Advanced Materials and Processes
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Lecture - 16
Rapid Solidification Processing

Another meta stable or non equilibrium process or one of the advanced process, which is used to generate number of novel materials. This is called mechanical alloy. As a name suggest, this is a way to bring two metals or two elements into the form an alloy by mechanical means. So, this is nothing but basically a high energy ball milling process, where you take pure metals a and b, put them in ball mill. And then allow the two metals to come together to form an alloy.

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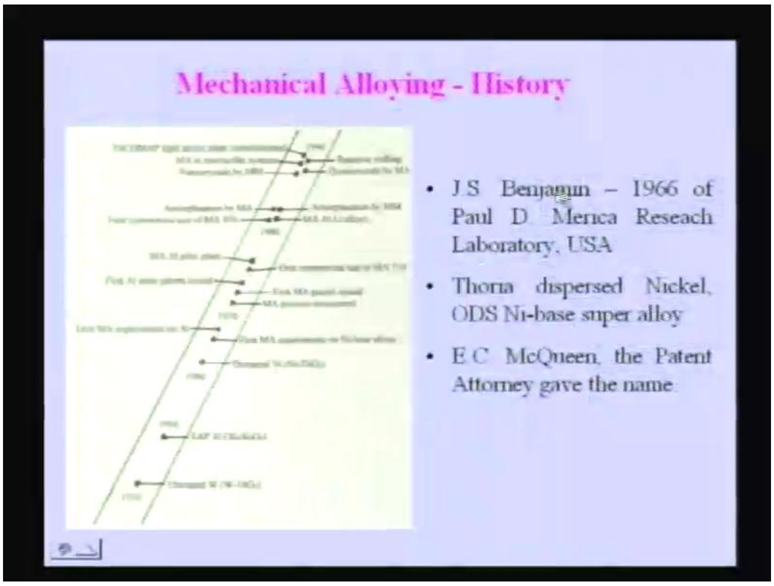

Mechanical Alloying - History

- J.S Benjamin – 1966 of Paul D Merica Reseach Laboratory, USA
- Thoria dispersed Nickel, ODS Ni-base super alloy
- E.C McQueen, the Patent Attorney gave the name

This field if you look at this view graph, this is field is a basically started with the person by name J. S. Benjamin in 1966 at the Paul D Mercia research laboratory in USA. Where, they wanted to generate nickel coatings on the thoria. There was a lot of work going on those days to somehow incorporate the thoria are eteria into the nickel base super alloys. To give the high temperature strength for these super alloys.

We know that most of the super alloys. They, get there high temperature strength from two basic components. One is the ordered inter metallic which is called gamma prime N i 3 A l, which is present in the nickel the base. So, you have in FCC nickel base matrix in which you have N i 3 A l ordered FCC particles, which are embedded in the nickel basic matrix. And that gives you very high strength.

But, we know that precipitation hardening does not really give you strengthening at very high temperatures. Because, the moment of you go to very high temperatures, you have either coarsening of the precipitate which occurs or desolation the precipitate. This is a typical problem with any precipitation hardening, but there is a small different between N i 3 A l precipitation strengthening. Because, N i 3 A l it is known. That it gives you an increase in the strength, with increasing in temperature at least within a small temperature domain of up to around 900 degree are so. But, if you want use these materials beyond this temperature, it is very difficult to use theme.

Because, at this high temperatures this precipitates will either dissolve or coarsen. As a result, what we see is people have thought instead of having only the N i 3 A l particles, if we can put some dispersoids, which are oxide dispersoids. Such as, eteria, throia one can have much better strengthening at high temperatures. And when they were putting these eteria particles into the nickel base super alloys, they found that the wettability is very poor.

So, in order to improve the wettability they thought, if they can coat it with nickel, they can improve the wettability. The way to coat it they thought could be a ball milling technique. Where, ball milling has been used for quite some time. Even in metallurgy we know, that most of the ores once we take it out from the ((Refer Time: 04:15)) we break them using a ball mill to make them finer sizes.

So, that they can be loaded into a blast furnace or something like that, any furnace further reduction, further the reduction. So, as a result they thought they will use the ball mill to coat nickel on the throia or on iteria. So, they were quite successful and then they thought, why do not we straight away make the ODS nickel base super alloy. What is ODS oxide dispersion strengthen. That means, eteria or alumina or thoria any oxides.

So, you disperse the oxides into the nickel base super alloy. That means, instead of first coating the compound with a pure metal, such has nickel. And then putting into a melt of nickel base super alloy, which is a two step process. Instead of that what they decided is two. Let us take all the elements, which are required for the nickel base to super alloy, put all of them into the ball mill. Along with that put all the oxides powders.

So, that you ball mill all of them together, when you ball mill all of them together, you can end up ultimately into a super alloy. Containing these fine dispersoids and that gives you very high strength. So, this was the origin of this whole thing and the actual term mechanical alloying was not given by Benjamin. But, patent official his name is McQueen, he basically thought let us call it as mechanical alloying.

Because, you are making the alloys using mechanical means. So, that was an idea which has given by the McQueen. So, if you look at how this whole field has evolved. If you look at the first experiment on mechanic alloying are around 1966 as you see here. And then the first patent in mechanical alloying came around in 1972.

And commercial alloys have started around 1974 are so. And the first pilot plant has come up around 1975. And then you have some interesting things that have taken place. For example, amorphisation phase by mechanical alloying all meta stable materials. In fact, before 1980s there all basically stable materials, people have never really thought.

That we can use mechanical alloying to produce novel meta stable material, such as either nano crystals or coarse crystal or amorphous materials. So, the first experiments were 1983 amorphisation by mechanical alloying. And almost the same year amorphous by mechanical milling. What it means is that, you take a compound keep on doing ball milling.

And the compound ordered compound transformer into an amorphous, first it becomes disordered and finally, it becomes amorphous. So, instead of doing mechanical alloying, where you take elements a and b. Whenever we take two or three or more than one element. And then put into the ball mill and then do ball milling we call it as mechanical alloying, because you have individual elements there. But, if you take a pre alloyed powder. That means, an alloy which is already made into a form of alloy, by some means by melting and casting root. And put that alloy powder into a ball milling and do the ball milling, we just call it as a mechanical milling. So, this is difference between these two.

And people have shown that even pre alloyed powders inter metallic compounds can made into an amorphous. An nano crystals by mechanical alloying has come around 1987. Coarse crystals by mechanical alloying also almost 1988, reactive milling has started around 88, 89, then mechanical alloying in amusable systems. That means, systems where the a and b do not dissolve into each other, under the normal conditions.

For example, they are number of systems which are more tic tic systems. We know in the phase diagram, there is miscibility gap in the liquid itself. That means, a and b do not dissolve even in the liquid state. Even such alloys can be made into an alloy by mechanical alloying, we will talk more about it later.

So, all these has happened before 90s. So, this feel has more or less got matured by 90s. And after 90s now there is lot of work going on, on trying to understand the process, because before this the understanding of the process was not really much. So, what is the energies that are going into, an how these energies are effecting the process. And so is there any co-relation between the energies, that we are putting in and the phase that is coming out. So, also this kind of fundamental understanding is has come in the last one decade.

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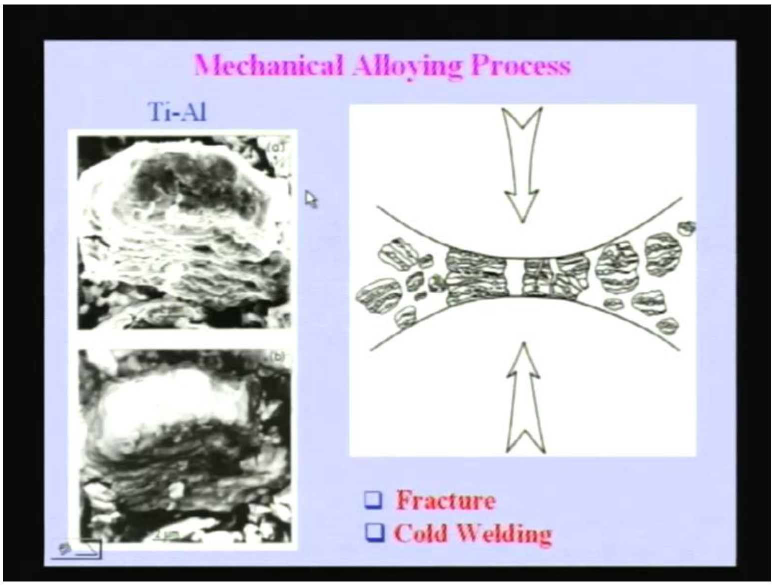

Mechanical Alloying Process

Ti-Al

- ☐ Fracture
- ☐ Cold Welding

If you look at what is this process. The process is basically composed of two basic process; one when a ball like this a section of the ball is shown here and another ball is shown here. Two balls there if they are heating of powder particles, what happens is two process occur.

One is a fracture of the particle, it is a breakage of particle. Second is cold welding of the particles. When a particle breaks depending on the type of particle, if it is ductile particle, it is becomes like a flake. Whenever, a ductile particle is hitting by a ball, it immediately becomes a flake.

And that flake if it comes across another flake, because it as large surface area to volume ratio a fresh surface is exposed. So, immediately there is a tendency for the welding to occur. And as a result, you can see here a pan cake type of structure happens, like a sandwich kind of structures.

So, you can see layered structures, this is a schematic diagram. And this is a the actual picture of one such system, this is a titanium aluminum system, where you can see layered structure within one particle. And this layered structure, if you carefully observe in a back scatted image in same. It shows you, the white and black contrast which clearly tells you, the compositional contrast, one of the elements white is one element and dark is another element. So, which basically tells you this comes because of the atomic number contrast. So, whichever has a higher atomic number, that will look bright. So, this is how we can find out that there are different elements. And alternate layers of these elements take place.

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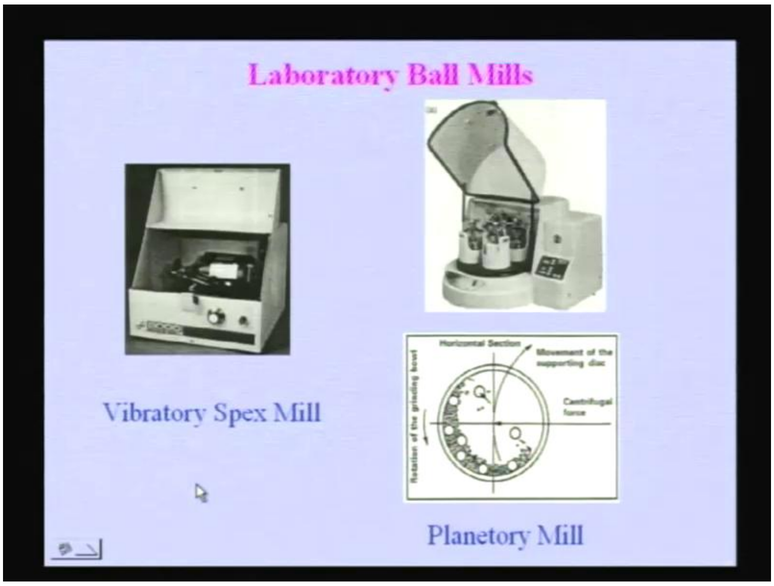

Laboratory Ball Mills

Vibratory Spex Mill

Planetory Mill

And once you get, that kind of things alternate layers any phase can form. We will come to what are the phases, that can come out of such a mechanical alloying. Before that, let us look at what are the types of mills that we use, one is called a vibratory mill. These are typical laboratory mills, there are two laboratory mills which people use usually.

