Advanced Materials and Processes
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Lecture - 7
Amorphous Materials Part – I

We are talking about the conditions for solid state amorphization, that means strain to get an amorphous space from a crystal in a solid state. As I told you before a one can get amorphous space from the three sources of the states of matter. Either from the vapor you can condense it. And get a nano crystals and if you go below a certain critical crystallite size.

You can go into an amorphous material or we can do the same thing from the liquid. Take a liquid rapidly cool it will come to the glasses in the next class. And today let us look at particularly the solid state amorphization. So, how to get an amorphous material from a solid state, and there are certain criteria involved in this and which is what we have talked in the last class. One is the thermodynamic criterion that the free energy of the amorphous phase should be lower than the starting material.

For you which is could be a pure metal mixture. During a high energy ball milling or it could be a solid phase. It could be a solid solution or an inter metallic, which is subjected to either high energy ball milling or may be electron bombardment. For example if you take a inter metallic compound. People have demonstrated this that you take an ordered compound. Keep on bombarding it with irons or electrons in a high voltage electron microscope.

So, what we basically do is that you introduce lot of defects into the material. And that as you keep on introducing defects into that ordered compound. It slowly becomes disordered is what is called the order parameter. You all are aware of long range order parameter. So, the long range order parameter keeps on decreasing. And finally, it becomes zero at some point of time. Suggesting that, the ordered compound completely becomes disordered. And finally, if you keep on increasing the amount of defects into the material, it at some point of time this disordered solid solution, which is still crystalline will undergo a transition and becomes amorphous.

So, this has been shown by a number of ordered materials. For example, one example is Ni3Al. People have shown in Ni3Al by such bombardment one can make ordered Ni3Al into first disordered Ni3Al. Or you can call it as a nickel aluminum solid solution. Once it is disordered it is no more kind of we cannot call it as a compound. Because, a the way the atoms are arranged they are disorderedly arranged inside the unit cell.

That means nickel can sit anywhere aluminum can sit anywhere. So, that is similar to a solid solution. But, the only difference is the composition is such that it is 75 percentage nickel and 25 percent of aluminum. So, the composition is same as that of the NiAl Ni3Al. But, the structure is such that the atoms of nickel and aluminum can sit randomly any where they want. And finally, we call it as a disordered compound or a solid solution.

And such a disordered state of matter, which still has a unit cell which is having a FCC unit cell. And that unit cell can further break down when you keep on increasing the defects. And finally, can become an amorphous state. So, this is what we call solid state amorphization. There are number of techniques by which people have observed this solid state amorphization. One is what I just now mentioned. That you bombard a material with some electrons or high energy particles they can be electrons they can be irons.

For example, this is one problem, which usually people face. When they do iron milling I do not know we you must have heard of iron milling, which people used to prepare TEM samples. So, when you want to see a sample by electron microscope. What you need is that you need a thin sample is it no, because if the sample is not thin enough the electron beam cannot transmit through the sample. That is a meaning of a transmission electron microscope.

So, if you want a material to be transparent to an electron beam, the thickness should be less than about 100 nano meters. So, every material if you want to see it under transmission electron microscope. It is thickness should be less than 100 nano meter. And this can be achieved by number of techniques. If the material is metallic you can do what is called electro polishing or jet polishing people usually refer to as where you take a sample.

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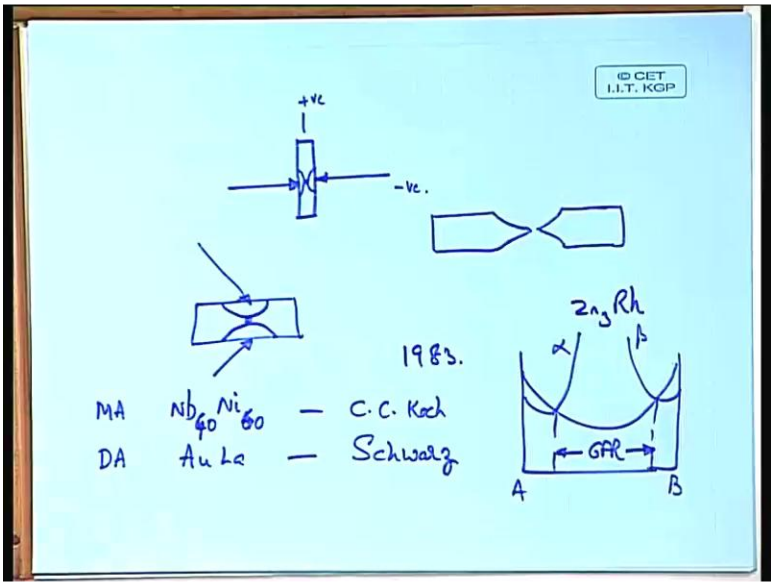

A material like this, put it vertically a thin disc. And that is subjected to a jet of electrolyte falling from both the sides. And you make your sample anode and the electrolyte around you the sample as a cathode. So, that this by anodic dissolution the sample dissolves, and because you are allowing the electrolyte to fall as a jet from both the sides. So, the dissolution occurs from both the sides. And finally, you make a hole here.

And near that hole, the region will be thin enough. So that means, finally, what you are getting is a sample of this size. If I exaggerate the sample configuration, it will look like this. So, this is the type of sample, you will get if you do electro polishing. And you look at this near this hole and if you look at near the hole. The thickness will be thin enough for the electron beam to be transparent.

And finally, you can see the micro structure of the sample. But, the problem would be with material, which are non conducting. If you want to use electrolytic polishing the material has to be conducting first. If it is not conducting then what do you do, that is where you have a new technique called ion beam thinning, where what you do is you keep your sample inside a chamber evacuate the chamber.

And introduce some organ into that and ionize this organ gas. And once you ionize this organ gas. And allow it to fall on to the sample as a jet or as a beam of beam of organ ions. And these that beam of organ ions once it falls on the sample it sputters away atoms.

So, you take a sample, and along a beam of organ ions to fall from top and bottom at a certain angle. This angle can be adjusted at least from almost 3 degrees to about 25 degrees one can adjust this angle. So, that as you now the if the angle is a very high; that means, if the electron beam is heating from vertically from top. Then the rate of sputtering will be more, when compared to when it is at a glancing angle.

But, if you want a very thin sample you need a glancing angle. So, if you want a large region having thinner region. Then what we need is a very shallow angle of the electron beam. So, as a result, what we usually do is we start with a high angle and slowly decrease the angle. So, that you get more and more thin region.

And finally, what you get is exactly similar to what you get in electron electro policing, that this region the sample is removed by sputtering. So, atoms are removed by sputtering, but the only difference between this and that technique, which we talk just now electro policing is that the sputtering technique is a very slow process. So, you may have to sometimes ion mill a material for about one day to get a thin sample. And a hole at the center finally. So, that the sample is thin enough, for the electron beam to be transparent.

Whereas in a electro polishing is just few minutes time. Provided you control the conditions, such that the voltage the temperature and many parameters one has to control. So, this is what is called the ion beam thinning, why we are talking about this is. Many times when the ion beam falls on the sample, there is a possibility of the destruction of the crystal structure. Sometimes, you get a thin amorphous layer on the sample.

Because the beam the electron is I mean the ion beam at a very high energy is falling on the sample sputtering away atoms. While doing that it also introduces defects into the top region. And once the defect concentration crosses in some localize regions. There is a possibility that the sample becomes amorphous. This has been observed in a number of samples. Particularly, wherever they prepare a sample by ion mill and if they prepare it by electro polishing the micro structure is different.

So, that ion milling sometimes introduces amorphization. But, that all depends on the conditions, if one can control the voltage and particularly the energy of the beam. So, one can reduce the destruction that is possible. So, what we are talking about is how to amorphize in the solid state. So, this is one technique. The second one is what we have been talking about is ball milling, that you introduce the defects into the material through ball milling. At the same time make them material nano crystalline.

And once the crystal size comes below a certain value then you get amorphization. I am going to demonstrate in a few cases how this happens, this is the second technique. The third technique which people talk about is, the diffusion technique which I talk to you in the last class, that means you take multi layers. For example nickel, zirconium, gold, lanthanum I gave you these examples in the last class, where you take such multi layers of gold, lanthanum, gold. This kind of multi layers, which are deposited by electro deposition or by vapor deposition PVD, CVD there are number of techniques available.

