generate by this rapid solidification processing. As I told you, so far whatever novel materials that we have discussed, such as either glasses or nano materials or quasi crystals.

These are all as I informed you before, that we can generate them from all the three states of matter. We can generate from starting from the vapors, you can take vapors condense them and you can get a nano crystal. Or you condense them you can get a quasi crystal or you can get a glass. Depending on the conditions, depending on the system everything depends on at that system, the thermodynamics of the system, the kinetics of the system.

So, but it is possible to have all three from the vapors, one can generate quasi crystals also from the ((Refer Time: 02:48)) if you choose the composition properly. That it corresponds to the quasi crystal in composition, you can generate vapors and condense the vapors and get a quasi crystal. Similarly, you can get nano crystals, we have already talked about it when we talked about nano crystals.

And amorphous many people have done thin films of amorphous by depositing the vapors. In fact, whenever you deposit vapors as thin films. Most of the time you get only amorphous, depends on the thickness. The thinner the film is the more the easier for the glass formation. Usually, when you look at very thin sections they are usually amorphous, because in thin sections the solidification rates are very high.

Whenever, you are condensing the vapors also it is basically cooling rates that matter there. Similarly, the second route is from the liquid. As I told you, you can take a liquid and some liquid cool it very slowly under equilibrium conditions. You get the equilibrium microstructures, you cool it slightly rapidly. Then, depending on the type of system and depending on the conditions of cooling, you can get any of these novel microstructures. Today we will talk about that.

Then, the third route is what is called the solid state route. You can take the solids and then those solids, you can convert the conventional solids in to any of the structures. For example, you can take a crystalline solid and introduce defects in to it by any means. And then make it in to amorphous, we have talked about that. Then, we can take a crystalline solid and break it in to smaller and smaller size.

And then make nano crystals out of it that is one technique which we call mechanical alloy which we will talk later. In fact, it is just ball milling, mechanical alloy is basically bringing a dissimilar metals. That is, more than one element brought together and then you induce alloying in to it.

So, like that we can again generate either nano crystals, quasi crystals, glasses or any other meta stable structures or for that matter simply just refinement of microstructure. You want a microstructure not to have 100 microns grain size. But, you want 10 microns grain size one can also achieve that. There are some applications, where you want oxide powders.

For example, paints think of paints, paints you need fine powders. There, min people are interested if you can bring down the powder size to 1 micron that is enough further for most of the applications. So, you need not have to really go to nano, but for such applications just you need to somehow make them to that.

Either you can do it from the solid state or if it is possible to melt such a material and then cool it rapidly, you can get such fine microstructures. Even by what is called rapid solidification. So, this is a technique which we learn. And what is the basic principles behind this technique. And what kind of advantages we gain by this technique.

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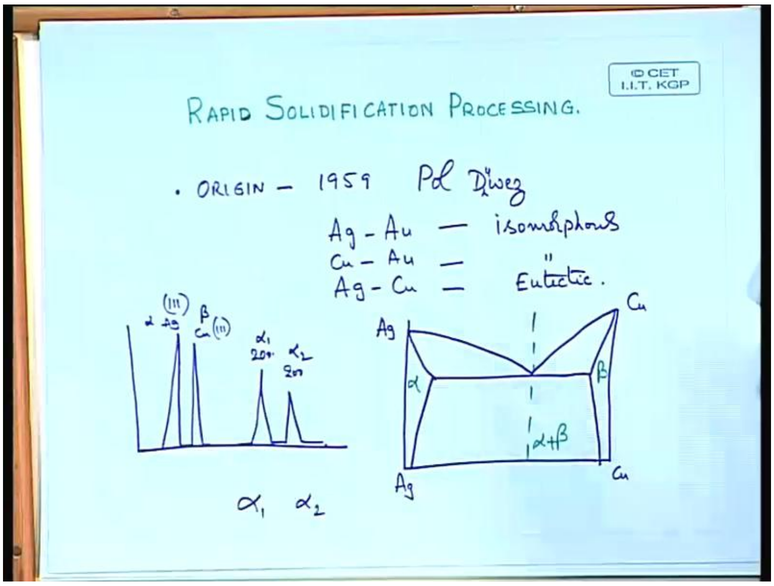

RAPID SOLIDIFICATION PROCESSING.

- ORIGIN – 1959 Pol Duwez

Ag - Au — isomorphous
Cu - Au — "
Ag - Cu — Eutectic.

Before we go in to that, let us just look at the origin of it as I must have mentioned it you some time back. The origin basically goes back to 1959 and a person by name Pol Duweg. Had looked at the silver copper system, we have talked about this problem some point of time, when we are talking about glass formation.

And so this is a system silver copper system. If you take silver, gold and copper gold and silver copper. If you look at these three systems carefully, these three systems, the silver gold and the copper gold are isomorphous, these two are isomorphous. Whereas, silver copper is a eutectic system, for many years people need not really understand, because it disobeys the Hume Rothery Rules. The Hume Rothery Rules we know which were in 1930s onwards, people know about them very well. That the solubility of a and b is decided by certain four factors, size factor, electro negativity, valence, structure, these are all the things which we know.