One is called as vibratory mill which is where basically you take a box, in which you put powder and balls. And then shake it at a very high speed something like 50 cycles per second. So, almost about 1200 RPM, if you want call to convert into RPM. So, you can have such high frequency impacts. Because, in each vibration there will be one impact at least.

So, balls impact the powder and because of which you get. So, if this is commercial ball mill called spex mill. This is an American mill which is very often use. But, the only problem with this mill is, the quantity of the powder that you can use is very small, not more than about 20 grams. So, if somebody is interested to make slightly larger quantities, he cannot use this kind of mill.

The next ball mill which is very popular is what is called planetary mill. This is one such planetary mill, where you see a disk a schematic picture is shown here. You have a disk, disk there, this black one that you are seeing here is a disk. And on that you see, four white colored jackets. And these are called bounce or wiles.

And these balls rotating a direction opposite to that of the disk, the disk rotates in one direction and the balls rotate in the opposite direction. And that is why you can see the disk is rotating in this direction. This is rotation and this is rotation of the grinding bowl and the moment of the disk is shown in the opposite direction here.

And because of this, the balls which are there inside the bowl will get some kind of a centrifugal forces. And because of this the balls will hit the powder and hence you get the energy transform to the ball. And this kind of ball mills, planetary mills are slightly having a higher capacity, then the vibratory mills.

And one can go up to about 1 kilo. If you put four bowls each one can take around 200 grams in principle, it depends on the type of materials and the density of material, because the volume is usually fixed. So, depending on the density of material one can go up to around 200 grams per bowl. So, approximately about 1 kg one can get.

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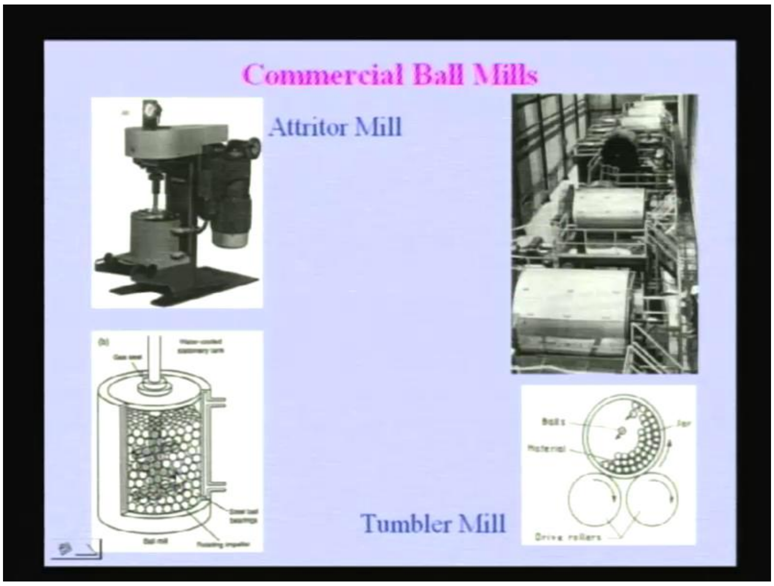

Commercial Ball Mills

Attritor Mill

Tumbler Mill

So, this is the laboratory mills. Now, let us come to the commercial type of ball mills. Commercial type of ball mills one ball mill is called as attritor mill. An attritor mill is something similar to a drilling machine basically. You have motor here and a shaft and this shaft in fact, the first attritor mills. Wherever, you go to any lab where you see attritor mill they basically converted a drilling machine into a attritor mill.

So, what you have this whole thing that you see here. This whole thing is nothing but a drilling machine. And what in a drilling machine you have shaft, where you put the drill bit is not it. So, here instead of drill bit what you do, is to that to shaft is you put some horizontal rods which are called impellers. You put horizontal rods to that shaft and then put a container here, this is the container here. And that container consists of balls and the powder.

And so when you are rotating the shaft, the impellers also move. And once, the impeller hits a ball, that ball goes and intern it hits a powder particle. There is a probability that a ball will hit a powder particle. So, at the same time there is also a probability that the ball will hit another ball. So, some energy is lost between ball to ball interactions. But, at the same time some of the energy also is transform to the powder.

So, as a result you get some transform of the energy. And the finally, the powders get converted to either nano crystals or quasi crystals or minter metallic or amorphous phases or anything that you are interested depending on the total energy that is transformed.

So, this is one type and here you can full go up to about 5 kilos. This is very common commercial mill. But, the energies here are usually lower, than what you get either spex vibratory mill or in this planetary mill. So, the laboratory mills usually have the highest energy. And this is another mill, which is a typically mill that every metallurgist knows.

What are called tumbler mills, in metallurgy what is called o dressing subject, if you have ever read in your B. Tech. You would have come across these tumbler mills. Because, we talk about this tumbler mills where the ore, which is taken out from the is broken into smaller pieces and that is what we use this.

So, basically you have two rollers on which you put a drum. And that inside the drum you put your balls and the powders, and when you operate this drum at the critical velocity, very close to the critical velocity, where the balls will thin to the wall of the tumbler mill.

So, just lower than that velocity if use, then the ball mill go up, up to the top. And then just falls from top and then gives you an impact. And here also depending on the size of the actual container, one can have the energies decided by that. Because, the height from which the ball drops is what is going to give it the kinetic energy to it.

So, as a result the energy of this mill depend basically on the diameter of the bowl. And at the same time it also depends on the speed of which the whole tumbler mill is rotating. So, you can see here, a series of such tumbler mills. This is a picture from INCO laboratories International Nickel Company USA. Where they have really made commercial mechanically alloyed products from the elemental powders. All super alloys have been made in this kind of ball mills.

So, here you can really have about 200 kilos without any problem. Only problem is whether the energies are high enough or not. So, whether we can use this kind of mills to produce either nano crystals or amorphous materials or not is something, which is what people are studying now days. In fact, within 15 days we have a small work shop on just to discuss that aspect. Whether we can produce such ball mills, which are commercial ball mills high scale ball mills. Where, the energies can be ((Refer Time: 17:43)) as much as you can put into these laboratory mills. So, if so how to design such a ball mill where the similar energies can be imparted, so that is there is a work shop going on that. So, hopefully people will come up with some idea.

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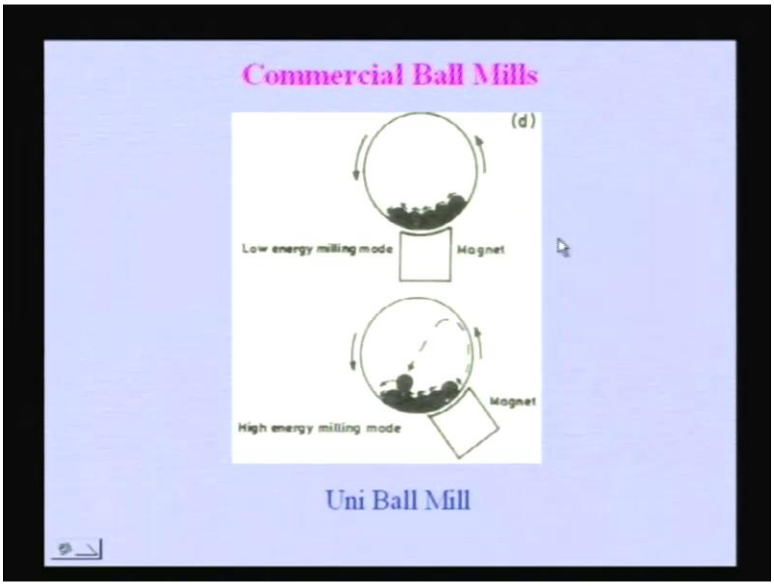
Commercial Ball Mills

Uni Ball Mill

So, the other type of ball mill is what is called a uni ball mill. This a special type of ball mill, which is different from the other ball mills in the sense. Here, the actual energy is imported because of the magnate which is kept here. So, you have a tumbler kind of mill here, circular or cylindrical shaft. In which you put balls and put a magnate here.

So, now, depending on where you place the magnate and start rotating the bowl or start rotating the container. The balls are taken to a higher position, depending on the position of the magnate. If the magnate is exactly at the bottom, then the definitely balls will not go to very high. Because, the magnate is attracting these balls and these balls are basically steel balls.

So, steel balls are attracted by magnate. So, the balls will not go to very high position here. And so basically they will keep on moving there itself. So, there is not much of impact, but only some shearing process will take place. So, one can control the type of the mode of energy transfer, whether it is just shear are an impact kind of energy.

So, one can change this energy mode by changing the position of the magnate. And that is why we call this as a low energy mode and high energy mode. So, if you put the magnate at some position somewhere here let us say, you will get much higher energy. So, like that one can control this. So, either shear mode or the impact mode. So, here also one can have large quantities produce something at least above 5 kilo or so one can produce this kind of a large quantities in this. So, these are the typical type of mills that we use. And now let us come to what you can achieve by this kind of mechanical alloying are milling process.

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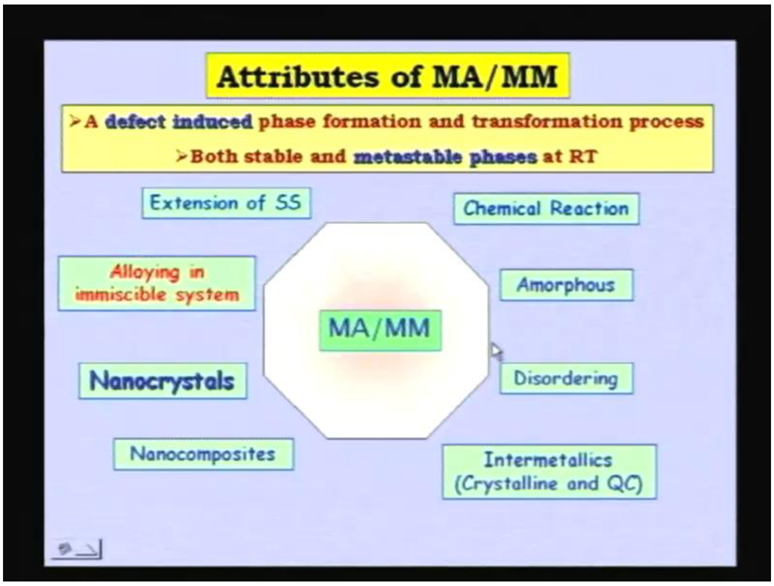

Attributes of MA/MM

➢A defect induced phase formation and transformation process

➢Both stable and metastable phases at RT

Extension of SS

Chemical Reaction

Alloying in immiscible system

Amorphous

MA/MM

Nanocrystals

Disordering

Nanocomposites

Intermetallics (Crystalline and QC)

If you look at the mechanical alloying or the milling process. Basically, it is a defect induce process. You are introducing lot of defects into the system, breaking the powder particles into the finer and finer particles. And during this fracture process, you are introducing lot of defects, such as dislocation, vacancies all kinds of defect are generated, and because of these defects, that you are putting. The phase formations are phase transformation are enhanced, because the diffusivity is enhanced. Infect people talk in terms of a special type of diffusion called pipe diffusion. Have you ever heard of pipe diffusion, if you have gone through diffusion course you could come across this.