One can deposit such multi layers and anneal it at low temperatures. And if you do it at low temperature both the thermodynamic and kinetic conditions are satisfied, particularly in those systems, where one of the element diffuses very fast into the second element. That is what is the kinetic condition that we have talked about in the last class.

And if that is satisfied then you get an amorphous phase by just low temperature diffusion. But, if you do at high temperature you end up in a equilibrium inter metallic compounds. So, that is the third technique of solid state amorphization. The fourth technique people have talked about is hydrogen induced amorphization. There are number of cases for example, inter metallic compounds, where the first inter metallic compound, where people have observed this is zirconium rhodium Zr3Rh, where they have annealed it in a hydrogen atmosphere. Unknowingly, that what would happen to it, when they anneal this compound in a hydrogen atmosphere to study it is you know phase transformation behavior. Then what they saw is that after annealing this material becomes amorphous. And they when they look at the x ray diffraction they saw a broad amorphous peak, which is typical of an material.

And from that point onwards in a number of materials people have shown. That when you introduce the hydrogen, because hydrogen is very small element which can easily diffuse into the material. But, at the same time it can introduce lot of defects. By it is movement through the lattice of the material. And these defects concentration once it crosses a particular a value then you can have amorphization.

So, these are the four different solid state amorphization techniques. And interestingly one thing is all of them have been discovered in 1983, very coincidentally all these things. Whether it is amorphization by mechanical alloying, starting from two pure metal mixture. The first such composition was nickel niobium 40 percent niobium and 60 percent nickel by a person by name C C Koch in North Canada University. This was the first report of mechanical alloying.

And similarly the gold lanthanum multi layers by a person by name Schwarz. in Calicut laboratory and that is also in 1983 this is what is called diffusion annealing. We can call it for multi layers and hydrogen indios amorphization is also almost a same year. So, that is the year of solid state amorphization I should say. Though amorphous materials are known for quite some time silicate glasses everybody knows about silicate glasses, but getting a glassy material. By making a crystal into a glass is something which has not been known to people. And that was the year when people have demonstrated it in a number systems and.

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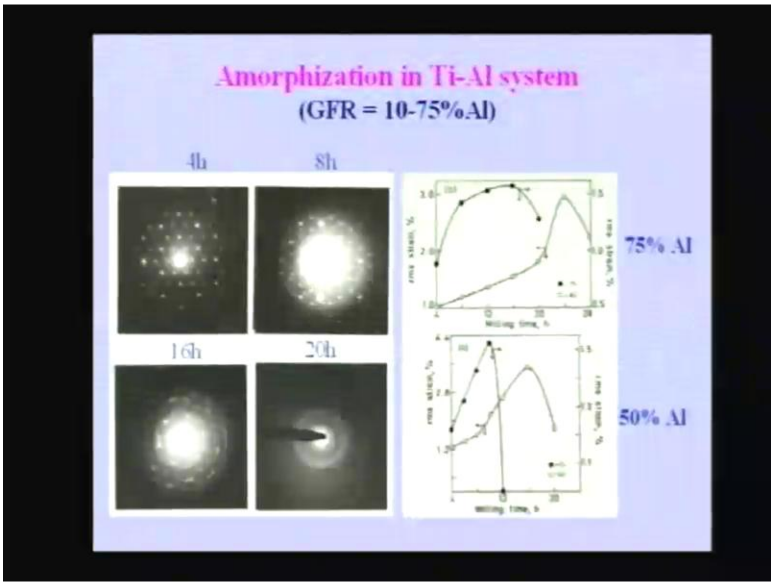
Amorphization in Ti-Al system

(GFR = 10-75%Al)

So, this is one example, which I have showed you in the last class titanium aluminum. How amorphization occurs, how the defects are introduced into a material. And finally, once you cross a particular strain that the material cannot take anymore strain. And the defects are, so high in the material that the crystal with. So, many defects becomes unstable and becomes amorphous.

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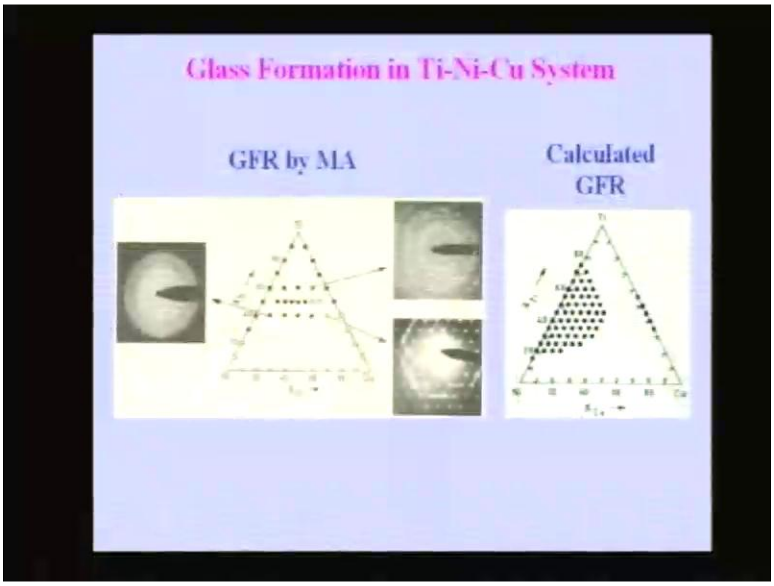

Glass Formation in Ti-Ni-Cu System

GFR by MA

Calculated GFR

This has been observed also in a number of other systems titanium, nickel, copper is here. A number of compositions are shown, some are glassy compositions, some are mixture of glass and crystal and some are the crystalline. So, this gives you an idea of what is called glass forming range. We talked about it in the last class Glass Forming composition Range are GFR which people usually refer in this particular field.

And one can do thermodynamic calculations and also show that yes the glass forming composition range. Basically, what we do in thermodynamic calculation is that you find out what is the free energy of an amorphous phase, and the free energy of the solid solution. Like I talk to you in the last class, basically you draw the free energy of the amorphous phase, and the free energy of the solid solution. Let us say alpha on one side, beta on the other side the two terminals solid solutions.

And then find out the composition range in which amorphous phase is most stable. Here, what we do is while doing the calculation for the amorphous phase. We assume the amorphous phase to be same as that of the liquid. Because, the crystal structure of amorphous phase is same as that of the liquid. We all know that because mostly amorphous phase is usually defined as that which is configurationally flows in liquid. We will come to it a little later, when we talk about metallic glasses. So, this is what is called the GFR. And this range would be different for different systems one can do it for binaries very simply like this AB. And for turneries one can calculate it at various compositions and show that, this is possible to have an amorphous phase like that.

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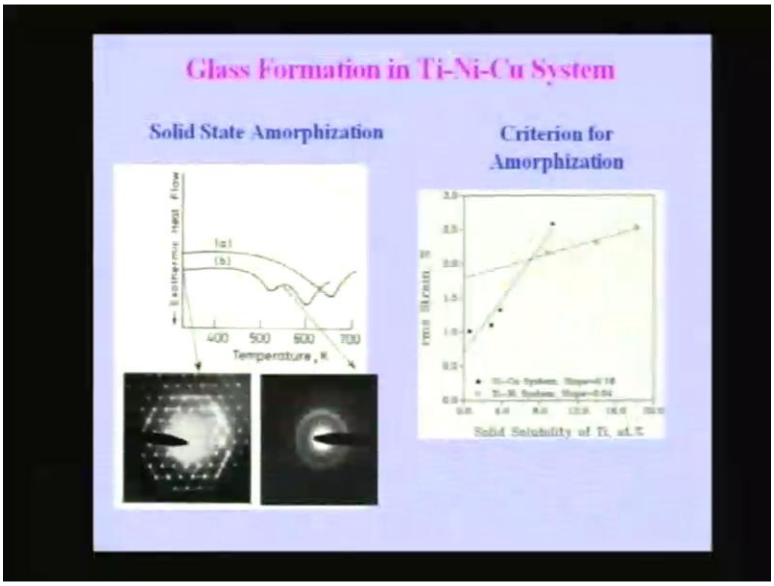

Glass Formation in Ti-Ni-Cu System

Solid State Amorphization

Criterion for Amorphization

And I also told you about this kind of situation, which is similar to a solid state amorphization by diffusion annealing. That means, if you do ball milling for a short period. What you get is a multi layered structure. Let us say A, B, A this type of a structure why does it happen, I told you already that.