Whereas, here is the case, where all the three elements have similar structure, they are all FCC, their atomic sizes are very close to each other, their electro negativities are very close to each other. But, still two systems among these three components will form isomorphous. As expected from the Hume Rothery Rules, where as the third system does not follow.

So, then Pol Duweg thought, if I can take this particular liquid. And then cool it slightly rapidly. It is possible that I may be ending up with a solid solution. So; that means, if you take that phase diagram. This is a typical phase diagram of silver copper, what is a melting point of copper.

Student: 1083.

1083 and that of silver 963.

Student: 963.

So, silver is a slightly lower about 100 degrees lower than that of copper. So, if you look at the phase diagram. The solubility of silver in copper at room temperature is approximately about 10 percent. This is silver on this side and copper on this side. Similarly, copper and silver also almost the same 9 percent, 10 percent that is a range that you get.

So, if you look at this, this is definitely not isomorphous. It is a eutectic, you can see that. So, what you thought is if I take this eutectic alloy, if you solidify it under equilibrium conditions. What should be the microstructure of this alloy at room temperature, can you tell me how many. This alloy, that you take eutectic alloy, if I solidify it under equilibrium conditions, at room temperature what will be the microstructure.

Student: It will be alpha plus beta.

It will be alpha plus beta, alpha beta if you think of it here, it will be alpha plus beta, only problem here is... We usually do not refer to this as alpha and beta. Because, both have same crystal structure it is like, alpha alpha dash, alpha alpha 1 something like that or alpha 1 alpha 2 people refer to as because both are FCC.

So, anyway, so there is two phase mixture alpha plus beta. And so if there is a two phase mixture. And if you do an X-ray diffraction of such an alloy, what will be the a typical nature of the x-ray diffraction. What do you observe in the x-ray diffraction?

Student: ((Refer Time: 10:35))

That is it simple, you will get peaks from alpha you will get peaks from beta. Interestingly, that alpha and beta being the same crystal structure; both are FCC, you will have the FCC of both. But, the only difference would be that if you look at the XRD Pattern and if I.... So, two peaks of FCC 1 1 1 peaks 1 1 1 of let us say silver.

At the moment we still do not know, which one will have a lower theta, which one will have a higher theta let us not bother about it. But, you will have two 1 1 peaks of silver solid solution. You call it let us say silver base solid solution, you call it as alpha let us say. And copper base solid solution if you want to call it as beta. Usually in metallurgy beta is reserved for BCC structures.

So, we do not use usually here beta. So, we usually refer to them as alpha 1, alpha 2. Because, alpha is for FCC beta is for BCC usually. So, anyway for that we it does not matter whatever is a notation. So, what you see is that two peaks of one solid solution and another solid solution in plane.

And then you will have the two 0 0 a peaks again one of two 0 0 peak of alpha 1 and two 0 0 peak of alpha 2 and so on. And if the latest parameter difference between these two is very close, then what you would see is simply that instead of two peaks like that.

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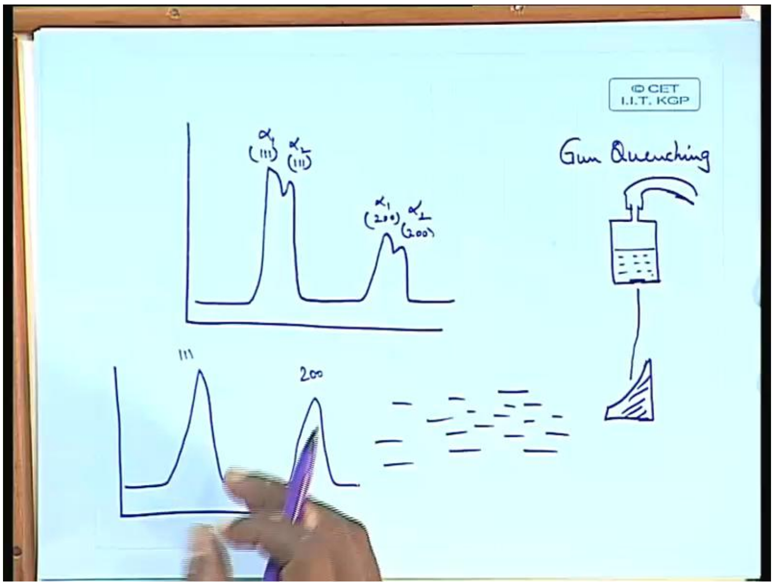

You will see this kind of a nature, you will see a shoulder in each peak, indicating that the lattice parameters of both are so close that they overlap with each other. And this means, that there are basically two peaks, one corresponding to alpha 1, 1 1 1 alpha 2 1 1 1 and alpha 1 2 0 0 and alpha 2 2 0 0 and so on 2 2 0 3 1 1 so on.

