Advanced Materials and Processes
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Lecture - 5
Nano crystalline Materials Part – III

Yesterday we were talking about various synthesis techniques for Nano Crystalline Materials preparation.

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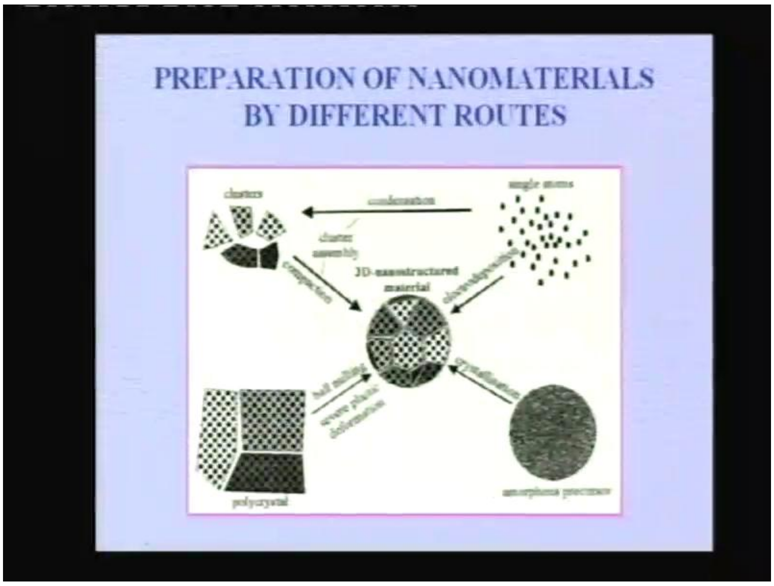

PREPARATION OF NANOMATERIALS BY DIFFERENT ROUTES

And we have talked about the techniques, which start from the vapors, and the techniques, which start from a liquid and the techniques, which start from a solid. So, basically the three sources for the synthesis of nano materials.

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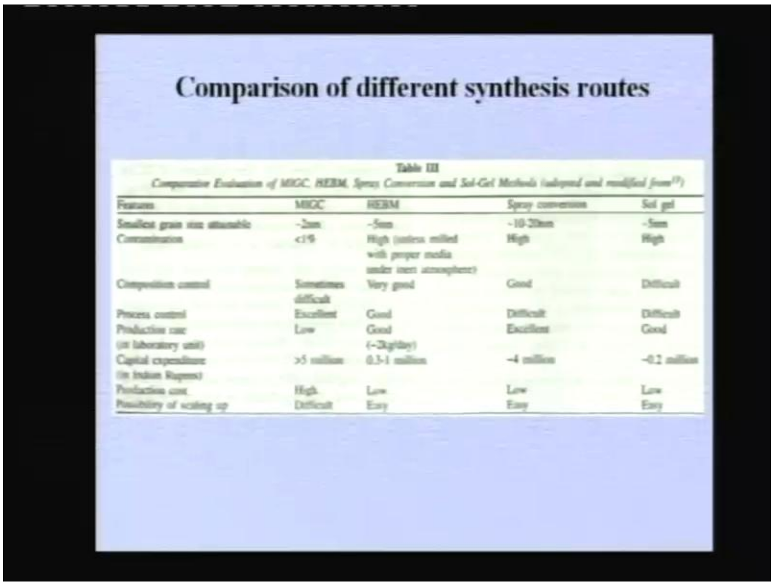

Comparison of different synthesis routes

Table III

Comparative Evaluation of MIGC, HEBM, Spray Conversion and Sol-Gel Methods (adopted and modified from[17])

Features	MIGC	HEBM	Spray conversion	Sol gel
Smallest grain size attainable	~2nm	~5nm	~10-20nm	~5nm
Contamination	<1%	High (unless milled with proper media under inert atmosphere)	High	High
Composition control	Sometimes difficult	Very good	Good	Difficult
Process control	Excellent	Good	Difficult	Difficult
Production rate (at laboratory unit)	Low	Good (~2kg/day)	Excellent	Good
Capital expenditure (in Indian Rupees)	>5 million	0.3-1 million	~4 million	~0.2 million
Production cost	High	Low	Low	Low
Possibility of scaling up	Difficult	Easy	Easy	Easy

I made a slide for you to understand, the comparison between these techniques. And this gives you some idea of various parameters. How we can compare different techniques, in terms of either there advantages or disadvantages over the other techniques. Here, we are comparing four different techniques, one is the modified inert gas condensation technique, which is people usually refer as MIGC.

Basically, it is a inert gas condensation technique. And has been improved to some extent by controlling the parameters inside to get a the best possible efficiency of conversion into nano materials from the vapor state. And the HEBM is basically high energy ball milling technique, which is from the solid state. So, one is from the vapor state, one is from the solid state. And the spray conversion technique and the sol gel technique are basically from the liquids.

So, only difference is in the spray conversion, you are basically taking the liquid and forming a spray. And then from that getting a nano crystals, this is similar to atomization. And then sol gel technique is basically a precipitation technique from the liquids. So, if you try to compare these on a number of parameters, starting from what is the smallest size that you can achieve.

You can see that, the gas condensation is the best. If you want to achieve the smallest sizes, because you are starting as I told you, it is basically a bottom up approach, this is what we talked yesterday. So; that means, you are starting from atoms. So, when you are starting from atoms, there is a chance for you to control the sizes to the smallest possible just stop them at the cluster stage itself, without allowing them to grow into bigger particles.

So, you can even achieve of the order of around 2 nano meters in such a technique. And ball milling is basically a top down approach we talked about it. So; that means, you are breaking down big crystals into smaller sizes. So, there you have limitations in reducing their sizes in principle, you can reach around 5 to 10 nano meters. So, it is very difficult to achieve very fine sizes in ball milling.

Particularly, we will talk about ball milling a little later, when we are going to talk about mechanical alloying. Here, what you have is when a ball hits a powder particle. A two process which simultaneously take place, one is the fracture, the particles fracture into smaller sizes. The second one is what is called the cold welding. Because, when a particle becomes a small fractured particle, there is a large surface area which is exposed now.

The surface area to volume ratio increases. When, the surface area to volume ratio increases, it becomes very reactive. And also it is surface area being very large, it can get welded to another particle. And as a result you have cold welding technique place, cold welding also occurs with the particles to the balls. That you are using for and also to the container walls. So, there is a possibility of cold welding of these particles to particles itself or to the balls or to the container.

So, this is one of the basic problems of if you want to say of the ball milling that you not only are grinding them to finer sizes. But, at the same time there is also a tendency of the particles to weld to themselves. And as result coarsening takes place. So, simultaneously reduction in the grain size and also coarsening takes place. And these to process simultaneously take place.

And depending on the actual conditions of ball milling, which one dominates is what is going to decide. Whether, you get the finer sizes or coarser sizes. If the rate of fracturing dominates, then you will get a finer sizes. And how does it depend on? That depends on the condition such as, what is the energy with which you are ball milling. And what is the temperature at which you are ball milling.

For example, if I do ball milling at very low temperatures. For example, there is a technique called cryomilling. That means, you do ball milling under a liquid nitrogen kind a conditions or at temperatures below the room temperature. Somehow you cool down the whole container and the balls and the powder. There are possibilities, that the whole container can be kept into liquid nitrogen or you can circulate liquid nitrogen, through the I mean on the walls of the container.

So, that you can cool the container. If you do that, we all know that every material becomes brittle at low temperatures. We have a that brittle transition temperature for every metal. So, because of that these powder particles become brittle at these low temperatures. And they can easily break. So, the rate of fracture dominates, rate of cold welding, because, at low temperatures welding cannot easily occur.