When you take a ductile particle and hit it with a ball immediately what happens to it is it becomes a flat. Like a flake. And once it becomes like a flake it has a large surface area to volume ratio. And once that happens it can easily get cold welded to another flake which has formed. So, it forms like a sandwich, which we see regularly.

So, that kind of a sandwich kind of a structure happens. And because there is an affinity for A element to interact with B element mode. So, you will see, the probability of having AB kind layers is much more. So, you have a tendency to have AB, AB, AB type of layers. And that kind of layers if the crystal size has not become really very fine, it does not become amorphous in the ball milling itself, because we told you I told you before. That unless it becomes nano crystalline amorphization does not take place, but if the crystal size has become fine enough.

What we can do is we can take such a multi layered structure which has formed by ball milling and heat it. When you heat it what happens particularly at low temperatures. Now, you are providing sufficient thermal activation energy for the atoms to diffuse through these layers. And then an amorphous phase can nucleate at this interface. The way it has formed in the multi layered structures, that you can see that an amorphous phase can easily form. And that is what you see in a differential scanning calorimeter.

What you have here ((Refer Time: 19:07)) is a differential scanning calorimeter result of one composition, which is a titanium nickel copper composition. There two compositions are shown here A and D, A is already amorphous in the as mild condition. And if it is already amorphous it gives you one peak, which is a exothermic peak, which means that that amorphous. Because, it is unstable or meta stable. I should not call it as unstable every amorphous or a glassy structure is a meta stable like our cementite.

And if you heat it to temperature which is called crystallization temperature. If you heat beyond the crystallization temperature, then that amorphous phase will transform to a crystal. And that gives you a exothermic peak because the enthalpy of a crystal is lower than the enthalpy of the amorphous phase. So, you have a delta h, which is released and you get an exothermic peak.

And if it is not completely transformed to an amorphous phase that it is still a multi layered structure like this in the as mild condition. Then what you see is that you get it two peaks two exothermic peaks. The first exothermic peak is for the multi layered structure to transform into an amorphous phase, because there is a decrease in the free energy. When a multi layered structure transforms to an amorphous phase. That is what I showed you before here.

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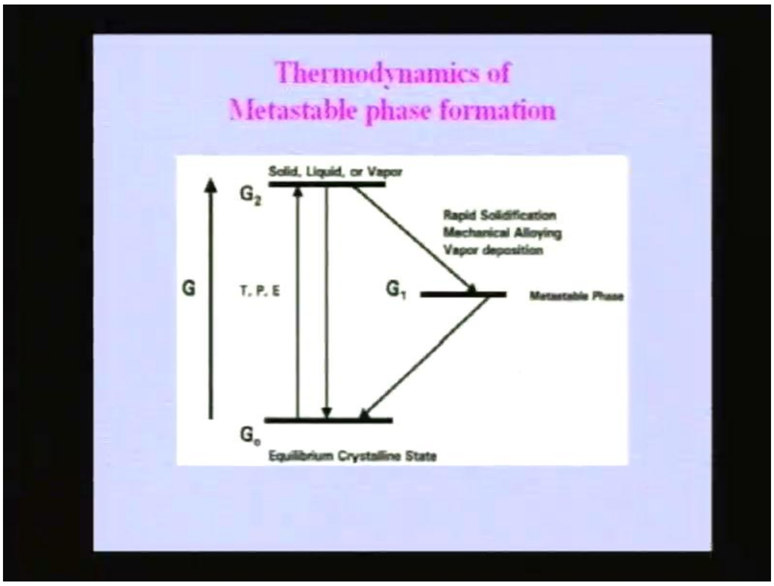

Thermodynamics of
Metastable phase formation

As you can see here. So, there is a decrease in the free energy.

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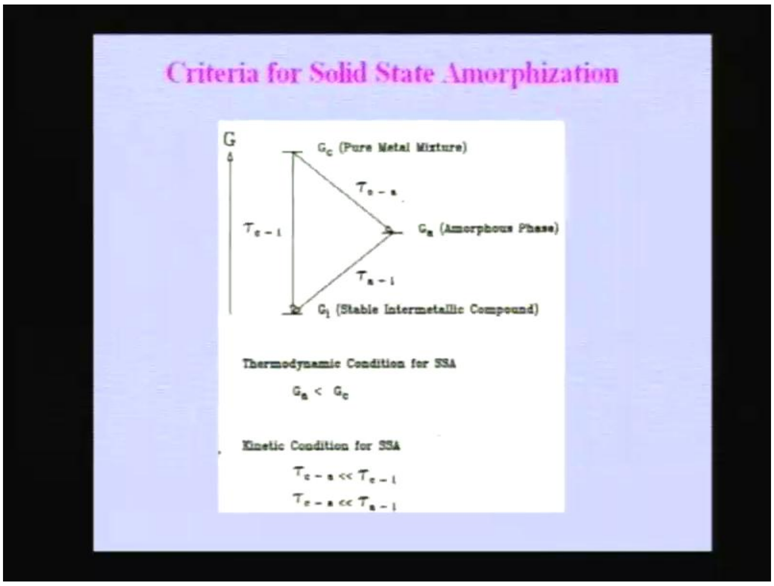

Criteria for Solid State Amorphization

Thermodynamic Condition for SSA

$G_a < G_c$

Kinetic Condition for SSA

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

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

That we are talking about it a pure metal mixture can go to amorphous phase. And then that will further go to a crystalline phase. And I am showing you ((Refer Time: 20:50)) two electron diffraction patterns here, which have been caught at those positions. One is in the as mild condition, before you start the DSC, what is you do when you see the electron diffraction pattern you see the crystalline pattern with a lot of defects in it. And what I can do is, I can heat it up to the end of the first peak and immediately cool it back.

And then take that sample and put it in the TEM. And look at the diffraction pattern and what I see is it amorphous ring.

And if I go to the second stage I get the equilibrium crystals back. So, we stop it at a particular position and have a look at it. And you can see this kind of solid state amorphization. So, this is similar to what is observed in the diffusion annealing. Only thing is this is, what we people usually in the mechanical alloying field called it as mechanically activated synthesis.

That means, you are not forming whatever phase that you want during mechanical alloying itself. You are stopping it at some stage and while doing that you are activating the system to a high energy level. So, that if you take that system with a high energy level.

And then heat treat it you get whatever phase that you want. The advantage of this is that probably the time required for mechanical alloying can be cut short. May be sometime for some of the phases to form, the time required could be very long during ball milling. And that can also lead to problem such as contamination. Because, the more you do the ball milling the more is the contamination. Some people want to avoid this contamination.

And as a result one can stop it in a short period get this kind of multi layers with a fine structure. And then immediately do a heat treatment. So, this is what is called mechanically activated synthesis. And what is important to know again here is as we talked in the last class also. That there is a critical strain irrespective of the system that we choose, that this is given for titanium nickel and titanium, copper that as we increase the percentage of titanium in copper. As more and more titanium goes into solution of copper the strain increases.

Why does the strain increases? When a titanium atoms sits in the lattice of copper it distorts it. So, you get in strain, but this strain keeps on increasing as you keep on increasing the titanium amount in the copper. But, beyond a certain level the strain reaches such a critical value. That the crystal with, so much of strain becomes unstable and it immediately transforms into an amorphous structure. And interesting thing is that this is not a function of the. Basically the elements that we are talking, but it is a function of only the structure, because here I am talking of copper and nickel.

