Nanotechnology Science and Applications
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Lecture - 06
Phase Diagrams and Stable Phases

Hello, we will now look at Phase Diagrams and what are Stable Phases. This is a very important step in understanding materials because this is a way of representing what is going to be stable and also tells us what is possible in the system. And therefore, it is worth spending some time, understanding what it is and then utilizing it.

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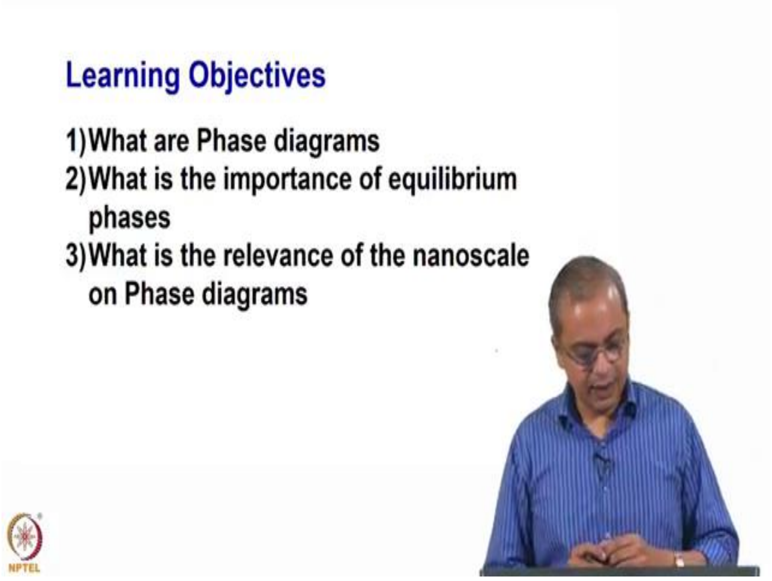

Learning Objectives

1) What are Phase diagrams
2) What is the importance of equilibrium phases
3) What is the relevance of the nanoscale on Phase diagrams

So, learning objectives are we will look at what are phase diagrams, we will get a sense of what it is. And, we will also look at what is the importance of equilibrium phases. And, we will also consider what is the relevance of the Nanoscale of on phase diagrams.

I must point out that this is a very brief look at the idea of phase diagrams and stability of phases. In reality, if you go to metallurgical engineering or materials engineering courses, anywhere internationally; these are complete courses this is like you can spend 40 hours looking at this 40 lectures, looking at this in great detail and in fact, there are other courses that, you can look at which do exactly that.

For us it is of relevance so, if you really want that background you have to look at those courses. Here, we will do a quick overview of what it is so, that you can utilize it effectively from the perspective of Nanomaterials and it helps keep the discussion complete. So, that is the reason why we will spend some time looking at it.

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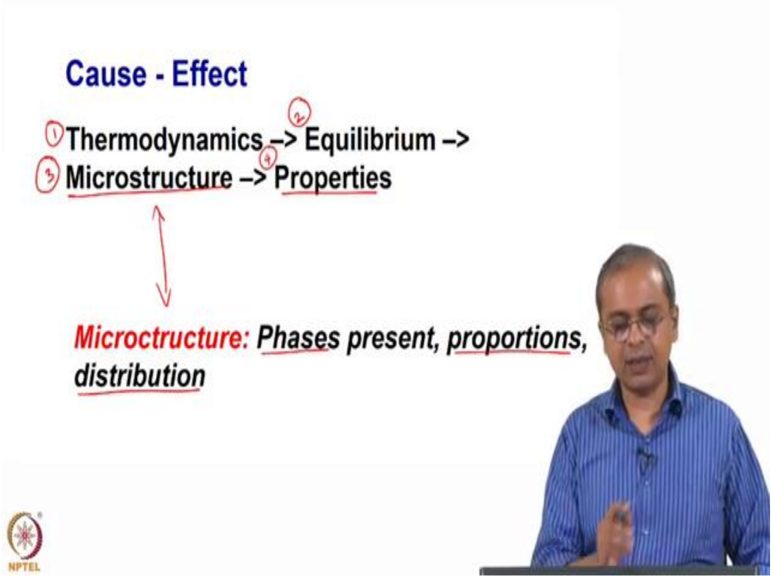

