Advanced Materials and Processes
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Lecture - 6
Nano crystalline Materials Part – IV

Various phenomena that occur when we take a material to the nano crystalline state. So, today we will continue with that. And try to see some more interesting things that happen. When we make a material nano crystalline. One of those things is what are called allotropic transitions. For example, we know there are different metals, which exist in different forms. Iron, for example we know iron at room temperature is BCC. And when you heat it beyond a certain temperature, it becomes FCC. What is that temperature?

Student: 910.

910 it becomes FCC and that form is stable up to about 1400. And then beyond that again you get a BCC form and finally, it melts at 1535. This is for iron, but not every metal exist in a allotropic form. But, there are certain metals, which have this kind of a allotropic transitions. Not only in metals, there are also a number of nonmetallic materials, such as oxides where such transitions occur.

For example, zirconia we know the monoclinic form and tetragonal form. And the transitions between them, which bring out what is called toughening of zirconia. So, these are all known to us. And what we see something interesting is that, there can be some metals, which do not have any allotropic transition up to their melting point. But, when we take these materials into the nano crystalline form, they show some new form which is does not exist, under the equilibrium condition.

One such example, I am going to show you is nickel. Nickel is FCC we all know up to the melting point nickel is FCC. The melting point is about 14, 50 or so. So, up to the melting point nickel is usually FCC under equilibrium conditions. But, the moment we take nickel to the nano crystalline state, immediately nickel transforms to a HCP form.

What is the basic difference between FCC and HCP? Can somebody.

Student: ((Refer Time: 03:00))

Yeah the stacking is different, yes that is a crucial point. The stacking of atoms is different in FCC and HCP. In the FCC it is ABC, ABC, ABC type and in the HCP it is AB, AB, AB type. Otherwise, mostly the structure is similar, the packing factor is also the same 74 percent of packing that we have.

So, the but you have is the packing density, I mean the sequence of packing or the stacking of atomic planes is going to be different. So, when we take a this nickel which is FCC, which has ABC, ABC, AB type of stacking. Once, you make it to nano crystalline state, you introduce lot of defects into the material. And because of which if imagine you introduce certain defects in the c layer, by chance if you introduce a lot of defects into a c layer. Then; obviously, if you imagine that the c layer goes from there, it becomes ultimately AB, AB, AB type of a stacking. So, you can convert an FCC structure to HCP structure just by removing the c layer there. So, if you can introduce lot of defects into the c layer preferentially.

That is one way of looking at how you can transform an FCC into HCP. Other way is that if you can introduce lot of defects into the FCC. It is free energy raises to such an extent, that this FCC with a lot of defects will have a higher free energy. Then, some other close pack structure, what is the other close pack structure that is possible it is only HCP.

And we know that, every system was to have as close pack packing as possible. So, once you have an FCC with lot of defects. And such a defective FCC structure would transform into a HCP structure. And that is what we see here and I also told you about what is the role of the free energy here.

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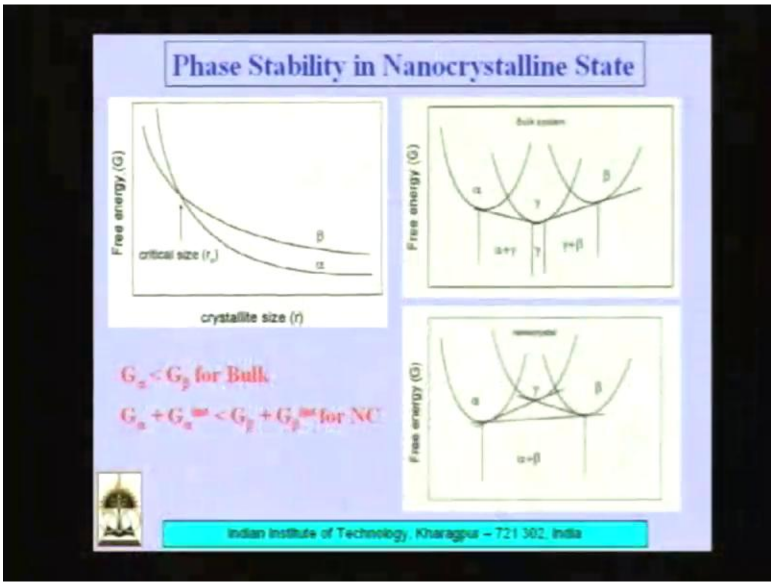

Phase Stability in Nanocrystalline State

$G_\alpha < G_\beta$ for Bulk

$G_\alpha + G_\alpha^{int} < G_\beta + G_\beta^{int}$ for NC

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As you can see here that when we take a material with a higher interfacial energy or higher surface energy. Once we take it into a nano crystalline state, that phase will not be stable. Because, it is over all free energy is going to be much higher. Then, another phase which has a lower interfacial energy, this is what we have talked in the last class.

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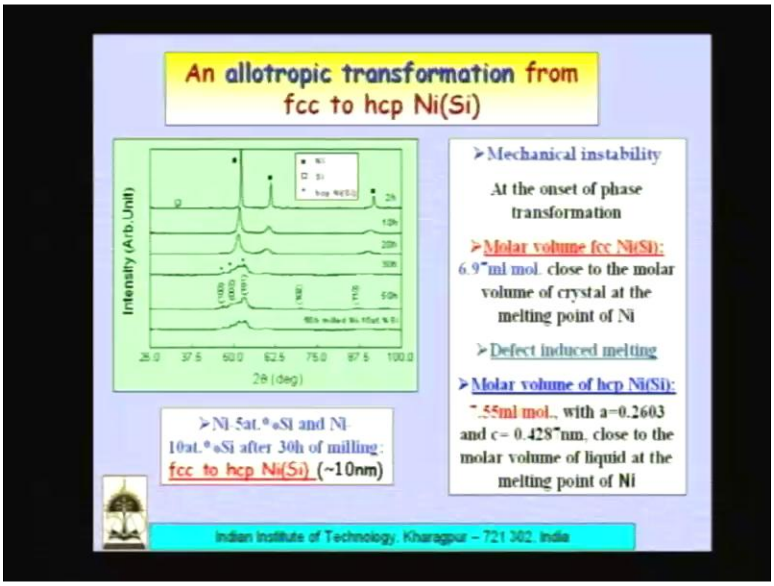

An allotropic transformation from fcc to hcp Ni(Si)

- Mechanical instability

At the onset of phase transformation

- Molar volume fcc Ni(Si):

6.97ml mol. close to the molar volume of crystal at the melting point of Ni

- Defect induced melting

- Molar volume of hcp Ni(Si):

7.55ml mol., with a=0.2603 and c= 0.4287nm, close to the molar volume of liquid at the melting point of Ni

- Ni-5at.%Si and Ni-10at.%Si after 30h of milling: fcc to hcp Ni(Si) (~10nm)

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So, what we see here in this particular nickel case is that, when you take nickel and keep on doing ball milling nickel powder. And we make it nano crystalline. And when it becomes less than 10 nano meters size, immediately that nickel transforms into a HCP. How do you see that? How do you recognize that, you can easily recognize it in an X-ray pattern in a XRD pattern an FCC metal, always shows the peak which correspond to FCC.

What are the peaks which correspond to FCC? 1 1 1 2 0 0 2 2 0 is a standard XRD pattern you all know. And the moment it transforms into a HCP, the peaks which are characteristic of the HCP would come into picture. And in any X-ray pattern it is very easy to recognize HCP. Because, HCP always will have three peaks close to each other.

