Advanced Materials and Processes

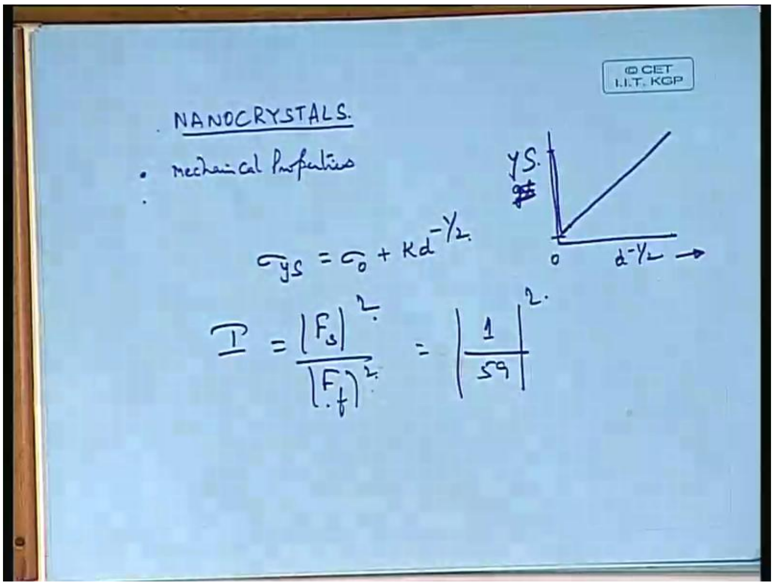
Prof. B. S. Murty
Department of Metallurgical Engineering
Indian Institute Technology, Kharagpur

Lecture - 4

Nanocrystalline Materials Part – II

Particularly for the last I would say the origin is basically I would say from a paper in 1981 by a person by name, Hulbert glitter. So, glitter from Germany was can be considered as a pioneer in the nano materials. And they have made nano material of various metals and ceramics, starting from 1981, the initial properties of general materials, once you take them to a nano regime. So, if you look at the mechanical property of any poly crystal material. We usually, correlate the mechanical property to the grain size, with a relation called Hall petch relation. You all are aware of it.

(Refer Slide Time: 01:48)



NANOCRYSTALS.

- mechanical Properties

$$\sigma_{ys} = \sigma_0 + Kd^{-1/2}$$

$$I = \frac{|F_s|^2}{|F_f|^2} = \left|\frac{1}{59}\right|^2$$

So, which looks something like this, that if you plot the grain size as a function of d to the power minus half. You get a straight line relation. This is commonly known to all of us. So, when the d to the power minus half is increases; that means, if the d is decreasing, then you have an increase in the strength. And this is basically attributed to the grain boundaries, acting as the pining agents, for the dislocation motion, these all known to all of us.

So, if you have more number of grain boundaries, by decreasing the grain size. You have more obstacles, for the other dislocation moment. And as a result, we say there is a decrease; there is an increasing in the strength yield. Strength of the material, as stress required for the further moment of the dislocation, which is basically, the yield strength of the material. So, if you extrapolate this two, the 0, d to the power minus half. What does it basically mean? When, you are extrapolating to the 0, d to the power minus half means, what kind of material it is.

Student: ((Refer Time: 02:55))

It is…

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

It is a single crystal, yes, when the d to the power minus half is zero. That means, you have the largest crystal possible, which is a single crystal. So, as a result, if you look at the intercept of the yield strength, the y axis as to be the heal strength of the material or the stress required for the deformation. The heal strength of the material, if you look at, what is the intercept?

That is, what we usually define as sigma y s as sigma 0 plus k 2 into d to the power minus half. This is the standard Hall petch relation, where the sigma 0 is nothing but the intercept on the y axis, which we can call it, as the yield strength of a material. When, the grain size is very large. But in principle, when you make a single crystal, a single crystal, most of the time, what we produce have almost 0 dislocations.

Or, usually, wherever a single crystal is a synthesized, it usually is nucleated on one of the screw dislocation. And it grows, that is what, people usually observe, whenever a single crystal is grown by any of the techniques, such as Czochralski technique and things like that. So, if you look at most of the single crystals, the number of dislocations is very few. When, the numbers of dislocations are very few, then how do, we at attribute the Hall petch relation to such a material, where the grain size is very large.

In principle, the Hall petch relation says that the strength should decrease and come to a very, low value. When the grain size is very large and when it becomes a single crystal, but at the same time, you will see that, when it becomes a single crystal. That it is a number of dislocations being so small, Hall petch relation it iself cannot really work. Because, Hall petch relation is based on the dislocations, being pinned down by the grain boundary.

If the there are no dislocations or there are very few dislocations in a material. In principle, we cannot really use the Hall petch relation. So, as a result, in principle, this plot, when the approach 0, should increase and then goes to a value, which is much higher, which is, what we call it, as theoretical cohesive strength of the material. So, that is what, exactly happens, when you go to very small number of dislocations, which are usually observed in crystals, which are signal crystals.

So, basically, Hall petch relation has a limitation. When, it is being used for a material, which has no dislocations or very few dislocations. So, single crystals really utilizing a Hall petch relation is very difficult. So, one has to remember this limitation, when we use a Hall petch relation. Similarly, on the other side, we are talking of nano materials. When, we go to nano materials of a very small sizes, we end up again in a similar situation, you think of a nano material of a 5 nano meters, let us say.

Imagine a material, a grain of a 5 nano meters. So, in a 5 nano meters, how many atoms, you can aspect in any particular direction. What is the usual inter atomic distances in a metal like aluminum, let us say. What is the usual inter atomic distance or if you think of a lattice parameter for an aluminum, which is nothing but a parameter. What is the approximate value? Anybody remember, in terms of nano meters or interns of angstroms, do you know.

Student: 3 and 4.

It is about 3 to 4 angstroms. Most of inter atomic distance in metals are about 3 to 4 angstroms. So, if you look at, such an inter, atomic distance, assume it to be around 4 angstroms. And if you take a 5 nano meter material in any particular direction, you cannot expect, more than above 12 atoms or 15 atoms. If you think of three dimensions, you have such a material of about 10 to 15 atoms in a particular direction.

In such a material, how much dislocation, you can really expect. We know that, whenever, you have two dislocations, two of different kind. Let us say, unlike dislocations. There is always an attraction between any two unlike dislocations and then they ultimately merge into each other and then a dislocation vanishes. If you consider a like dislocation, any two like dislocations. There has to be a minimum distance, between any two like dislocation.

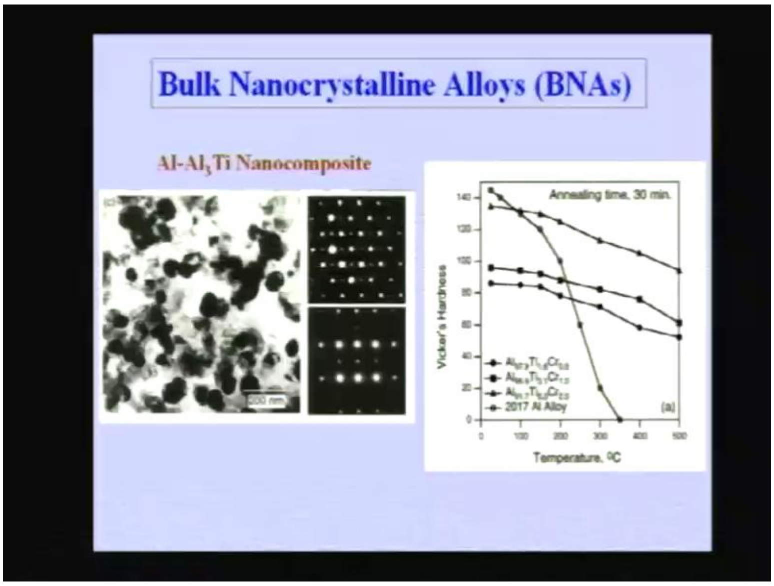
Because, of the repulsion, between the two like dislocations, there has to be a minimum distance. And this minimum distance is usually of the order of 4 to 5, inter atomic distances. So, if you think of about 5 inter atomic distances. You cannot expect in a particular direction, more than 2 or 3 dislocations in a material of about 5 nano meters. So, if you really go to such fine scale of nano materials the number of dislocation itself or so few. That one can really talk about dislocations, being you know obstructed by the grain boundaries.