Both are FCC and if you look at the strain of about 2.5 percent which is the critical strain is reached by putting 8 percent of titanium into copper and by putting about 18 percent of titanium into nickel is it not. The amount of titanium in copper and nickel is different, but what you see is that once the 2.5 percent is reached. Then suddenly you will have a transformation of the crystal to amorphous, which is only a function of the structure. So, FCC can take some amount of strain into it. BCC can take some amount of strain. HCP can take some amount of strain and. So, depending on the type of material the strain is fixed, and that is what is we call the critical strain.

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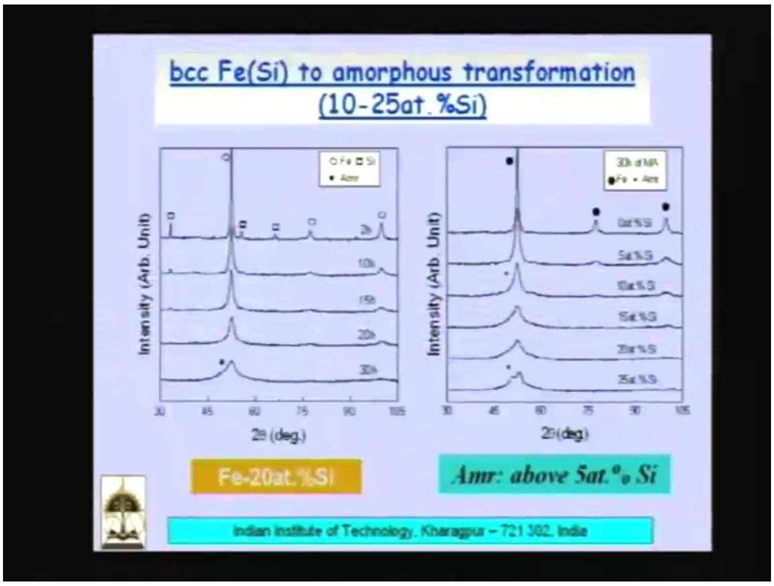

bcc Fe(Si) to amorphous transformation (10-25at.%Si)

Fe-20at.%Si

Amr: above 5at.% Si

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And this has been observed in a number of systems I give you one example of iron silicon, which is as a function of composition. You see here a number of compositions and on the left side you see for one particular composition, which is 20 percent of silicon. As you keep on increasing ball milling starting from 0 hour means it is just a pure metal mixture of iron and silicon, which gives you all the x ray peaks of iron, and the x ray peaks of the silicon.

And as you keep on increasing ball milling times the silicon peaks vanish suggesting that silicon goes into solid solution of the iron. And the peaks of iron becomes broad suggesting that it is becoming nano crystalline. And once it reaches a particular value you start getting a know a shoulder on the left side. And that shoulder is nothing but an amorphous hump. And which is more clearly seen in the right side for the 25 percent case, where you can see a shoulder of amorphous phase in addition to that solid solution of the BCC iron. So, the BCC iron solid solution once it reaches a critical value of crystalline size.

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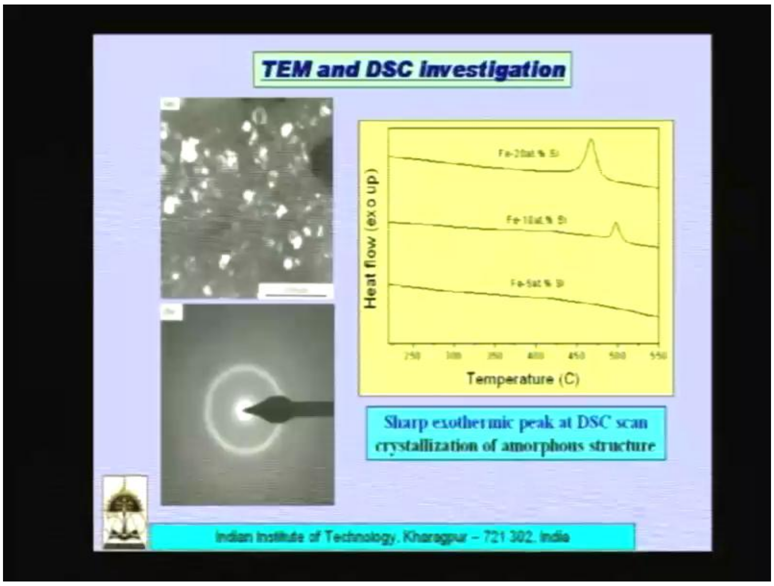

TEM and DSC investigation

Sharp exothermic peak at DSC scan crystallization of amorphous structure

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We will see it in a minute that it transforms to an amorphous phase. What you see here is an electron micro graph of those BCC crystals, which are very fine of the order of around 10nano meters are so. And that if you continue ball milling a little bit it becomes amorphous. You can see from the diffused ring. And that is also clear when you take the DSC.

In the DSC when you look at it 5 percent silicon which does not form any amorphous phase, it gives you a flat signal. Suggesting that there is no amorphous space it is an equilibrium structure. Whenever I take a equilibrium structure and heat it, it does not transform to anything. So, it does not give you any exothermic peak or an endothermic peak.

But, if I take a phase which is amorphous when I heat it at a particular temperature it gives you an exothermic peak, and if I go to from 10 percent to 20 percent the amount of amorphous phasing increases. And because of which you get a bigger peak, adjusting that more amorphous phase is there which transforms to a crystal and give you get a bigger peak. So, from the from the peak size, one can talk about the volume fractional the amorphous phase, but what is important to know, that this happens under two conditions.

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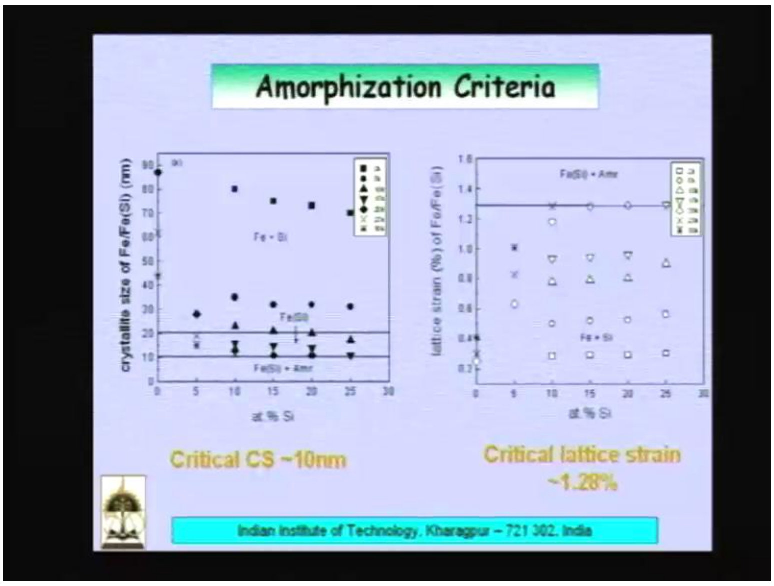

Amorphization Criteria

Critical CS ~10nm

Critical lattice strain ~1.28%

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One is the crystallite size, as you can see here we are showing all compositions 5 percent, 10 percent, 15 percent, 20 percent, 25 percent of silicon in iron. And in all these cases as you keep on increasing the milling time the crystallite size keeps on decreasing. Let us take up any one case, let us say ten percent this is the top point is for 2 hours and is keep on increasing the milling time, the crystallite size is decreasing.

And, but the moment you reach around 20 nano meters, it becomes solid solution. As I told you the solubility starts increasing only below a certain crystallite size. Nano crystallization is a prerequisite for alloying, this is we talked about it. So, you start seeing alloying below a critical crystallite size, irrespective of the composition.

And once you reach a above 10 nano meters. All this compositions which can reach 10 nano meters they all will transforms to amorphous phase. For example, if you take 5 percent, 5 percent even after 30 hours of milling it is only about 50 nano meters. So, as a result that 5 percent composition could not transform to an amorphous phase. But, if I can somehow make that 5 percent silicon also below 10 nano meters, which is possible probably by long milling or doing cry milling.

We talked about it before. So, if I can do that probably I can bring it below 10 nano meters. And once I reach I can see that it becomes amorphous So, for example, here you can see 25 percent case just by ball milling for 10 hour itself. This point is a 10 hour point that you see. So, the inverted triangle field triangle and that clearly tells you that by just a ball milling for 10 hour itself. You have reach 10 nano meters immediately transforms to a amorphous.