Cause - Effect

①Thermodynamics –> ②Equilibrium –>
③ Microstructure –> ④Properties

Microctructure: *Phases present, proportions, distribution*

So, when you look at a material and you are trying to put it to some end-use. So, that is basically what we at the end of the day that is what material science is all about you have some end-use.

So, some specifications are there saying that I want a material that has properties of a certain kind, that will help me carry out some function. So, that is the end-use that you have. We would like to understand from where we have to approach to arrive at that end-use. So, that is the thing that we need to understand.

So, to do that we the general sequence by which you understand what is happening is to see, what is the thermodynamics of the system. So, that is the first thing that we have to understand what is the thermodynamics of the system. Then based on the thermodynamics we understand, what will the system do, when it is at equilibrium. So, you take that system whatever is that material system that you are trying to put it to use, put to use, for in some location; it is a turbine blade in an aircraft engine. So, you have some material system that can potentially be used as a turbine blade for an aircraft engine.

So, you look at that system you understand it is thermodynamics and what is going to be the equilibrium state of that system, under the conditions of operation of that turbine system. So, the turbine engine the turbines of that engine. So, whatever pressure it is going to see, whatever temperature it is going to see, under those conditions what is the equilibrium state of the system.

So, this is something that we need to understand. Then, as we discussed in our in an earlier class, we also have to keep in mind that many times the system may be in a non-equilibrium state. So, and that is perfectly fine. So, we should also look at this system and consider if within this system there is a non-equilibrium state, which is more desirable for the turbine blade. And, therefore, you should see if you can direct the system towards this non-equilibrium state.

So, when you process that material, you direct it towards this non-equilibrium state. So, at the end of it all what is the result of doing all this direction of knowing this and then carrying out this directed activity on that material directed treatment of that material, the result is that you arrive at a microstructure. So, we will see what is a microstructure in a moment, but you arrive at a microstructure which is the way in which that material ends up being so, that you can actually use it and that microstructure results in some properties so, that is what you get.

So, that is the cause-effect kind of flow. So, you have the thermodynamics, you have equilibrium, you have any related non-equilibrium, you can decide what you want between them, and then that results in some microstructure, and then from that microstructure; you get some properties. So, this is the sequence with which you have to deal with the material. And, what is the microstructure? Microstructure simply indicates what phases are present.

So, a phase it is a region in a material where properties are uniformly constant. And, you can have a more technical definition of it and essentially you have some phases that are present; you can have them in differing levels of proportions. So, it may not just be pure iron, it could be iron carbide; it could be something like that. So, you have a definition of a phase and then, what proportion of those phases are present?

So, you can have more than one phase. So, will you have 50% of this and 50% of that or 20% of this 80% of that you may have three different phases. So, how what is the relative proportion of those phases so, that is important information.

And, how is how are they distributed? Are they uniformly distributed or is one phase in the form of small particles that are located at specific locations, the other phase is a larger phase, that occupies most of the space and so on. Or is one there along the boundaries if do you have one phase in larger sections and in the boundary between two particles of that larger phase you have the second phase that is present so, this is called distribution.

So, microstructure includes all this, what are the phases present, what is the relative amount of those phases and how are they distributed. So, this is the idea of a microstructure so and that is what is present here. So, the thermodynamics gives you an idea of equilibrium and equilibrium you can associate with kinetics and then you can see if you are actually attaining equilibrium or you are attaining a non-equilibrium state.

And, with respect to that, you see what is the microstructure, which is what you see here and then from that microstructure you get some properties. And, this is how you use the material?