So, what you can clearly see here is, you will definitely get the peaks corresponding to both the phases. And that is a signature of a two phase mixture always. So, what he thought is, if I take this alloy. And then solidify it rapidly, what is the time going to end up with. So, he took this alloy and what he did was using a technique called gun quenching.

What he basically did was to take a crucible with a small aperture at the bottom. And then close this aperture with some kind of a metallic foil very thin metallic foil. And then put the silver and copper in to this and melt it. So, you have the liquid of silver and copper in to that, with a eutectic composition.

And what you do is, once you think it is molten. You introduce argon into the system. Pressurize this liquid with argon and when you pressurize this liquid with argon, what happens is... The liquid immediately pierces that foil. And then falls on to a copper block which is kept below. You know copper has a very high thermal conductivity.

So, as a result if you put a copper block and allow this liquid to it is like a gun, you are piercing the foil through a high pressure argon gas. So, like a bullet it comes out. In fact, you can hear that sound of the piercing and then the liquid comes out like a bullet and falls on that. So, at a very high rate high velocity and once it falls on to that. Obviously, whenever a liquid droplet falls on to that, it becomes like a flake a thin flake.

So, you will have a large number this kind of flakes falling here, you will never get a continues ribbon here. A large number of flakes just fall on the floor there and you just collect these flakes. And then try to do an X-ray of these flakes and if you do an x-ray of these flakes interestingly what he saw, was that he saw just peaks like that.

Just single peaks of 1 1 1 2 0 0 and so on instead of getting the peaks like this ((Refer Time: 16:46)) what we saw before. He now got peaks like this, if slight broadening suggesting that the grain sizes are much finer here. And why does this whole thing happen, this happens because of two reasons, one there are two aspects which take place here.

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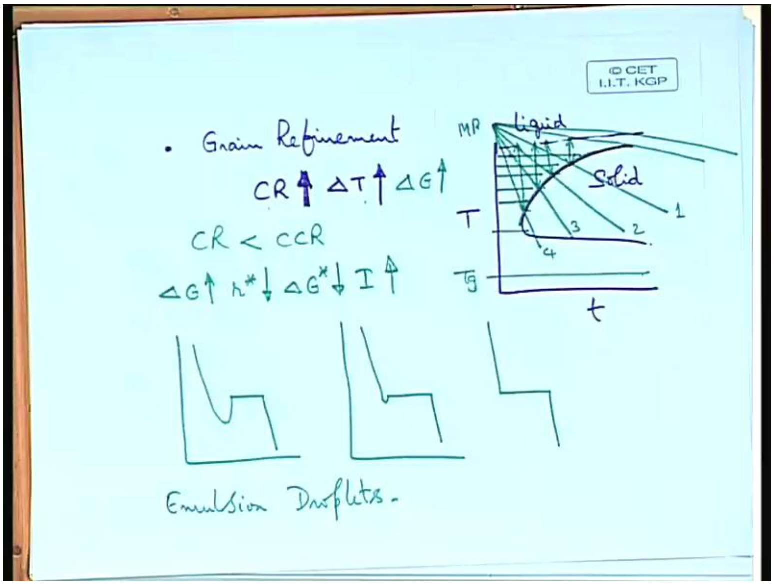

One is what is called grain refinement as I might have told you before, grain refinement during rapid solidification is related to what.

Student: ((Refer Time: 17:31))

Is related to the under cooling. So, we have seen that if the cooling rate increases. Then, that delta T increases, there is a direct correlation between the cooling rate and under cooling. Because, as you are cooling it faster the liquid does not want to solidify at the equilibrium melting point. Because of the inertia in the system and so it gets under cool to below the melting point.

And then starts solidifying and because of which you will see that there is something called an under cooling. And the higher the cooling rate, the higher will be the under cooling. Because, the higher will be the inertia you are not providing sufficient time. As you are increasing the cooling rate, the time available for the nucleation to occur is very small is not it.

And if the time available for the nucleation to occur is very small, you have to really under cool it to very high low temperatures. In fact, the this is not really true up to very large under cooling's. Because, we know this TTT diagram, let us imagine that there is a liquid here, there is a solid nucleation. This is the standard temperature time diagram, which we all know about it. When we talk about a austenite to paralite we talk about this regularly.

So, if you look at this you can see from here, the time required for the nucleation. Or for the start of the solid formation, keeps on decreasing like this, as the temperature decreases is not it. So, you need lesser and lesser time, as you come to lower and lower temperature. And that is what we call incubation period. So, when you are cooling rapidly the liquid, because the time required time available is very small.

For example, let us say you take a liquid and rapidly cool to this temperature. And if the time that you are allowing is very small, because of that cooling rate at that particular temperature, at any temperature we can calculate what is called residence time at any temperature, whenever you are cooling it very rapidly.

So, basically the cooling rate divided by the temperature if you do it. Basically, you get some time a temperature divided by the cooling rate, then the time goes to the numerator. So, you will get that what is called residence time, if that residence time is smaller than the incubation period, then there will be no solidification.