So, the time required for amorphization is going to be different for different compositions, because different compositions need different time to reach that crystallite size. So, if I have more a alloying element into it. So, I have more solid solution strengthening. And if it is having higher solid strengthening, it becomes more hard. And if it is more hard it can become nano crystalline more easily. So, within a short period, it becomes nano crystalline. And once it become nano crystalline below a certain critical crystallite size it becomes amorphous.

The same thing is true in terms of strain, here you can see that as we increase the milling time for different compositions. The strain keeps on increasing. And once you reach a critical strain of about 1.3 percent or. So, then immediately you will see it becomes amorphous. So, this is true for any system only thing is the particular values may be different for different systems. For example, in case of titanium copper nickel, we have seen their that the strain there you need is about to 2.5 percent. So, if you put in about 2.5 percent it could transform into an a amorphous phase, whereas here it is about 1.3 percent. So, because here we are talking of BCC iron where silicon is going into. So, the structures are different. So, as a result the strains are different.

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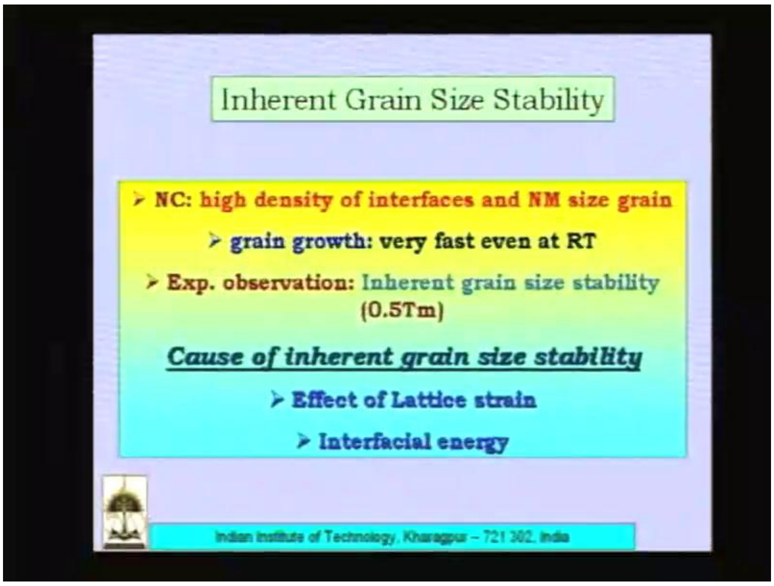

Inherent Grain Size Stability

- NC: high density of interfaces and NM size grain
- grain growth: very fast even at RT
- Exp. observation: Inherent grain size stability (0.5Tm)

Cause of inherent grain size stability

- Effect of Lattice strain
- Interfacial energy

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So, this is about nano crystals becoming amorphous. The next point which is important in the nano crystalline materials before we go into the next topic, which is the glasses. Is the stability of these nano materials. Let us say we have produced these nano materials we want to use them, but we know that a nano material is always meta stable is it not.

So, how does it grow, under what conditions we can somehow control its growth. So, that we can retain it as in the nano crystalline form. And utilize the advantages that we can get from the nano crystalline nature of that material. That is a challenge for the engineers, a scientist will make a nano material. But, then he is not really concerned about the growth much, because he is more interested in the phenomena.

That happens at the nano crystalline state, but if somebody wants to use an engineer. So, he would like to retain them in the nano crystalline state at high temperature. And most of the time what we see is that, if you take pure metals nano crystals they grow very rapidly. For example if you take a nano crystalline aluminum or nano crystalline copper. By the time you reach around 300 degrees or so it becomes from if you start from about 20 nano meters.

Or so it becomes more than 100 nano meters just by heating it by to about 300 to 400 degrees. But, there are ways to control it. What are the ways? One is what is called alloying when you put for example, an alloying element into the solvent. What we know is that, whenever a solute goes into a solvent. The diffusivity gets restricted. And we know clearly that if the grain growth has to occur atoms have to defuse if the atoms do not defuse.

Then the grain boundary cannot migrate. And if the grain boundary does not migrate then there is no chance of grain growth. So, the crux is how to control, the grain boundary migration. One possibility is to reduce the diffusivity by putting elements which have high melting points. For example, if I take a aluminum and alloy it with titanium and get a aluminum titanium solid solution. Let us say I make it, in the nano crystalline form. Then that aluminum titanium nano crystal solid solution would not grow at the same rate as aluminum.

Because, see you have a titanium there, which has high melting point it is diffusivity is very low. And in addition because of the strain, that it is generating by sitting in the lattice of aluminum, it prevents the diffusion of aluminum itself. So, it reduces the diffusivity of aluminum. So, both the diffusivity of aluminum is lower and the diffusivity of titanium is lower now. And because of which you can have a lower growth rates. And we have seen in a particular case earlier for example, if I remember right the sliver copper I think we have seen, yes here.

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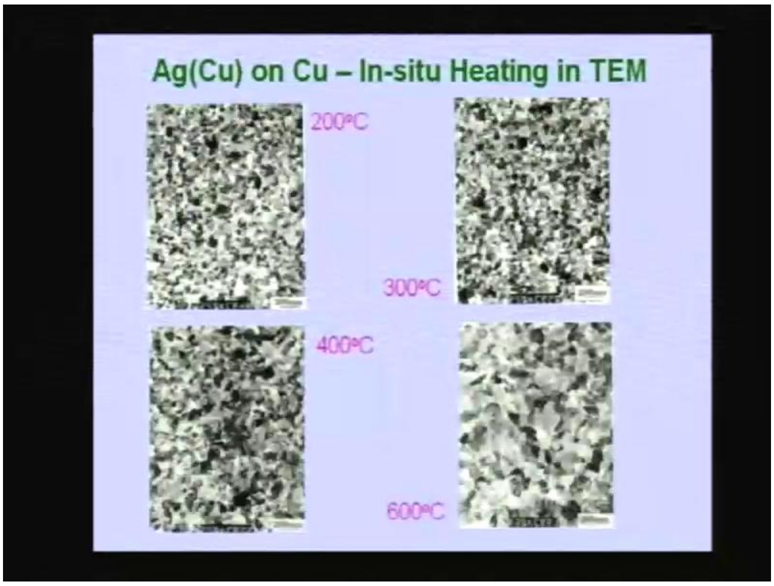

Ag(Cu) on Cu – In-situ Heating in TEM

This is the case for sliver nano particles, which are heated to about 600 degrees centigrade. And there is another case where sliver alloyed with copper which is heated to various temperature. And 600 is also shown here.

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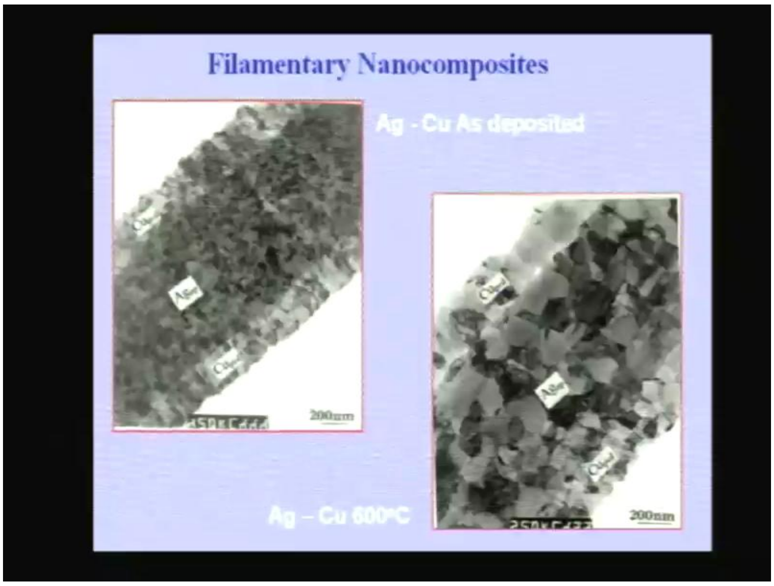

Filamentary Nanocomposites

Ag - Cu As deposited

Ag – Cu 600°C

And if you compare this grain size with the grain size of pure silver, heated to the same temperature both are deposited under the same conditions by vapor deposition. You will see that the grain growth is much lower here this is what is called Zener pinning. So, you have what is called kind of a pining of grain boundaries. Because, of low diffusivities the other possibility is to put some Zener pinning. The other possibility is to put some particles at the grain boundaries.