So, as a result you will have more of fracturing taking place. So, one can really reduce the sizes to a very low level. In addition, there is also one more factor which controls. What is the size minimum size that you can achieve? That is, the melting point of the metal itself, which you are grinding. If I am comparing aluminum with let us say tungsten. I have taken aluminum powder, ball milling it I am also taking tungsten powder ball milling it.

So, the finest size that I can achieve in ball milling is going to be different for tungsten and for aluminum. Why is that so? Because, the melting points of these two are widely different. And because of that, at the temperature of ball milling, ball milling we are doing at room temperature is not it, at that temperature, whatever temperature that we are using for the ball milling, if that is closer to the melting point of the metal. Then, there is a lot of diffusion that can occur. And as a result, you have more feasibility for the cold welding to occur. So, as result if I am melting ball milling low melting metals, the tendency for cold welding is more. And if I am ball milling high melting metals, then the tendency for fracture is more.

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For high melting metal is much more. Because, if I am ball milling at room temperature. Room temperature is like a we can consider it as a, you know cold deformation for tungsten. And if I am ball milling, let us say tin or led for example, it is like a hard deformation is not it, because I am already above the re crystallization temperature.

So, that controls whether you have more of grain growth and cold welding to occur. So, that the grains are going to be coarser. So, one can if you plot the what is ever is the smallest size, that one can achieve. As function of the melting point, you will see that there is an inverse relation between the size, that you can achieve to the melting point.

The higher the melting point, the lower the size that you one can achieve. So, one has to remember that, this there is when I say the smallest size is about 5 nano meters. That is, basically for the high melting metals. But, if it is a very low melting metal like led or tin that you are ball milling it. Obviously, you cannot achieve as fine as 5 nano meters may be above 10 or 20 nano meters. So, one has to remember that.

Then, spray conversion is basically atomization technique, were one cannot really achieve very low sizes. And then sol gel technique is again another technique. Where, it is a precipitation kind of technique form ions. So, as result one can really achieve finer sizes as fine as what you probably can achieve in the gas condensation, but not really.

So, fine because here you have precipitation from the liquid state. Whereas, in a gas condensation you have precipitation from the gaseous state, where they are really atoms or molecules which are in the gaseous state individual atoms are there. Because, we know in the liquids there is always a short range order. Because of the short range order there are already clusters in the liquid, whereas in the gas you have individual atoms which get separated out. So, one can talk of finer sizes in a gas condensation. Then, any technique that we can think of... And come to the other major problem of this kind of a technique is what is called contamination; contamination from the environment, during the process of synthesis of these nano materials, because whenever you are making a nano material.

For example, if want to make a silicon nano particles. For some electronic applications, such as may be some semi conducting applications. You do not want any other element to come into picture, because that is going to effect the properties of it. So, chemical contamination from the environment, whether it is the gaseous environment, that you have inside the chamber, which you are using for synthesizing.

Like a for example, oxygen contamination or hydrogen contamination or nitrogen contamination. That is one problem depending on the type of material, that you are synthesizing. For some materials may be contamination may not be a real problem depending on the real application. But, in some cases contamination can be a major problem.

The other thing could be from the tools, that you are using for synthesizing. For example, in ball milling we are using the balls, which hit the powder particles to make them final. So, depending on the material that we use for the balls, if that balls material is not very hard and if it is soft, there is possibility of erosion of these balls. And that can come into as a contamination.

So, if you look at the contamination basically gas condensation gives you the lowest contamination. The other techniques always give you contamination. Even, for spray conversion, we are basically doing atomization kind of thing using nozzles is not it. So, there can be contamination from the nozzles, because high melting liquid is going through the nozzles. So, one can have contamination from there.

So, in sol gel technique there can be contamination from the un reacted products is basically what you are doing is.. You are splitting a particular liquid into a nano particles of a metal and something is left out. That can contamination the powders. So, that you can have some un reacted products, which are left out in the material. So, that is one of the measure problems one has to control that then comes to composition control. We have more or less very good control in most of the techniques. Excepting, the sol gel as I told you, because always un reacted products are left out. So, it is very difficult to have a good composition control.

In such a thing unless, there is a way to separate them out very easily. Otherwise, in ball milling spray conversion and also gas condensation more or less you can have good control, but the only problem in gas condensation, particularly when you want to make compounds. For example, I want to make a nickel aluminum compound NIAL. How do I make a NIAL by gas condensation technique? One possibility is to take NIAL melted in gut, which is already melted by some other method.

And put it in a crucible melt it. And then allow it to evaporate and these vapors are allow to condense on a your cold finger. But, then when the these vapors are condensing, the vapor pressure of aluminum and the vapor pressure of nickel are different. Once, it is evaporated, the aluminum and nickel are there in the vapor as separate entities. And these two are suppose to come together and form a again NIAL compound nano particles.

So, as a result you may not exactly get the 50, 50 composition, but slightly a different composition. So, that is one of the problems and to avoid this people also do another technique, that they melt the two separately. So, you have two crucible inside the chamber, you separately melt nickel at a different temperature, aluminum at a different temperature two different heaters are provided.

And then these two vapors go and mix inside the vapors state. And then they are allowed to form the nano particles. But, their also a good control becomes very difficult. So, as a result the control of composition is to some extent is not very easy, particularly when you to want form compounds. If you want to form pure metals there is absolutely no problem.

And we cannot even talk about composition control, in case of pure metals. Only, when we are talk of alloys, then the question of composition control comes into picture. So, that is something which is important to note. And then process control is excellent in most of the techniques. Particularly, the gas condensation and high energy ball milling, we can control the process parameter very easily spray conversion also it is easier, because of the high temperatures, that we are using in spray conversion. The process control becomes slightly difficult. And the sol gel, as we see that it is a precipitation technique. And controlling the conditions such that, only one of those required element precipitates is parameter one has to really control. So, that nothing else precipitates out, but whatever there should be a selective precipitation of what you are interested in.

So, that has to be controlled very well. Then, the production rate this is an important thing as for an engineer or for someone who wants to commercialize the process. It is very low in gas condensation. We know that it is the gases we need a huge chamber to produce a small quantity of nano particles there. And then ball milling is good, but not very high, we can produce about 1 to 2 kg of powder in a day.

And then you have spray conversion and sol gel techniques, which are basically atomization and chemical deformation techniques, were one can have larger quantities. In principle these two techniques can have a higher. But, at the same time considering the difficulties with the other techniques people do not really readily go into these techniques unless, you are specifically looking for one particular type of a metal, which is easily can be made by these techniques and an a larger quantities.

So, one has to always consider many aspects not just the production rate. In fact, next month we are going to have what is called a one day workshop on how to improve the production rate of ball milling. So, how do we scale it up, we are going to come it in a minute. That possibility of scaling up, it is very difficulty in gas condensation.

Because, you know that if you want to really scale it up, the chamber sizes that are required are huge. And the whole chamber has to be evacuated, because you have to evaporate the metal. So, as a result it is very difficult. But, the other three techniques are much easier and we are looking at what are the problems that we are going to face, when you are scaling it up and to larger quantities.

Particularly defense people are very much clean to produce these nano composites on a larger scale. They, have given as a big project and they want us to look in to the all the aspects of what are the problems, that you will face. If you scale it up to let say about 50 kilo's or so per day. So, if you want do that what kind of a ball mills that even has to consider.

What should be the design criteria of such ball mills. And what are the contamination problems, that you can face and how to overcome such a problems. So, we have going to have a one day workshop, where the experts in ball milling are going to come here. And going to deliberate on that and discuss about this particular problem.