For example, as you can see here the dots which are kept there or the hexagonal peaks. And the peak which is in the middle indicates that some FCC phase is still remaining. That means, it is a two phase mixture probably, if somebody goes to still lower crystallite size. You can have complete conversion from the FCC to HCP. And one can do that by going to lower crystallite size by cryomilling or it can be obtained even by normal inner condensation technique.

You see, it is not that it one has to do only ball milling to obtain this. What is important to realize is, this is happening only because of the defects. And people have shown also in a number of other systems. Where, people have obtained by gas condensation technique. The moment you go below certain critical crystallite size. And that critical crystallite size may be different for different systems.

It is not that, that 10 nano meter is a sacrosanct number that you have to go only below that. So, depending on the system that particular number depends. Because, it is a surface energy which matters as I told you before. So, the surface energy is a system dependent property. So, because of that for some systems may be if you come below 20 nano meters itself, maybe there is a phase transition.

But, in this particular case nickel if you come below 10 nano meters people have observed. And there are other cases also such as niobium, which is usually BCC. If you take it below a certain critical crystallite size it transforms into a HCP structure.

Student: ((Refer Time: 08:01))

That is, what I am telling below a certain crystallite size, it is not that it has to be 10 nano meter. But, when you go below certain crystallite size what you see here is going to happen. There is a critical size at which, there is a change over from the free energy takes place ((Refer Time: 08:22)). That the free energy of the meta stable phase becomes lower than the free energy of the other phase, which is stable under equilibrium conditions.

So, there is a critical crystallite size below which this free energy becomes lower. It is like our melting point. We know that below the melting points all you has a lower free energy, than the liquid, whereas above the melting point liquid has a lower free energy than the solid. So, that particular point is fixed. So, similarly here there is a critical crystallite size below, which such a thing happen.

And what is interesting is that, this in this particular system. This has not happened in case of pure nickel. If happened when you add a small amount of silicon to it. This is a particular case, where about 5 percent of silicon has been added. The problem with pure nickel is, pure nickel we all know is a ductile metal. In a ductile metal, when you try to do ball milling as I explained you before in the last class.

That you cannot really make it very fine a ductile metal unless you go to very low temperatures, which is called cryomilling. So, if you go to cryomilling then definitely it is possible to go to such a low crystallite size. Otherwise, usually nickel you cannot go below 20 nano meters, it is very difficult to go below around 20 nano meters, so but if you add a small amount of other alloying element. Then, you can have solid solution strengthening taking place. Because of which the particles can go to a lower crystallite size, very easily and that is what you see here. That when we take a nickel silicon and then take it to around 30 hours of milling or so immediately the crystallite size goes below 10 nano meters. And what is important to realize is that there is a molar volume expansion which happens.

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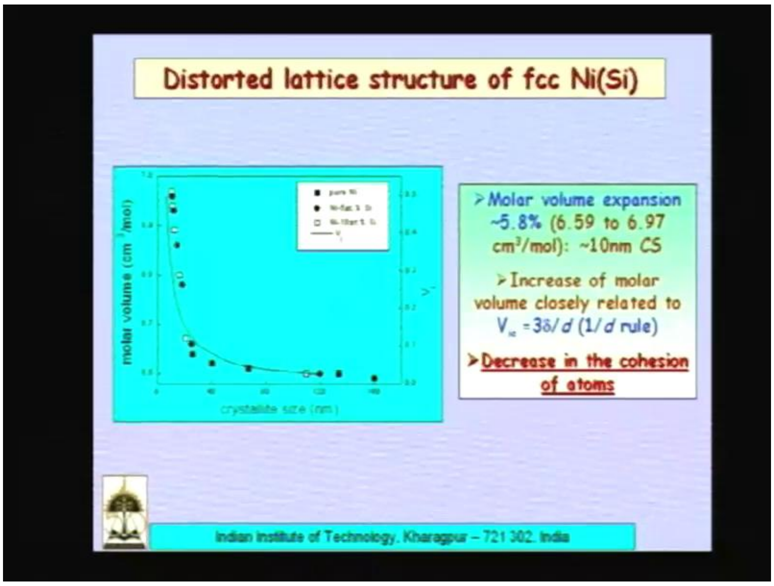

Distorted lattice structure of fcc Ni(Si)

- ➢Molar volume expansion ~5.8% (6.59 to 6.97 cm^3/mol): ~10nm CS
- ➢Increase of molar volume closely related to $V_{ic} = 3\delta/d$ (1/*d* rule)
- ➢**Decrease in the cohesion of atoms**

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When you take this material into a nano crystalline state, because as you keep on decreasing the crystallite size, you imagine the crystals becoming smaller and smaller. The grain boundary volume is increasing continuously, when this happens the overall volume. You imagine a small nano crystal, when you imagine a small nano crystal the grain boundary is a random nature it is a disordered nature.

So, because you have a disordered region around the grain., and within the grain you have a crystalline region, this crystal as you keep on decreasing the crystallite size, there is a volume expansion that takes place. This is similar to what you see, when you take a metal and keep on heating to higher and higher temperature, when you take a metal and keep on heating to higher temperature more and more defects which are nothing but, the vacancies come into picture.

And as vacancies concentration keeps on increasing, the metal expands. And we see in most of the metals. The room temperature volume and the volume at the melting point is always different. The metal always expands. In fact, that is one of the reasons why, if you take the steels, the room temperature BCC, the solubility of carbon in BCC is much lower, the maximum solubility is 0.025 in alpha.

But, the same BCC structure, when you look at the delta which is also BCC, the solubility of carbon there is higher. The maximum solubility is how much 0.1 percent, it is four times higher. This is just, because the same BCC structure is in a expanded form at high temperature. And because of the volume expansion the ((Refer Time: 12:09)) become bigger and as a result carbon can dissolve more.

And same thing happens with most of the metals, that we always have what is called a positive coefficient of thermal expansion for every metal. Most of the metals expand as you keep on increasing the temperature. And this is exactly, because the there are defects which are introduced. And we know the vacancy concentration is a function of temperature.

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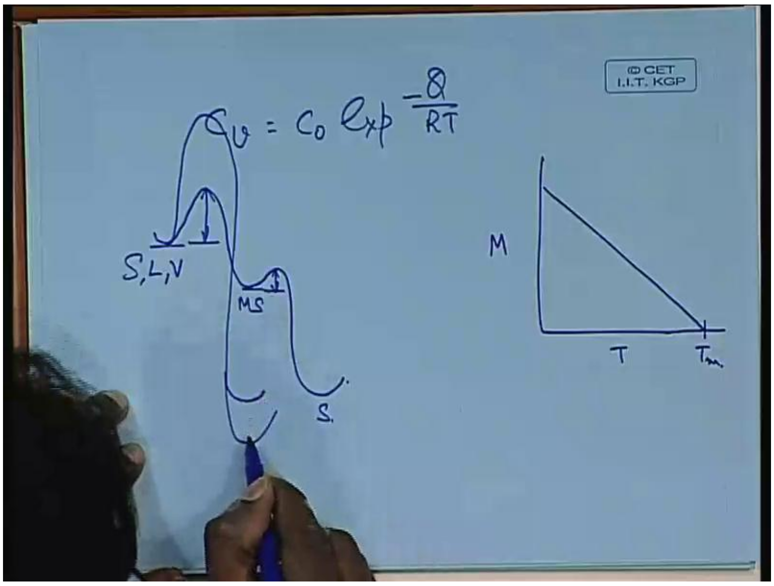

For example, we have talked about it before and concentration of vacancies can be written as C naught into exponential minus Q by R T we all know this. Similarly, this we are doing it as a function of temperature. Here, we are not doing anything with temperature, what we are just doing is reducing the crystallite size. As we are reducing the crystallite size, we are introducing more and more defects into the system.