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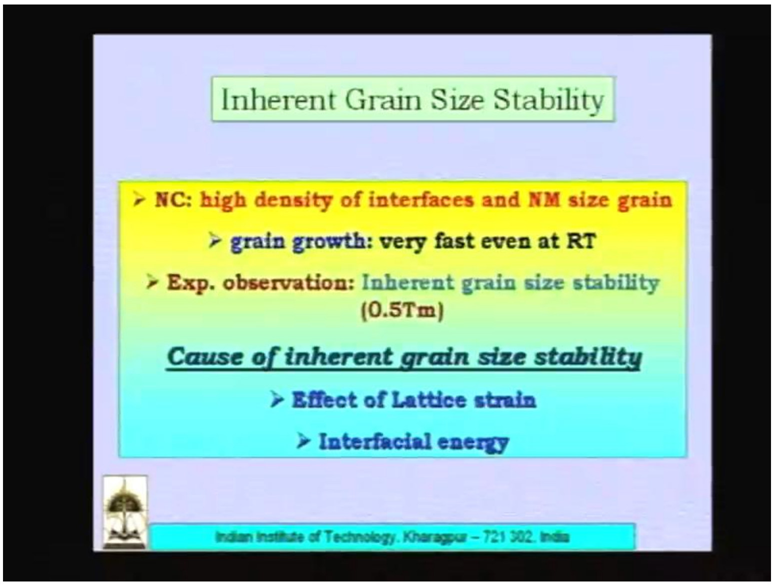

Inherent Grain Size Stability

- NC: high density of interfaces and NM size grain
- grain growth: very fast even at RT
- Exp. observation: Inherent grain size stability (0.5Tm)

Cause of inherent grain size stability

- Effect of Lattice strain
- Interfacial energy

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If you put certain particles hard particles high melting particles at the grain boundaries, which we all know in the case of high strength low alloy steels HSLA people have done it. And the same thing can be done in nano materials and a number of people have chosen this path by putting some. For example an alumina particles in a nano crystalline copper. So, if you put alumina particles fine particles of alumina into introduce them into the nano crystalline copper. That means if you are doing by ball milling technique. Let say what you do is you put the alumina particles along with copper and ball mill it.

So, that these alumina particles are refined and uniformly get distributed into the copper and then you can compact it. And then start sintering at high temperature. And you still see that the copper does not grow. Because, there are hard particles at the grain boundary which pin the grain boundaries, this is the second method. And people have done it in a number of cases.

If that is ball milling other possibility is if it is any other method let us say gas condensation technique. What you can do is take fine alumina particles and nano particles of copper and mix them together. And then compact them together and then sinter them together, that is another way. So, this execute addition and if it is ball milling one can generate such a composite in situ by ball milling them together.

So, such nano composites can be obtained. And in such nano composites the growth rates are much lower than the monolithic nano materials. Monolithic nano materials means, basically single phase materials. If you take single phase material, particular single phase pure metals. If the single phase is an alloy, then again it is the go coarsening kinetics are going to be lower, when compare to a single phase pure metal.

We also see under certain conditions. The nano crystals do not want to grow without going into the two situations that I have told you, so far. The conditions under which they do not want to grow is when they are strained for example, you see here. When there is a strain inside a material. There is a inherence stability for the nano crystalline material towards grain growth, that means the nano material do not want to grow when they are strained. And the other possibility is when the interfacial energy is very low, I give you an example for these two.

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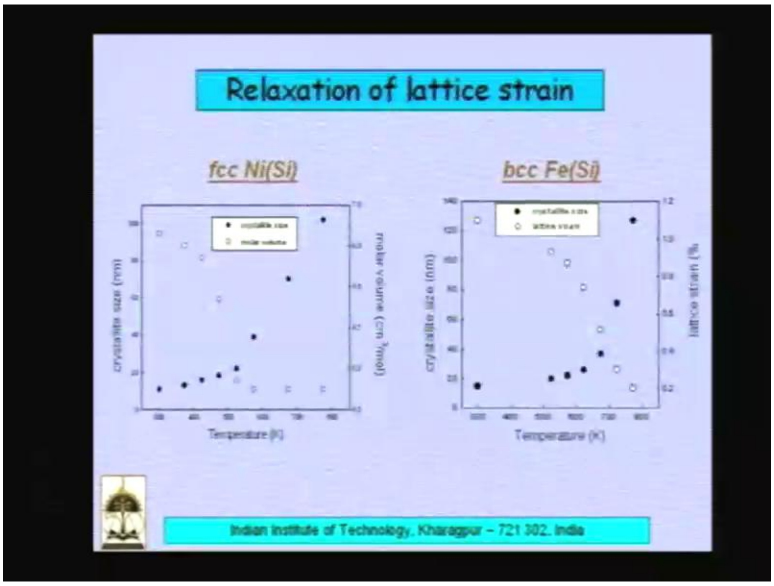

Relaxation of lattice strain

fcc Ni(Si)

bcc Fe(Si)

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One example I am giving you is an FCC nickel solid solution and BCC iron solid solution, both with a small amount of silicon in it. What you see here is that there is material in the as prepared condition is nano crystalline. It is crystallized size is of the order of around 15 nano meters here and about 18 nano meters here. And it is strain is very large you can see the molar volume on this side. And the lattice strain on this side both of them are very large. The white circles are the strain and the black circles are the size crystallites size.

So, in the as prepared conditions they have a large amount of strain and very small crystal size. And as you keep on heating it, you see the strain starts falling suddenly beyond a particular value. Because we know whenever you heat a material with strain material there is recovery that happens is it not. Recovery happens when you reach particular temperature. And once the recovery take place; that means, once the strain reaches a very low value, and that is the time at which the crystals start growing, till then the crystals do not grow.

So, the crystallite size if carefully observed it is very low, up to the strain falling to a very low value. Once the strain falls to a low value, then suddenly you will start seeing the crystals growing. This is because when a strained lattice is there, because of the strained lattice the diffusion gets restricted. And if the diffusion is restricted then the grain boundary movement gets restricted and as a result grain growth cannot take place.

So, whenever you strain a material. In fact, even alloying is also one way of straining the material, when you put a solute atom into a solvent atom. You are straining the lattice and once you have strained the lattice diffusion is restricted. And that is what is happening, when what is called is solute drag effect. I used a different term earlier the Zener pinning is basically for the particle pinning, when you have solid solution. We call it as solute dragging effect.

That means the second alloying element makes a situation such as there is a kind of a drag for the atoms to move. That means, some kind of restriction for the atoms to move and that is what is usually referred to a solute drag effect. So, solute drag effect and Zener pinning effect these are the two crucial techniques by which one can control the grain growth in nano materials. And this is another example of straining a material. And this strain how do you introduce by introducing defects into the material by deforming the material. During ball milling that is what we are doing? We are deforming the material. So, you are introducing strain into the material.