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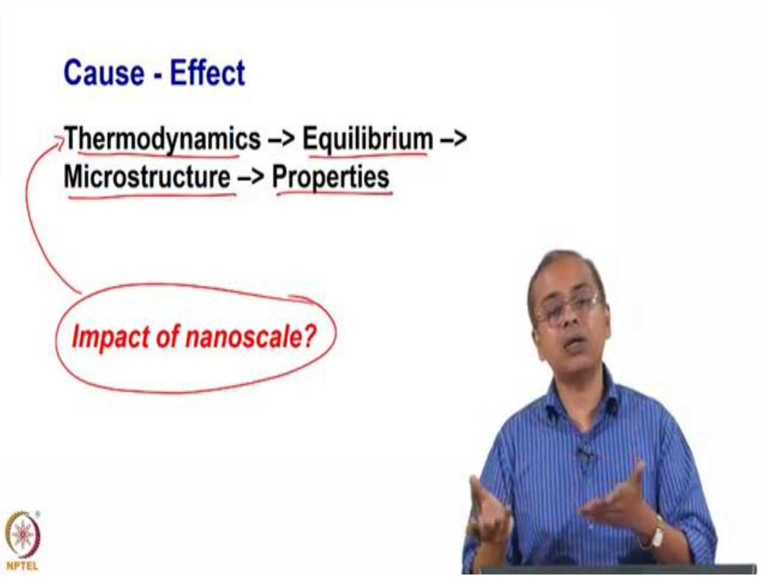

Cause - Effect

Thermodynamics –> Equilibrium –> Microstructure –> Properties

Impact of nanoscale?

So, now what is the impact of Nanoscale? So, this is the point that we wish to understand we wish to address what is the impact of Nanoscale. So, and what we will see is that the Nanoscale starts impacting us at a very fundamental level because it effectively starts impacting the thermodynamics of the system itself.

As I mentioned in a previous class, the typical it is not the thermodynamics is changing in any fundamental sense, it is exactly the same. It is just that when we look at thermodynamics of macroscopic materials, which are not at the Nanoscale microscopic materials. Then, there are certain terms that we do not have any relevance or rather are extremely small in value. And, therefore, we ignore those terms.

But, when you go to the Nanoscale, the same those that some of the terms that you ignored actually start having some significant value and, therefore, they affect the result that you get from the thermodynamic equation. The thermodynamic equation is exactly the same, but you start getting some additional value for a certain, terms and then that starts affecting the result that you get.

Therefore, in the presence of Nanoscale suddenly your equilibrium changes. So, the point you have to understand is typically so, if you look at Nanomaterials in general. The why this has become big why is it your thermodynamics book has not really addressed this much typically in a general sense, you will find that most of the books in thermodynamics were written as because thermodynamics is such a classic subject, they have all been the best books, they have all been written 50 years ago or we were more and they are the kinds of traditional excellent books in that subject.

And, that is the kind of book that we learn from. If, you see on the other hand the whole field of nanotechnology has really come about only in the last to say 20 years. That is when we all became suddenly very alert to this idea of nanotechnology that it can do so, many interesting things for you and then we should utilize this opportunity to work with Nanomaterials.

So, therefore, the books in thermodynamics have typically dealt with systems, where particles were in the macro scale or materials had microstructure at the macro scale. They did not have really any Nanoscale materials. So, when they wrote equations and they looked at the systems that they were traditionally looking at, they did not see the impact of terms associated with small scale, because they were not working with systems in the small scale.

And, therefore, they focused only on those terms which affected the systems in the larger scale. And, therefore, that is how they wrote the equation. Now, when you look at nanomaterials, you understand that some of those additional terms which could have been there in the original equation but were ignored because they had minuscule values. Now have significant values and therefore, you add them.