And because of it there is a overall molar volume expansion. And that expansion can be of the order of around 5.8 to 6 percent. So, when you take the crystal from the normal bulk state ((Refer Time: 13:18)) to above around 10 nano meters, if you can take nickel can expand almost by about 6 percent. This is just by making the grains smaller and smaller equivalent to...

In fact, if you carefully see, the amount of volume expansion that you see. When, you take a metal up to its melting point is usually of that order. And in fact, whenever you take a metal liquid which solidifies, during solidification there is always a shrinkage is not it. That is, because when a solid transforms to a liquid, excepting a few solids such as ice, there is a volume expansion, because liquid occupies more volume than the solid, why? Because it is more defective structure. So, liquid occupies always a higher volume and that volume difference is usually of the order of around 6 percent. So, that is why whenever in a foundry people when they try to make castings. They always consider this shrinkage that 6 percent shrinkage. And we add extra metal in the form of risers to take care of that 6 percent volume contraction that takes place.

So, you need to provide extra liquid. So, that you can take care of that shrinkage cavity. So, that is exactly because the volume of the liquid is higher than that of the solid, which is basically coming because of the large volume expansion that occurs, when a solid transforms to a liquid. Similarly, when a solid is heated from room temperature up to it is melting point, there is always an expansion.

And this is what you see here, what you see is that. As you keep on decreasing the crystallite size below a certain crystallite size around 20 nano meters or so there is a sudden raise in the molar volume to a large extent. And almost you reach around 6 percent expansion, if you compare from the lower level 6.6 it is going up to 6.95, which is almost about 6 percent of volume expansion.

And this can be correlated to what is called 1 by d type of a root. Because, what you see on the right hand side is the grain boundary volume, inter crystalline region V i is the grain boundary volume or volume of the interface. So, if you plot the volume of the interface or the volume fraction of the interface, that also almost follows the same rule, because it follows 3 delta by d type of a rule which we talked about it earlier. And that if you put that line, what you see that solid line is nothing but V i. And that if you superimpose on this the way molar volume is increasing. You see both of them fit into it each other very well. So, the molar volume increase is basically coming from the...

Student: Increase in the grain boundaries.

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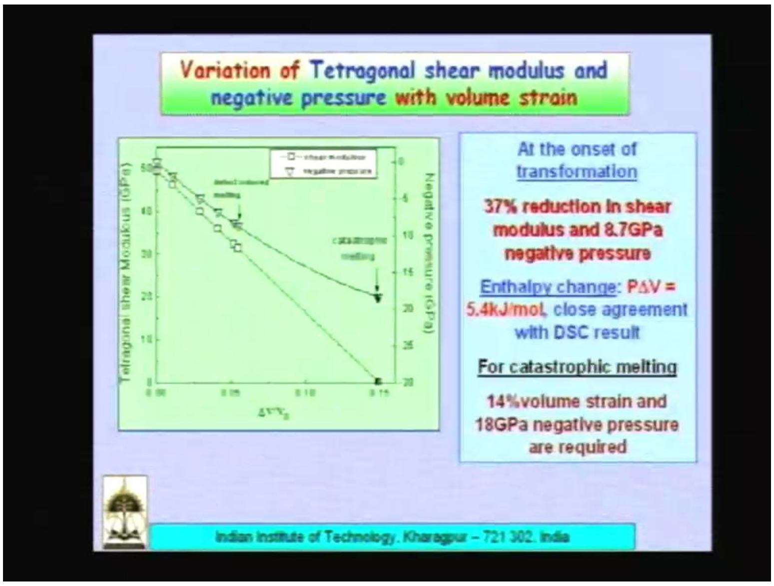

Variation of Tetragonal shear modulus and negative pressure with volume strain

At the onset of transformation

37% reduction in shear modulus and 8.7GPa negative pressure

Enthalpy change: P∆V = 5.4kJ/mol, close agreement with DSC result

For catastrophic melting

14%volume strain and 18GPa negative pressure are required

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Increase in the grain boundaries, the volume fraction of the grain boundaries. And this results in what is called a decrease in the shear modulus. Whenever volume is expanding, it means a shear modulus is decreasing. In fact, how do we define a liquid. A liquid is one whose shear modulus is 0 is not it that is how we define a liquid. In fact, there is a mechanical definition of melting point people call it.

The mechanical definition of the melting point is that, it is that temperature at which the shear modulus goes to 0. If you plot the shear modulus of a solid as a function of temperature. You will see, there is a temperature at which if you keep on plotting the shear modulus ((Refer Time: 17:01)) as a function of temperature. You will see, it goes to 0 at a particular temperature and that temperature is nothing but the melting point.

And that melting point is very close to our thermodynamic melting point, where we say the free energy difference between the solid and liquid is 0. These are very close to each other and one many people particularly physicist are more worried about this kind of mechanical instability they call it. That means, a solid as you how do we define a solid, solid is something is rigid, that is a solid.

And as I keep on heating the that solid, it loses its rigidity. The two such an extent, that at a particular point it can just flow like a liquid. Where, it is shear modulus goes to 0. And that is that temperature, where we call it as a melting point. So, if you plot this molar volume convert that molar volume into shear modulus. There are formula available which is called equation of state.

And if one can use that kind of formula and then calculate the shear modulus as a function of molar volume expansion. We see that the shear modulus continuously decreases. As a function of the expansion molar volume expansion, as we keep on increasing the molar volume, the shear modulus keeps on decreasing. And what you see finally, when you reach about 14 percent of volume expansion. Then, the shear modulus goes to 0 and that is the melting point.

And here, because we have not at gone up to that stage. We say, there is what is called a defecting used amorphisation. Becoming a liquid is equivalent to calling it as an amorphous. Liquid and amorphous are always consider to be having the same crystal structure is not it. So, here people also explain this in terms of the FCC crystal, as we keep on putting more and more defects it is molar volume expands.

And at a particular point it cannot remain as an FCC crystal. And it immediately melts and becomes amorphous and from that amorphous the HCP phase comes out.

Student: ((Refer Time: 19:24))

Because, HCP phase has a is also one of the closest pack system. Among the all the crystal structures that are available HCP and FCC are the most closest pack, among the various crystal system. So, when FCC is becomes unstable, the next phase that can come out which is also equally close pack is the HCP structure ((Refer Time: 19:57)).

So, this is one way of talking about it, basically in terms of the shear modulus one can also give in terms of the thermodynamic explanation, what we talked about it earlier. And one can also give an alternate explanation ((Refer Time: 20:04)) which is in teRMS of the shear modulus, that as you as the molar volume keeps on increasing.

Once you reach about 6 percent of molar volume expansion, you have about 37 percent reduction in the modulus, which will lead to what is called the liquidification or the amorphous phase formation. And finally, you get into what is called the HCP phase.