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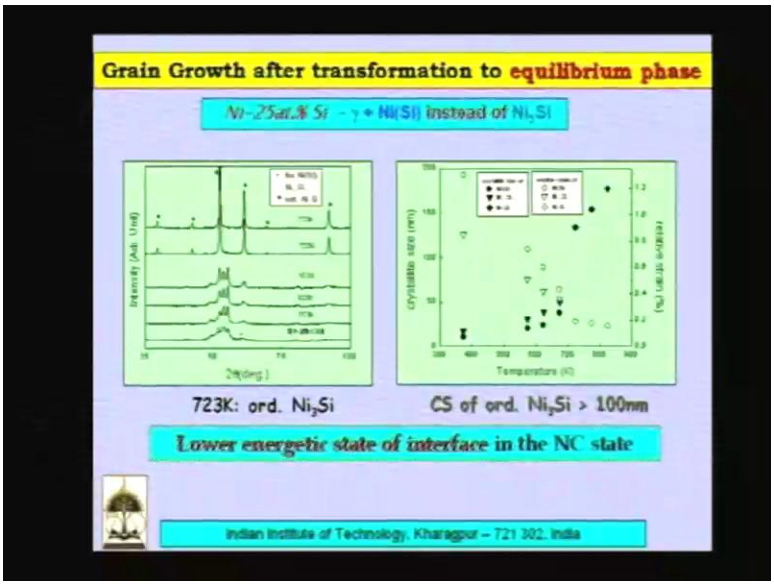

Grain Growth after transformation to equilibrium phase

Ni-25at.% Si – γ + Ni(Si) instead of Ni_3Si

723K: ord. Ni_3Si

CS of ord. Ni_3Si > 100nm

Lower energetic state of interface in the NC state

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The other possibility is what is called the effect of low interfacial energy. I told you before if you can make nano materials which are inter metallic compounds, which are congruent inter metallic compounds. These have very low interfacial energies, we talked about it earlier. I told you that in a nano crystalline state only congruent melting compounds form and non congruent melting compounds do not form, because they have low interfacial energies. So, if I take a material here is an example of nickel silicon, which in the nano crystalline state it has a gamma phase, which is a congruent melting compound. All the peaks that you see here are all gamma peaks. And this gamma phase is a nano crystalline phase, which I have shown you before about 20 nano meters or so. And when you start heating it up to 673 it remains as it is.

Excepting that the grains cores into some extent, but beyond that when you go from 673 to 723 Kelvin. Then immediately that particular phase transforms to the equilibrium Ni3Si phase equilibrium Ni3Si is non congruent melting phase. That is why it cannot form in the nano crystalline state. So, that is why during ball milling that never forms because inter metallics always form in the become nano crystalline. So, in the ball milling condition when it goes to a nano crystalline state Ni3Si cannot form only the gamma phase, which is Ni31Si, 13.

That is the phase which usually forms, but when you start heating beyond the certain temperature the Ni3Si forms. And once the Ni3Si forms the crystal size suddenly start growing you can see here very clearly, that as you increase the temperature, what you are seeing is the crystalline size of the gamma phase and nickel phase, nickel solid solution. There are two phases in as mild condition the two phases there crystallite sizes are very low below 50 nano meters up to 673.

But, the moment you go to 723 the crystal size becomes almost equivalent to 120 nano meters. So, once a non congruent melting compound comes into picture. It has a high interfacial energy. And a high interfacial energy boundaries can easily migrate when compared to a low interfacial energy boundaries. This is what we see usually during ageing also, during ageing the coherent precipitate do not grows much is much easily. Whereas the incoherent precipitate can grow because in coherent precipitate the interfacial energy is very high. If the interfacial energy is very high it becomes incoherent. And once it is incoherent it can easily grow. Whereas, if it is coherent there is strain involved at the interface and because of the strain involved, at the interface the growth of such precipitate is very slow and that is what you see here.

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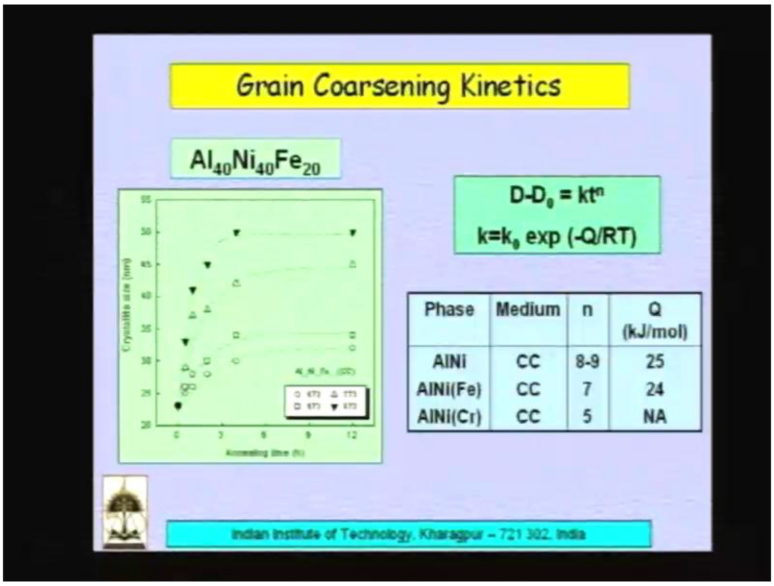

Grain Coarsening Kinetics

$Al_{40}Ni_{40}Fe_{20}$

$D-D_0 = kt^n$

$k=k_0 \exp(-Q/RT)$

Phase	Medium	n	Q (kJ/mol)
AlNi	CC	8-9	25
AlNi(Fe)	CC	7	24
AlNi(Cr)	CC	5	NA

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And one can do kinetics of this growth here is an example of NiAl the b 2 ordered compound. Where you we have put in some iron into it. So, it is NiAl compound basically with a lot of 20 percent of iron into it. And if you see how the crystallite size changes, as a function of temperature 573, 673, 773 and 873 and the time shown here you can see the higher the temperature the higher, the crystallite sizes which is expected, because at high temperature there is more growth of the grain size. And if you put all these values of grain size into a growth expression, this is a typical growth expression D minus D not is equal to k into t to the power n, where n is called growth exponent. You must have studied kinetics or probably kinetics course is going on now.

So, when you do kinetics course you will look at this kind of equations, which are growth equations, where D is the grain size at any point of time. And temperature, D not is the starting grain size and k is a parameter, which takes into account the activation energy for the grain growth, which is given here k equal to k not into exponential minus Q by RT. Where Q is the activation barrier for the grain growth or activation barrier for grain growth is usually activation barrier for diffusion.

And n is the growth exponent and the value of n tells you how fast it is growing or how slow it is growing. If you look at here one is AlNi, another is AlNi with iron into it, the AlNi with chromium into it.

And if you look at the growth exponents for these two last two cases and compare them with AlNi. You see the growth exponents are smaller with iron and chromium into the AlNi, when compare to AlNi itself. This clearly tells you that when an iron or chromium goes into it. They introduce some kind of solute drag effect. And as a result the growth cannot happen at the same rate as that happens in case of aluminum and nickel. And that is why you have a low growth exponents here when compare to that.

CC is a I know cemented carbide; that means, tungsten carbide. Where all ball milled under the same condition. So, that because the problem is if you use a stainless steel, as I told you before some contamination can come into picture. So, we will talk about those things later, when we talk mechanical alloying as a technique. We are at the moment not using talking about that. We are just basically looking at nano crystals the technique by which we can make them.

And then looking at the various nano crystal materials phenomena that occur in the nano crystal materials, and we are referring to the word mechanical alloying, once in a while only because that was method that is used for some of these materials. And we have also shown you examples of materials nano materials, which are made by the gas condensation technique. I will also show some examples later, where the nano materials made by the crystallization of the metallic glasses. When you start of talking about glasses, will start showing you that that. One can crystallize these glasses and get nano crystals in a glassing matrix. So, it is like a composite know, so such possibilities are also there.

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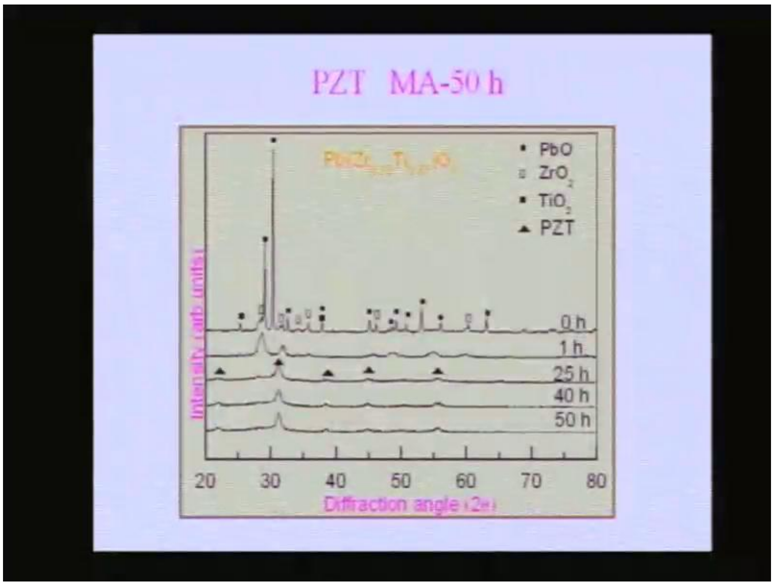

PZT MA-50 h

Another example of nano materials is the ceramics we have so far talked about basically metallic materials. I want to give you some flair of on the materials which are ceramics where many interesting phenomena take place one such example is what is called the PZT. It is a p j electric material and ferro electric material 2. And what is PZT is a lead zirconium titanate. So, PbO ZrO Zr2 O3 and let us TaO2. So, if you take a mixture of them and from a compound which is a spinel type of a structure. So, that is called lead zirconium titanate.