So, therefore, Nanoscale affects thermodynamics. Therefore, it affects the equilibrium; because it affects the equilibrium, it affects the microstructure. And, because it affects the microstructure, it affects properties. And, that is the reason why when you go to the Nanoscale; you suddenly have exactly the same material in terms of composition, suddenly giving you properties that it did not previously give you.

So, that is the whole idea of nanotechnology and in these classes, we are trying to look at how the thermodynamic aspect of it can be understood. how it can be looked at. And therefore, in any other system we will look at some examples, but in any other system also if you take that approach you can begin to understand, what is the impact on thermodynamics from the Nanoscale. So, this is the idea.

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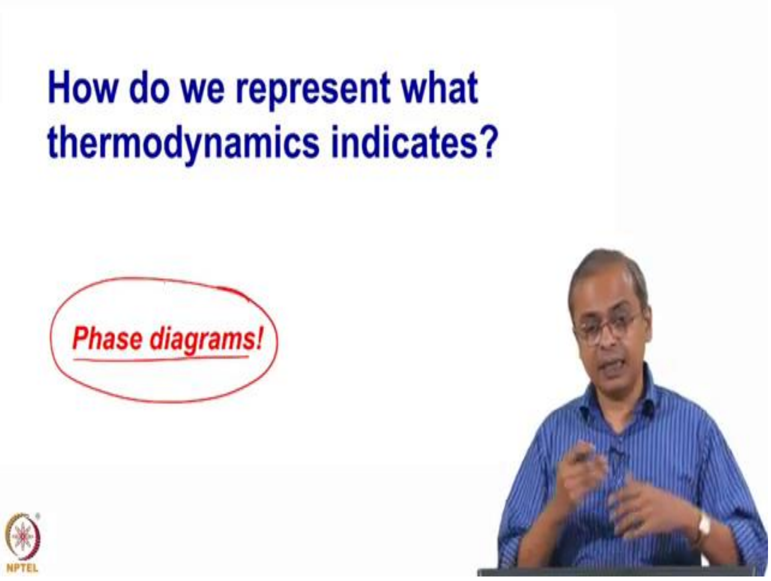
How do we represent what thermodynamics indicates?

Phase diagrams!

So, how do we represent, what thermodynamics indicates? So, this is the point that we would like to address here, how do we represent, what thermodynamics indicates. So, typically we do that using phase diagrams.

So, we do that using phase diagrams. So, as I said we are looking at thermodynamics talks of equilibrium, it tells you what is going to happen under the conditions where you have given enough time for all reactions to occur. And, they have finally, reached their resting state. I mean they have done all the reactions possible maybe I mean in principle you are even talking of you have given in 100s of years etcetera. I mean you are not going to run an experiment for 100s of years, but in general that that kind of time scale you think off, you say that give it infinite time what will it do. This is what it will do.

So, that is decided based on the change in free energy and what is the lowest free energy the system can adapt. And therefore, the equilibrium state of the system. And, then once you decide on the equilibrium state of the system.

You have a range of compositions the system can take for each composition you try to understand, what is the equilibrium state of the system. And, then you put that all that information together in a single pictorial representation. And, that pictorial representation is this phase diagram. And, that very nicely captures the thermodynamics of a system.

So, we need to understand a little bit about phase diagrams. And, and therefore, on that basis, we understand and then look at maybe what does the Nanoscale do to it.