A pipe diffusion is a diffusion through dislocations. A dislocation is what is nothing but a row of vacancies is not it. So, you can imagine a dislocation as nothing but an empty pipe is like a just a cylinder. This is an empty cylinder a like tube. So, you can imagine dislocation as a tube, so where the diffusion can occur very fast. So, if you have large number of dislocations inside a material.

So, diffusion can occur very fast. And at the same time when you are decreasing the size of the crystals, we know diffusion is always basically a phenomenon, which is driven by two things.

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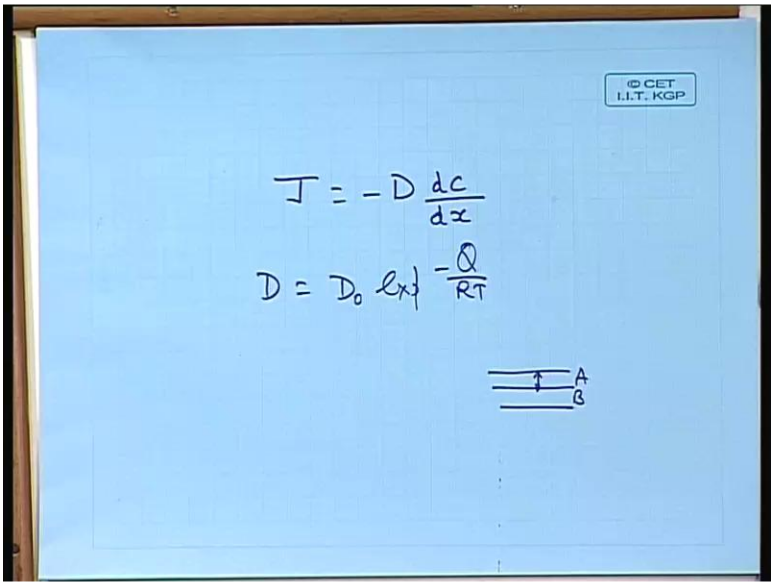

$$J = -D \frac{dc}{dx}$$

$$D = D_0 \exp -\frac{Q}{RT}$$

One is diffusivity, another is concentration gradient. In fact, we should not call it as concentration gradient we call it as potential gradient. For a binary system a potential gradient is equivalent to the concentration gradient, not potential gradient in principle, it is chemical potential gradient, whatever it is we talk about only chemical diffusion.

So, we do not talk about any electrical diffusion also. So, here potential is not a voltage potential, but it is chemical potential. So, d c by d x is equal to d mu by d x in principle for a binary system, but for a turnery system it is not so turnery or ((Refer Time: 22:06)) system. So, let us consider it is... So, it is a function two things, the flux is diffusivity and concentration gradient depended.

So, diffusivity depends on the temperature we all know basically and also the concentration of course. Because, diffusivity we can think of as a concentration dependent or concentration independent, when we try to calculate. All of you have gone through diffusion course any type at some point of time. Or a part of metrology course some metrology course, you must have come across diffusion any way.

So, fix laws of you must be aware of. So, basically diffusivity more or less people take it as temperature dependent process, where D is equal to D naught into exponential minus Q by R T. So, where temperature comes into picture, Q is called activation barrier for diffusion and D naught is what is called the pre exponential term. So, now, d c by d x is very crucial in this kind of situations.

When you are decreasing the size let us assume that in a ball milling you are forming alternate layer like this A and B. If you are doing continuous milling, the thickness of A and B keeps on decreasing, because there is continuous breaking an again re welding taking place. So, because of which there is a continuous decrease in thickness of individual layers, and if there is continuous thickness decrease. Then, you can see what is called the d c by d x increases tramendarly, because the d x is decreasing. As you can see the d x is nothing but the diffusion distance. The distance over which the diffusion as to occur, in a laired structure like this, the diffusion has to occur in this thickness is not it.

So, if that thickness can be reduced, then the d x is decreased. And if the denominator decreases, then the whole fraction increases tremendously and as a result the flux increases. So, that is one of the reasons, why you have the defect induced ((Refer Time: 24:21)) phase formation and transformation, which gets enhanced because of the defects.

And the decrease in the size of the crystals, that occurs during ball milling. And because of this you can have either stable phases forming. And meta stable phases forming, at room temperature this is very crucial. All this phases are not really happening at high temperature, they are all happening at room temperature or close to the room temperature.

We will talk about the temperature during ball milling at some point of time. So, you can take it granted that more or less temperature is close to the room temperature. So, all this process occur at near the room temperatures. So, on what can happen as I told you it can give you a nano crystals, it can give nano composites, if you putting more than one type of material. So, you can have nano composites for example, if you take nickel base alloy.

So, nickel and etria if you take it, you can break it two very fine size. And ultimately if the energies are very high enough, you can make a nano composite of nickel into which you can have etria. So, you can make nano composites and you can have what is called alloying. And because of that alloying, you can have extension of solid solubility, rapid solidification processing you have talked about extension solid solubility.

Similarly, hear also we have extension of solid solubility, in rapid solidification processing. The concept which tells you about a extension solid solubility is T naught concept, we have talked about T naught concept. Here, we are forcing the atom to come together and form an alloy. So, that is why we call it as mechanical alloy, you are mechanically bringing the A and B atoms to come together and form an alloy.

And so that is how you can have large extension of solid solubility's will come to each of these one by one. And one can have alloying in the immiscible system. This is one thing which rapid solidification process cannot do it. Because, rapid solidification processing, you are starting with what, you are starting with liquid. You are starting material is liquid, if in the liquid if the two elements do not dissolve, then you cannot help it.

So, if the two elements have not dissolved in the liquid state, then you cannot have solubility of A and B in the solid states. Because, you already starting with two liquids. And those two liquids if you are cooling it fast, those two liquids may give you two solids. So, ultimately you end up it in two solids instead of one single solid. Whereas, here it is not such a thing.

That even if the two elements are immiscible in the liquid state, you may end up in a solubility. And in a number of systems people have really ended up in a good solubility in such systems, we will give you examples of that also. Then, one can have disordering before that I should say. One can make inter metallic's, after alloying, after solid solution formation. The next possibilities is inter metallic's, one can make inter metallic's.

Whether, they are crystal in inter metallic's or quays crystal in inter metallic's. We have talked about this at some stage, when we are talking of nano crystalline materials. One can have disordering in the inter metallic's, one can take an ordered inter metallic's make it disordered. I told you, why we want to make it disorders, because a disordered compound is more ductile.

So, if you want to introduce some ductility into a compound, if you can take an ordered compound and put it into a ball mill, one can make it is disordered. And one can make it completely amorphous and one can also introduce chemical reactions. So, these are all one can do.

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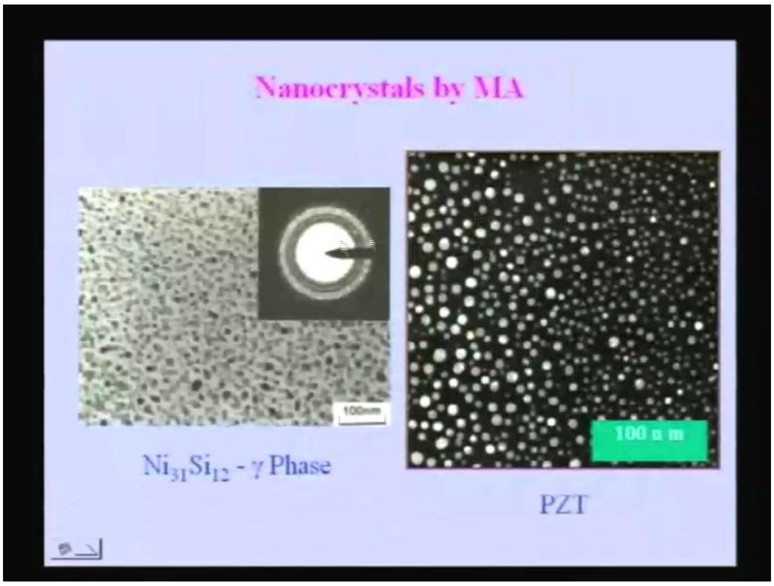

Nanocrystals by MA

$Ni_{31}Si_{12}$ - γ Phase

PZT

And these are the some of the examples nano crystals, one can make this is in the metallic system, this is in a oxide system PZT.

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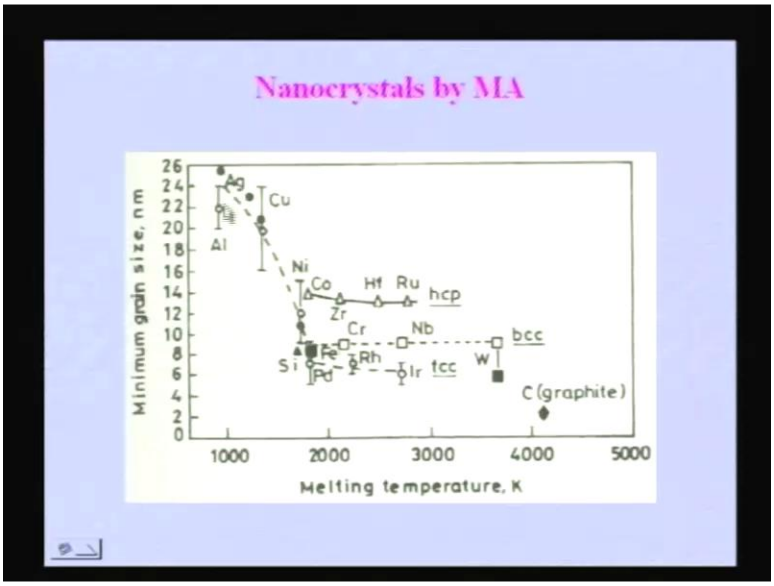

Nanocrystals by MA

And the nano crystal, the crystal size that you can achieve by mechanical alloying is always a function of melting point. The higher the melting point for example, graphite, tungsten have a very high melting points, one can achieve very low crystal size.

Whereas, if you take aluminum, copper, silver they all cannot have very low crystallite size you have a high crystallite size that is one.