So, what will happen is that liquid will not undergo solidification at that temperature. But, liquid will cool further. And then come to such a temperature, where the time that you are allowing is equivalent to the incubation period. At that temperature it will start solidifying. So, if the cooling rate is higher and higher, because you are providing lesser and lesser time.

So, it will keep on going to lower and lower temperatures up to this low temperature. In fact, if the cooling rate is much higher. Then, even this solidification will not occur, then you will come to a situation, where you will hit the T g and get the glass. So, as long as your cooling rate is below the critical cooling rate.

You can see clearly, if I use this liquid and draw different cooling rates. You can see from this, for this cooling rate let us say call it 1, 2, 3, 4. You can see from 1 to 4 is a cooling rate increasing or decreasing.

Student: ((Refer Time: 22:11))

It is increasing, because the slope of this line is nothing but, the cooling rate. So, as you are increasing the cooling rate, you can clearly see here. The delta is automatically increasing. If you look at where this cooling curve hits the start of transformation, that will tell you, what is the temperature at which transformation is happening? If your cooling rate is very slow very, very, very slow.

That means, if the cooling rate is very, very, very slow then the transformation will occur at the equilibrium transformation temperature, which is nothing but, the melting point. That is what we call the equilibrium transformation, when the cooling rate is very slow which is called equilibrium cooling rate equilibrium conditions, then the transformation will occur at the equilibrium transformation temperature, otherwise if the cooling rate is higher. So, the higher the cooling rate, the higher the under cooling. So, you can see there is a direct relation between cooling rate and under cooling. Because, this is the temperature at which transformation is occurring at these cooling rates.

And higher under cooling the transformation will occurring at a lower temperature. And an delta T is nothing but, the equilibrium transformation temperature minus the temperature at which transformation is taking place. And that becomes larger if the cooling rate is larger. So, as a result we know that if the cooling rate increases delta T increases.

And if delta T increases, we have already seen before that delta g increases, which is the driving force. And if the delta G increases, we know the r star decreases and the delta G star decreases. And finally, the I increases, all these are connected, there is a chain of events that take place. Once, the delta T everything is related to just one parameter that is a delta T.

That is why under cooling is crucial in that is why people say now a days, after almost know how many years more than 45 years, let us say close 45 years. After rapid solidification has started 1959. Now, people know that you need not have to even cool it rapidly. If there is any way to give high under cooling to the liquid, without cooling it rapidly. You can get all the advantages that you can achieve, with high under cooling with a rapid solidification, by just giving high under cooling. You heard of such techniques, how do you achieve high under cooling without cooling it fast.

Student: ((Refer Time: 25:21))

Bulk metallic glass is a...

Student: ((Refer Time: 25:26))

Yes, including inoculation no, no.

Student: ((Refer Time: 25:32))

If you are putting inoculation it is a heterogeneous nucleation. So, heterogeneous nucleation will only make the grain size smaller, it will not give you high under cooling. In fact, it will decrease under cooling, if you think of the cooling curve, this is a typical cooling curve for a homogeneous nucleation.

And for a heterogeneous nucleation the cooling curve is either very small like this or sometimes it will be just like this, because you are providing the substrates. So, under cooling does not take place the way to do is...

Student: Pressure.

Not pressure.

Student: ((Refer Time: 26:18))

That is, what he said bulk metallic glasses putting large number of elements, but that as nothing to do with under cooling. That is, only makes the nucleation more difficult of solids. And as a result you get glass, that is only to make a glass, that is not to make under cooling higher.

So, here what you do is when this under what conditions, the under cooling the gets reduced it is by inoculation, as he has pointed out Nirupam just now. So, the way is the reverse remove the inoculates, if you can somehow remove any heterogeneous nucleating sides, inside the liquid. Then, the liquid has no other solution.

But, to get under cooled to very low temperatures up to what is called homogeneous nucleation temperature. That is what people do, by what is called emulsification of the liquid. Droplet emulsion techniques they call it emulsion techniques what they do is, they take liquid. And immediately emulsify the liquid. How do you do that, there are different techniques one is atomization.

What you can do is, you allow a liquid to fall through a nozzle and then inject a gas to that. So, that the liquid breaks the liquid breaks and then becomes very fine droplets. And now if you look at these fine droplets, there is a possibility, that some of the droplets will not have any heterogeneous nucleating sides.

The point is whenever you melt a liquid, there is always bound to have some kind of inclusion particles. Unless you really do under very highly controlled conditions, vacuum and you have some waste. For example, you must have heard of secondary steel making, just to remove inoculates. It is a very tough process, they go through a number of techniques, vacuum re melting, electro slag refining there are so many techniques people use just to remove inoculates.

Because, there are some steels where the inoculate percentage has to be kept very low. Because, we know that these presence of these second phase particles are the ones where the crack initiates. So, you do not want such a thing to happen. So, they for some strategic applications people give in the design parameters itself. The inoculants they are the what are called second phase particles or the oxide particles should not cross a particular limit.