So, in principle, in a number of cases, there have been a few of example also, where people have seen that, there is a lattice softening that occurs. Lattice softening occurs, basically because, when you have a large grain boundaries. The material flows like a viscous material. Because, the grain boundaries are something like an amorphous structure or like a liquid structure.

So, when you have such a disordered structure at the grain boundaries. There are number of examples, which are available, where people have showed, that the material becomes really soft. So, as a result, again we have a limitation on the Hall petch relation. So, Hall petch relation, basically works in domain of let us say, something like about, as large as a grain size. But, not a single crystal of any grain size, poly crystal in material, from that level up to around, may be about 50 nano meters or so.

If you really go much below to around 20 or less than 20, you end up into problems. So, here, we see one example, where the strength improves to a large extent, particularly, and strength at high temperatures, by making a nano composite.

(Refer Slide Time: 10:05)



Bulk Nanocrystalline Alloys (BNAs)

Al-Al_3Ti Nanocomposite

This is an example of aluminum alloy, with the AL 3 Ti particles unit, these are nano particles. You can see, the scale there, is of the order of around 200 nano meters scale. In which, if we look at individual particle sizes, there of the order of the around 50 to 20 nano meters, they are different sizes in the range of 20 to 50 nano meters. So, such nano particles, if they are embedded in aluminum matrices and these particles are ordered AL 3 Ti particles.

These are FCC ordered structures, which are called the L 12 structures. When, you come to inter metallics, we will talk more about, what is this L 12 structure. Basically, if you take an FCC structure, order it. In such a way, that all the face centered atoms are occupied by one type of atom. And all the body corners are occupied, one type of atom, this is what is called an L 12 structure.

In an AL 3 Ti, you have three atoms of aluminum, one atom of titanium. And the titanium occupies all the body corners and the aluminum occupies all the face centered. That is, what is called an FCC ordered structure. And such an ordered structure, if you subject it to diffraction. You will see, if you look at any of these two diffraction patterns, you will clearly see, there are faint spots.

In addition to the major spots, which you can see there, for example, the top one gives you, three fold, symmetry or the six fold symmetry, which is characteristic of the 111 pattern. And you have fine spots at the centre and those fines spots are, what are called the super lattice reflections. We know in an x ray or electron diffraction, in any diffraction, whenever you have an ordered structure. You get extra peeks or extra spots, which correspond to the ordered nature of the particular compound.

So, once a compound is ordered, you get extra spots. Because, of the ordered nature, which I think, we will talk at some point of time, probably in x, anybody has done x ray course, here. So, have you heard about, super lattice reflections. For example, FCC, what kind of super lattice reflection, you can expect, what are the fundamental reflections in FCC?

Student: ((Refer Time: 12:25))

In FCC.

Student: ((Refer Time: 12:30))

That is for h square k square plus l square. So, if you look at the real h k l, what are the peeks, that you can get? 111 peek. 200, 220 these are the first three peeks, that you can get in FCC. And the 110 peek and 100 peek, these two peek are the forbidden peeks, in case of disordered FCC, the moment you order it. The structure factor changes and from the structure factor, one can really prove, that you can see the 100 and 110 reflections, as supper lattice reflections in an FCC structure.

Similarly, in a BCC structure, you do not usually see the 111 peek, under the normal conditions. If it is a disordered structure, once you make a BCC into order BCC. Then, you can even see the 100 and the 111 peeks in a BCC. Here, is an FCC structure, which is an ordered FCC structure. And all those faint spots, that you see, are the super lattice reflections.

The only difference between super lattice reflections and fundamental reflection is that, their intensity will be very low. Because, the structure factor is usually the difference of the atomic scattering factor of the 2 and because, it is the difference and intensity is nothing but the square of the structure factor. So, you will see, there the intensity of a super lattice reflection is much smaller than the intensity of a fundamental reflection, which is nothing but the summation of the atomic scattering factor of the two elements.

Student: ((Refer Time: 14:06))

Yes, from the extra lines, one can see, but the important thing is that, the extra lines or so faint. That in some cases, you may not even see, for example, if you take copper zinc, a typical example of brass, we all talk about beta brass. Beta brass can be ordered at high temperatures, around 550 degrees or so. If you take to a temperature, below 550, you have usually an ordered BCC structure, which is beta prime, people call it are beta dash.

And if you go to higher temperature, you talk of disordered structure. And if you compare, the crystals, the diffraction patterns of these two by x ray, you will not be able to see any difference. Basically, because, copper and zinc are next to each other in the periodic table. And the atomic size, atomic number, difference between these two, is just 1. So, as a result, if you consider the structure factor difference is basically 1.

So, if we talk of the intensity, intensity is nothing but the square of the structure factor of the super lattice reflection by the fundamental reflection. If you look at the square of these two and this is atomic size difference is only one. Whereas, this is nothing but the summation of the 2, which is 29 plus 30, the atomic numbers is 59. So, it is 1 by 59 square of it. You can see, the intensity ratio, between the fundamental reflections on the super lattice reflection, for a BCC structure.

Like such as, the copper zinc beta brass is so small, that one cannot really see the super lattice reflection. If you use an x ray, one can go to electron microscopy, where the incident beam itself, as so much high energy, because you are using about, 100 kilo volts there. So, because of which, you are able to see, the super lattice reflection also more easily.

Otherwise, if you go to other compounds, which are also called BCC based. But, the two atoms or far apart in the periodic table, for example, nickel aluminum Ni AL. You must have heard of Ni AL is also ordered bcc structure. And such as ordered bcc structure there, you will be able to easily see it because; nickel atomic number and aluminum atomic number are vastly different. So, you can easily see the fundamental reflections and the super lattice reflection, in such a case. So, one has to remember this aspect.

So, these super lattice reflections always have a lower intensity. Because, as I told you, the structure factor basically is different for super lattice reflection, for a fundamental reflection factors is much bigger than that for the super lattice reflection. But, what is more crucial here, because we are talking about the nano material is that, when you put such an ordered nano particle in an aluminum matrix. You see much higher improvement in the strength, particularly at high temperature, for example, if you look at this plot, which is shows the hardness.

Because, hardness of a commercial aluminum alloys 2017 alloy, which is nothing but aluminum copper alloy, the most popular aluminum alloy. For aerospace space industries, aluminum copper alloy, you all know that. If you take, such an aluminum copper alloy, take it to the peak aged condition and look at it is hardness, as a function temperature. You will see that it hardness falls very rapidly, because we talked about it in the last class.

Why does the aluminum copper alloy lose it is strength, when you go to high temperature?