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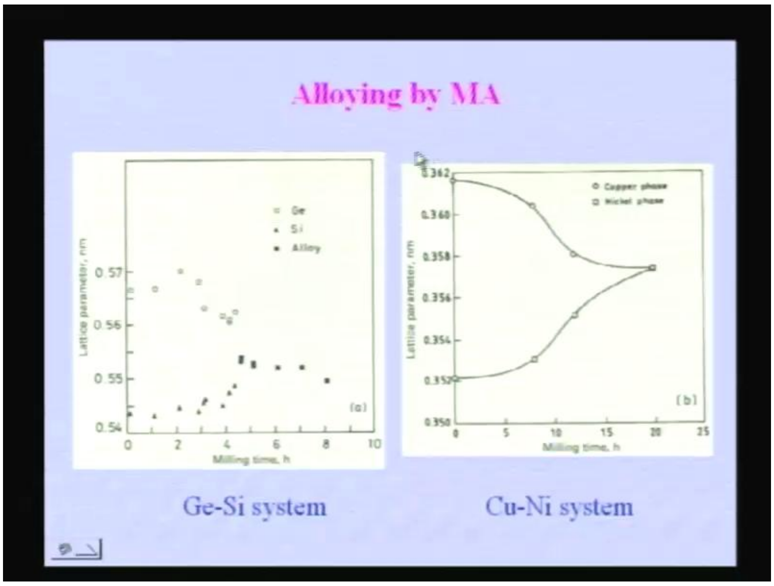

Alloying by MA

Ge-Si system

Cu-Ni system

Coming to alloy, alloying basically occurs by two different process I said continuous diffusive mixing and discontinuous mixing. Sometime, we have talked about it, this is an example of such a continuous diffusive mixing. Here, lattice parameter of copper and nickel is plotted as a function of milling type. You can see, one of them the lattice parameter decreases another lattice parameter increases.

And at some point of time they become same. And that is the time when the alloying is taking place. Similarly, this is germanium silicon, this is germanium, this is silicon, one increases another decreases and finally, you get an alloy.

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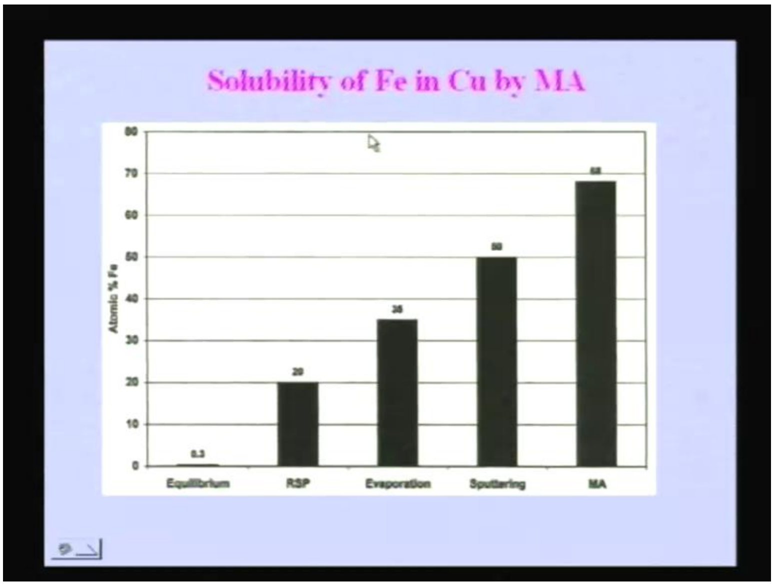

Solubility of Fe in Cu by MA

And this is tells you, how much solubility you can achieve. This is iron copper, iron copper is suppose to be a immiscible system. Lot of people are working on this immiscible systems now. Particularly to put a small amount of copper into iron interstitial free steels lot of people are working. Where, they want to put small precipitates of copper, particularly nano crystalline copper into iron.

So, that they can increase the strength of the interstitial free steels. So, if you look at what is the equilibrium solubility is only 0.3 percent. Only 0.3 percent of iron can go into copper under equilibrium conditions. By rapid solidification one can go 20 percent, by evaporation 35 percent, by sputtering about 50 percent, by mechanical alloying one can go to 68 percent. You can imagine from 0.3 you are going up to almost 68 percent. So, this all because you are just forcing the atoms to come together. So, that is an advantage of mechanical alloying.

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And similarly I told you earlier, nano crystallization is a pre requisite to alloying. We have talked about it when we were talking about nano crystals. I thought we will just bring it here, because this is something to do with mechanical alloying. So, when the crystal size decreases to a critical value, suddenly the solubility occurs. This is true whether this is a copper zinc system or copper nickel system or this is iron silicon system.

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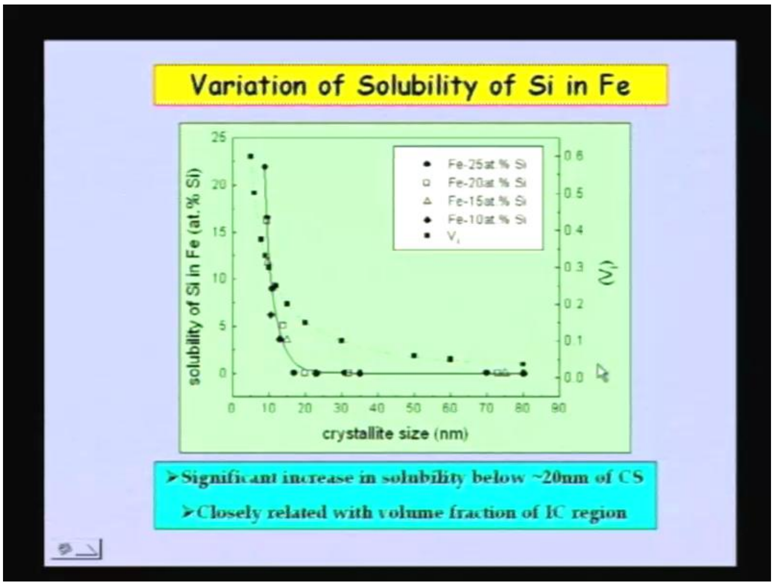

Variation of Solubility of Si in Fe

- ➢Significant increase in solubility below ~20nm of CS
- ➢Closely related with volume fraction of IC region

So, the solubility if silicon in iron suddenly increases, when the crystal size comes below 20 nano meters up to 20 nano meters there is no solubility, below that suddenly there is a solubility. So, this we have already talked some time.

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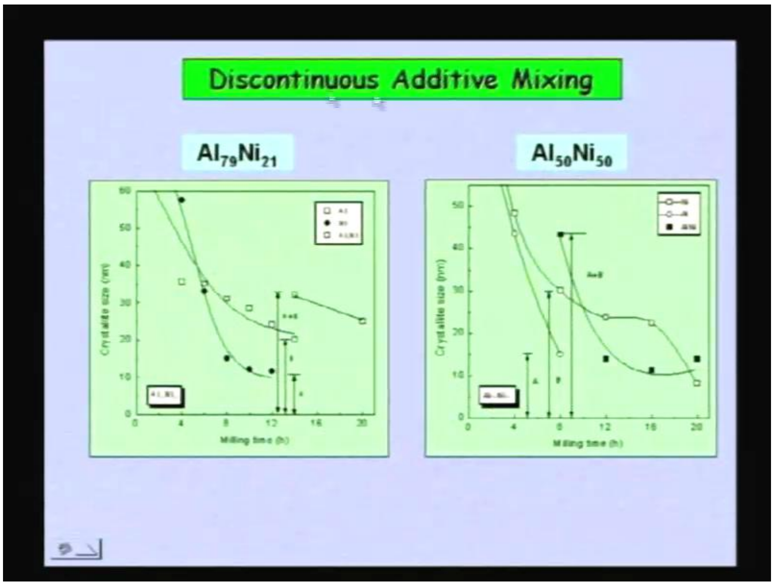

Discontinuous Additive Mixing

$Al_{79}Ni_{21}$

$Al_{50}Ni_{50}$

And then discontinues solid mixing is another which we talked. So, this another mode of alloying, which occurs during mechanical alloying. In case of ordered compounds, not for solid solutions, but in case of ordered compounds with high negative enthalpy of mixing, you get this kind of discontinuous additive mixing.

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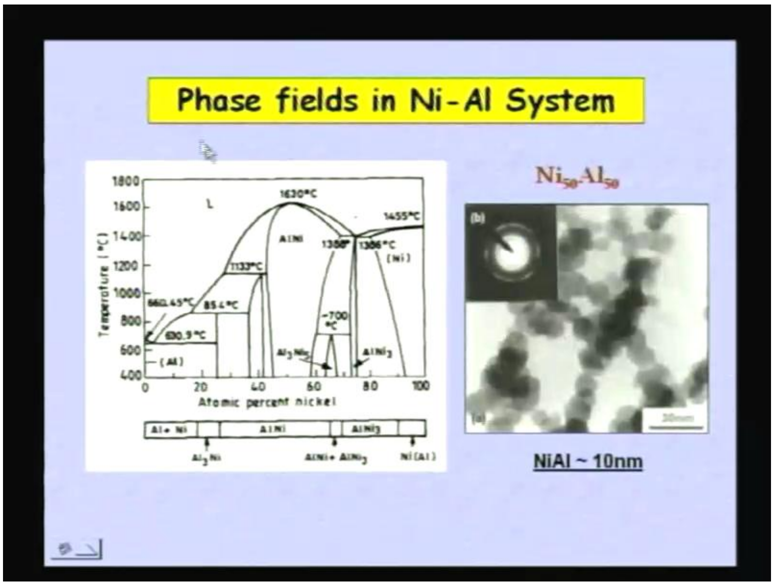

Phase fields in Ni-Al System

NiAl ~ 10nm

And one can have extension of phase field in the inter metallic's also. We talked about extension of solid solubility in solid solutions. But, one can have extension of solid solubility in inter metallic's. For example, N i A l is one such example. Where, equilibrium conditions you get a solubility from 45 percent to 50 percent.

Here you can get from 25 percent 65 percent, a very large extension. And it is all because of nano crystals. And one can show, that when you make it nano crystal, the phase field becomes much larger. This is very easy to show. And one can introduce disordering. But, the extent of disordering, that you can introduce into ordered compound, depends on the ordering energy of that compound.

How ordered is that particular ordered. Because, some of the if you compare some a inter metallic's compounds. For example, let us take beta brass, beta brass if you start heating beta brass. It is ordered at room temperature, once you cross a particular temperature what temperature is that?

Student: 450.

About 450 centigrade’s it becomes disordered, where as N i A l if you take, you take it up to the melting point. Only at the melting point it becomes disordered and melts. So, it does not become disordered up to the melting point, so because the ordering energy is different for different ordered compounds.

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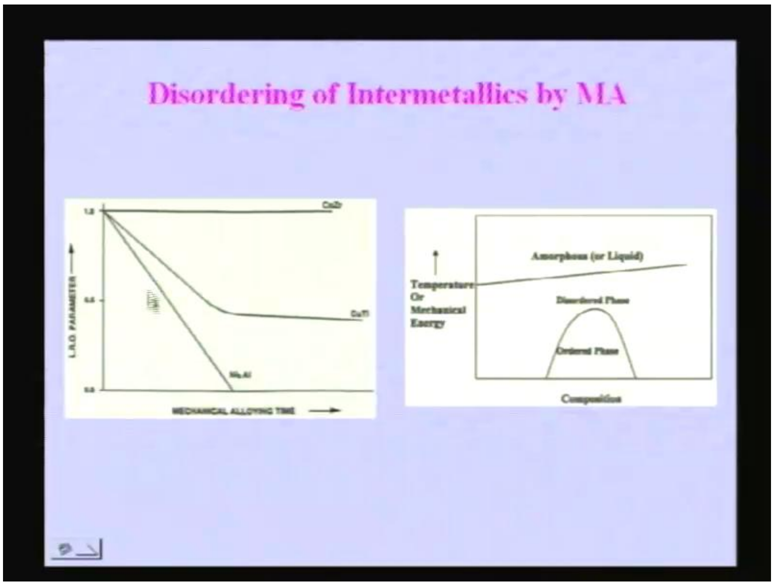
Disordering of Intermetallics by MA

So, if you look at it here, this is one example N i 3 A l copper titanium, cobalt zirconium. Three different ordered compounds have been ball milled. As you are increasing the milling time, the order parameter, long range order parameter decreases. In one case it continuously decreases and becomes 0. In one case it decreases and more or less reaches a saturation below that it does not decreases much.