So, as a result you have to refine to remove this, there are techniques to do this. So, here what you do is, you just emulsify the liquid. And as you decrease the particle size of the liquid droplet size of the liquid, the probability of finding at particle inside the droplet; obviously, decreases. The bigger particle will can have more particles, a smaller particle will not have particles I mean may not have particles.

So, if you look at these solidified particles, people have seen. The smaller particles are the ones which have really solidified at high under cooling. How do you know that they are solidifying at high under cooling, is there any way to find out. This is like postmortem, like failure analysis. After the thing has happen you try to find out what is the cooling rate or you try to find out what is under cooling, because there is no way to directly find out measure the under cooling in a droplet. How do we find out, we look at the microstructure. There has to be some correlation of the microstructure to the under cooling. Particularly, if you look at the what is called the eutectic microstructures. Let us say or if you look at the dendritic microstructures, the inter dendritic spacing’s. Or the what is called secondary dendritic all spacing SDS people call it, dendrite arm spacing.

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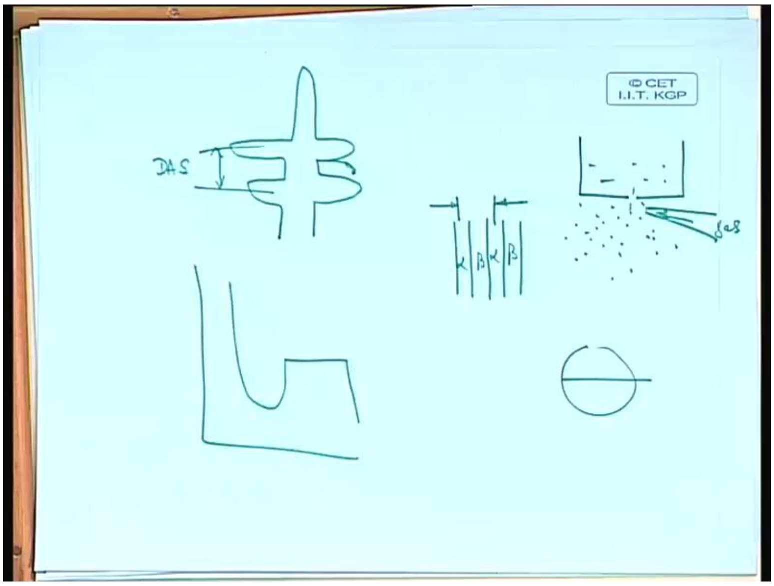

That means, if you look at a dendrite, this is like a typical dendrite let us say. So, this spacing between these two is called Dendrite Arm Spacing DAS people usually measure. And this dendrite arm spacing is always a function of the under cooling, the higher the under cooling, the higher the nucleation rate and smaller the r star. And because of which this decreases.

Similarly, if you look at the eutectic microstructures. If you take a eutectic composition and then try to solidify, the what is called inter lamellar distance, you know whenever there is a lamellar eutectic that forms, the inter lamellar distance between any two. For example, if you look at the paralite which is does not really form from the liquid anyway we should not consider that, but if you take any simple microstructure, such as aluminum copper. Aluminum copper is a dendritic is a lamellar eutectic. So, you look at alpha, beta, alpha, beta this kind of a eutectic microstructure. And this distance between any two alpha is what is called inter lamellar distance. The center of the one alpha lamellae and the center of the another alpha lamellae.

So, if you look at the alternating alpha lamellae. And look at the distance between them, that will give you what is called inter lamellar spacing. And this inter lamellar spacing and this dendritic arm spacing are directly related to under cooling. So, there are actually a number of experiments people have done. And we already have a lot of database on what is the correlation between these two.

So, from that if you do if you measure the actual the DAS or the actual inter lamellar spacing, one can go back calculate. What should be the cooling rate or what should be the under cooling. Cooling rate is a one way, as I told you basically it is a under cooling. And there are methods to measure also.

For example, there was one technique which people have used what is called drop tube technique. Have you ever heard of this, have you heard of container less solidification. So, where people electrostatic or electromagnetic limitation they do. So, they take a metal a piece, it has to be very small otherwise it is very difficult to levitate it because of the weight.

So, you try to apply some electrostatic forces or electromagnetic forces. So, that piece is levitated; that means, it floats in the atmosphere. And then through laser or through some kind of a heating means you melt it. So, it is floating and then it melts now. A number of experiments people are doing on this,aAnd now if you allow it to solidify.

That means, you allow it to cool remove that heating source, people can melt it through laser, electron beam. There are many ways of melting such levitated particles. Now, if you allow it to cool, it does it they there is no container inside which this droplet is solidifying now. So, once there is no container, then there is no heterogeneous nucleation’s.

Usually, we know whenever you pour the liquid into a mold. The mold wall itself acts as a nucleating sight. So, here there is no mold wall nothing. So, the liquid droplet now solidifies, just keep on observing people can put thermocouples or; obviously, thermocouple cannot touch the sample.