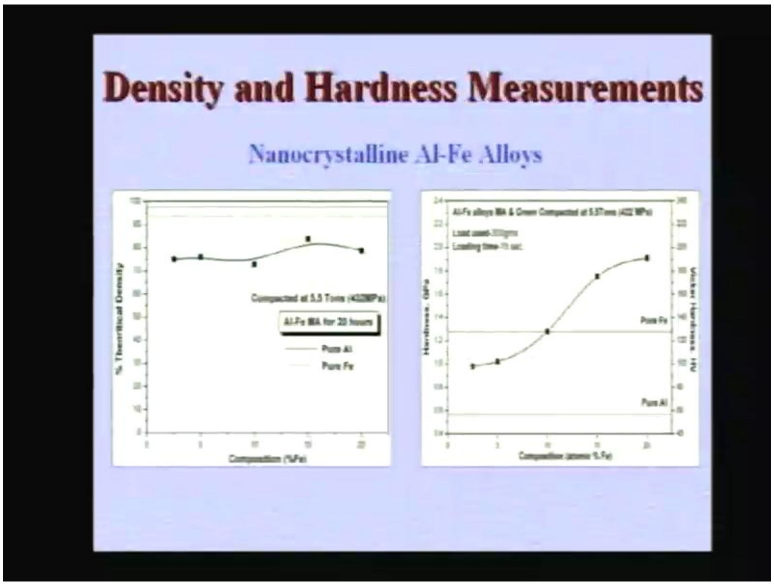
Student: ((Refer Time: 17:56))

Because of the particle coarsening or particle dissolution, these are the two crucial important parameters, which affect the strength of the aluminum alloy, at high temperature. The particles, which are the theta double prime or theta prime, that we talk about either the coarsen or dissolve depending on the temperature. Because, of which, the strength more or less, drastically falls.

But, if you take this kind of a composite, nano composite, you see, these AL 3 Ti nano particles, remains, inside the aluminum matrix, without any dissolution or coarsening. And then can give you strength, at even temperatures of the order about, 500 degrees. You cannot imagine, using an aluminum copper alloy at 500 degrees, impossible, the maximum temperature is about 300. Nobody can imagine using an aluminum copper alloy, at high temperatures.

That is why there is a lot of work nowadays, on trying to develop high temperature alloys using such composites structures, nano composites structures.

(Refer Slide Time: 19:08)



Density and Hardness Measurements

Nanocrystalline Al-Fe Alloys

So, this is one of the advantages of such, a nano composites, other thing is also there are. There is another example here, aluminum iron, alloy, where what we see on the left side is nothing but an aluminum iron nano composite, which is compacted. And gives you an idea of, what are the densities that are the achieved in the green condition. That means, as compacted condition, without a centering.

That, you can reach densities of the order of around, 80 percent or 85 percent and such a green compact, if you look at the hardness of it, you see that, the hardness. You can reach, almost about 2 giga Pascal, which is very high for any aluminum alloy, these are just green compact single, without centering. So, one can achieve, such high strength levels in a nano composite. So, that is one of the fundamental reasons, why everybody is existed about nano composition, as for as a metallurgical applications are concerned.

Yes, physical properties are also much improved properties, people have found. But, as a metallurgist, we are more concerned about, how to improve the strength of the material. And how to control the micro structure of a material, so that, you can achieve a particular mechanical property, enhanced mechanical property. This is one of the things, you may, also ask me, what about the creep resistance, in such a nano material.

We will talk about it, when we talk about grain coarsening in these materials and how to control the creep in such materials. Because, we know that, if you have a fine grain material, the material easily creeps. So, at high temperature in principle, you should lose the strength. But, in some of these materials, even the high temperature strength, as I showed you in the previous case is also much higher.

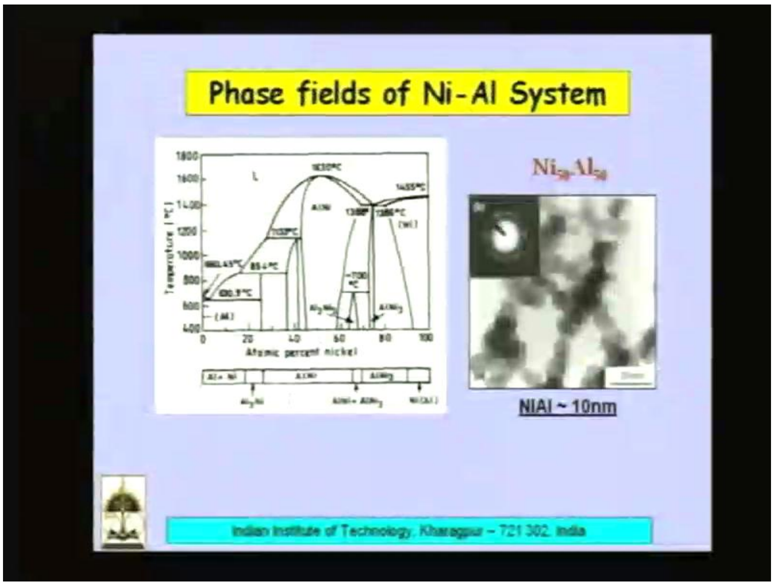
How is that, you are able to achieve, such high temperature strength, without any creep occurring. That is, basically because, when you put these hard particles, they not only coarsen. Because, their solubility in aluminum is very small, you have to remember that, the coarsening of a particle has a direct relation to the solubility. For example, in dispersion strengthening, the particles do not coarsen.

When, I put atria into nickel based super alloy, the particles remains, what they are, whatever you have put, they do not coarsen, basically because, atria does not dissolve into nickel. So, the coarsening is largely related to the dissolution. Because, coarsening occurs by diffusion, particle coarsening, if at all particle has to coarsen, the atoms have defuse.

So, that is related to the dissolution or the solubility of any of the element inside the particle. For example, in case of the aluminum copper alloy, the particles, that are coming out or basically A L 2 c u. So, it is the solubility of copper in aluminum, which controls the coarsening. Of course, the diffusivity also is crucial, the temperature is also crucial. But, at the same time, one of the most important parameter is solubility.

So, if you take those systems, where the solubility is very much restricted. Then, in such systems, the grain coarsening or the particle coarsening is can be controlled. This is one of the reasons, why if you have such AL 3 Ti nano particles, they do not coarsen. At the same time, they act as pinning agents, for any grain boundary sliding, which is the phenomenon for the creep. So, you can control the creep. So, one is able to achieve high strengths in these materials, even at high temperatures, by controlling the grain boundary sliding. So, that is one of the advantages in these materials.

(Refer Slide Time: 23:02)



Phase fields of Ni-Al System

$Ni_{50}Al_{50}$

NIAl ~ 10nm

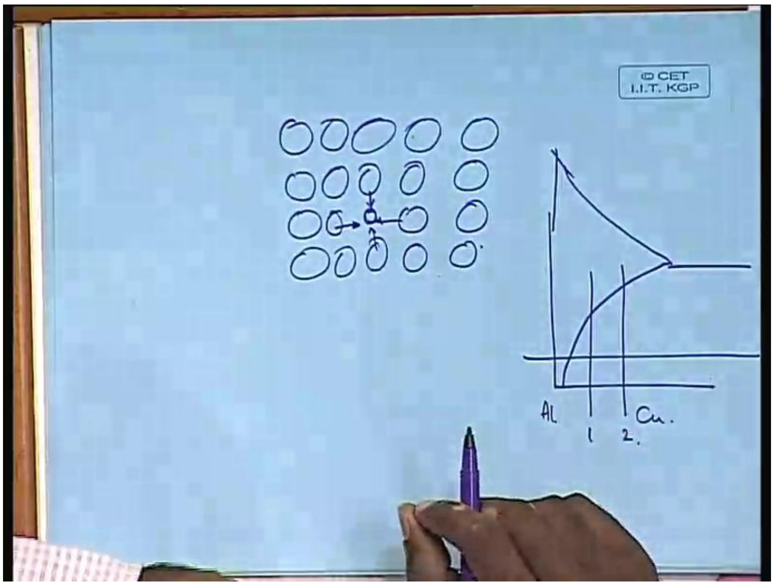
Indian Institute of Technology, Kharagpur – 721 302, India

There are also additional things, when you go to a nano regime, one can achieve, wide range of phase fields. For example, if you know talk about the solubility of a metal a, in another metal b, this is decided usually, by what is called the Hume Rothery rules. We all know about them, the four Hume Rothery rules, which are crucial in deciding the solubility. And this is true, also for inter metallic compounds and also for the sol gel solutions and this can be extended, when you go to a nano regime.