And in one case it does not decreases to at all, because this is a very strong ordered compound. So, you it is very difficult to introduce disordered into such some strong ordered compound. N i A l is one such compound N i A l, N i 3 A l can made very easily disordered, but N i A l cannot made disordered.

Similarly, if you look at an ordered phase, and start increasing the temperature, we know usually there is a temperature at which it becomes disordered. And if you start increasing this temperature, further it becomes liquid is not it. Sometimes, in some cases this disordering temperature. And the melting point both might be you know overlapping with each other in some kind of compounds.

In case of copper zinc kind of beta brass, this is this temperature there is difference in this temperature. Because, the melting point is difference the disordering temperature is different. So, similarly here there is an enology between the temperature and mechanical energy. If you keep on increasing the mechanical energy, the ordered phase becomes disordered.

And this disordered phase if you keep on increasing the mechanical energy further, it becomes amorphous, which is similar to that of the liquid. So, this is something similar to what happens, if you keep on increasing the temperature. An ordered phase becomes disordered and becomes liquid. So, instead of liquid in a mechanical energy, it becomes the amorphous. So, that is one way one can do. At one can talk in terms of what happens, when you put these powders into a ball mill. And look at how various milling parameters effect, the type of phases that are forming.

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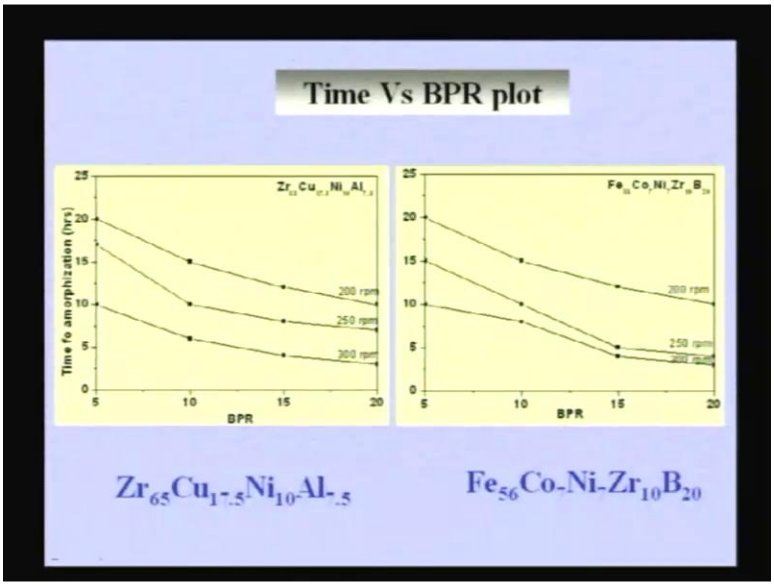

Time Vs BPR plot

$\mathrm{Zr_{65}Cu_{1-.5}Ni_{10}\text{-}Al_{-.5}}$

$\mathrm{Fe_{56}Co\text{-}Ni\text{-}Zr_{10}B_{20}}$

This is one such example, which tries to show you different milling parameters. One is called in ball milling, the different milling parameters one is the speed of the mill. The RPM and the ball to powder weight ratio. So, if you are increasing the speed of the mill, definitely you are increasing the energy is not it. And the if you are increasing the ball to powder weight ratio.

That means, for small amount of powder, if you have more number of balls, then the possibility of a ball hitting another ball increase. That is one possibility, at the same time there are less number of powder particles, which receive impact. So, as a result the possibility of each powder particle, receiving more impacts also increases. And because of which the total energy transferred to the powder over a period of time increases.

As a result, the higher the ball to powder weight ratio, the higher the energy transferred. But, the that same time there is a critical limit, because you keep on increasing a ball to powder weight ratio. Then, the numbers of balls have increased to such an extent, there is no ball to powder impact at all, all ball to ball impacts take place. So, ultimate effective energy transform will come down.

So, there is an optimum level, we have done a lot of studies on that. This is one such example, where you can see the time required for amorphization keeps on decreasing. As you increase the speed 200, 250, 300 RPM and as you increase the ball to powder weight ration and this is for two different systems.

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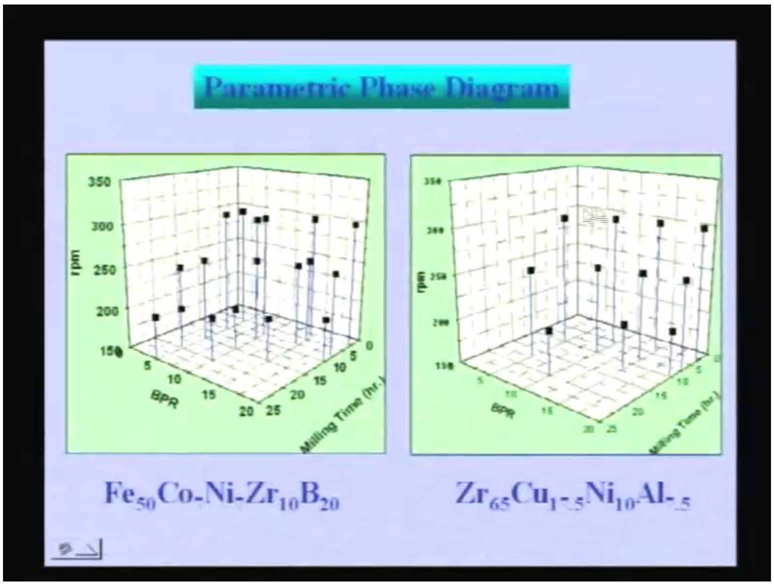

Parametric Phase Diagram

Fe$_{50}$Co-Ni-Zr$_{10}$B$_{20}$

Zr$_{65}$Cu$_{17.5}$Ni$_{10}$Al$_{7.5}$

And similarly, one can put the RPM ball to powder weight ratio. And the time required for the amorphization all of them together. And see basically similar results.

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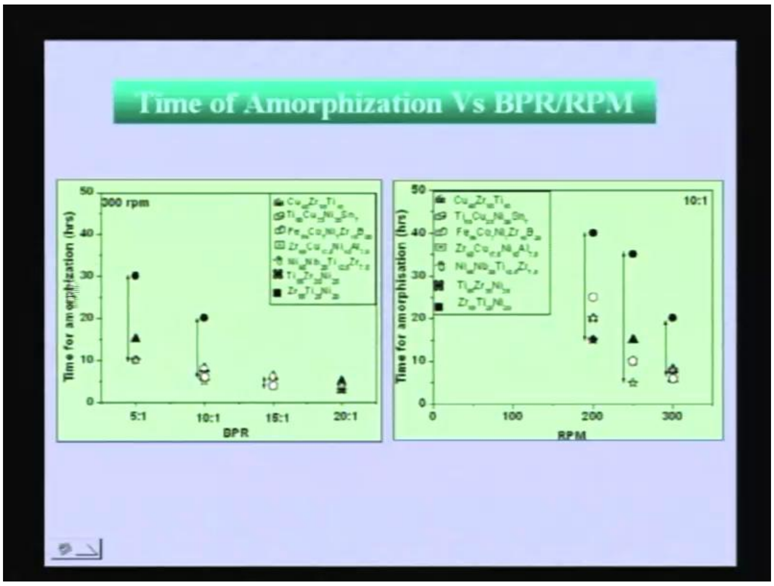

Time of Amorphization Vs BPR/RPM

And the again the time required for amorphization. If you look at for various systems, one can see that at very high milling energies. That means, high ratios and high RPM, the overall time required for energy for a amorphization is a same irrespective of the system that you choose. When, you are putting in so much energy every system becomes amorphous very easily.

So, whether it is a easy glass forming system as I told you, if you use a laser for rapid solidification. Even a pure metal can become amorphous. So, whether it is a easy glass former or non easy former both of them will easily become a glass, when you use very high cooling rates of the order of tender of 12 or 10 to the 14.

Similarly, when you are putting very high energies, whether it is a easy glass former or non easy glass former. If for example, here when you are putting small amount of energy, easy glass former will take less time a glass, which a is a not easy glass former will take more time. But, when you are very putting very high energy all of them more are less take very low amount of time.

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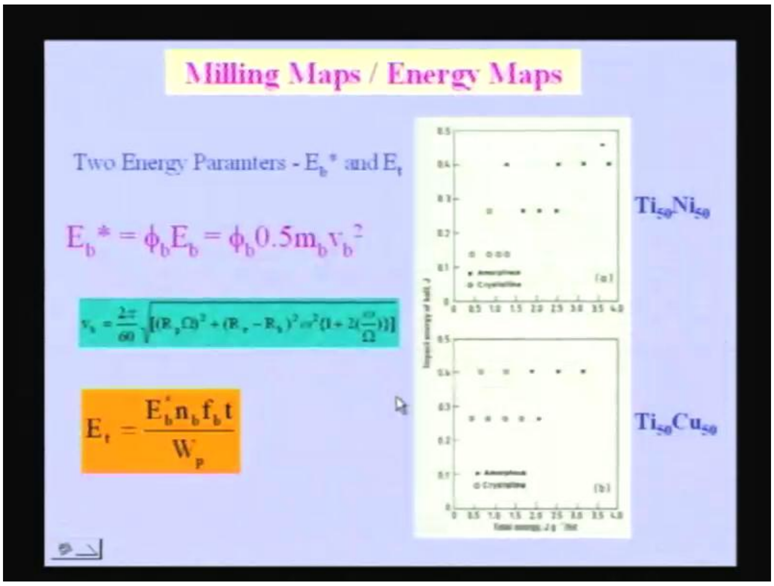

Milling Maps / Energy Maps

Two Energy Paramters - E_b^* and E_t

$$E_b^* = \phi_b E_b = \phi_b 0.5 m_b v_b^2$$

$$v_b = \frac{2\pi}{60}\sqrt{[(R_p\Omega)^2 + (R_v - R_b)^2\omega^2(1 + 2(\frac{\omega}{\Omega}))]}$$

$$E_t = \frac{E_b^* n_b f_b t}{W_p}$$

And one can put all these into energy parameters. There are basically two energy parameters during ball milling. One is called impact energy, which is called E b ball impact energy. That means, when the ball hitting a powder what is the energy of the ball, how do we know that it is nothing but half m v square.

The impact energy of ball is nothing but half m v square. So and if you know the mass of the ball, if we know the velocity of the ball one can calculate half m v square. And in addition one has to consider also ball to ball impacts, because some energy is lost when a ball hits another ball. So, because of which effective energy transferred from ball to powder is decreased.

So, because of which we multiply with a parameter called phi and that is decreases the overall impact energy of ball. So, this E b star is nothing but the effective impact energy of the ball. And one can calculate phi b very easily depending on the extent of filling of the container. And the ball to powder weight ratio and things like that.