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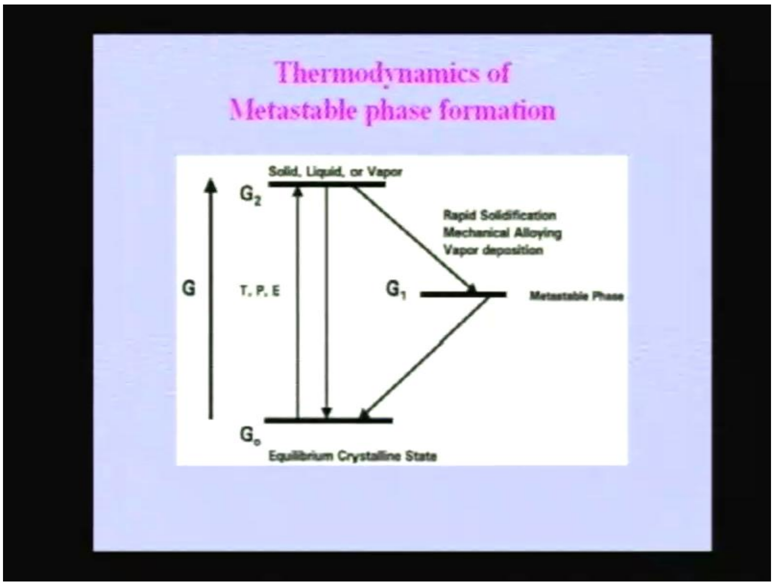

Thermodynamics of
Metastable phase formation

Now, come to various meta stable phases, that we get when we make any material into nano crystalline. If you want to look at from the thermodynamic perspective, a meta stable phase always has a higher free energy, when compared to an equilibrium phase. Imagine there is an equilibrium crystalline state, which has a lowest free energy.

And this if you compare it with respect to the liquid or vapor or solid with a higher free energy. Let say I take a pure metal mixture, during ball milling, that is one way of making a nano crystalline material, if I may be ball milling may be some other method. For example, if I take a solid and keep on bombarding with a lot of irons or electrons.

Then, what I generate is a solid with a lot of defects in it, it has a much higher free energy, when compared to the equilibrium crystalline state. And such a solid with a high defects or a liquid or a vapor can they have two possibilities. They can either directly go to a equilibrium crystalline structure or they can go to a meta stable state, depending on what is the activation barrier for the particular transformation.

For example, if I take a and b metals put them together. And from that if an equilibrium inter metallic compound has to come out. Let us imagine a case of nickel plus aluminum, if I take nickel plus aluminum powder mixture put it in a ball mill and keep on doing ball milling. There are two possibilities for it, one is it can become a crystalline N i A l which is a equilibrium compound, which has a lowest free energy.

Because, it is an inter metallic compound it has low free energy, high negative enthalpy of mixing. It can also form an amorphous phase, which is somewhere probably in the middle. Because, it has a higher free energy, if I take a pure metal mixture and keep on putting defects into it, ultimately it has two possibilities.

This pure metal mixture with lot of defects, if it has higher free energy than an amorphous phase. I can probably go to an amorphous phase, rather than going to an inter metallic compound. Basically, because if an inter metallic compound has to come out, it has to nucleate and grow a particular crystal structure has to nucleate and grow.

For example, most of the inter metallic compounds are ordered. So, that means an ordered structure has to nucleate and grow from a two pure metal mixture. Such a thing needs a lot of activation barrier, because you need the atoms to come together to form that particular unit cell. And that unit cell has to grow is not it. So, for such a thing the activation barrier is usually much higher than, what is required for an amorphous structure to form.

For an amorphous structure you do not need to really move the atoms to such an extent. That you need a particular unit cell to form and that unit cell has to grow, there is no unit cell in an amorphous structure. So, like that this is just one example of a meta stable phase. There can be many more meta stable phases, not only amorphous phase.

So, any meta stable phase if you can imagine, it always has a kind of an intermediate free energy, when compared to what you are starting with such as a liquid or a vapor. And then that liquid or a vapor or a solid instead of going straight away into the equilibrium phase, it can come to a meta stable phase by any of these processes, either rapid solidification or mechanical alloying or vapor deposition.

These are all what we can call them as non equilibrium processes, because they are generating non equilibrium phases. A meta stable phase is always a non equilibrium phase. So, we can generate a non equilibrium phase by any of these processes from starting from either liquid or solid or a vapor. If we are starting from solid, we call it as a mechanical alloying. If we start from the liquid it is a rapid solidification, if we are starting from the vapor it is a vapor deposition.

So, depending on the type of source with which we start or type of starting materials with which we start. We can have various process, which can lead to the meta stable phase formation. And that meta stable phase is definitely a meta stable phase, it is not a stable phase. So it has to finally, go to a stable state and that is what is a second part?

That meta stable phase, if you hold it for a long time at high temperature, will ultimately give you an equilibrium state. But, how fast it will give you an equilibrium state depends on, what is the activation barrier for this meta stable state to transform to an equilibrium state. This is similar to what we say here ((Refer Time: 25:53)).

If you start from the solid or the liquid or the vapor, you come to a meta stable state, whose activation barrier is this. And from the meta stable state you come back to the stable state with another activation barrier. This would be always easier than transforming the liquid directly into the solid state.

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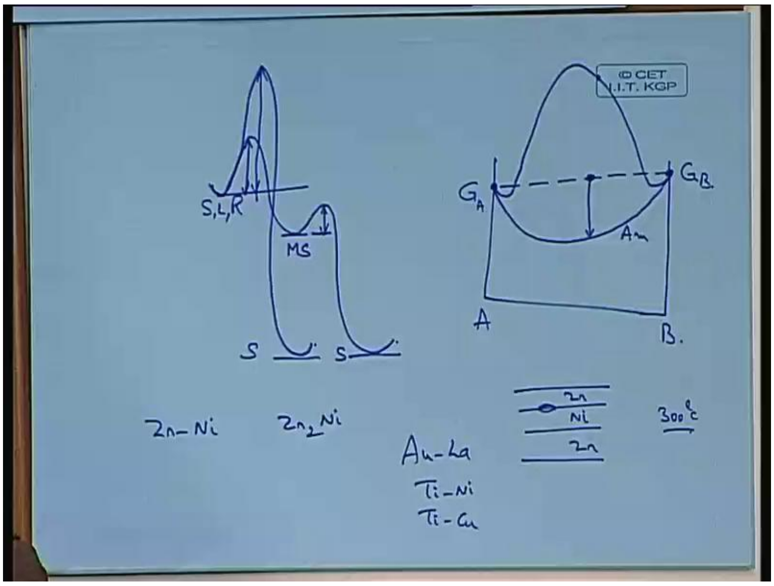

If you think of the solid liquid or vapor, coming directly to the solid state, the activation barrier usually would be much higher. Then, what it is required when it transforms to a meta stable state. And from the meta stable state you get into a stable state. This is what is called, you usually hear this when we are talking of age hardening. Super saturated solid solution of alpha does not directly go to a theta.

But, goes in a number of steps g p joules, theta double prime, theta prime and finally, to theta. This is what people call it as Ostwald Step Rule.

Student: ((Refer Time: 27:35))

Need not be, it depends on the actual process. But, it could be in some cases, but it need not be exactly. Because, it all depends on what are the actual kinetic process that are involved. If it is a diffusion control, if both are diffusion controlled then the summation would be equal. If one is the diffusion controlled, if another is a interface controlled, then the situation will be different. So, it all depends on the type of process.

So, what you see basically is that, if one can go from the meta stable state to the equilibrium state, with another activation barrier. And but if this activation barrier is larger the meta stable state will stay for a long time, like what we see cementite. We see that cementite is stable more or less, though we know it is a meta stable phase. But in for all practical purposes we see cementite almost like a stable phase. So, that is the typical nature of the phase transformation.