And come up with some solution to overcome, that they are willing to give you an a few cores to set up a plant on producing larger quantities of such nano composites. So, an production cost if you consider it is very low for the three techniques, which are ball milling, spray conversion and sol gel. Sol gel basically you need only chemicals nothing else.

So, if you as long as chemicals or not costly, which you are considering it is a very low cost process. But, gas condensation as you know you need a lot of both capital cost and production cost are going to be very high for the gas condensation technique. Expecting that, gas condensation technique is only technique. When, you want to really produce few clusters. So, that one has to remember that depending on the actual requirement. So, one has to chose, one cannot say that this technique is better than that technique. So, there all complementary to each other depending on the type of application one has think of it.

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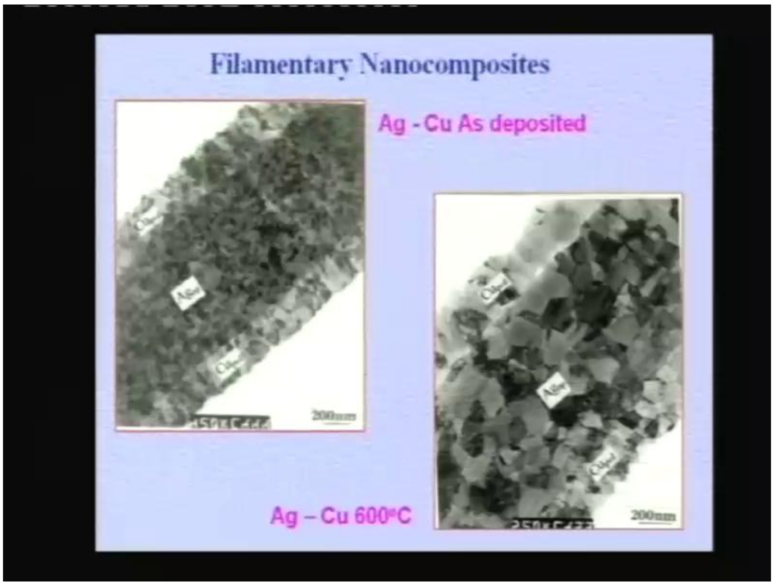

Filamentary Nanocomposites

Ag - Cu As deposited

Ag – Cu 600°C

So, then we were talking about various nano materials. That one can synthesis, this is one example of what are called filamentary nano composites. One can produce as I told you layered structures. This is such a layered structure, which is cross section. So, layer structure of for example, copper nano layer and sliver nano layer have been produced. And which have been section and we are looking at one of those sections and one can do.

For example, in TEM what is called In-situ heating experiments? Have you ever come across characterization using TEM. If you go to TEM, there are certain transmission ultra microscopes available. Where, there is a possibility of heating the sample to at least above 700, 800 degrees centigrade or so. And when you kind of heat these nano particles from room temperatures, you can really see in-situ how these nano particles grow.

What is the tendency of these some of the a particles have a tendency to grow very fast. Particularly, nano crystalline pure metals grow very fast and nano crystalline alloys have a tendency to have lower growth rates. Particularly, because the diffusivities or restricted when you alloy an element with the another solute.

So, unless both of them defuse very fast, you cannot have a growth. Because, any grain growth has to be controlled with basically the diffusion rates. So, as a result if you put either alloying elements which is called solute drag effect. So, whenever you put a solute atom into that. So, the growth rates are restricted, because of what is called solute drag effect.

And the second way of controlling the grain growth is what is called putting some pinning agents, which is people usually refer to as gene pinning effect. So, when you put some hard particles at the grain boundaries, which prevent the grain growth of these particles will come to those things a little later. So, this one such example of sliver copper as deposited and heated to 600 degrees in-situ.

So, what happen how the nano particles grow. You can see when you heat to around 600 degrees centigrade which is almost more than half of the melting point of sliver. So, you still retain above 52,000 nano meter particles. When, you start with about 10 to 20 nano meter particles.

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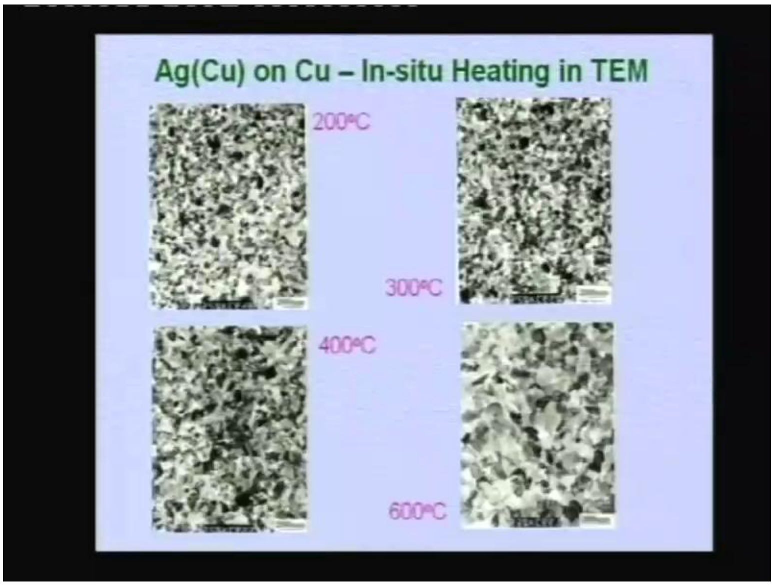

Ag(Cu) on Cu – In-situ Heating in TEM

And one can do in-situ various temperatures. So, the same sliver the only difference is sliver copper alloy has been deposited on copper here. And what we are looking at is a sliver copper alloy region. The copper substrate is not shown here. And if you look at that, heated to 200 heated to 300, 400 and 600 how the grain growth occurs. One can talk about, what are called growth kinetics.

What are called grain coarsening kinetics, one can do all that as a function of a temperature. And usually in these materials for example, if you compare this with the previous picture this is also 600 degrees. And here you have on the right bottom is also 600 degrees. You can see, the grain sizes here are much finer than what you see ((Refer Time: 22:18)) in the pure silver which is deposited on copper. So, that can give you an idea, that if you have such a alloying elements induced into the copper into the silver you can reduce the grain growth.

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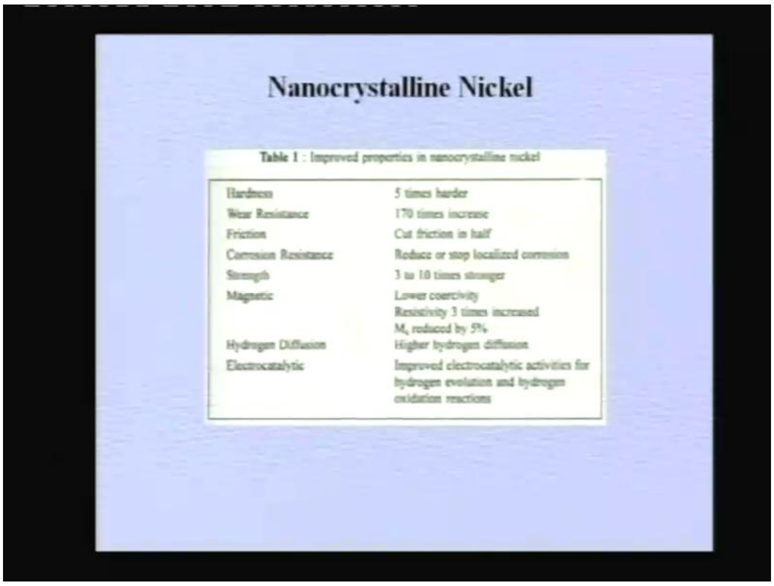

Nanocrystalline Nickel

Table 1 : Improved properties in nanocrystalline nickel

Hardness	5 times harder
Wear Resistance	170 times increase
Friction	Cut friction in half
Corrosion Resistance	Reduce or stop localized corrosion
Strength	3 to 10 times stronger
Magnetic	Lower coercivity Resistivity 3 times increased M_s reduced by 5%
Hydrogen Diffusion	Higher hydrogen diffusion
Electrocatalytic	Improved electrocatalytic activities for hydrogen evolution and hydrogen oxidation reactions

There are also additional advantages. Here, is a one case of nickel. If you make a nano crystalline nickel, what kind of advantages one can achieve. When, compared to normal, typical, poly crystal in nickel. If you look at, the hardness the hardness would be above 5 times higher. And look at the wear resistance is about 170 time increase you can achieve.