How do, we extend it, we can extend it because, the grain boundaries volume fraction increases to a large extent. We have talked about it in the previous class and when you increase the grain boundary volume fraction and we know that, the grain boundaries are more open structure. When, you have such a large fraction of open structure in a material, the solute atom can easily dissolve.

Why is that the solute atom, there is a restriction on the solubility. Because, whenever a b element dissolves into the a element, we know that the atomic size of b is different from that of the atomic size of a. And as a result, when put a b atom into an, a atom, there is a stress involved.

(Refer Slide Time: 24:35)



For example, if you look at the atomic arrangement, for example, something likes this, a type of atoms. And if you have a small, b atoms, which is not really interstitial, but at the same time, substitutional, but it is size is smaller than the remaining atoms. Then, you see that the moment, you put a small atom there. The other atoms around it, are attracted towards that, because there is always some kind of a delta h mixing, associated with any a and d atoms.

And because of that, there is either an attraction or repulsion, depending on the situation; whether it is delta h mixing is positive or negative. We know about it in the thermodynamic class, we have talked about it. And so if you look at, such a situation this, when the atoms are either attracted or repulsed, there is some strain. That is associated with it and this kind of a strain prevents more dissolution. Because, whenever there is a strain, inside the lattice, the lattice becomes unstable.

So, as you put more and more atoms into it, there is more and more strain and the moment, the strain crosses a particular critical value. Then, the solubility, there is, you reach a maximum on the solubility. That what we call the solubility limit has been reached. And so as a result, for any given crystal structure, there is a maximum solubility for a particular solute in a solvent. And this basically depends on the atomic size, difference between a and b, what is called the misfit parameter, size factor, people call it.

So, as a result, here whenever we talk about, two elements, in a normal crystal, where the items are periodically arranged, in such a case, there is a restriction on the solid solubility of a b in a. But, the moment, you have a random structure. Obviously, such a strain generation, you cannot expect a lot of strain being generated, because the atoms are randomly arranged.

So, as a result, there is no real pushing of atoms, when a large atom is sitting, large solute atom is sitting or the atoms being pulled to a large extant. When, a small atom is sitting, because the total strain gets uniformly distributed, inside the material. When, you have a random arrangement, this is true in the liquids also. We always see the solubility of a particular solute in a solid is much lower than in a liquid. Why is that so the same thing that in a liquid, there is no strain generated, when a solute dissolves? So, you can have a larger solubility in a liquid.

Exactly, similarly, because the grain boundary structure is similar to that of a liquid structure is like an amorphous structure, you can expect a large solubility. That is why, in most of the cases, we will also see in the coming slides. That the solubility can be enhanced to large extent and here is an example of a nickel aluminide, Ni AL, intermetallic compound.

We just now talked about it, the b 2 type of a compound; that means, ordered BCC compound, which under equilibrium conditions. You see the phase diagram; the solubility is from about 45 percent to about 55 percent. So, the room temperature solubility, if you look at it, not really room temperature, we have the phase diagram only up to 400 degree centigrade. But, if you go to lower temperature, it is further gets reduced.

We know that, solubility is much lower at low temperature and usually increases at high temperature. Basically, because the lattice expands, when the lattice expands, the system can accommodate more strain. So, more solubility can be achieved. So, as a result, if you see the solubility is higher at higher temperature and at low temperature. It is much smaller and that is 45 to 55.

But, the moment, I make them in nano crystalline form, what you see the picture on the right side. The nano crystal Ni AL made and it is solubility range, varies from about 25 percent here. The bar, which is given on the bottom, please have a look at it and you the phase field of Ni AL, varies from about 25 percent to about 65 percent. So, one who can have a very wide range, starting from 25 percent of nickel to about 65 percent of nickel, possible, by just making it, nano crystal?

So, one can increase the solute solubility, you may say, what is the kind of advantage, that I get by doing that. The advantage, that I can get is, that Ni AL, if I want to produce it. I can produce it, only on an limited range, there are a number inter metallic compounds, particularly, which are called line compounds are you aware of them, what are line compounds?

Student: ((Refer Time: 29:36))

Fixed composition, correct, their composition is fixed. They have a very narrow composition range and such compound, if you want to make it; it is very difficult, because you have to control the composition carefully. So, that you have exactly that for example, Fe 3 c, you take it semantic, it is a line compound, n b 2 Si is a line compound there. So, many line compounds like that, Al 3 Ni is a line compound. These are all line compounds, which fixed compositions.

If you want to make them, under normal conventional condition, you have to really control the composition. So, that, exactly you are at that composition to get that compound, single phase compound, if you want to make. But, if you go to the nano regime, even if the composition is slightly on the either side, you can still produce that particular compound, because that compound can exist over a range of composition.

One can produce such compounds over ranges of composition and one can extend the face fields. One can have large phase fields possible in this kind of thing and when, we are talking of solid solutions, what is the advantage of extending the phase field, in case of a solid solution. If you have an extended solubility, what kind of an advantage, you can get?

Student: ((Refer Time: 31:00))

More strengthening, not only because of solid solutions strengthening, but also, you can precipitate larger volume fraction of the precipitate, because the volume fraction of the precipitate. That you can generate at any given temperature, during aging depends on the solubility. For example, if you look at this, the typical aluminum copper phase diagram, we know that, if I take this alloy, if I am talking doing aging at this temperature.

If I take these two alloys, alloy number 1 and alloy number 2. In alloy number 2, I can have a larger volume fraction of the precipitate, when compared to alloy number 1. So; that means, if I can have a super saturated solid solution with higher amount of solute. Then, in such a super saturated sol gel solution, if I can do aging, I can have larger volume fraction. And the volume fraction, if it higher, I can have higher strength.

So, if I can have a higher super saturate solubility an extended solubility, one can have a not only an increased strength, because of the sol gel solution formation itself. But, sol gel solutions, we know always have a lower strength, when compared to a precipitation harden alloy are a desperation handed alloy. So, as a result, one can increase the strength of the sol gel solution by precipitating a larger volume fraction of the precipitate, if you can have an extended solubility.

So, that is why, the extended solubility, not only has can give you an improved strengthening. But, also can help you in producing these compounds, over wide ranges, particularly in case of line compounds, where you have limitation in making. For example, AL 3 Ni, we have a lot of problem in making Al 3 Ni, because aluminum has a low melting point, nickel has a very high melting point.