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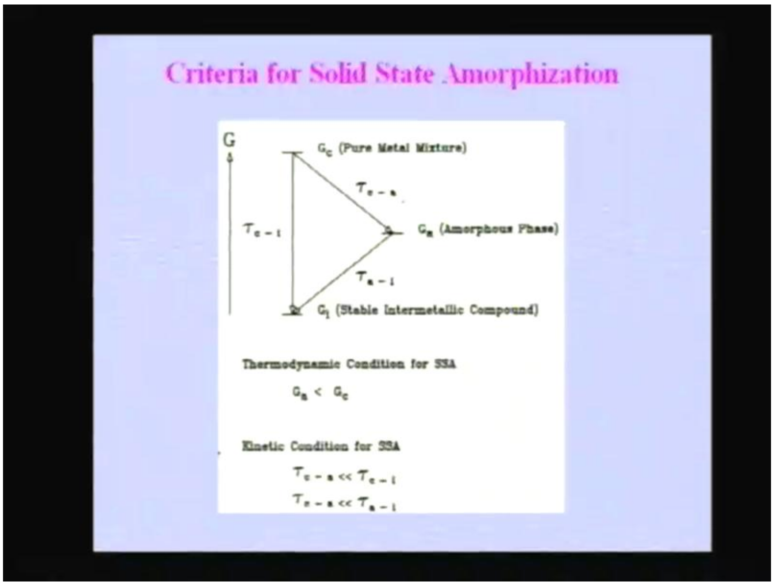

Criteria for Solid State Amorphization

Thermodynamic Condition for SSA

$G_a < G_c$

Kinetic Condition for SSA

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

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

If we come to specifically for solid state case, forget about the liquid and the vapor case. Look at only the solid state and start from a pure metal mixture, such as a ball milling condition. If I start from a pure metal mixture, I can get either inter metallic compound from the pure metal mixture or an amorphous phase depending on two conditions.

There are two criteria, what are these two criteria, one is that free energy criteria is that. The free energy of the amorphous phase should be lower than the free energy of the pure metal mixture ((Refer Time: 29:35)). If I start if I say take pure A and pure B. And look at the free energy of the two metals G of A and G of B, the free energy of the amorphous phase, if I take a line joining these two points.

At any particular point the free energy of the mixture is given by the point on the straight line. This we know from our thermodynamics. So, if I draw the free energy curve for the amorphous phase, if the amorphous phase has such a free energy curve. So, that there is a driving force. Then, only the amorphous phase will form, but if the amorphous phase has a free energy like this.

Such that, the amorphous phase having that particular composition has a much higher free energy, than this phase pure metal mixture. Then, you will not have an amorphous phase formation. This is the first criterion. But, just because it has a lower free energy it will not form. That is only a thermodynamic criteria, that is why we always say thermodynamics is in the subject of impossibilities.

It will tell what is not possible, but it will never be able to tell what will happen. For example, if this is the free energy curve for amorphous phase, this particular from this we can say amorphous phase cannot form from the pure metal mixture, that I can say. But, whether something else will form what will really form depends on the kinetics actually.

If there are two or three possibilities, all of them having a lower free energy, than the parent phase. Then, among these three, what will form depends on the kinetics that is what is the second condition? What is that second condition? The second condition says, whenever a phase has to form there is what is called an incubation period for the phase to nucleate. The tau that you are seeing here is basically nothing but, the incubation period ((Refer Time: 31:50)).

If the incubation period for the crystal to amorphous, if that is much smaller than, if the incubation period for the crystal to inter metallic then the amorphization will occur. I will try to repeat this, what we are saying is from the thermodynamic point of view. If I look at the pure metal mixture, pure metal mixture would always tend to go to an inter metallic, because that has a lower free energy than the amorphous state is not it. Amorphous state is having a free energy higher than that of the inter metallic. This is true in all the cases, because amorphous phase is always a meta stable phase. Amorphous phase can never be a stable phase in any system it is always a meta stable phase. So, because of it, it is free energy is higher than the stable inter metallic compound.

So, under thermodynamic conditions, if I look at it then I will say that only inter metallic should form under these two conditions. That, because amorphous phase though it has a free energy lower than that of the pure metal mixture. But, because inter metallic has a much lower free energy in principle inter metallic should form. But, under many conditions you do not see inter metallic forming.

Particularly when the two elements that you are choosing, the two pure metal metals that you are choosing. If their diffusivities are such that, one element diffuses very fast when compared to the other element. If you choose such a system, where we say what is called anomalous diffusivity. That means, the diffusivity of A in B is much higher than diffusivity of B in A or vice versa ((Refer Time: 33:40)).

If you consider that kind of a system for example, one such example is zirconium nickel, if I look at zirconium nickel system. The diffusivity of nickel in zirconium is much faster than the diffusivity of zirconium in nickel. All most four orders difference you will find.

The diffusivity of nickel in zirconium is very fast, when compared to that of zirconium in nickel. What should this do, what will this do in terms of the phase formation.

What you see is that under this condition. If an inter metallic has to form, let us say Z r 2 N i. You choose your composition in a such a way that it is Z r 2 N i type of a composition. If I take that composition and take pure metal mixture 66 percent of zirconium, 33 percent of nickel put them together. And do either ball milling or let us say vapor condensation, whatever it is.

Here we are talking of only solid states. So, let us stick to solid powders starting a ball milling or it can be another process which we will come to it a little later. That if you start doing that kind of a ball milling let say. Then, what you see is that ((Refer Time: 34:52)) if an inter metallic Z r 2 N i has to form. The zirconium and nickel atoms have to come together from the unit cell of Z r 2 N i and then it has to grow.

For this to happen zirconium or nickel atoms have to diffuse together. At almost similar rates, if one of them is diffusing very fast when compared to the second element Z r 2 N i nucleus cannot really form. Particularly at low temperatures, where ball milling is usually done room temperature, at such low temperatures such as room temperature.

Zirconium is very highly melting metal, it cannot diffuse as fast at that low temperature. Whereas, nickel has a lower melting point it can diffuse much more easily. So, because of such a situation, then you will see that, that both of them cannot come together to form a unit cell. But, for an amorphous phase to form it is much more easier.

Because it does not have any unit cell. So, that is why the activation barrier for the amorphous phase to form will be lower. Or in other words, the incubation period for the amorphous phase to form will be lower than the incubation period for the inter metallic to form. That is why, you see this happening. People have seen this a very interestingly in what is called multi layers also ((Refer Time: 36:19)).

For example, if I take a multi layer of zirconium, nickel, zirconium deposited by let us say vapor deposition thin films, you all know about thin films. So, let us say I deposit on some sub state a zirconium thin film. On that I deposit nickel thin film, again zirconium. And I take this kind of a couple, put it in a furnace at low temperature. Such that around 300 degrees centigrade or so.

What we see interestingly is that, at the inter phase between zirconium and nickel, at this inter phase. You will see an amorphous phase formed. How did people do this, what they did is that after these are deposited. They have sectioned it the way I showed you before and put it in a TEM. Where, you have a hitting facility possible. And in situ heat that sample and keep on observing what is going to happen to the inter phase.

And you will see at that inter phase an amorphous phase will nucleate and start growing. And how do you know that it is amorphous phase, simply you can find out by taking a diffraction pattern from that region, whereas the zirconium and nickel will be crystalline. And that particular region where amorphous phase has nucleated you will see it as amorphous.

Zr 2 Ni will not nucleate or any other inter metallic will not nucleate, it is the amorphous phase that will nucleate, but if I take this to high temperature. Let say 600 or 700 degrees centigrade, at that temperature instead of amorphous phase nucleating, you will see an inter metallic will nucleate. Why, because at that temperature the two elements start diffusing more or less at the same rate.