So, you can have optical pyrometers and measure the temperature. And try to see how it cools as a function of time and then plot what is called the cooling curve. And if you plot the cooling curve, you can find out to what temperature it has really under cooled. So, you will get this kind of a cooling curve.

If it is a pure metal and from that one can really measure what is the under cooling. And then if you look at the microstructure of that. And correlate now the under cooling to the microstructure. So, like that people have this is one technique levitation is one technique, people have used. Another technique is what is called drop tube technique, what they have done is they have taken long drop tubes 100 meter drop tubes are available.

In fact, there was an a proposal to have a drop tube in IIT Kharagpur our main building, the old building people wanted to use it as drop tube. That means, you put a furnace on top. And then allow the metal to melt small piece of metal, allow the liquid to drop in a tube up to the bottom. And when it keeps on dropping, there will be a condition. This is has been done not just for finding out, what is called the under cooling.

But, to understand what happens under microgravity conditions. There is a lot of research going on about microgravity. We know one of the measure problems in solidification is what is called segregation. If you are melting a two elements, such as led and let us say copper alloy, led has a much higher density than copper.

So, when both of they are solidifying, the alloy is solidifying. There is always a tendency for what is called gravity segregation is not it. So, because of which the composition is not uniform throughout the sample. And we know that, that kind of a situation can be completely removed if you have a loss of gravity.

That means, if you have 0 gravity condition and people are doing experiments on the International Space Settle ISS, they call it. And in addition there are number of people who try to simulate such conditions on the earth using this kind of drop tubes. For example, I do not know whether you heard of if you go in lift keep on falling in a lift from a very high, particularly in places like abroad.

I have seen places like in Japan, where 98 floors, from there if you are falling. You will definitely experience a few microseconds of microgravity condition. So, it is like that. So, many people are studying that and try to see, what kind of different microstructures that you get. Similarly, for example we talk of inoculation, inoculation has something to do with interfacial energies is not it.

W know that the interfacial energy between the inoculating particle. And the solid is much lower, that is why the solid is nucleating on the particle. How is this going to be effected under loss of gravity. Whether the inter facial energies have something to do with gravity or not. These are all mostly academic research frankly speaking, number of people who object to them.

But, then NASA is doing lot of research on this, one of our own faculty members in IIT Kharagpur, Professor Dhinda does a lot of research in collaboration with NASA on this microgravity. So, what kinds of microstructures are developed under microgravity and how to generate microgravity. That is one aspect.

And what is the science of solidification under microgravity conditions. How does solidification occur. Particularly, when I composite solidifying what kind of a microstructures are generated. Whether, the particles are pushed to the grain boundaries. And you do not get a uniform distribution or whether the particles are engulfed what kind of conditions that happen. And what is the rate of solidification under microgravity conditions, when compared to normal solid conditions.

So, lot of research is going on one such aspect is under cooling. So, in the drop to when you keep on fall allowing the particle to fall which is nothing but, a container less solidification, the droplet is just falling without any container. So, it will under at some point of time. And at various heights people put thermocouples to measure the temperature of this part droplet that is falling.

That means, you put pyrometers; obviously, you cannot put thermocouples which touches that particle, you put optical pyrometers. And put pyrometers and measure the temperature of droplet. And find out at what temperature it has started solidifying. And then from that deduce what kind of microstructures you have got, after the particles has really solidified what you do is just cut the particle look at the microstructure.

And you can identify, what is the microstructure, what is the dendrite arm spacing or what is the inter lamellar spacing. And from that, you correlate it to the under cooling. And different type of particles, different sizes of particles will have different under cooling’s and will have different microstructures.

So, ultimately correlate the microstructure to the under cooling. And correlate the microstructure to cooling rate, if people do fast cooling experiments. So, fast cooling is one technique. But, because we know fast cooling basically gives you high under cooling, if even if you do not do fast cooling, if you just have high under cooling possible. But, this kind of high under cooling can be achieved only in special conditions.

For example, levitation is a not a condition which is easily possible for large quantity of materials. Similarly, if you want to do droplet emulsification. That is one technique which is not very difficult. But, the point is different particle sizes will have different under cooling’s.

For example, atomization if you do atomization liquid is atomized by a gas. You have this kind of a nozzle, liquid is here, the liquid is allowed to fall. And then you have a jet of gas allow it to fall on that liquid which is falling. So, immediately the liquid gets emulsify like this becomes droplets. But, you will have different sizes of droplets.

But, one can do a lot of engineering on that to control the narrow down the size range, a lot of people who are doing DMRL is one place, where lot of work is going on, on that. And atomization is a standard technique to produce powders, metallic powders. Most of the metallic powders are produced by atomization is a standard technique.

So, in that but most of the atomization techniques that are used are for sizes which are of the order of the around 100 microns or more than 50 microns. People do not really go to less than submicron size, when you really go to submicron size. That is when you will really see, the particles without having any inoculants. And that is when, you can really achieve very high under cooling's and achieve novel microstructures.