And that lead zirconium titanate, one can make it in nano crystalline form by starting with the PbO ZrO zirconium oxide and titanium oxide. All the three oxides and make a composition of this kind of a composition as I have shown here Pb Zr 0.53 titanium 0.47. And oxygen three that is a typical spinel type of composition ABO3 ABO3 is the spinel composition usually. So, we can make such a ABO3 type of a composition and if you take the individual oxide mixture. And finally, keep on doing ball miling you end up in a nano crystalline PZT.

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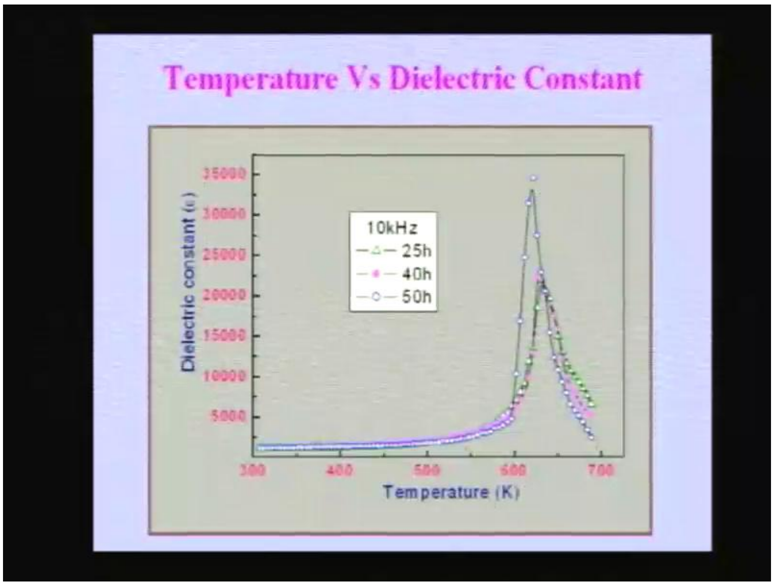

Temperature Vs Dielectric Constant

And that nano crystalline PZT incidentally has the highest dielectric constant, which has been reported, so far in the world. It has about 33000 which is really an amazing number for any dielectric material which is possible because of the nano crystalline nature.

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TEM of PZZT MA-50 h

As you can see very fine nano particle of PZT of the order 5 to 10 nano meters and they can lead to really very high dielectric constant. And that is dependent on the time of milling of course, because the as you keep on milling after 50 hours complete transmission to PZT take place.

And at lower timing the complete transmission does not occurs some of the reactants will remain. And because of which you will have a lower dielectric constant. But, once a complete nano crystalline PZT forms you can have a very high dielectric constant.

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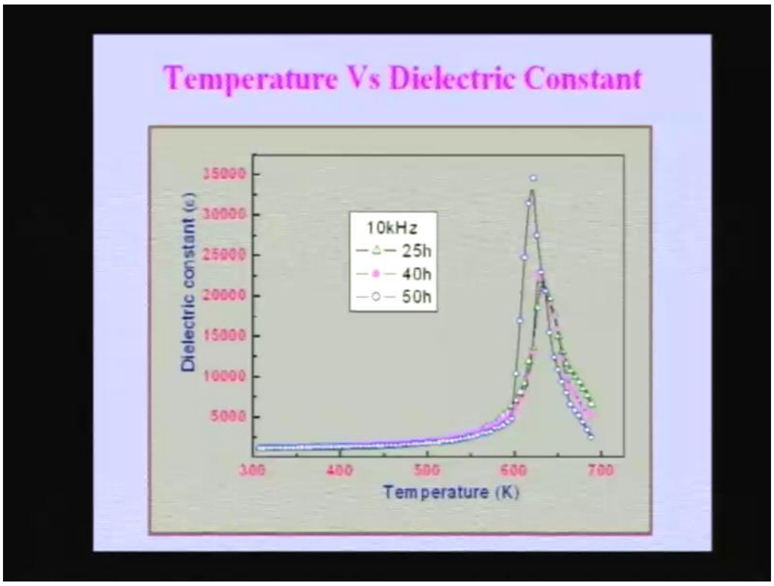

Temperature Vs Dielectric Constant

And they are even after sintering, this dielectric constant that we are talking is after sintering not just in the ball milled condition. They are have been sintered at 1200 degree centigrade for about 2 hours. So, even after that they still retain the nano crystalline nature. And the SEM pictures also show that they are about 0.5 to 1 micron. And some of them 2 microns also, but these one has to remember these are agglomerates. The actual nano crystals within each agglomerate either of the order of around 10 nano meters or so. These are all different timings, you can see 25 hours low magnification high magnification 2000, 6000 magnification can you see there.

Student: ((Refer Time: 53:11))

So, you can see it is basically low magnification and high magnification kind of situation and there are…

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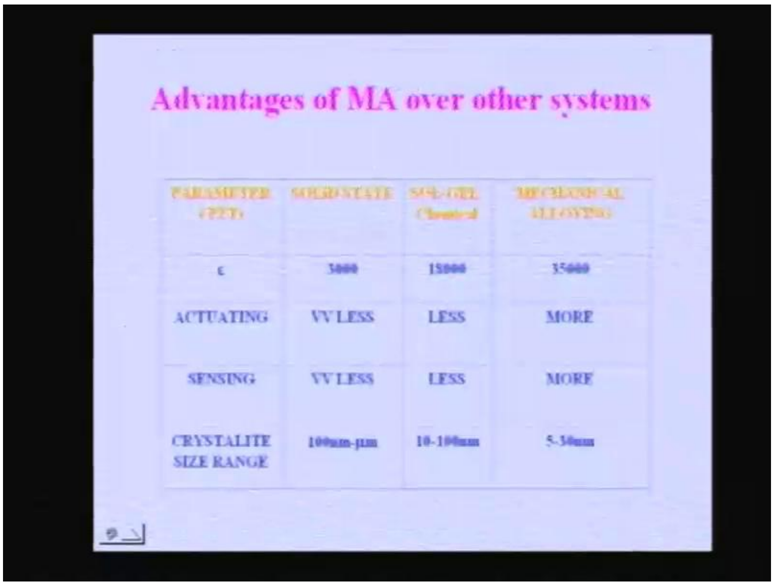

Advantages of MA over other systems

PARAMETER (PZT)	SOLID STATE	SOL-GEL (Chemical)	MECHANICAL ALLOYING
ε	3000	15000	35000
ACTUATING	VV LESS	LESS	MORE
SENSING	VV LESS	LESS	MORE
CRYSTALITE SIZE RANGE	100nm-μm	10-100nm	5-30nm

Number of advantages by doing this, that for example, there are different techniques by which you can make these PZT, nano PZT. If you make it by normal solid state route; that means, you take these individual oxides compact them.

And sinter them you can make a PZT by that, but you can get very low dielectric constant. And if you do by chemical route such a sol gel technique you can get a higher value, but still much lower than what you get by mechanical alloying. And the actual properties are very less here. Where much better there sintering properties are much better and the crystallite size is much lower, which is what really controls it.

The difference comes basically because of the crystallite size, you can see here a crystallites size here is much higher. And if you go to sol gel it is lower and if you go to mechanical alloying you get much lower and that is what controls. We will stop here and then take up the next class later.