The diffusivity of both elements will come closer to each other at high temperatures. And once that happens the nucleation of an inter metallic compound becomes very easy. So, people have shown in a very simple experiment by just changing the temperature. That at low temperature you get an amorphous phase and at high temperatures you do not get it.

A number of systems for example, gold lanthanum is another example, nickel titanium is another example, titanium copper is another example, and many such examples, where people have shown that the diffusivity of one element is much higher than the other. And because of which an amorphous phase forms very easily.

There is a second kinetic condition also ((Refer Time: 38:55)). What is the second kinetic condition, that says that if the incubation period for the crystal to amorphous is much lower than amorphous to inter metallic. Then, only amorphous phase will form. What is the meaning of the second condition. Let us say the first condition is satisfied, if the first condition is satisfied what will happen, amorphous phase will form.

First condition is what, incubation period of crystal to amorphous is much lower than crystal to inter metallic. That means, if I take a pure metal mixture, for it to transform to an inter metallic. The incubation period is much larger, whereas for it to transform to amorphous the incubation period is much smaller. So, amorphous phase will form.

But, the moment this amorphous phase is will form, if the incubation period for the amorphous to inter metallic. Because, amorphous phase is meta stable we know. So, it wants to transform to a stable state, what is the stable state? Stable state is that inter metallic compounds in any particular system, and if this transformation from amorphous to inter metallic, if the incubation for period for that, if that is very small. Then what will happen, the amorphous phase immediately after forming, it would immediately transform to an inter metallic. Before you take it out and then do an X-ray, it may immediately transform to an inter metallic.

So, you will not be able to see whether amorphous phase has formed at all or not. Even if it has formed, before you take it out and put it into a DSC and see. This is the situation is similar to what I talk to you in thermodynamics class about the finding out the C p of a liquid. You want to find out the C p of a liquid heat capacity of a liquid, you put in a calorie meter and you want to heat it and find out that what is the heat capacity of it?

But, before you measure it, it transforms to a solid. So, you are not really measuring the heat capacity of the liquid. But, you are measuring the heat capacity of the solid. So, similarly here you make an amorphous phase, but if that amorphous is highly unstable let us say ((Refer Time: 41:04)). That it is transformation to inter metallic needs very small thermal fluctuation. That it can easily transform into an inter metallic compound, then you will not be able to see really amorphous phase.

So, as a result the second kinetic constraint is also very important, if an amorphous phase has to form. This all happens in the nano crystalline state, that is why we are referring to this. So, when you take a material to nano crystalline state. That nano crystal being having a very high free energy like G c here, it can either become an inter metallic or it can become an amorphous depending on any of these two conditions.

And in fact, both the conditions have to be satisfied if an amorphous phase has to come. If the amorphous phase has to come, then first the free energy of the amorphous phase should be lower than that of the nano crystal. Second the activation barrier for the amorphous phase to form should be lower than the activation barrier for the inter metallic to form from the nano crystalline state.

And the third another condition is that, the activation barrier for the amorphous to inter metallic also should be large. Or in other words the incubation period for the amorphous to inter metallic should be larger than the incubation period for the crystal to amorphous. So, imagine that on top instead of a pure metal mixture, you have a nano crystal there. Exactly, whatever we have talked here will stick to that particular condition, that we can take a nano crystalline material and do all this. And that is what I am going to show you as a few examples.

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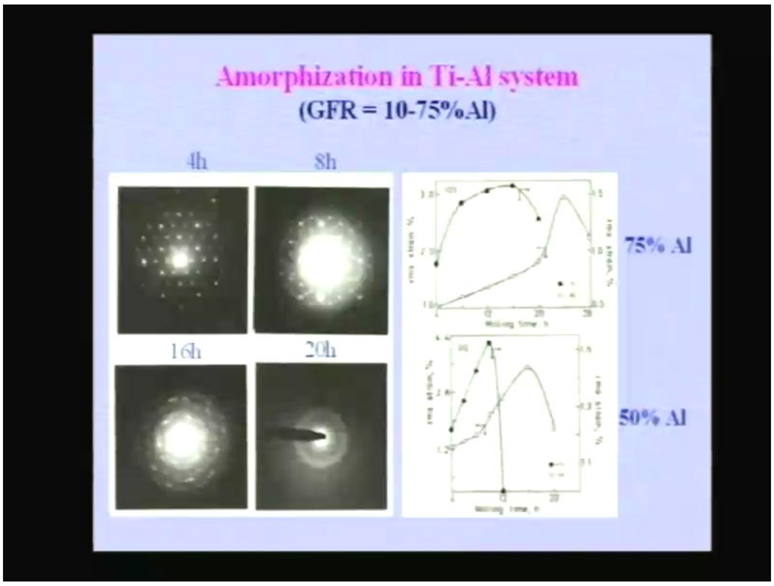

Amorphization in Ti-Al system

(GFR = 10-75%Al)

One such example is here, titanium aluminum. What you see here is that, we have taken a particular composition, this is let say T i 50 A l 50 kind of a composition. And start doing ball milling. You say, initially it is crystalline 4 hours you can see that, you come to 8 hours, there are more and more defects come into picture from the diffraction pattern you can clearly see.

And then come to 16 hours you see there is lot of rings forming, what is the meaning of rings forming? That means, they are becoming finer and finer nano crystalline. Nano crystals always show as rings in any SAD pattern. In a selected area diffraction pattern in any term, you will always see rings which correspond to nano crystal.

And the thickness of that ring is similar to the breadth in any X-ray peak. And so the thickness of the ring is an indirect evidence for the nano crystalline nature. And one can calculate the actual crystallite size from that thickness. Or in a X-ray from the peak broadening we can calculate the crystallite size, we know the Shearer formula.

So, similarly here it gives you an idea that they are becoming nano crystalline. And finally, it becomes amorphous, amorphous how do you distinguish in a X-ray.

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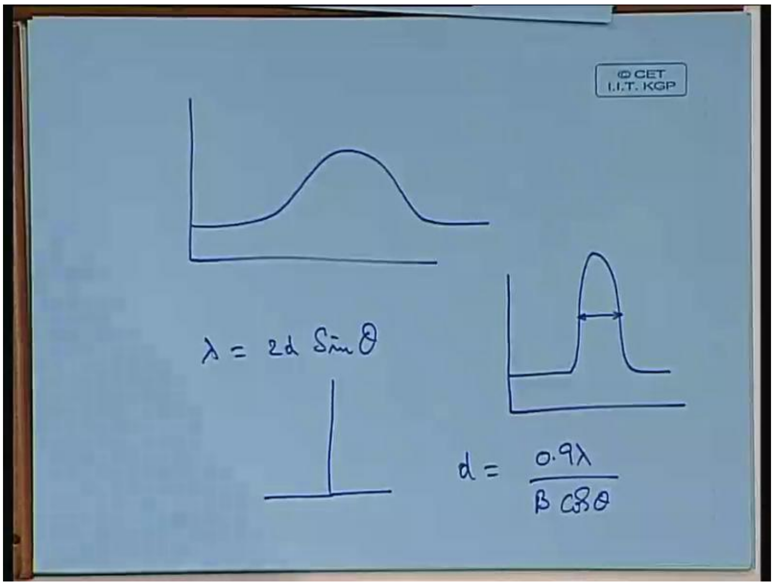

In an X-ray diffraction amorphous structure always gives you a broad peak like this. And in a electron diffraction, it will also just give you what is called a halo. That means, a thick ring, a diffused ring. The difference between a nano crystal and an amorphous in a electron diffraction is that nano crystal rings are sharp they are never diffused.