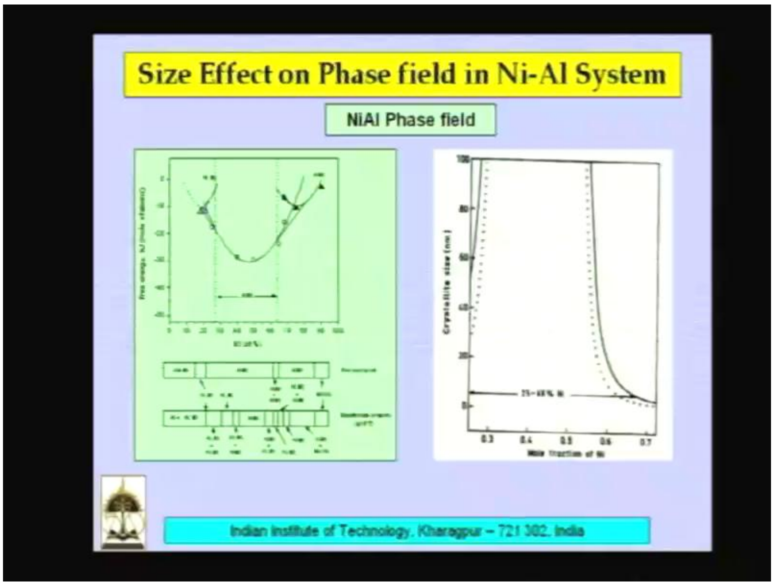
If you want to make them by melting root, you have to melt aluminum and nickel together. Obviously, then you form a compound in the liquid state and then cast it. So, that, you can get an AL 3 Ni compound. If you want to make such a compound, by the time is the aluminum starts and the nickel starts melting, there is chance, that some of the aluminum starts boiling.

So, it is very difficult to control the composition, how do you know, how much of aluminum has boiled. So, that, if you want to know make Al 3 Ni, you need to know, how much of aluminum, you should to take, how much of nickel, you should to take. So, that, both of them can give you the Al 3 Ni, single phase compound and there is a lot of difficulty. By such a normal conventional roots to make the single phase compounds, which are particularly, line compounds.

Whenever, the situation is such that, one of the elements has a much lower melting point, when compared to the other. The problem gets aggravated in these cases, even otherwise composition control is very difficult, during the liquid metal is in the root. Because, we always know, during solidification, there is always segregation that occurs. So, once the segregation has occurred and then you it is become very difficult to produce a particular composition.

And ultimately, you may not end up in a single phase, but you end up in a two phase mixture and if your goal is to make a single phase, you have a problem in making it. So, as a result, nano crystal materials have an advantage, one can have a wider range of compositions and still, have such a compound formation.

(Refer Slide Time: 34:38)



Size Effect on Phase field in Ni-Al System

NiAl Phase field

Indian Institute of Technology, Kharagpur – 721 302, India

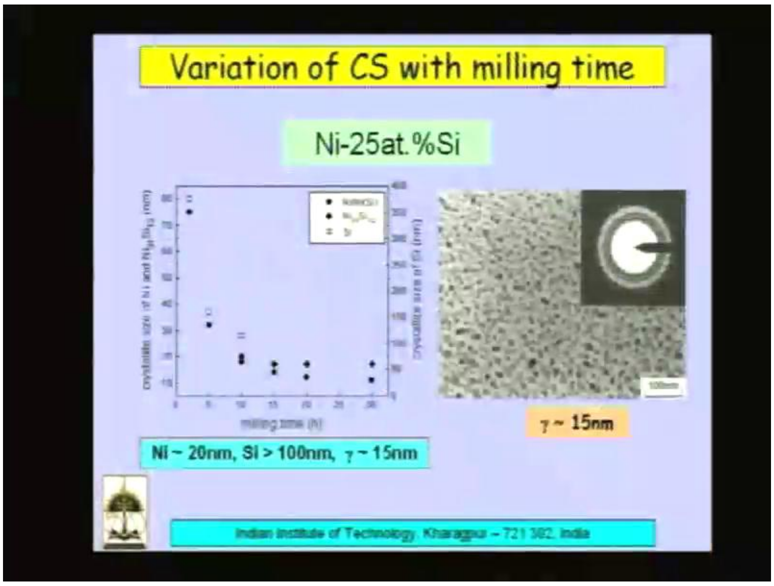
One can also do a lot of thermodynamics and to show that, yes, if you take it to a nano crystalline state, one can have a wider composition range. For example, one can calculate the free energies of the nano materials. Particularly, in case of metallic materials, it is very easy to calculate the free energies. We have talked about it in our thermodynamics class.

And so that, when you decrease the crystallite size, the plot on the right side, if you have a look at it, when you decrease the crystallite size, what you see is the phase field of this is the phase field of Ni AL. We are showing that the distance between the two curves, gives you the composition range, for which Ni AL can be stable and that composition range becomes larger and larger.

If you come to lower and lower crystallite size and when you reach a crystallite size of about 5 nano meters are so which is, what has been shown to you before. For example, if you look at the previous lecture, most of the particles are of the order of 5 to 10 nano meters. And if you look at, such a fine particles of 5 to 10 nano meters, their phase field extends some almost 28 percent to 68 percent.

So, which is what, we have observed under experimental conditions. So, one can do thermodynamics and show that what to see experimentally is not anything, which is unexpected. But, from thermodynamics, one can really prove that such a thing is possible.

(Refer Slide Time: 36:13)



Variation of CS with milling time

Ni-25at.%Si

Ni ~ 20nm, Si > 100nm, γ ~ 15nm

γ ~ 15nm

Indian Institute of Technology, Kharagpur – 721 302, India

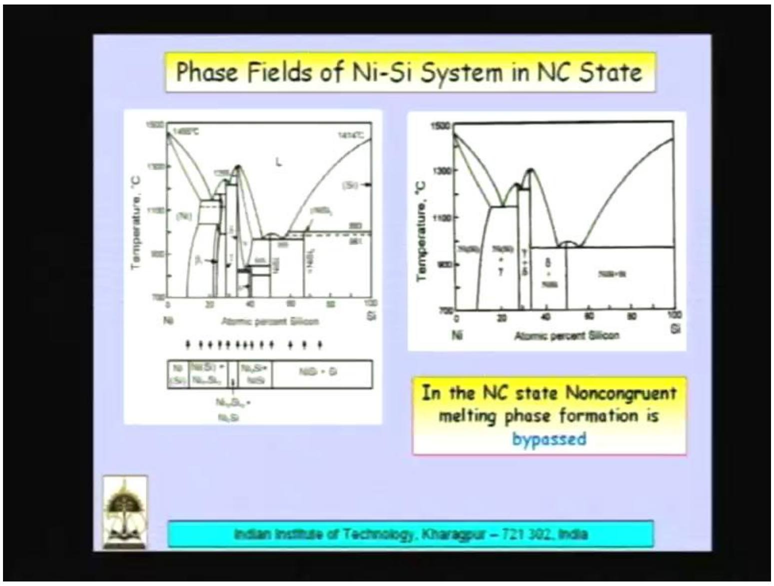
One can also produce very fine particles. For example, this is another example of a nickel silicide, nickel silicide which is called a gamma phase Ni 13, 31 Si 12 phase, which is called gamma phase. One can produce very fine particles of them and what is important is, that this is produced by a technique, what is, I call you top down approach. That means, you take a macro crystals and break them down by what is called a ball milling technique.

And you can see, with increasing milling time, one can decrease the particle size and reach a level of almost about 10 to 15 nano meters. And what is important is that, such phases, such as these inter metallic compounds form, only when the crystal size comes to a size of around 20 nano meters. If you start with nickel and silicon, let us say and start doing milling them together. You have a nickel powder, silicon powder, putting them together and doing ball milling.

And if you do that, when you bring the crystal size of nickel to a level of around 20 nano meters, that is the time, when suddenly, there is a reaction between the nickel and silicon and the inter metallic compound comes out. So, in a nano crystalline state, the formation of inter metallic compounds, largely depends on what is the crystallite size. Because, below certain crystallite size the surface area to volume ratio is so large, the particles become unstable.

And start reacting with the environment, whatever is there around it, in this particular case, silicon is there around it and it reacts with that silicon. And then forms a compound, which is more stable, under these particular at that composition, under equilibrium diagram, if you look at it, at that particular composition of about 25 percent. What phase is more stable, if you look at it? That is the phase, which forms by such a reaction. But, what is crucial to understand is that this always happens, only in a nano crystal state.