So, if you achieve high under cooling what are the things that you can get, one is as I just now pointed out, yes here one is this ((Refer Time: 43:33)). That r star decreases and I increases, that gives you what grain refinement. That is one of the whole story, that is not the complete story.

So, you can get grain refinement or micro structural refinement. Grain refinement is in case of pure metals. But, most of the engineering materials are not pure metals, you use alloys, many times multi component alloys. So, you want microstructure refinement, you want the grain size or if it is a eutectic microstructure, you want in fine inter lamellar spacing.

Because, you know that if the inter lamellar spacing decreases, the mechanical property increase. We know this, there is a direct relation between this. And similarly, if you have a two phase mixture, you want fine precipitates to be uniformly distributed. So, all this refinement of microstructure is one way, which can be achieved by under cooling.

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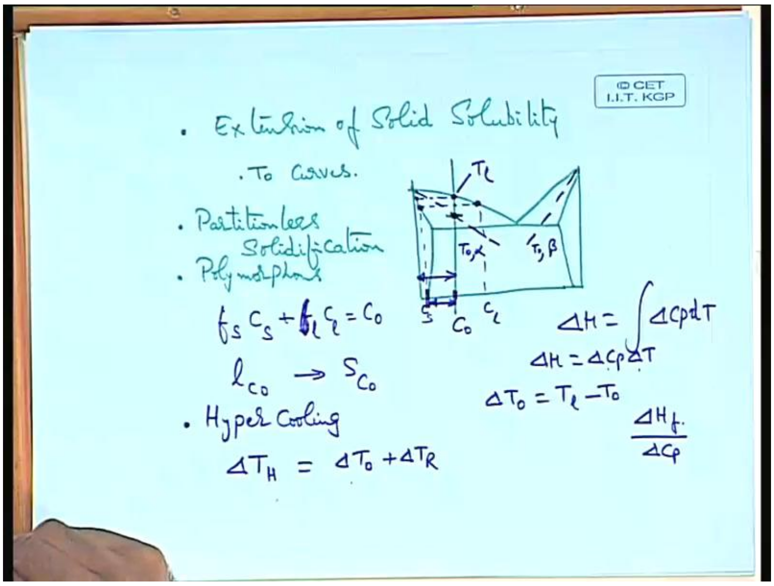

- Extension of Solid Solubility
  - T_0 Curves.
- Partitionless Solidification
- Polymorphous

$f_s C_s + f_l C_l = C_0$

$l_{C_0} \rightarrow S_{C_0}$

- Hyper Cooling

$\Delta T_H = \Delta T_0 + \Delta T_R$

$\Delta H = \int \Delta C_p dT$

$\Delta H = \Delta C_p \Delta T$

$\Delta T_0 = T_l - T_0$

$\frac{\Delta H_f}{\Delta C_p}$

Second thing is what is called is extension of solid solubility. This is another advantage of rapid solidification process. And why do you get this, this comes again because of high under cooling. Whenever, you have high under cooling, we have talked about the T naught curves in the thermodynamics class. So, it is all related to the T naught curves.

Let us look at one example of a T naught curve. So, if you look at a eutectic phase diagram like this with a T naught curve, which goes like this let us say. This is T naught for alpha, this is T naught for beta, T naught alpha. If you look at these T naught curves. If I am cooling it rapidly I am providing high under cooling.

If I am having a under cooling, let us choose a composition like this, if I choose a composition like this, if I can under cool below this T naught. Then, definitely there is a driving force for what is called partition less solidification. We have talked about this probably some time back, it is also called polymorphous solidification.

But, mostly partition less solidification is a regular term. That is used because polymorphous transformation can be used for any type of transformation. What is a polymorphous transformation Yamini?

Student: ((Refer Time: 46:54))

Where the composition remains the same and the structure changes, that is a polymorphous of transformation, where only structural change is taking place that is why this is polymorphous morphous, morphous is structure. So, structure changes from one to the other. Here, what is a change, it is changing from liquid structure to a crystalline structure.

But, the composition remains the same, that is polymorphous structure.

Student: ((Refer Time: 47:21))

Polymorphic transformations people say anything, polymorphous transformation, polymorphic transformation just the same it is only terminology. So, this is nothing but, the partition less solid. Partition less means, there is no partitioning of the solute into the liquid and to the solid. Usually, whenever you take this liquid, under normal conditions what happens is the moment you reach this temperature.

Solidification starts, under equilibrium condition. And you will see a solid having this composition comes out, and if you come to a lower temperature like this. Now, liquid will have this composition, solid will have this composition is not it. The solute if you call this as C naught composition. That C naught is getting a partition between the liquid and solid.

Solid will have C s composition this is C s composition let us say, I bring it down and call it C s and this is composition is called C l composition. So, that the C naught gets partitioned between the C s and C l. And in principle, we can draw the what is called the mass balance equation which is nothing but, the fraction of the solid multiplied by the composition of the solid. Plus fraction of the liquid multiplied by the composition of the liquid should be equivalent to the C naught.