But, if it is an amorphous, the amorphous always gives you a diffused ring ((Refer Time: 44:53)). And that gives you an idea of how such a transformation takes place. So, but this is important to remember, that this happens only after the crystals become nano crystal. So, it has to become a nano crystal, then only it will become amorphous.

Unless it becomes nano crystal, the free energy will not be so high. That it is free energy will be higher than that of the amorphous phase. Unless you reach such a condition, the free energy of the crystal is higher than that of the amorphous phase. You will not have transformation from the crystal to this. And this happens only when you take it to nano crystalline state.

And similarly, you will see also there is a condition of the strain as you keep on doing ball milling, you are putting lot of strain into the system. We know, that whenever we deform a material, you are straining the material, strain hardening we say. So, similarly whenever you are putting in lot of ball milling. Where, the ball comes and heats. So, there is a deformation, because of which strain comes into picture ((Refer Time: 45:59)).

In fact, one can calculate from the X-ray peak broadening. Whenever, you have an X-ray from the peak broadening that you have full width at half maximum we say, one can calculate both crystallite size and strain. Because, strain can also give you peak broadening. In fact, do you know what are all the things that can give you peak broadening in X-ray.

Crystallite size strain I have already told about these two, there is also something else. Instrumental broadening, this is very important to note. What is instrumental broadening, whenever I am sending a particular radiation of a certain wavelength lambda we should get a peak, but if this lambda is not a fixed lambda. But, has certain range plus delta lambda minus delta lambda.

The moment I am sending a radiation not having a fixed wavelength, but having a range, then immediately the theta that you are going to get from backsaw ((Refer Time: 47:01)) we know equal to lambda equal to 2 d sin theta. For a given d there has to be a theta, when you use a certain lambda. But, if I am using a range of lambda, there will be a range of theta for the same d is not it.

So, that will range of d theta will give you a broadening in the peak. Otherwise in principle, if you take a coarse material without any strain in it. How do you obtain that by annealing a material at high temperatures, we can make a material strain free completely. And at the same time, because we are annealing at a high temperature, you can make it a very coarse material.

Such a material, if you do X-ray you should get peaks which are just like that something like a delta function should be sharp. It should not have any broadening, but whenever you have done any X-ray, if at all you have done X-ray anytime before. You would always see, it has some broadening, you will never see without any broadening 0 broadening is very rare to observe.

And that broadening is coming path basically from the instrument, if the nano crystallite is not there. If there is no nano crystallite, if there is no strain, the broadening that comes is basically from the instrumental broadening. And if we can measure that, that can be deducted from the actual broadening, that you are observing in a nano crystalline material. And the whatever is the difference that you are finding that can be attributed to the nano crystalline nature.

And one can calculate using the Shearer formula, which is nothing but, d crystallite size or grain size is equal to 0.9 lambda by beta cos theta, this formula all of you know. And there is also a way to calculate the crystallite size, I mean the strain which I will talk to you when we talk about mechanical alloying to produce nano crystalline materials. Or we can take it up even right now. Basically, there is there are ways to separate these two contributions.

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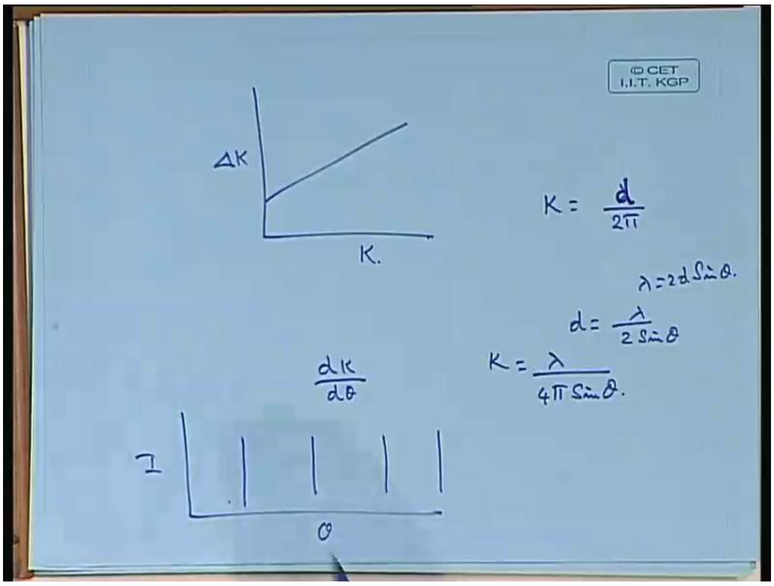

How to separate strain and crystallite size, there are certain ways to separate these two one way is what is called, if you calculate what the delta K verses K plot it. What is delta K, delta K is K is nothing but the wave number. Wave number is lambda by 2 pi and lambda equal to 2 d sin theta wave number equal to d by 2 pi let me tell you that d by 2 pi.

And so lambda equal to 2 d sin theta and so d is nothing but, lambda by 2 sin theta. So, if you put that, you will see that K is equal to lambda by 4 pi sin theta. If you plot this, this is called a wave number with respect to the delta K. Delta K is nothing but, d if you do d K by d theta. That means, differentiate K with respect to theta, what you get is delta K. So, this delta K verses K if you plot for a number of peaks in a X-ray diffraction, when you do X-ray diffraction intensity verses theta. You get a number of peaks for each peak calculate the peak broadening.

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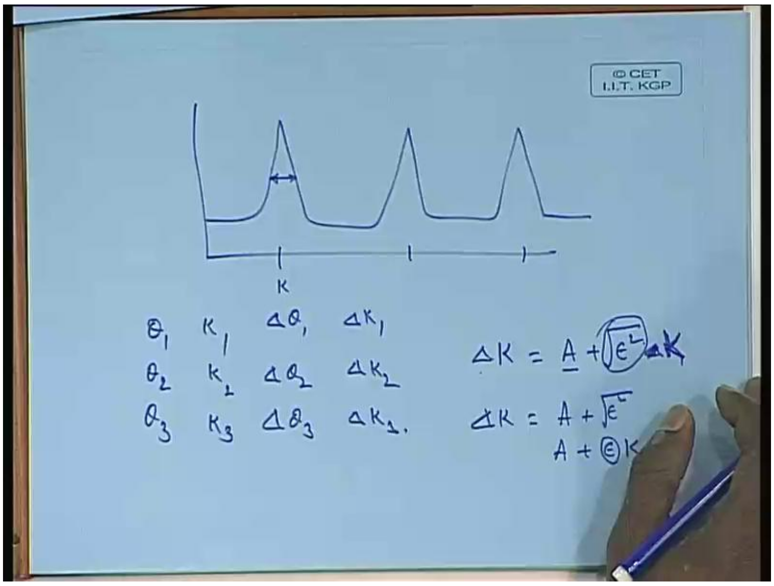

Let say you get peaks like this, like this for each peak calculate, what is the delta theta. And calculate what is delta K from that. Once, you know delta theta you can calculate delta K, and that delta K. If you plot as a function of K for each peak, you can get K for this, and delta K, K for this and delta K, K for this, and delta K. So, for each peak you can calculate what is the K? Because, you know the theta. So, from theta 1, theta 2, theta 3, one can calculate K 1, K 2, K 3 and from delta theta 1, delta theta 2, delta theta 3 one can calculate delta K 1, delta K 2, delta K 3. And if you can plot all this, what you see is the slope of this will give you the strain.