This has been experimentally verified and these are the results obtained from the experiments. So, one can really think of a wear resistant coatings on surfaces of some substrates, wherever you want to increase the wear resistance a with nano coatings of some material such as nickel.

Nickel is a pure metal, definitely if you can have a compound counted on substrate, you can have much higher wear resistance. Even with pure metal, if you can achieve about 170 times higher wear resistance. You can imagine, definitely with inter metallic compounds are some oxide nano particles. You will achieve much higher wear resistance, then frictional coefficient decrease by half.

So, you can have very smooth surfaces without any friction, because the grain sizes very small. So, you can have much better smoothness as the as per as the surfaces is concerned. And once, the frictional coefficient decreases you can have better wear resistance. Because, wear resistance is also connected to the frictional coefficient.

Then, corrosion resistance this is another interesting thing. Though we think of you are making it nano. That means, the grain boundaries are increasing the number of grain boundaries are increasing. And we know that, each grain boundary acts as a reason for corrosion. But, at the same time when you increase such large number of fine grain boundaries.

You can improve the corrosion resistance of material. We our self have seen a number of alloys that the corrosion resistance and oxygen resistance of a material increases when you make it nano. Because, basically what you are doing is... You have definitely each grain boundary will act as a nano and corrosion will definitely occur. But, corrosion now occurs uniformly throughout the material on a very fine scale there is no localized fitting that takes place.

And because of that, you can have an improvement in the corrosion resistance of the material. So, one can improve the corrosion resistance. And strength; obviously, increases to the large extent 3 to 10 times increase in the strength one can achieve. And they effects on the magnetic properties, coercively decreases, resistivity increases. And the magnetic saturation, saturation magnetization reduces by about 5 percent.

And this is one more important thing that, one of the measure advantages of using nano crystal materials is for there. What kind of a application? Can you think of the first application that one can think of the moment, you think of a nano material is a catalytic application. Because, you have a high surface area to volume ratio forget about grain boundary properties and all, just using the high surfaces area to volume ratio. One can think of them, as good catalyst and they have been compared with a number of commercial catalyst. We our self have done it in here. And we see, that the catalytic properties are improved to a large extent I will show you one more slide later. How one can improve the catalytic property and you can see hydrogen evolution can be improved and oxidation reactions. And any reaction where catalyst is involved can be improved by using nano crystalline materials.

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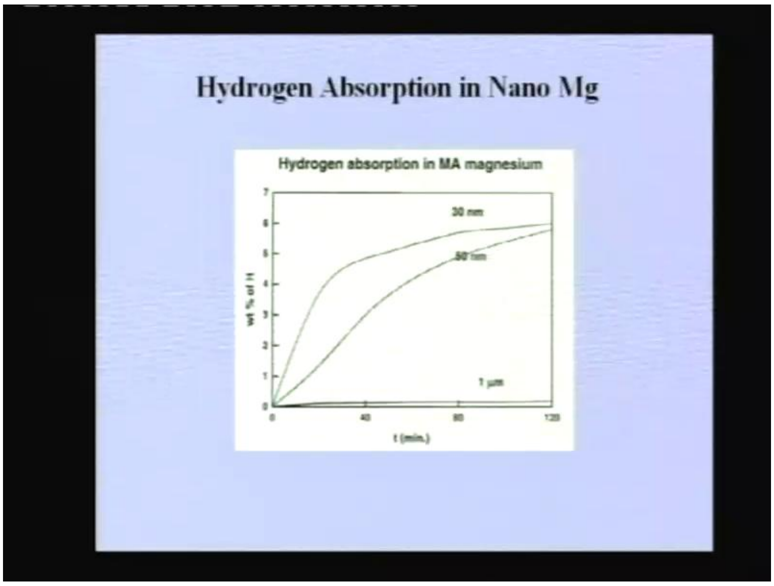

Hydrogen Absorption in Nano Mg

Here is one example of how a micro material compares with a nano material for hydrogen absorption in magnesium. So, if you consider a micron sized magnesium, and how it observes hydrogen, you can see the amount of hydrogen observed is very small. This is the effect of surface area to volume ratio. And the moment you make it about 50 nano meters you can see almost about 5 percent of hydrogen can observed depending on the time of absorption.

So, if you can have a longer time of folding. Obviously, you can observe more, but at the same time there should be a saturation limit at higher longer time. And the saturation limit is of the order of around 5 to 6 percent. When, compared to almost about 0.1 or 0.2 percent, that one can achieve in a bulk material.

So, one can see that there is a lot of advantages of using these nano materials. For example, you might have heard of the new materials which are coming up batteries, which are based on hydrogen absorption, absorption desorption. People think that, this is going to be a new energy source in future. Where, we are going to have problems in terms of the petrol, the amount of petrol being depleting in the surroundings.

So, as a result at some point of time may be about after 50 years also. We may not have any petrol or diesel left out in the crust. And under those conditions, one has to think of alternate energy sources. So, hydrogen can be one, where there are materials now a day's available such as magnesium, magnesium nitride zirconium alloys. Some lanthanide alloys available, which can absorb and desorb, the hydrogen depending on the condition that you are using.

So, we can use it as a source like a capacitor. Capacitor is nothing but basically where you can store the electricity. And then give out electricity whenever you want give out. So, same thing like a capacitor you can really use it to absorbed all the hydrogen, under certain conditions. In fact, there is one professor in BHU in Prof Oham Mohan.

Student: ((Refer Time: 28:45))

Yes correct.

Student: ((Refer Time: 28:49))

Correct.

Student: ((Refer Time: 28:52))

Yes, there is one professor O M Srivastave in BHU. I have seen in his lab. He keeps a motor bike, which runs on this hydrogen. He has made a number of magnesium based alloys and which can observed this hydrogen. So, there instead of a petrol tank you have a tank containing this material.

So, you have a hydrogen it is like a whenever the you need hydrogen to be charged into the material. You take it filling station, like you take your car to you are filling station to fill it with petrol. You fill it with hydrogen. And once it is filled for a number of cycles it can work out. And once, you think that because of leakage or whatever it is the hydrogen is depleted. Then, you again take it a filling station again fill it with hydrogen.

And once, you fill it with hydrogen at some point of time during the process, it can desorbed the hydrogen. And the once the hydrogen is desorbed. That is used for oxidation and then it generates energy. And with that energy one can move the vehicle. So, there is a vehicle like that in India itself people have done a lot of work on that. So, these are new things that are coming up, particularly with the invention of nano materials.

Because of these nano materials are available. You can have large surface area to volume ratios, grain boundaries are more open structures, large volume fraction of grain boundaries. One can have large absorption of hydrogen, only thing that you need is a material which can also desorbs.

Depending on the conditions, if it only absorbs and does not desorbs, you will have a problem. So, if you can change the conditions, we should be able to the give out hydrogen and if it can give out hydrogen we can use that. So, this is a new energy source that is coming up. And particularly because of these nano materials, we have talked about this.