And the total energy of the ball is crucial, total energy of the ball is nothing but the impact energy of the ball, numbers of balls the frequency of impacts. And time of milling, all of them will come in the numerator. And weight of the powder comes into the denominator. That means, if you put large amount of powder, then the total energy transferred for each powder particle; obviously, decreases, because there are too many particles to receive the impacts. If you less number of powder particles. Then, less number of particles are receiving more impacts. So, each particle receives more number of impacts. So, as a result the totally energy transferred to the powder particles are more. So, like that one can two put these two energy parameters.

And try look at come bring in all the milling parameters, into these two energy parameters. And look at what happens, when you plot these two energy parameters y axis the impact energy of the ball, x axis the total energy. And try to see under what conditions you get an amorphous phase.

You see, that irrespective of the impact energy. There are three different or four different impact energies here, different levels of impact energies. And at each impact energy, the total energy is increasing in this direction. And you can see, that there is a critical value of total energy, beyond which the amorphous phase forms, below it that it does not form. You can see, this is copper titanium nickel, this titanium copper.

So, you can see below this particular, if you put a vertical line like this, below that line all are white circles. That means, they are crystalline they have not yet formed amorphous. And beyond that line you have a amorphous phase formation. That means, there is a critical energy beyond which they. So, the actually impact energy of the ball is not crucial. What is the total energy transferred to the powder over a period of time what is crucial for any a phase formation.

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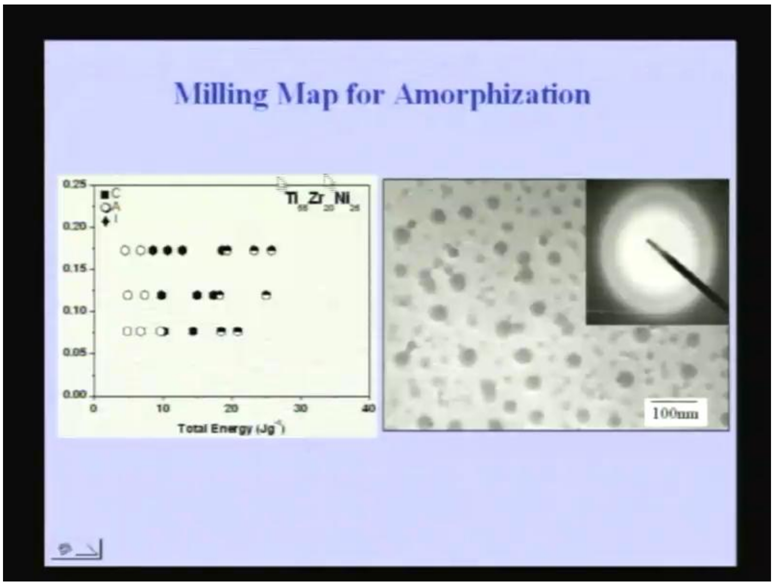

Milling Map for Amorphization

And one can do this for various glasses. This is another turnery kind of a glass, where a nano crystal becomes a glass, after certain period of milling. And again here also you can see there is a minimum total energy beyond which you get a glass. But, interestingly you can see, that here also you see this half field circles means, that the amorphous phase that has formed in this domain, crystallizes when you put very high energy these also another interesting thing.

Any amorphous phase that forms is not a stable phase. It transforms into a crystal, when you heat an a amorphous phase Because, we know whenever a glass is heated a glass becomes a crystal. So, if you heat this a glass it becomes a crystal. So, similarly when I am putting more and more energy, more and more defects are coming into a picture. And these defects, enhances the diffusivities.

And the because the diffusivities are so enhance. So, crystallization can come occur very easily even without increasing the temperature. So, the amorphous phase can become a crystal in see too in the ball milling itself, without taking out and heating it into a DSER doing are a annealing.

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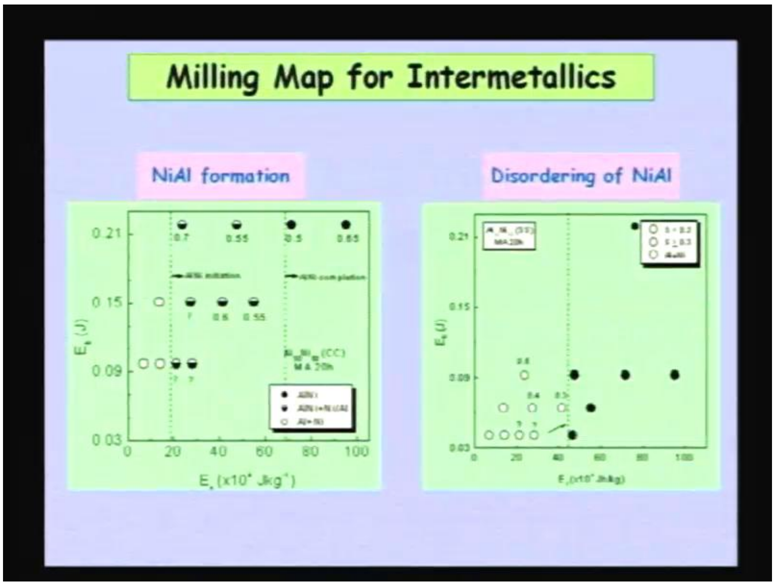

Milling Map for Intermetallics

NiAl formation

Disordering of NiAl

So, this kind of in situ crystallization. So, one can do all that and one can also show that there are milling maps for inter metallic's. This is one such inter metallic's N i A l, you can see that irrespective of the impact energy of the ball. There is a minimum total energy, where the initiation of the A l N i phase formation occurs.

And there is a minimum energy beyond which there is a completion of the reaction. So, the reaction starts and the reaction completion, always occurs beyond a particular energy. Similarly, there is a minimum energy beyond which complete disordering of the ordered N i A l occurs. Below which the order parameter is higher than 0 and beyond that the order parameter becomes 0. So, suddenly there is a complete disordering occurs and that is again a function of the energy.

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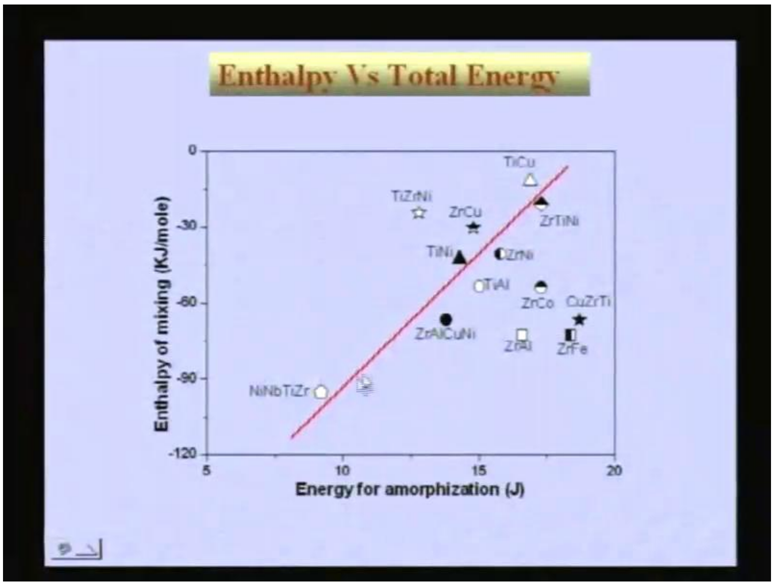
Enthalpy Vs Total Energy

And one can correlate the energy required for amorphization to thermodynamics. And show, that this for amorphization one van do similar thing for any phase formation. There is always say a direct correlation between the thermodynamics and the energy required for any phase formation. So, one can have a strong correlations.

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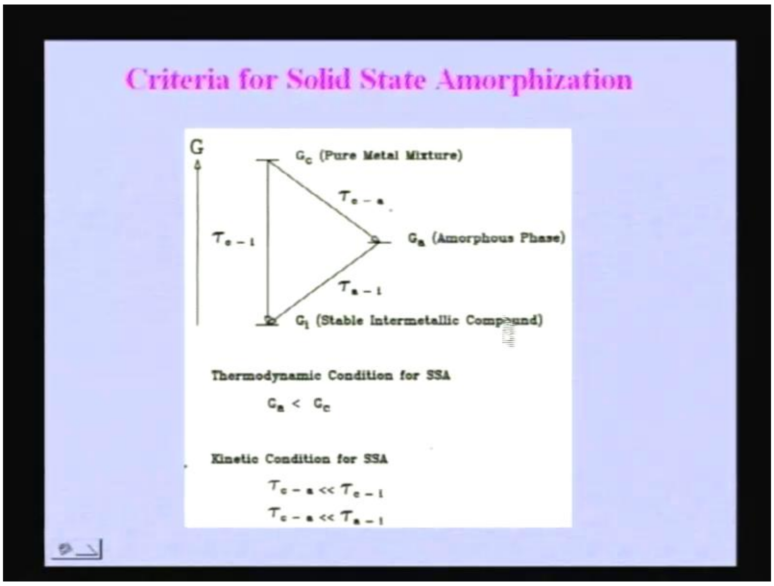
Criteria for Solid State Amorphization

Thermodynamic Condition for SSA

$G_a < G_c$

Kinetic Condition for SSA

$\tau_{c-a} << \tau_{c-i}$

$\tau_{c-a} << \tau_{a-i}$

And this is one thing which have talked about this it is some point time, what are the criteria for some amorphization, one thermodynamics criteria, kinetic criteria.

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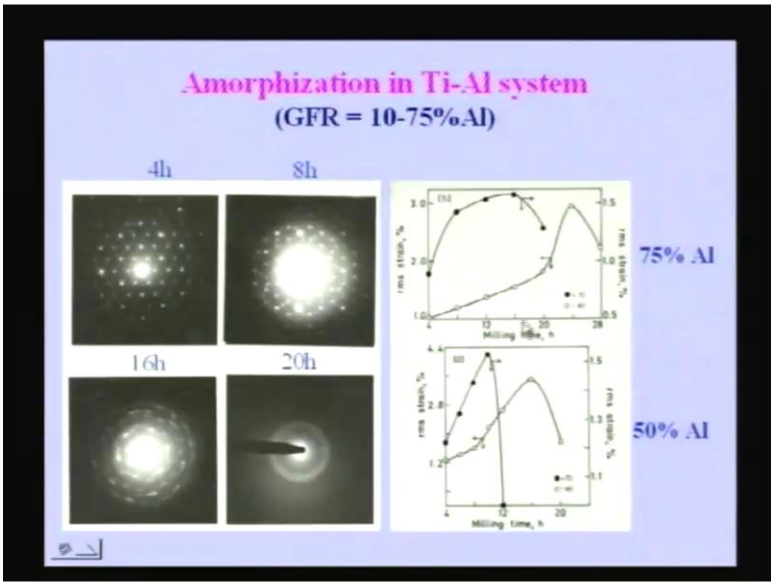

Amorphization in Ti-Al system

(GFR = 10-75%Al)

And we have also talked about, what is the strain critical strain that is required for amorphization to occur.