And the intercept gives you the peak broadening coming, because of the particle size. This is what is called Friedel’s Law. So, there is a formula called delta K is equal to some constant A plus strain square root of exclaim square they call it RMSS strain versus by delta K1 .

So, if you plot delta K verses K here it is K. If you plot delta K verses K, then you will see that there will be a straight line. And the slope of the straight line is nothing but, this and the intercept is what you will see...

Student: ((Refer Time: 53:05))

No, K is outside see delta K is equal to A plus epsilon square or you can even call it as just epsilon K which is nothing but, the strain and K is nothing but, the wave vector. So, one can do this kind of a thing, there are also other methods. Whenever, we come across ball milling we will talk about this more.

Student: ((Refer Time: 53:03))

That is what is called RMS square, RMS strain. So, RMS strain if basically because you have strain in all the three directions x y z. So, that is why we call root me square strain. So, root me square strain one can calculate, because we are not talking of a strain in any particular direction, we are talking of the bulk strain inside the material. So, that is always called RMS strain.

So, that is why here you are plotting the RMS strain ((Refer Time: 54:03)). So, if you calculate that RMS strain, you will see that RMS strain reaches a particular maximum. And immediately after it reaches a maximum there is an amorphization. So, once the strain reaches a critical value immediately, there is an amorphization. You will see that a little later also this is a shown in to difference compositions.

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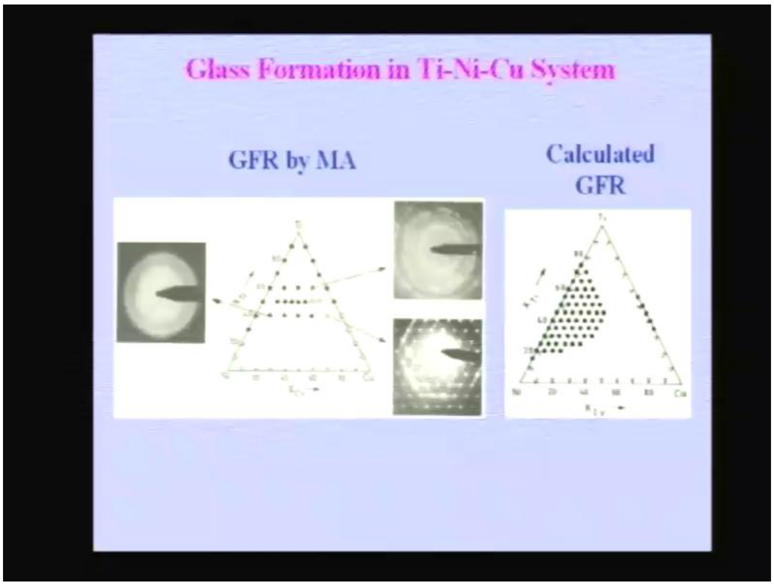

Glass Formation in Ti-Ni-Cu System

GFR by MA

Calculated GFR

And I will show you in a another system also a similar thing happening. That once you reach a critical strain, you will see amorphization taking place.

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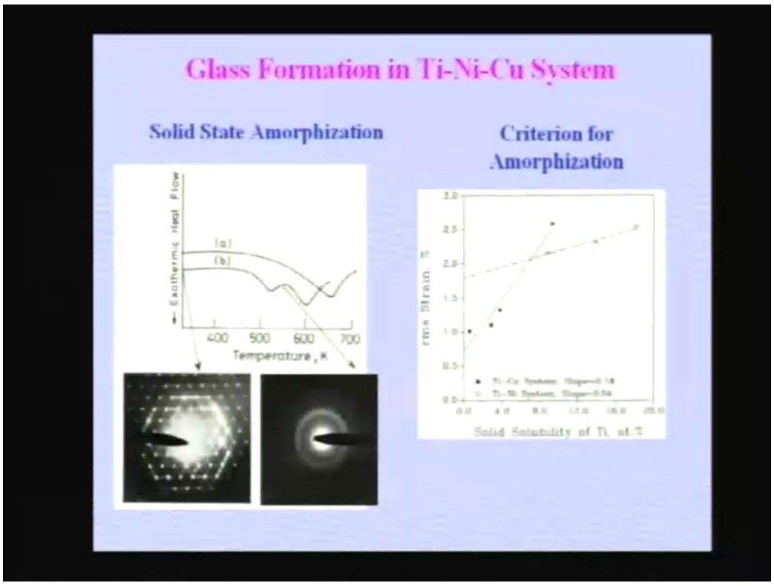

Glass Formation in Ti-Ni-Cu System

Solid State Amorphization

Criterion for Amorphization

This is also for example, here this is a titanium copper and titanium nickel case. So, as you keep on increasing the solubility of titanium in copper or nickel. You will see the strain keeps on increasing, but the moment the strain reaches a critical value immediately it become amorphous.

That, whether it is titanium copper or titanium nickel irrespective of verse system, that we are choosing. And I have shown you earlier titanium aluminum case, that in both the cases the strain at which the amorphization occurs is always the same, about 2.5 percent.

So, when you reach around 2.5 percent of strain inside the material. Then, imminently the crystal with this much strain becomes unstable. And immediately it will transform to a amorphous phase. And this is happens in all the cases and one can do it in a number of ternary systems also this is one such ternary system titanium nickel copper. Where you take different compositions and show that some compositions are completely amorphous. And some are completely crystalline and some are a mixture of amorphous plus crystalline. And one can do thermodynamics and calculate what is called glass forming composition range.

That means, what composition range in which you can get a glass and compare it what with what you get experimentally. And one can show that this is feasible. How do you know what is the glass forming composition range, what we do is that take a free Energy composition diagram.

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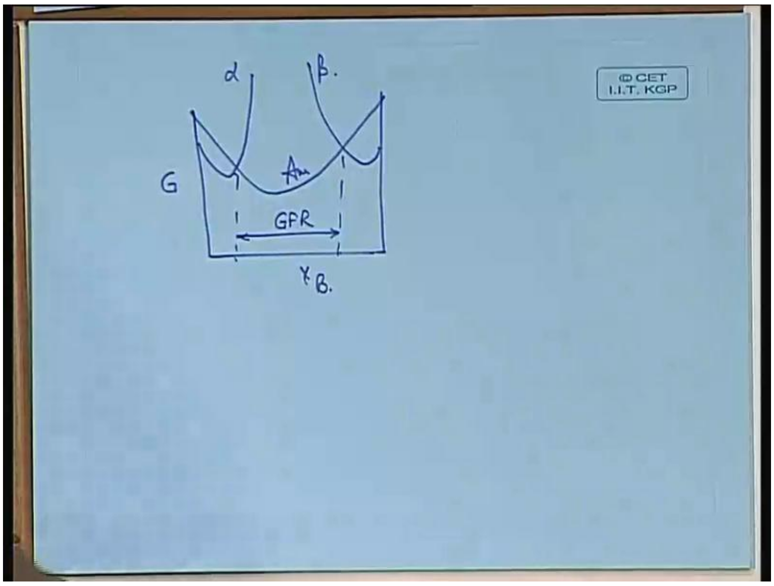

G verses composition X B and plot the free energy of alpha, free energy of beta and free energy of the amorphous phase, if I do this. This particular composition range is what is called the GFR. That means, the composition range between the two T naught one is the T naught with the alpha, another is the T naught with the beta. So, that composition range is the GFR. Why, because within that composition range free energy of the amorphous phase is always the lower. So, that is why we use that as the GFR. We will start stop here and then start next class.