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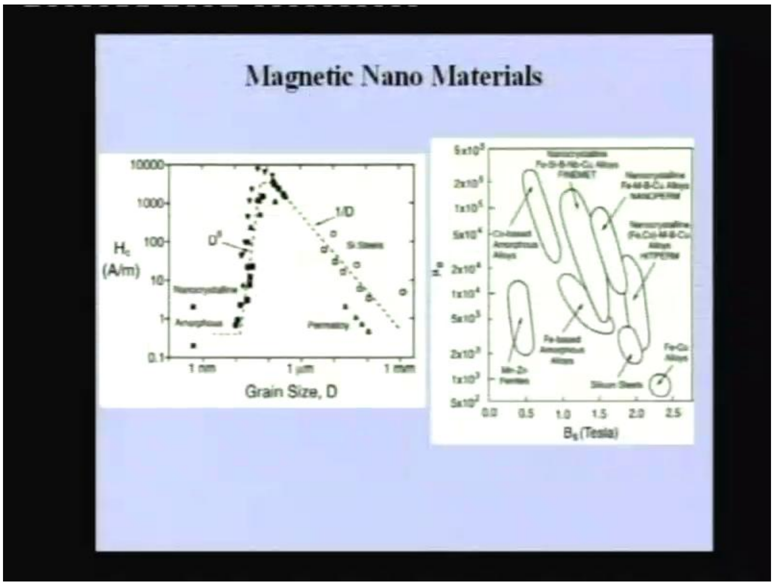

Magnetic Nano Materials

This is again magnetic nano materials. There is a lot of work going on magnetic nano materials. When, you come to the nano materials there is some interesting things that happen in a magnetic materials. You know about the traditional magnetic material, what is the most commonly used soft magnetic material. You all know about it.

Student: ((Refer Time: 31:14))

Iron.

Student: Silicon.

Iron silicon alloy with about 4 percent silicon. All our transformer force are made of aluminum silicon alloy. So, their actually what we do is that, we try to grow as big crystals as possible. In fact, there is a process by which you role it and nil it to generate force grain structures. Why, because if the grain size is smaller you have higher coercivity.

If you have higher coercivity the material does not behave as a soft magnet. But, it tends to become a hard magnet and the hesitancies loop becomes larger. The higher the coercivity means, the larger the hesitancies loop. The larger the hesitancies loop means higher losses. And these losses resulting heating up your magnet during the process.

So, as a result a soft magnetic material is always characterized by the smallest hesitancies loop is not it. So, if you want to have a smallest hesitancies loop, you have to have course grain material. What you see here is a plot on the left side, which shows how the coercivity changes as a function of grain size. As you decrease the grain size, you see that there is a d 2 the power minus one type of a law that the coercivity increases with decreasing grain size up to a certain level. Till recently when the nano crystals have not really evolved, people worked only in that domain. Where, people know only that yes the coercivity increases with decreasing grain size. And then so that is why everybody was interested only how to decrease the coercivity by increasing the grain size.

But, when you come to at region, where the grain size comes closer to the domain size magnetic domain size. Then, you have because of the thermal excitations inside the material, you will see that the coercivity drastically falls. You will have a d to the power six type of a law instead of b to the power minus 1. And the coercivity suddenly starts dropping, when you come to a nano region.

And now, people are able to generate very high magnetization materials, soft magnetic materials with very low coercivity using nano materials. But, there is a limit, if you go to a very small sizes of the order of less than 10 nano meters or so. You go into another domain which is called super magnetic.

Where, the coercivity is almost 0 and material does not behave really as a magnetic material. But, it become super para magnetic material. So, because the grain size is so small, that it is much smaller than the domain size and yes.

Student: amorphous.

Amorphous materials.

Student: ((Refer Time: 34:18))

That is, basically because you are using on a especial type of material which are iron based materials, which have high magnetization. So, if you use such material such as iron, cobalt based, nickel based which have very high magnetization, one can really use them. Otherwise, usually when you go to very small sizes particularly, in the case of hard magnetic materials, when you go to very small sizes it does not behave as a good magnet.

So, people want to really avoid such small sizes. But, again as you if you into amorphous state as he pointed out there are advantages. For example, that is one of the reasons why metallic glasses have really prospered. And there is a lot work that has gone into by making the metallic glasses, particularly iron, boron type of glasses, which have been made as transform core material.

And with a very low loses, the lowest loses that people have made is with those bulk metal metallic glasses. Those days there were no bulk metallic glasses, only metallic glasses made of the melt spinning.

Student: ((Refer Time: 35:26))

The inversion occurs basically, because when the grain size comes closer to the domain size. When, you are talking of about domain sizes are of the order of about 20 to 50 nano meters most of the materials. Or about 100 nano meters depends on the type of processing conditions of course. But, it is always less than 100 nano meters the magnetic domain size.

So, when the grain size is much bigger then magnetic domain size, within a grain there are a number of domains. So, as a result the magnetic domains when you apply a magnetic field. They, get aligned into the direction and the grain boundaries do not really increase the magnetization, but at the same time act as obstacles for the magnetic flux to flow.

And because of which the coercivity increases, but when the grain size become almost equal to that domain each grain becomes a domain. So, as a result that grain acts as a magnetic particle, each domain acts as each grain acts as a magnetic particle. And because of which the grain boundary effects get reduced. And then you will see that the coercivity drops significantly.

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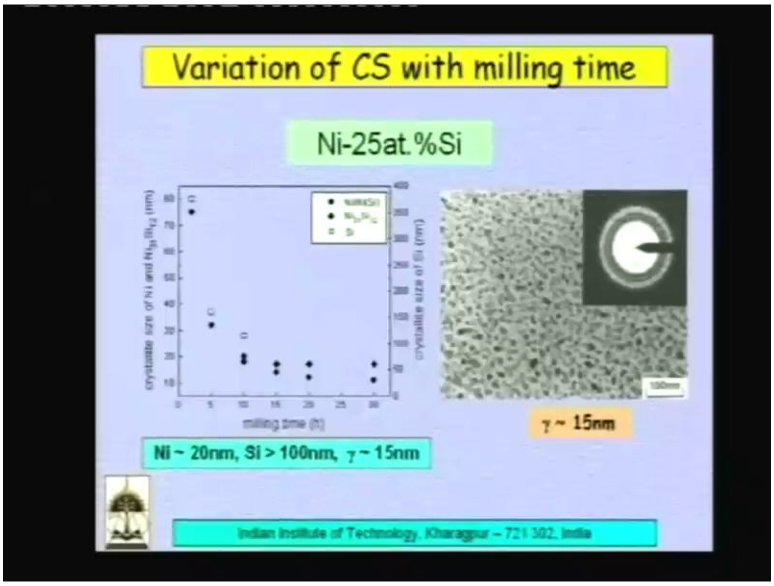

Variation of CS with milling time

Ni-25at.%Si

γ ~ 15nm

Ni ~ 20nm, Si > 100nm, γ ~ 15nm

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So, there has been a lot of studies on a number of materials. Where, people have proved that it comes down. This is, that plot that I have shown you is not just for one material, the points that are there on that plot are a combination of a large number of alloys. So, irrespective of the alloy people have seen similar affect we have talked about these things.