That is nothing but, what is called the mass balance equation, from where we derive what is called the lever rule is not it. So, this is under equilibrium conditions, but if you cool it very rapidly under rapid solidification conditions. You come to below the T naught, if the tall you come below the T naught, then there is a possibility for partition less solidification.

That means, liquid having C naught composition will transform to solid having C naught composition. And we also talked about, what is called hyper cooling during our thermodynamics class probably. That hyper cooling tells you, what is the critical cooling that is required.

The delta T hyper cooling is nothing but, the critical cooling under cooling. That is required for having partition less solidification, which is equivalent to delta T naught plus delta T recalescence. Where, delta T recalescence is nothing but, T liquid us temperature minus T naught temperature for that composition, for a particular composition for example, this C naught composition. T liquid us temperature is what, this is a T liquid us temperature, T naught is this temperature. So, this difference between these two is delta T naught. And what is delta T recalescence is nothing but, delta H fusion divide by delta C p.

Because, we know that delta H is equal to integral delta C p d T. And we can write always the delta H equal to delta C p delta T. So, delta T is equal into delta H by delta C p. What is this recalescence, we know that when liquid gets under cooled. And a solid is nucleated, the moment solid is nucleated there is a heat which is released.

And once a heat is released, the liquid which is surrounding that solid which has nucleated it is temperature will go up. And once, it is temperature goes up and if it goes in to the regime above the T naught. Then; obviously, partition less solidification cannot occur. As a result, you need to be below the T naught temperature for that particular composition. Even, after the recalescence has occurred.

So, if you want to make sure that this happens, it can happen only when this difference between these two is also considered. And then if the total under cooling is equivalent to these two. So, this is what is called extension of solid solubility. Because, if you can under cool a liquid up to the T naught definitely you have been able to achieve solubility, which is equivalent to this much liquid of C naught composition has solidified into solid of C naught composition, whereas the actual equilibrium solubility at room temperature is only this much. Now, your solubility is this much. So, this is the extension of solid solubility. So, you are able to extend a solid solubility, what is the advantage of extension of solid solubility?

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

Yes, you can get solid solution hardening, you can get precipitation hardening extra precipitates you can get volume fraction of the precipitates can be more. So, that is one another way.

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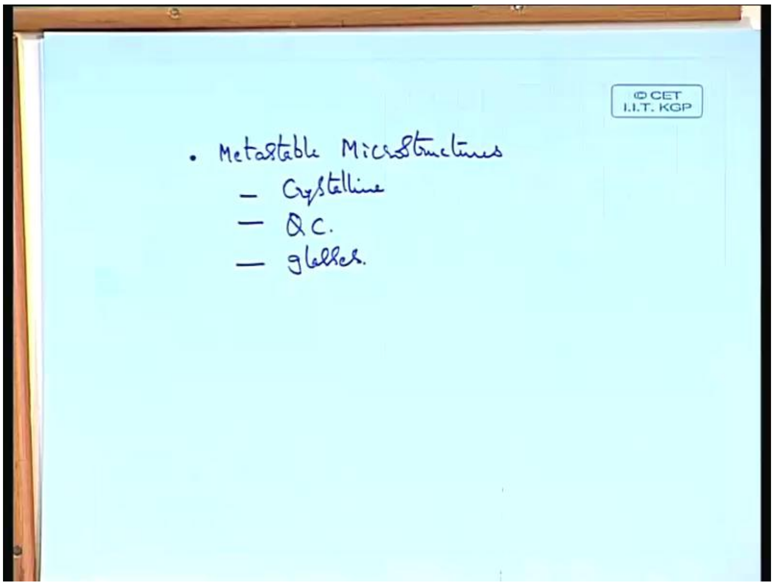

- Metastable Microstructures
  - Crystalline
  - Q.C.
  - glasses.

Then, what is the other advantages, the other advantages is you can get meta stable microstructures. Meta stable, they can be crystalline microstructures, they can be quasi crystalline they can be glasses. That means, when you under cool the liquid very rapidly to very high under cooling’s.

At that high under cooling’s, once you are at a very low temperature, at that temperature solidification is occurring. Then, there is a competition between a equilibrium solid that is coming out and some other non equilibrium solids, and if the non equilibrium solid has a lower activation barrier. That will form more easily than a equilibrium phase.

So, as a result, you may have non equilibrium crystalline structures, which may not exist in the phase diagram. For example, as I must have mentioned you many times. When, we are doing age hardening. Instead of the equilibrium structure some other non equilibrium structure comes out.

For example, aluminum copper instead of the theta, theta double prime or g p joules. They do not exist in the phase diagram, but they come out. So, like that during cooling also if the activation barrier for such phases is lower. So, you may get such meta stable phases.

And you can get quasi crystal in phases and if the cooling rate is still faster, you will end up in glasses, we have talked about all this before. So, with this we will stop and then will continue in the next class.

Thank you very much.