(Refer Slide Time: 38:29)


Phase Fields of Ni-Si System in NC State

In the NC state Noncongruent melting phase formation is bypassed

Indian Institute of Technology, Kharagpur – 721 302, India

So, making nano crystals is crucial for such compounds.

Student: ((Refer Time: 38:32))

This is mechanical alloy, yes; this is what is called mechanical alloys. We will talk about it a little later. Today, I do not want to bring that into picture, because let us take it generally, as nano crystals. And then look at how these nano crystals have interesting features, when you take any material into a nano crystal state. This is another interesting feature, that when you see a phase diagram. There are many phase diagrams, where you see a large number of inter metallic compounds.

This is one such phase diagram, which is the nickel silicon phase diagram, which has a number of compounds, which are shown there, beta 1 phase, which is nothing but Ni 3 Si kind of phase. And then you have a gamma phase, you have a delta phase and you have a epsilon phase, you have an Ni -Si phase and you have Ni -Si 2 phase. A number of inter metallic compounds, but there is a difference between these compounds.

That some of these compounds are congruent melting compounds, some of them are not. What is the congruent melting compound? A compound, which melts at a fixed composition, is called a congruent melting compound. So, in this phase diagram, if you look at it, there are basically only three congruent melting compounds. One is the gamma phase, another is the delta phase.

And finally, the Ni -Si phase, only these three are the congruent melting compound. Whereas, the other compound such as Ni -Si 2 or beta phase, all these phases are non congruent melting compound. Usually, a congruent melting compound has always a large negative enthalpy of mixing. Because up to the melting point, it is not changing to anything else, it is able to be stable up to the melting point. This happens, only when the delta h mixing is largely negative.

So, when you look at such inter metallic compounds, which has a large negative enthalpy of mixing, they are very stable compounds. And in a nano crystalline state, not every compound becomes stable. When, you take a and b elements, bring them into nano crystalline state and a and b, have to react with each other and form some compound. The compound that forms is always that, which is a congruent melting compound, near to that particular composition, whatever composition you have chosen and not a non congruent compound.

For example, if I take a nickel and silicon in the ratio of 3 is to 1, Ni 3 Si. At the Ni 3 Si composition in the phase diagram, what I have is a beta phase and beta phase is a not a congruent melting compound. So, if take a 3 is to 1 and take them to nano crystalline state, what I see is that beta phase does not come out. But, whatever is the closest composition, congruent melting compound. That is the compound, which will come out. That compound is nothing but the gamma in this particular case.

That is why, in the previous case, what we have seen is the composition, that we have chosen is Ni 25 percent silicon, which is the Ni 3 Si composition. But, the phase, that is forming is, really a gamma phase, which from the diffraction pattern, one can prove it, x ray diffraction also one can do and can prove it. And so you can see that true, not only in case of gamma, but also in case of delta and also in case of Ni -Si.

So, what you have on the right hand side is a kind of a meta stable phase diagram, because nano crystalline materials are meta stable. So, in a nano crystalline state, the equilibrium phase diagram is not always valid. It is not valid for one reason, that as I told you not all compounds are feasible in a nano crystalline state. We will come to it a little later.

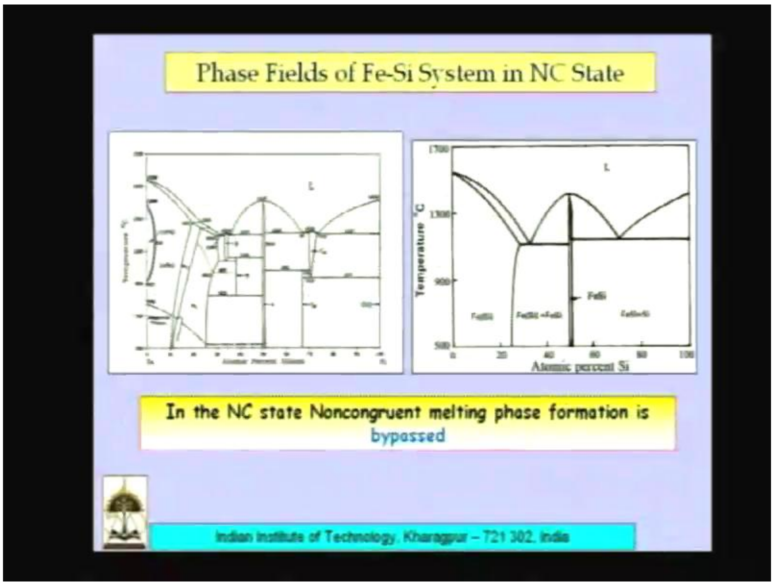
Thermodynamically, we will try to show why not all compounds are feasible. And second is that, when you have extension of sol gel solubility’s possible, again we can see that the equilibrium phase diagram is not valid. Because, in an equilibrium phase diagram, there is a limitation on the sol gel solubility, there is a restriction on the sol gel solubility.

Whereas, when you take it to a nano crystalline state, there is an extension on the sol gel solubility. So, you can generate newer phase diagrams, which one can call it them, as meta stable phase diagram. For example, what do you have here is a phase diagram, which consist of only three compounds. One is gamma; another is delta and another Ni Si, which are the phases, which are possible, under a nano crystalline state. And all other phases, one can remove it from that phase diagram and one can think of this.

But, one has to remember, that it is still metastable. It is like our iron cementite phase diagram. We know that iron cementite is is a meta stable phase diagram and if you allow equilibrium to be achieved, ultimately that iron cementite phase diagram is not valid. And you have to talk in terms of the iron carbon phase diagram.

So, similarly, this is valid only as long as you are in the nano crystalline state. Once, you grow the crystals to a bigger size and then you revert back to the old phase diagram, the equilibrium phase diagram.

(Refer Slide Time: 43:45)



Phase Fields of Fe-Si System in NC State

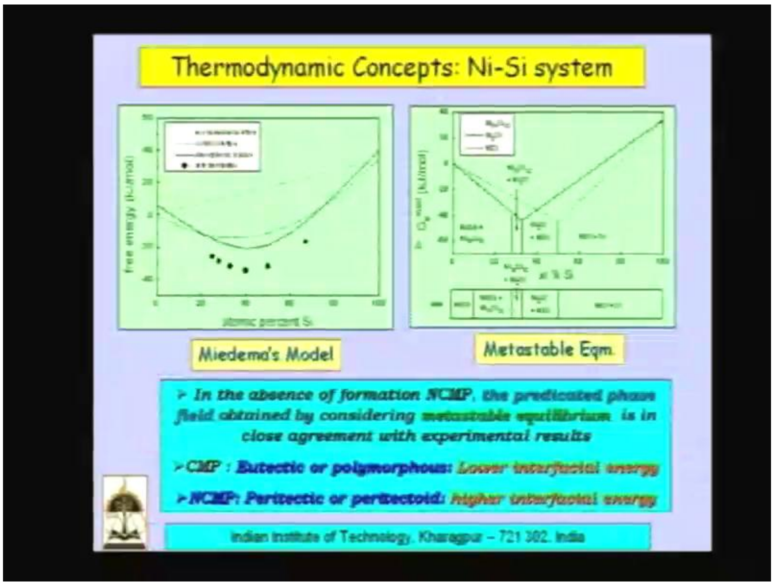
In the NC state Noncongruent melting phase formation is bypassed

Indian Institute of Technology, Kharagpur – 721 302, India

This is true, that in a number of systems, this is another system, which is an iron silicon system. In an iron silicon system, there is an only one congruent melting compound, which is Fe Si. And when you take iron and silicon into the nano crystalline state, the phase that forms is always the Fe Si phase, not all other phases, which are exist 3 is to 1 thing in the phase diagram.