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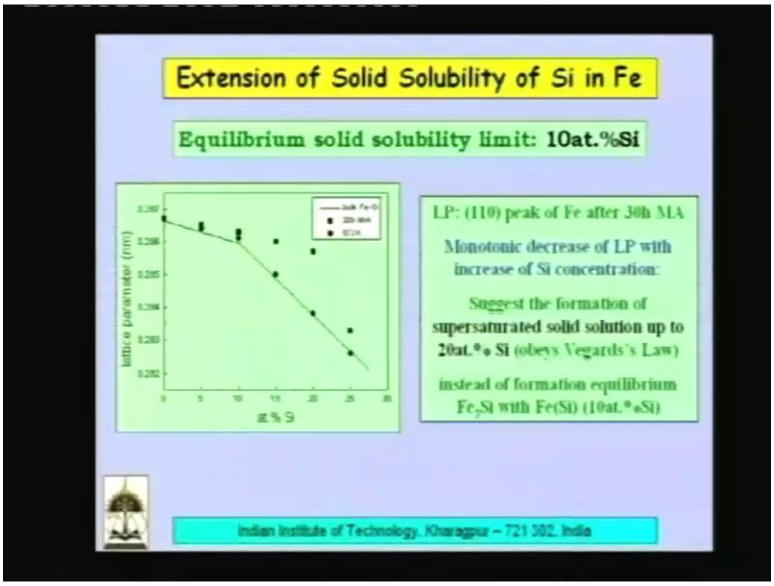

Extension of Solid Solubility of Si in Fe

Equilibrium solid solubility limit: 10at.%Si

LP: (110) peak of Fe after 30h MA

Monotonic decrease of LP with increase of Si concentration:

Suggest the formation of supersaturated solid solution up to 20at.% Si (obeys Vegards's Law)

instead of formation equilibrium Fe_3Si with Fe(Si) (10at.%Si)

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Let us talk about the solubility, one of the very important thing for a metallurgist. When you want a an element to be soluble in another element. We have a limitation in terms of the Hume Rothery rules is not it. We know that Hume Rothery rules give us a restriction on what is the solubility limit.

Some elements are able to be this soluble in another element very easily. Whenever, the size factor is very small, whenever crystal structure of the solute is same as that of the solvent. And particularly, the other two factors which are the electro negativity factor and the valence factor are favorable.

So, when you have all favorable conditions, then only you get a large solubility copper nickel is one example. But, there are also exception such as silver, copper. Where, we know that though most of the conditions are more or less satisfying. But, you do not get a isomorphs system there, but you get a eutectic system there. In fact, that is in the reason for the development of a new field called rapid solidification.

When, we come to the RSP we will talk about it that silver copper was the starting point for fall though way to develop this new technique of what is called melt spinning or gun quenching technique. So, we will come to it a little later. But, the thing is that as I told you, if you can have a larger solubility. You have advantage on two accounts, one is that solid solution strengthening can be improved.

Second you can have a large volume fraction of the precipitates, which can give you higher strengthening, so in order to achieve that people want to have larger solubility. But, hume rothery rules say that no, no, no sorry this is not possible. Under equilibrium conditions mind it, it is all whenever we talk Hume Rothery rules they are all under equilibrium conditions.

Now, if you can do non equilibrium processing such as rapid certification or ball milling or any such process, one can have extension of solid solubility. We are now not talking about that. But, we are talking about nano crystalline materials, that in a nano crystalline material. Because of the large volume fraction of the grain boundaries, which are much more open structure. Then, the grain boundary itself we can have a larger solubility possible.

And that is what you see in this particular plot, that what is plotted is the lattice parameter of a an iron silicon alloy with a different amounts of silicon. If you take different amounts of silicon starting from 0 to up to above 25 percent, and plot the lattice parameter achieved during ball milling, this is done by ball milling as a function of the silicon, what you see is that lattice parameter continuously decreases with a change in the slop at 10 percent, basically that is coming.

Because, that is a equilibrium solid solubility. And this is the plot that you get, if it is under equilibrium conditions. But, if you take a as mechanically mild condition, what you see is those square dots that you see there. So, there is a continuous decrease in the lattice parameter, which indicates a continuous solubility of silicon into the iron. Suggesting that, you can have an extension of solid solubility up to above 20 percent in such a iron, without really the Hume Rothery rules coming into pictures.

Under equilibrium condition, you cannot have more than 10 percent. What you see the circular dots or equilibrium condition, which are obtained by heating the same alloy to high temperature. If you heat same alloy you lose the extension of solubility, this we know. Because, extension of solid solubility is only meta stable extension.

If I heat it the second phase, which is in this particular cases, the second phase if F e 3 S i which precipitates out. And then you lose the solubility expression of solubility. So, but under the all mechanically alloyed conditions, because you are producing nano material and you can have a extension of solid solubility.

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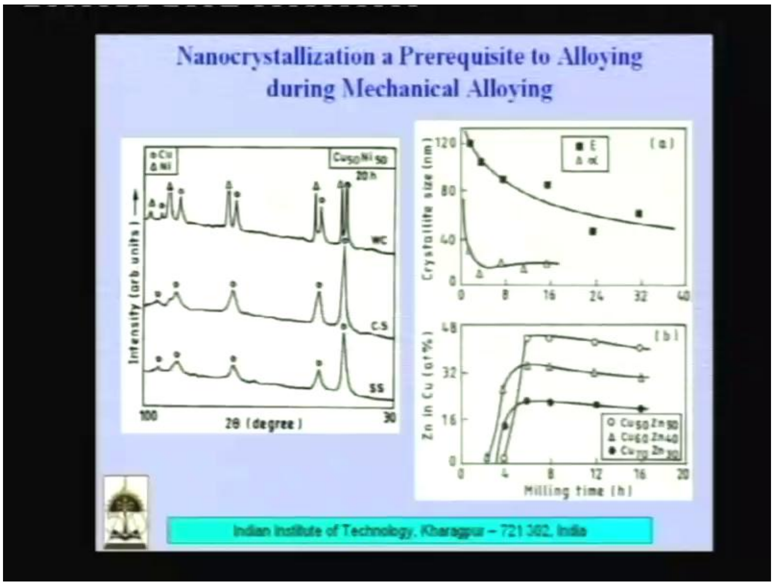

Nanocrystallization a Prerequisite to Alloying during Mechanical Alloying

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And this can also be seen in a number of systems. This is one example of copper nickel and copper zinc. Where we say nano crystallization is a prerequisite for alloying. If you want alloying to occur large quantity of solute atom to dissolve into the solvent atom, you need nano crystallization to occur.

So, that is the first step unless it becomes nano crystal, it does not the solute atom does not dissolve into the solvent atom. And that is proved by this plot will try to have look at the right plot. Where, you see the crystallite size of let us say alpha in copper zinc, what is an alpha phase, in a copper zinc phase diagram what is an alpha phase.

Yes, you all have seen copper zinc braces are known to you. Any one, alpha phase is a solid solution of zinc in copper, it is a terminal solid solution. So, look at the crystallite size of the alpha phase, which is shown here, that when the crystallite size of the alpha comes to as increase the ball milling time. The crystallite size decreases and when you reach around 4 hours or so the crystallite size reaches about 20 nano meters.

The lower values are not really shown here. And it more or less asymptotically increases at lower time. So, when you reach around 20 nano meters, you will see suddenly the solubility of zinc in copper suddenly increases. How do you know that this is happening? When you look at the X r d pattern, how do you get this crystallite size. Do you know how to people calculate the crystallite size.

Student: ((Refer Time: 43:43))

Peak broadening from the peak broadening one can calculate the crystallite size. So, if you look at the copper peaks. You will see that as you keep on doing ball milling, the peak broadening increases. And the moment the broadening reaches a particular critical value, suddenly the peak start shifting. The peak shift basically means what, the lattice parameter has changed. And why does a lattice parameter changed, when an element dissolves into it.