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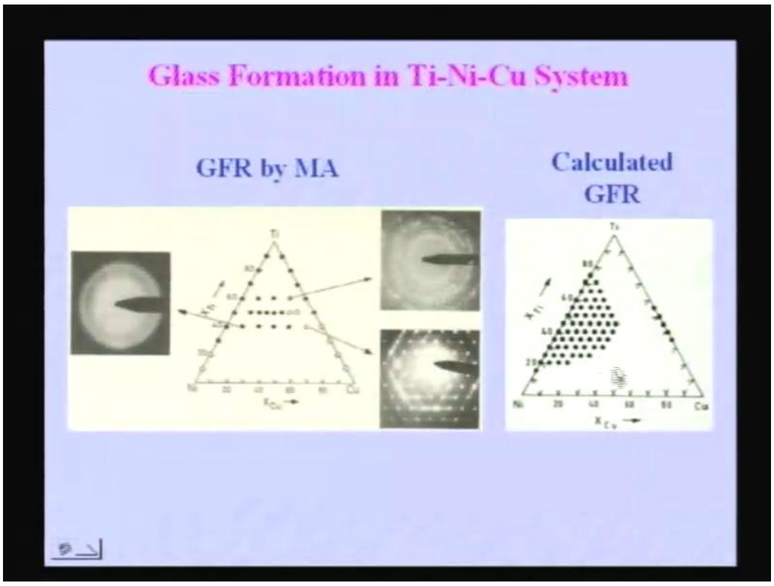

Glass Formation in Ti-Ni-Cu System

GFR by MA

Calculated GFR

And we have talked about, the calculated glass forming ranges thermodynamics. And which can be compared with the experimental glass forming ranges.

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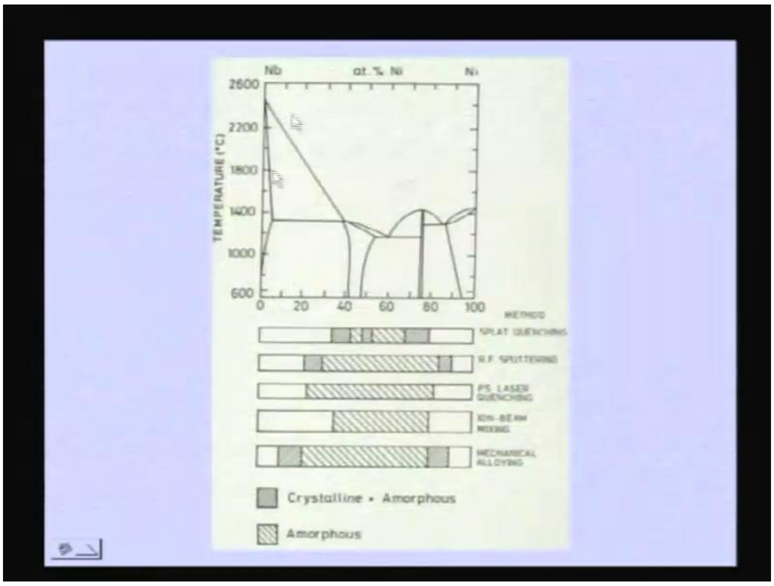

And this is another interesting thing. For one particular system, this is a nickel niobium system, where we are showing you what are the glass forming ranges that you can get by different techniques. You can see all these hatched once the big hatched once is all amorphous composition range.

So, you can see that range is very small for splat quenching, splat quenching means gun quenching, and then if you do r f sputtering or laser quenching or iron been mixing and mechanical alloying. Mechanical alloying shows you very wide composition range. So, the glass forming range can be very wide, and interesting thing also that by liquid metallurgy route.

That means, if you use rapid solidification, the glass formation always occurs near the eutectics. Particularly near deep eutectics. Why, because that is where liquid is stable and that is, where the T g is close to that of the T l. And that is why we have talked about glass forming criteria, such T r g reduce glass transition temperature. That is very high at the eutectic temperature.

So; that means, in case of nickel niobium, this is the composition around 60 percent is a composition, where you can easily get a glass by splat quenching. For example, you can see this is range by rapid solidification. Whereas, in case of mechanical alloying there is no such restriction, you can get it over a wide composition range.

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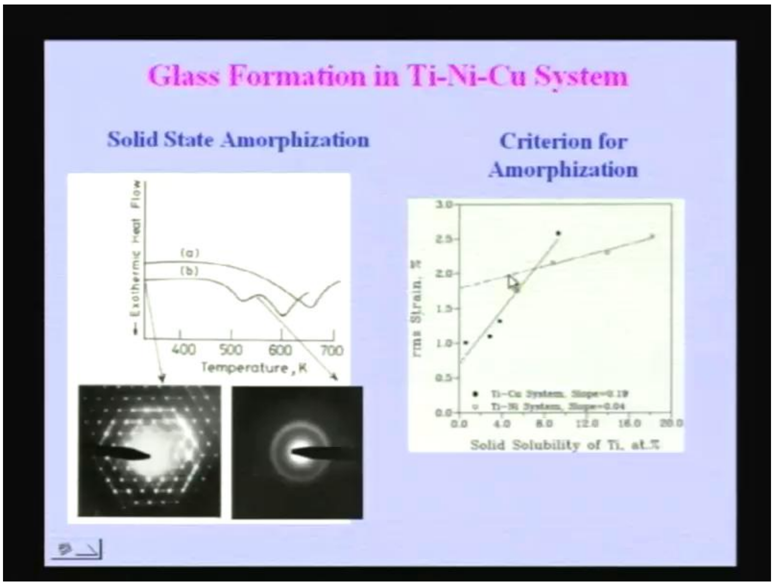

Glass Formation in Ti-Ni-Cu System

Solid State Amorphization

Criterion for Amorphization

And this is another criterion for amorphization, the strain criterion, which we have talked about it before.

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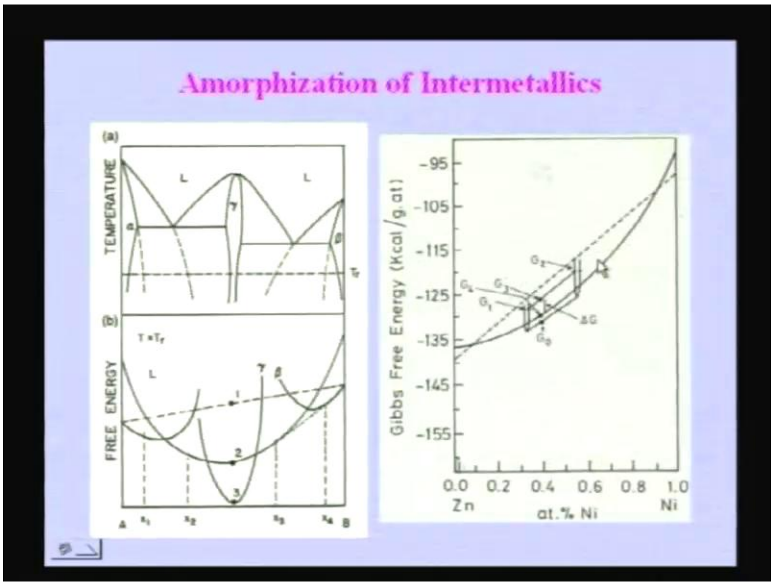

Amorphization of Intermetallics

And this is how an inter metallic can be made into an amorphous. We usually know if take a system like this, you have two solid solutions and both the ends. And one inter metallic at the middle. And if you draw the free energy composition curves, you can see an inter metallic has lowest free energy.

If you take the inter metallic has lowest free energy. And the liquid has a free energy like this. And the solid solution have a free energy like this, it is a easy for a solid solution to become an amorphous, beyond the T naught curves. If you choose this T naught curves, beyond that the solid has a higher free energy then the liquid. So, you can easily get a amorphous phase.

But, an inter metallic if has to become a liquid, it is not easy. Because, there is no direct driving force, the liquid always has a higher free energy then the inter metallic or the amorphous phas, has always say higher free energy then the inter metallic. So, what do we do? What we do is, when take such a inter metallic. And start doing ball milling, what happens is you are putting so much of the energy into the in to the system.

And because of the defects that you are putting when you put so many defects into the inter metallic. The inter metallic free energy goes up and when the inter metallic free energy goes up, it will you will come to certain condition. Where, the free energy of the inter metallic goes beyond that of the amorphous phase.

And once that happens, then suddenly there will be a driving force for the inter metallic with so many defects to transform into an amorphous phase. That is what exactly happens, when two inter metallic. When, an inter metallic tries to transform into a an amorphous phase. And when you take a mixture two inter metallic's.

Let us say two inter metallic's have been chosen here, one is this inter metallic another is this. And solid curve that you are seeing here is a free energy of the amorphous phase let us say. and the mixture of two inter metallic's has always the lowest free energy. Now, if you take the mixture of two inter metallic's, again start doing ball milling.

Then, the free energy of the inter metallic's goes up. And again, if you look at after some time of milling the free energy of the mixture of a inter metallic become something equivalent into the G 3. And that G 3 from G 3 to G 4, G 4 is the a free energy of the amorphous phase, there is a driving force. So, now the transformation can occur.

But, directly from the mixture of the inter metallic's one cannot have a amorphization. So, one has to put in some amount of defects. So, that the free energy can go up and then transformation can happen.

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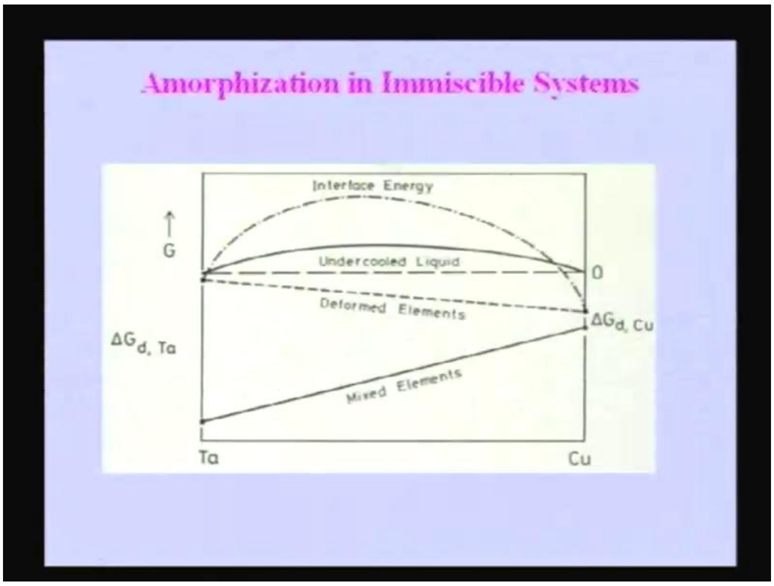

Amorphization in Immiscible Systems

And one can also have amorphization in immiscible systems. An immiscible system is like this for examples, if I take copper tantalum system, it is an immiscible system. And if take the tantalum metal and the copper metal, the free energies are given here. The free energy of the mixture is given by this, the line joining these two free energies.

And if you look at the free energy of the amorphous phase, the free energy of the amorphous space is something like this. Because, it as a positive enthalpy of mixing and positive of free energy of mixing. So, the free energy does not go like this. But, the free energy goes like this. And if the free energy goes like this, when you deform the individual metals.