One can prove this in a number of systems and we have our selves have done it in a number of systems. This is an example like that. So, non-congruent melting phases are always bypassed, when you go to a nano crystalline state.

(Refer Slide Time: 44:25)



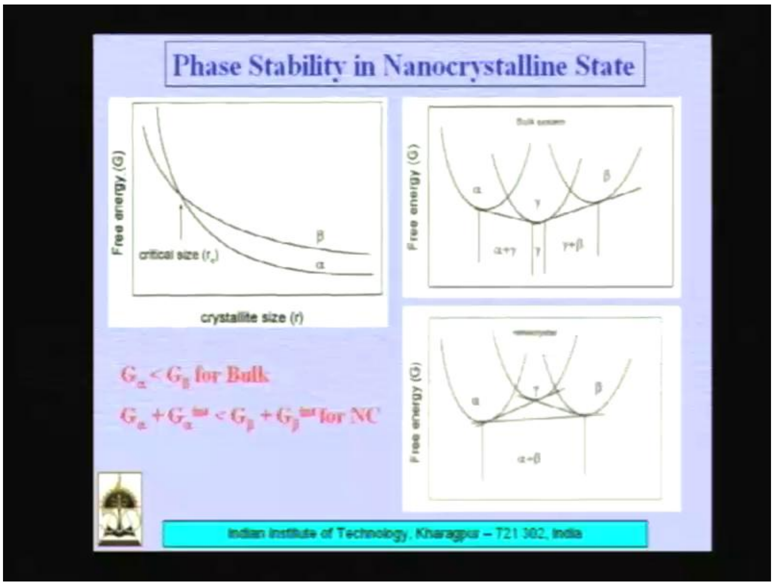
Thermodynamic Concepts: Ni-Si system

- In the absence of formation NCMP, the predicated phase field obtained by considering metastable equilibrium is in close agreement with experimental results
- CMP : Eutectic or polymorphous: Lower interfacial energy
- NCMP: Peritectic or peritectoid: higher interfacial energy

Indian Institute of Technology, Kharagpur – 721 302, India

This is also can be proved using thermodynamics and one can talk about phase fields in a nano crystalline state, what happens. And one can prove that, only congruent melting phases are possible. Particularly, because in the non congruent melting phases, always have a lower inter facial. Because, of the large negative enthalpy of mixing, their interfacial energies are very low. In a nano crystalline state, what is crucial is the interfacial energy, I think some point of time, I will just show you.

(Refer Slide Time: 45:05)



Phase Stability in Nanocrystalline State

$G_\alpha < G_\beta$ for Bulk

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

Indian Institute of Technology, Kharagpur – 721 302, India

Have a look at this picture, what you see here is that, two phase's alpha and beta and we are plotting the free energy as a function of crystallite size, when we talk of stability of a phase. How, do we define the stability of a phase, whichever phase has a lower free energy that phase is more stable. That is how we defined the stability of a phase. But, whenever, we talk of free energy, we usually talk of bulk free energy, volume free energy of a material.

But, when we take a material to the nano crystalline state, we need to consider, also what is called the interfacial free energy or the surface energy. If you add the surface energy to the system and then define the stability criterion, you will see that in the nano crystalline state, if the g alpha plus g alpha interfacial energy. If that is lower than g beta plus g beta interfacial energy, then we can say alpha is more stable.

If a combination of the interfacial energy plus volume free energy, if that combination is lower that phase is more stable. If you look at two phases alpha and beta, it is possible that alpha is more stable, then beta in a bulk state. That means, when the grain size is very large, but the moment, you take it to into a nano crystalline state, the beta, may be more stable than alpha. Why, because it is possible, that alpha has a higher interfacial energy or a higher surface energy, then beta.

If the surface energy is higher, the free energy increases more rapidly, as you decrease the crystallite size. So, when you keep on decreasing the crystallite size, the rate at which the free energy increases, with decreasing crystallite size is the function of the interfacial energy or the surface energy. So, if a particular phase has a high surface energy, you will see it is free energy raises very rapidly, when compared to another phase, which has a lower free interfacial energy or lower surface energy.

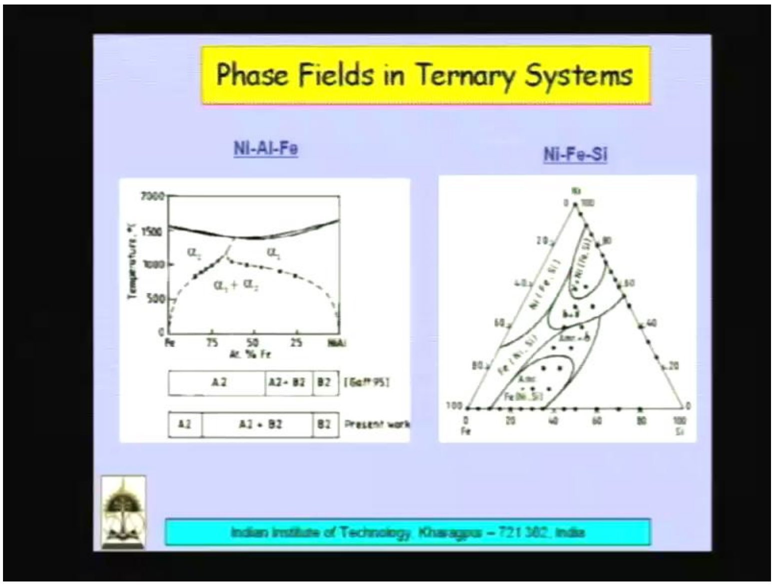
And you come across a critical point, where the free energy of the both phases become equal and below the particular crystallite size. You will see the phase with a lower interfacial energy or the lower surface energy becomes more stable than the phase with a higher interfacial energy. In a nano crystalline stage, the phase always that is stable is the one with the lowest interfacial energy.

And the congruent melting compounds are one of those examples, which have the low interfacial energy. And that is why, you do not you see, that those phases only exist and the non congruent melting phases do not exist. Same thing, can be observed here, for example, you imagine there is a situation of three phases existing in a system, alpha, beta and gamma. Let us assume that gamma is a phase with a high interfacial energy.

The moment, I take it this system into a n nano crystalline state, the gamma will have much higher free energy, when compared to alpha and beta. And you see that in a bulk state, you have a phase field of alpha, gamma, gamma and gamma plus beta, under equilibrium conditions. But, the moment you take it to a into nano crystalline state, gamma goes to a much higher free energy level, that you have a situation of alpha plus beta being more stable, than the gamma.

So, this kind of a situation occurs, that is what exactly you have seen in the previous case, where the non congruent melting phase, it is free energy goes up and it is no more stable. And the congruent melting phase becomes stable, though at that composition in principle, it is not suppose to be stable. For example, if you look at this particular composition, where gamma should have been a stable phase, you will see at that particular composition. Now, instead of gamma, it is a alpha plus beta mixture, which is more stable. So, this kind of phase, changes are possible in a nano crystalline state.