So, you see that the peak shift occurs only when the broadening crosses a critical value. That means, when the crystallite size reaches a critical value. Till then the peak does not shift and the solubility is 0. This is true irrespective of the composition that you choose. For example, here 30 percent zinc, 40 percent zinc, 50 percent zinc, three different compositions are compared. For all of them, you see the similar plot suddenly there is a jump in the solubility.

So, once you reach that particular critical crystallite size, suddenly you see that zinc starts dissolving into copper. And then till then it does not dissolve. This is true, even in copper nickel, if you have a look at this here is an example of one composition, which is ball milled in three different milling media. That means, the balls and the container that is used is called milling media.

Here, one is tungsten carbide W c and chrome steel and stainless steel. You may asked, why should there be an affect of the milling media. You can see interestingly, that if you look at the top one tungsten carbide, you see the peaks of copper and peaks of nickel separately. That clearly tells you, that the alloying has not taken place. Copper is remaining separately nickel is remaining separately.

The both have not really become an alloy, there is a pure metal mixture of copper and nickel, but if you look at the bottom two. The two peaks have merged into one peak; that means, an alloy are solid solution has formed. And if you carefully look at it, the peak broadening here in the bottom two cases is much larger than the peak broadening the top two cases.

That mean, the crystallite size in the two bottom cases is much smaller than the crystallite size in the top case. In fact, when we have calculated the tungsten carbide case keeps you about 200 nano meters, in that bottom two you get about 20 nano meters, why is this so. This happens basically, because when you ball milling in a chrome steel or a stainless steel. There is a contamination of iron coming from the balls.

When, the iron goes into copper and nickel, there is a solid solution strengthening that takes place. When, iron which is coming from as a contamination from the balls into the copper powder, dissolves into it immediately there is solid solution strengthening. Once, that happens the powder particles become more hard they become harder.

And if they become harder, they can break more easily. The rate of fracture increases when it become harder. So, as a result you will see when the particle when there is a contamination particle become harder. And when they become harder, the grain size decreases more rapidly. That you can easily achieve nano crystals in such a condition, when compared to tungsten carbide, where there is no contamination.

And unless you go to lower temperatures, you cannot achieve the low grain size there. Because, copper and nickel are ductile materials, usually in ductile materials the fracturing does occur very easily. Only in brittle materials like, oxides are real brutal materials. You can easily have more and more fracture. And finer grain size that can be achieved.

So, this is one again indirect prove to show you, that nano crystallization is a prerequisite for alloy. Unless it becomes nano crystal alloying cannot occur. This has been observed in a number of cases. So, you can see once a material becomes nano crystal so many things happening. Magnetic properties, physical properties and mechanical properties and even alloying itself is going to change, when you go into a nano crystal design. So, there are, so many fascinating avenues that open up when you go to nano crystal.

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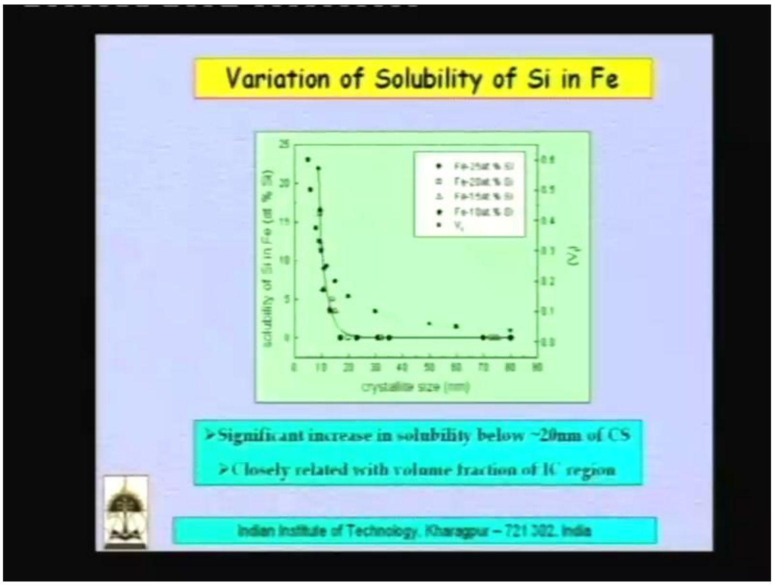

Variation of Solubility of Si in Fe

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

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This is another example to show you, hear what we shown is a solubility of silicon in iron as a function of crystallite size. A clear demonstration of how crystallite size again affects the alloying. You see that, until you reach around 20 nano meters, the solubility is almost 0. The silicon solubility in iron is almost 0 up to about 20 nano meters, starting from about 100 nano meter.

One can even do how a larger sizes, you see again there will be almost low solubility. But, once you come below 20 nano meters there is a sudden raise in the solubility. And as you go to lower and lower sizes, there is more and more solubility. And you also see a dotted line here and dotted line is nothing but the volume fraction of the grain boundaries calculated volume fraction of the grain boundaries.

As I told you, one can calculate once you know the grain size assuming a certain thickness for the grain boundary. Yesterday we talked about it, what is the volume fraction of the grain boundaries, which is 3 delta by d approximately. So, that 3 delta by d if we can use that formula, one can calculate the how that volume fraction of the grain boundaries changes. And that more or less goes almost in the same fashion.

So; that means, this increase in the solubility can be directly attributed to the increase in the grain boundary volume fraction. In fact, the difference between these two curves is basically, because of our assumption that the delta, which is the grain boundary thickness is constant throughout the region. In principle, if one can consider the variation of the grain boundary thickness as a function of the grain size itself.

We know that as grain size decreases grain boundary thickness increases. If one can consider that the these two curves will almost merge. But, there is no real evidence available on how the grain boundary thickness varies with the grain size. Though people no theoretically it should be increasing with decreasing grain size. But, the actual numbers are not available.

So, as a result at the moment we have only used at fixed grain boundary thickness. And with that you can still see that there is a clear one to one correlation between the grain boundary volume fraction to the solubility.

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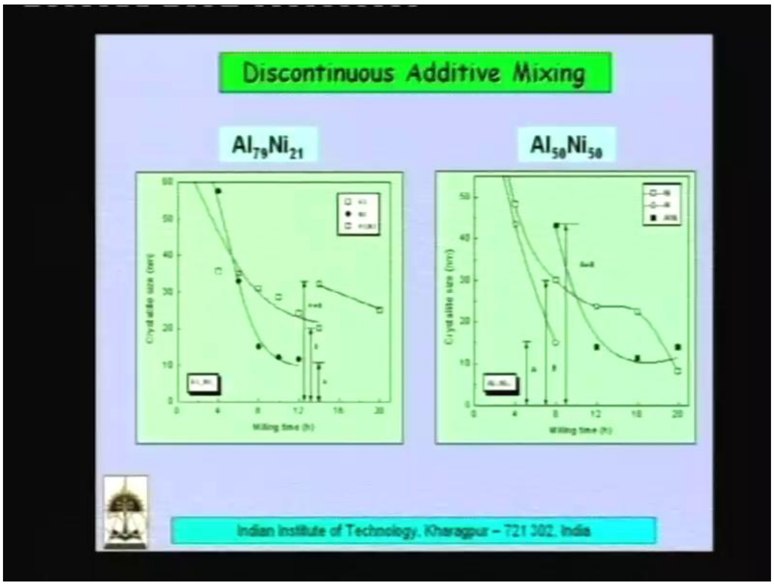

Discontinuous Additive Mixing

$Al_{79}Ni_{21}$

$Al_{50}Ni_{50}$

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And there is another interesting phenomena that one can observe when you go to nano region. Particularly, when inter metallic compounds are formed. Here is an example of two inter metallic compounds, one is an Al 3 Ni compound, another is Al Ni compound. When you look at these two compounds, what you see interestingly is that when you start ball milling.