And depending on the type of metal, copper cannot be easily deformed when compared to tantalum, tantalum has higher melting point. So, you can make it nano crystalline much more easily. So, as a result it becomes finer much more easily. So, it is free energies goes up to much higher level, than the free energy of the copper going up.

So, the dash line that you are seeing is a free energy of a mixture of the deformed metals. That means, where the defects have been introduced, and if you look at that and then put in the interfacial energy into it. There interfacial energy because of the nano crystals, whenever you have nano crystal you have a interfacial energy.

So, when you look at that over all free energy, because of the interfacial energy. And the defects everything put in. Then the overall free energy will be higher than that of the amorphous phase. And then you will have a driving force now for the such a deformed material with a lot of defects, and nano crystals to a transform into an amorphous phase. So, even in immiscible system can be transformed, this is not possible by rapid solidification.

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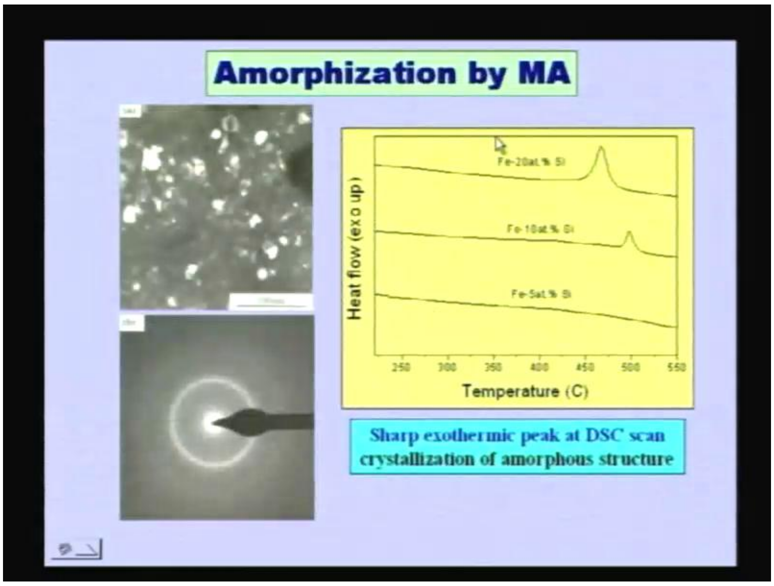

Amorphization by MA

Sharp exothermic peak at DSC scan crystallization of amorphous structure

And one can have amorphization by mechanical alloying below a certain a crystallite size we have seen this before.

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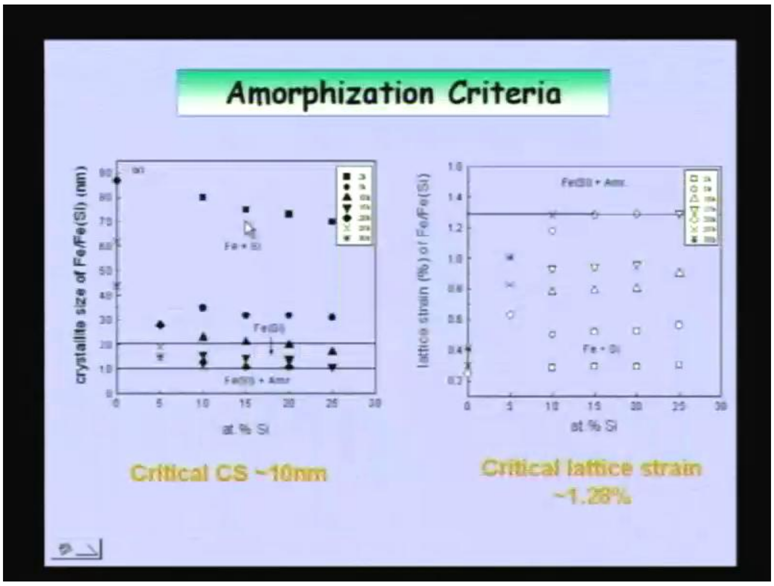

Amorphization Criteria

Critical CS ~10nm

Critical lattice strain ~1.28%

When you bring the nano crystals bellow a certain size of about a 10 nano meters or so. Sudden it becomes amorphous phase. And similarly beyond a certain strain it becomes a amorphous phase.

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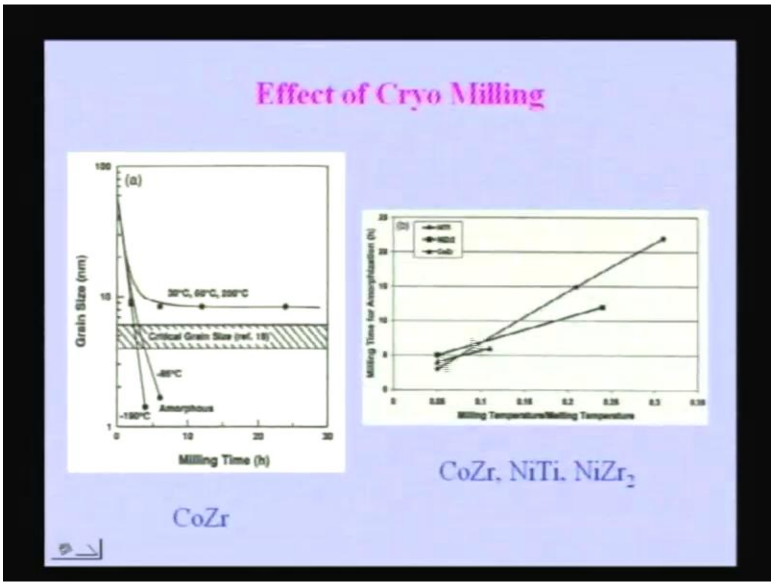

Effect of Cryo Milling

CoZr

CoZr, NiTi, $NiZr_2$

And similarly here is an example of the effect of cryomilling. When, you start ball milling at room temperature. This is a cobalt zirconium, you cannot a bring the crystallite size to very low level. The crystallite size is only above 10 nano meters or so, when you ball mill at 30 degrees or 60 degrees or 200 degrees these are all milling temperature.

But, if you reduce the milling temperature do cryomilling. For example minus 85 degrees and minus 190 degrees, the rate of decreases in the crystallite size can be very fast. So, as a result you come to that below the critical crystallite size, so that amorphization can be easily occur. So, cobalt zirconium can be amorphous very easily. So, similarly you can see, so the time required for amorphization is inversely prepositional to the melting temperature. The lower the melting temperature, the faster the amorphization will occur.

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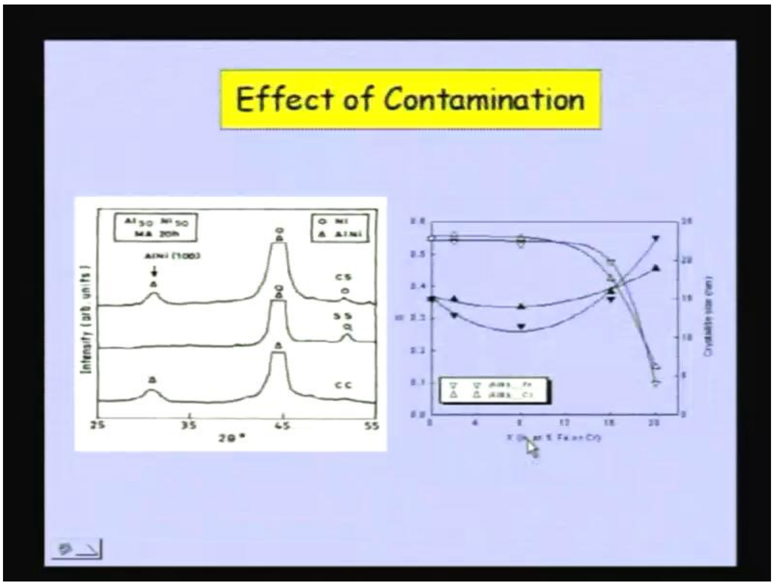

Effect of Contamination

And this is the effect of contamination. We know the contamination is one of the major problems by ball milling. But, sometimes contamination can be useful we have talked about it some point of time. Here, contamination can lead to what is called disordering into a compound. If you ball mill a N i A l into a tungsten carbide, you get an ordered a super latish reflection.

But, if you ball mill it in a stainless steel, you will never get a super latish reflection. That means it is completely disordered. That is, because the iron goes into the contamination, the iron coming from the balls. And the container it goes into the N i A l and reduces the ordering energy. And because of which the ordered the N i A l completely becomes disordered.

And once it becomes disordered it becomes ductile. And again another last point is the temperature of ball milling. Lot people have studied about this temperature, initially people thought the temperature will be very high. But, then later people have thought about it a lot and did a lot of modeling. And also some experiment there were some very ingenious experiment.

Such as taking a marten site, putting the marten site into the ball mill and start doing ball milling. And try to see what is the microstructure of this marten site, after some time of milling. And we know that marten site get’s tempered to various difference structure depending on the temperature of the tempering. So, if you look at the tempered structure, we can find out what is the temperature of tempering. So, what was the temperature during ball milling one can find out. What was the temperature at the impact of the ball to the powder. So, people had looked that and then could see that the temperature never goes beyond about 300 degree and so...

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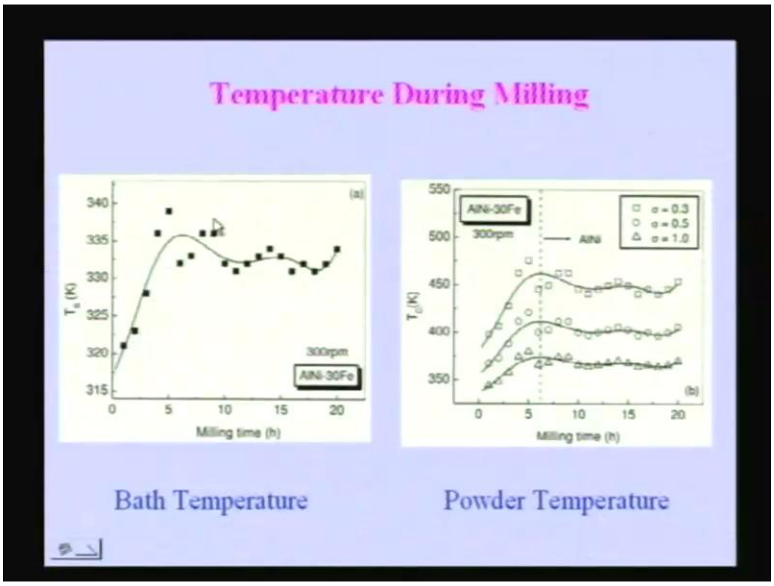

Temperature During Milling

Bath Temperature

Powder Temperature

And we did a lot of modeling. And try to measure the temperature of the tolvin bath. And try to have an equation, which correlates the actual temperature of the powder to the temperature of the bath. And we could see, the temperature never goes beyond 450 Kelvin, 450 Kelvin is about 200 degree centigrade.

So, you can never go beyond this. So, that is a kind of a temperature rise, that you can think of. So, in temperatures are never very high. So, everything is happening more or less at room temperature. But, why these kinds of process are happening at such low temperatures is because of the large diffusivities, because of the large number of defects that we are introducing. And the fine scale that has been generated, because of the generation of the nano crystals with this we will stop.