(Refer Slide Time: 49:23)



Phase Fields in Ternary Systems

Ni-Al-Fe

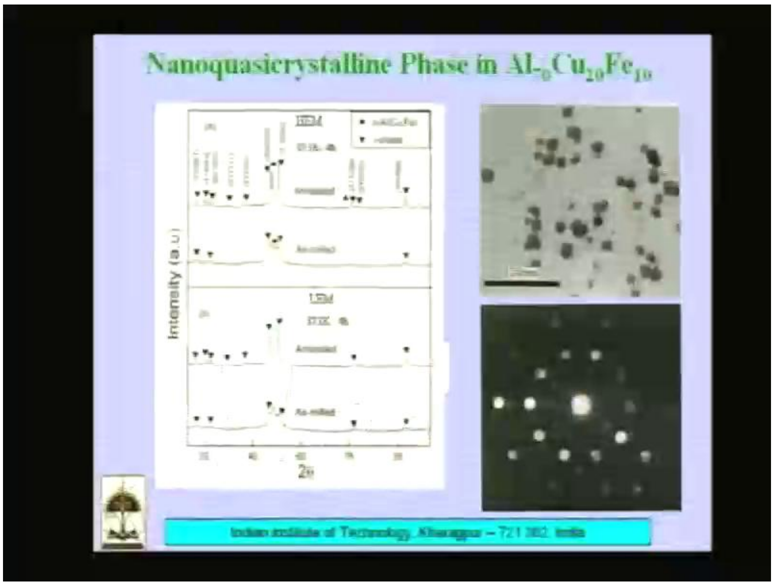
Ni-Fe-Si

Indian Institute of Technology, Kharagpur – 721 302, India

Because, of the presence of congruent melting and non-congruent melting compounds. This is true, not only in a binary case, in a ternary case also, one can show that always only congruent melting phases are possible. And this is one example of nickel iron silicon and nickel iron aluminum. That always, only the phases which are congruent melting forms, you can also produce nano crystals in a quasi crystalline state.

We talked so far about crystals, which are in the nano crystalline states. You can also have quasi crystals in a nano crystalline state and one can show, with that such quasi crystals can have a better properties. Particularly, physical properties, people have seen that such in materials behave like semi conducting materials. And people are trying to use them, as good semi conductors, with better properties than the conventional semi conductors.

(Refer Slide Time: 50:28)

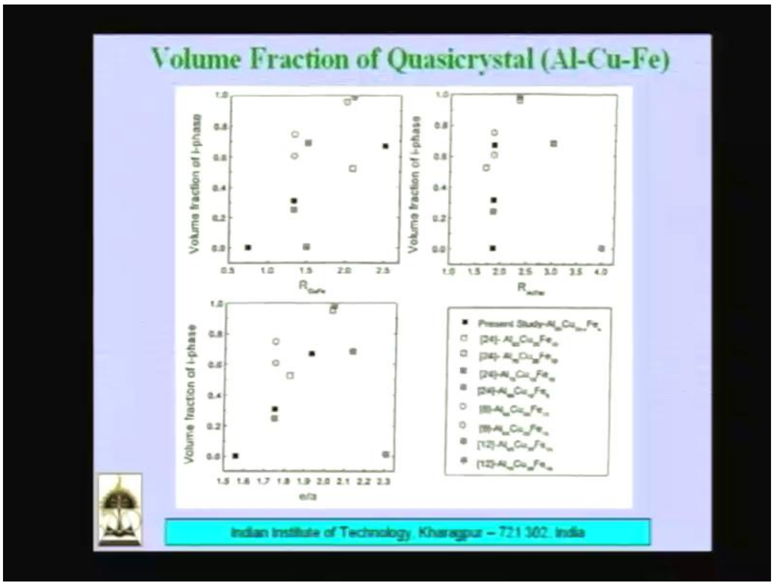


Nanoquasicrystalline Phase in $Al_{70}Cu_{20}Fe_{10}$

Indian Institute of Technology, Kharagpur – 721 302, India

You can see this case, were you can have a nano particles of a quasi crystalline case, as I told you last class. That you can see that, the diffraction obtained from a quasi crystal is entirely different from that of a crystal. Why, because you have a special rotational symmetry in a quasi crystalline. That is fivefold symmetry and you can see here, that you look at the transmitted spot and count, that total number of diffracted spot around that, you see 10 diffracted spot. This is what is the 10 fold symmetry? We call it and that is the classic example of a quasi crystalline and this kind of particles can be made.

(Refer Slide Time: 51:09)



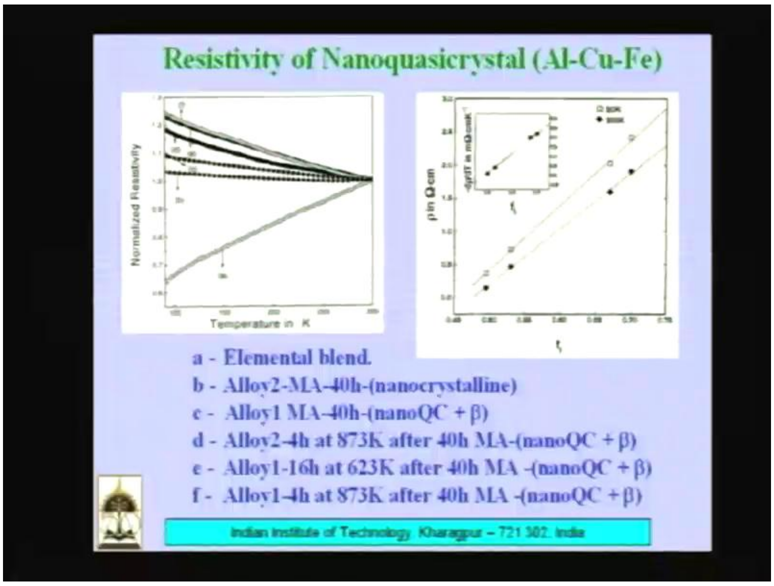
Volume Fraction of Quasicrystal (Al-Cu-Fe)

Indian Institute of Technology, Kharagpur – 721 302, India

And these kind particles, one can show that they form at a fixed e by a ratio. We talk about e by a ratio, as a crucial parameter in the formation of inters metallic compounds. Quasi crystals are also interring metallic compounds; basically most of the quasi crystals occur at fixed e by a ratio. And you can see that, for example, in copper zinc, we all know, copper zinc you have beta brass, you have a gamma brass and you have an epsilon brass, which are all occurring at fix d by a ratios.

And you can see that, this in this particular case also, the quasi crystal, the volume fraction of the quasi crystalline phase keeps on increasing and reaches almost one percent. When you vary the e by a ratio and when the e by a ratio reaches about 2, you will see exactly, that is the state at which you have the 100 percent quasi crystalline nano quasi crystalline phase, which is possible under the nano crystalline state.

(Refer Slide Time: 52:07)



Resistivity of Nanoquasicrystal (Al-Cu-Fe)

a - Elemental blend.
b - Alloy2-MA-40h-(nanocrystalline)
c - Alloy1 MA-40h-(nanoQC + β)
d - Alloy2-4h at 873K after 40h MA-(nanoQC + β)
e - Alloy1-16h at 623K after 40h MA -(nanoQC + β)
f - Alloy1-4h at 873K after 40h MA -(nanoQC + β)

Indian Institute of Technology, Kharagpur – 721 302, India

And they have as I told you a semi conducting nature, as you can clearly see here. If you take a mixture of aluminum plus copper plus iron, it will always show a metallic nature. That the resistivity increases with increase in temperature, which is the characteristic of every metal, but the moment, you take these three and make it into a quasi crystalline state. Immediately, you see, it will have a negative coefficient of resistivity as a function of temperature.

Thus, the resistivity decreases with increasing temperature and in fact, the resistivity increases with increasing volume fraction of the quasi crystalline phase. And also, the negative coefficient of resistivity also increases with increasing volume fraction. So, as a result, one can really show that these nano quasi crystalline phases can have different properties than that of the normal metals.

You are starting with the same metals, these aluminum copper iron, these are all metallic elements. That we know. And they behave like a metallic nature, when they are in the just mixed condition. But, the moment all of them are brought into an alloy form with a quasi crystalline nature. But, the moment you make this alloy into a crystalline nature, again you come back to the normal metallic behavior. Only when it is in the quasi crystalline state, it behaves in a semi conducting nature. We will stop at this point and continue in the next class.