Aluminum and nickel together choosing the composition, which is shown there one gives you A l 3 N i phase another gives A l N i phase. You choose the composition accordingly. So, that you get these two phases. And what you see is that the crystallite size of aluminum and the crystallite size of nickel decrease continuously. And you can see that crystallite size of nickel is smaller than that of aluminum, which is again corresponding to what I have told you earlier.

That nickel having a higher melting point, it will have a lower crystallite size than aluminum having a lower melting point. So, but what is more interesting here is not that fact. The more interesting thing is that, once the two crystallite sizes reach a critical value, suddenly there is a reaction between the nickel and aluminum.

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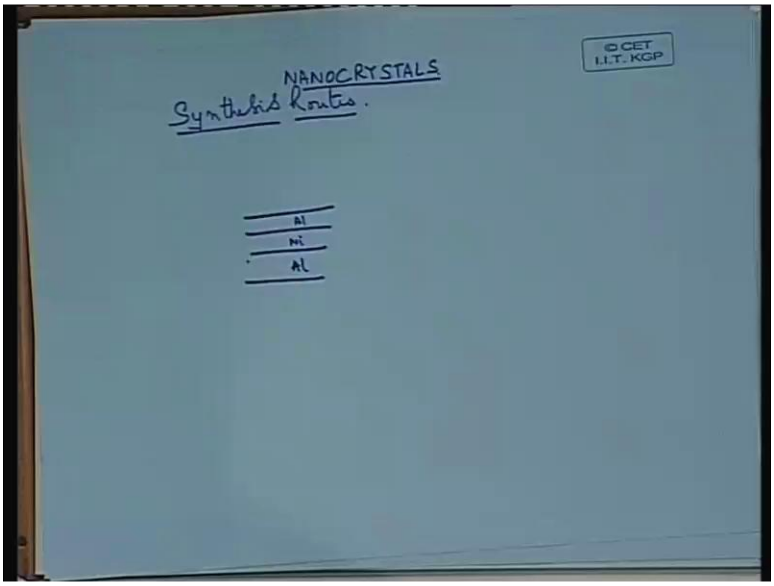

So, what you see here is that if you think of the nickel aluminum. Nickel aluminum alternate layers which form during ball milling you always know that the nickel and aluminum both of them are refined made finer. And when a ball hits a ductile powder particle, it immediately becomes a flake. And these flakes get ideal to each other and form what are like a sandwich kind of a structure, and within this sandwich structure, when the crystallite size becomes very fine. There is a sudden reaction between these two. And then formation of a compound that occurs, but this occurs exactly at a critical crystallite size. And that is what you see here, this what we call it as discontinuous additive mixing, because there is a discontinuity in the crystallite size there.

And there is a kind of an addition of the two crystallite sizes. And the crystallite size of the inter metallic that is coming out is, equivalent to the summation of the two crystallite sizes. That means, if you assume two layers and the two layers and the two layers react with each other and you have an inter metallic compound forming. And it is crystallite sizes is nothing but the summation of these two crystallite sizes.

And this is what is called ((Refer Time: 53:26)). And this observed in all ordered inter metallic compounds with a large negative enthalpy of mixing. And in fact, we have also seen that, the higher the negative enthalpy of mixing. We all know though that if the enthalpy of mixing of an compound if it higher, it has a greater driving force performing is not it.

When the enthalpy of mixing of an inter metallic compound is large. We can say its driving force is large. And if it has a large driving force for it is formation, it can form even at a coarser crystallite size. So; that means, the critical size is a function of the delta h mixing of the compound.

That, if the compound has a low enthalpy of mixing, you need to take the particles to lower and lower sizes for the inter metallic compound to form, which may not be possible under normal milling condition. That may you have to do probably cryo milling. But, if the enthalpy of mixing is very largely negative. Then, even under normal conditions at a larger crystallites as itself, you may be able to make these compounds and we have done a number of cases.

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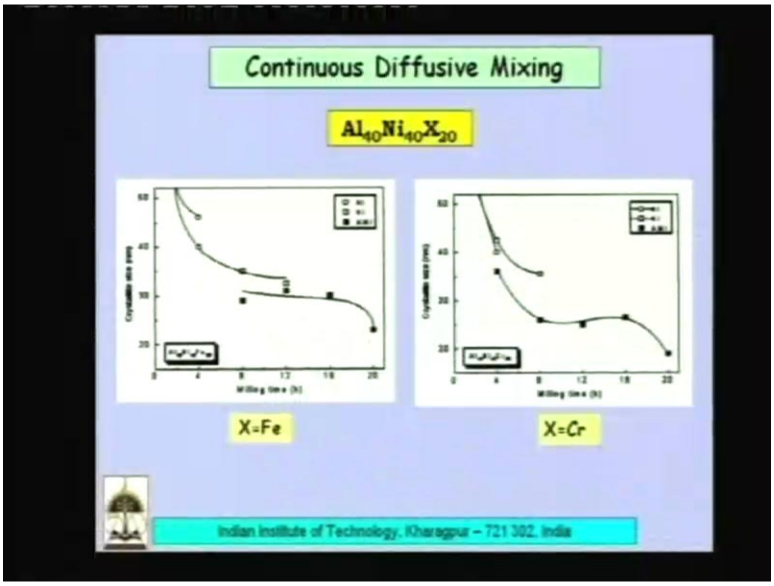

Continuous Diffusive Mixing

$Al_{40}Ni_{40}X_{20}$

X=Fe

X=Cr

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And we have seen that, if the compound is disordered. You do not have this kind of a situation that here is an example. Where, we have taken a aluminum, nickel and put chromium and iron into it. The moment you put chromium and iron of a particular concentration, it becomes disordered.

Once it become disordered it behaves like a solid solution, there is no discontinuous additive mixing kind of thing. Then the what you see is that with decreasing crystallite size, once the crystallite size reaches below a certain value. There is a continues shift of the peaks. And a continue of solubility that occurs and there is no reaction and formation of a new compound.

So, this is one of the major changes that you see, when you go from a ordered compound to a disordered compound. Disorder compounds are behave like solid solutions, ordered compounds were reactive mixing occurs. This is similar to self propagating high temperature synthesis.

You must have heard of some of the people must have heard of what is called self propagating high assume ((Refer Time: 55:39)) synthesis. Where, you take individual elements heat them to high temperature. And immediately they both of them react with each other. And when there is a reaction between each other, then the compound forms.

When the compound forms, then a enthalpy is released, because this is an exothermic reaction. And when there is a released of enthalpy, that enthalpy will help in the further transformation of the remaining material. So, that it is a self propagating wave. Once, the wave is ignited, once a reaction is initiated. Then, the energy that is released will be sufficient to overcome the activation barrier for the rest of the material to get ignited.

And you have a continues formation of these inter metallic compound. A number of such inter metallic compounds are being made with this kind of a process. But, here the interesting thing is everything is happening at room temperature. Just, because of you are making it into a nano. Here, it is not happening because you are igniting it with high temperature.

No, we are not igniting it, the ignition is taking place because of the crystallite size being very low. Where, the surface area to volume ratio is so high. That, ignition occurs automatically because of the nano crystallite size. So, you can see that nano crystallization is again a kind of a first step for such a ignition to occur, and formation of such compounds.

And this has been proved in a number of cases you can see here. This is a kind of summation of study and a number of systems, that you see that as long as they ordered. You have a discontinuous additive mixing. And if they are disorderd, you have a continuous additive mixing, will stop here and continue in the next class.