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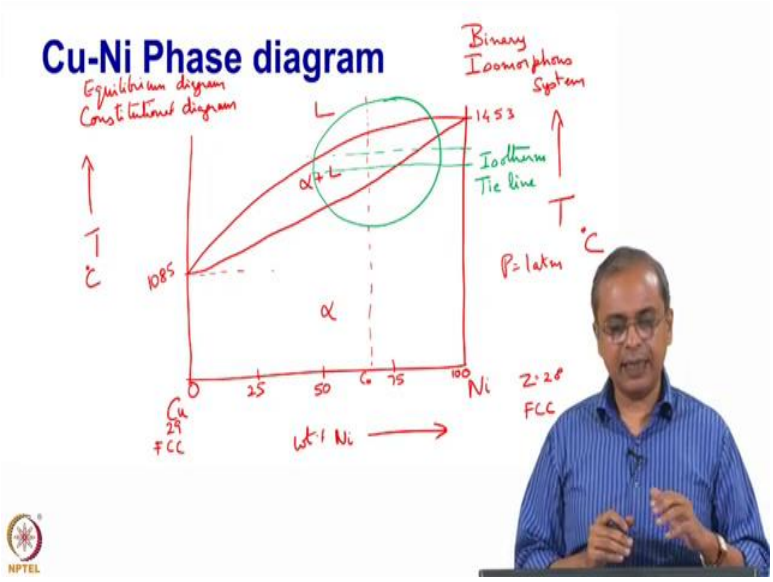

Cu-Ni Phase diagram

So, to do that let us just take an excuse simple example of a copper-nickel phase diagram. So, you understand what does the phase diagram provide us. And, therefore, you can begin to see what the Nanoscale might do to it. So, that is why we would like to look at it. So, to do that this is an interesting phase diagram to look at because it also happens to be a very simple phase diagram to look at.

So, what we need to have is we have to have temperature, you would have composition. So, this is temperature on the y-axis both sides and we will start with pure copper and we can go up to. So, this is weight% nickel heading that way increasing weight% nickel. So, this is 0% Nickel. So, this is half way there. So, this is 50% nickel and this is 100% nickel, 100% nickel. So, you go this way and so, this is 75 and here we put 1-meter mark 25.

So, this is what we have and you will see here we have a temperature of about 1085, this is all degree centigrade, the temperature in degrees centigrade; this is also in degrees centigrade. And, you have 1453; 1453 is the melting point of nickel 1085ºC is the melting point of copper. So, what you normally see is a diagram for this system which looks like that, it is correct that a little bit.

So, something like this is a hand-drawn diagram, but this is basically what you are looking at a phase diagram. The copper-nickel system is fairly interesting to look at because their atomic numbers and crystal sizes are crystal structures are very similar. So, you are looking at an atomic number of Z is 28 atomic number and it is 29 for copper, and both of them have FCC structure. And as a result, you can start putting nickel into copper and you can keep on adding nickel, it is called a solid solution.

So, in the crystal structure you remove some copper atoms you put nickel atoms, you keep on doing this you can go from 100% copper to 100% nickel. And, they will dissolve in each other completely; this is not true for many other systems it happens in this system. So, therefore, you get this kind of a diagram and this is called a binary isomorphous system. So, this is called a binary isomorphous system. so, binary isomorphous system. So, this is the system that happens, because of the differing details associated with copper and nickel. So, you get this system here.

Now, what happens is generally as you go to higher temperatures, you are going to have the liquid phase. So, actually if you are at this kind of a temperature above 1453, you are always in the liquid phase; does not matter what the composition is if you are above 1453 you are in liquid phase. If, you drop below 1453 then of course, again it depends then it starts depending on composition, but you will you can begin to have mixtures of a liquid and solid phase.

So, but that is not exactly below 1453 it depends on the composition. If you go below 1085 then you only have solid phase. So, this is solid. So, we would call this α. So, this is α phase. In intermediate temperatures, you have both phases α + liquid. And, we so, this is how this is this happens, and you can take any given composition. So, let us just take some composition C_0. So, C_0 and then with respect to that we can do some discussion.

So, this is called putting this information together like this as a plot which shows you at which temperature what face is going to be present is called a phase diagram. I must also alert you to the fact, that there are other experimental conditions that you can control and that could be, for example, pressure. In this case, we are assuming in most metallurgical systems such as the one that you see here, the assumption is that the pressure is one atmosphere. And, that is generally and very convenient assumption to make in these systems. Because, this is molten metal, metal solid metal, and molten metal and we really do not have much I mean ability or interest in adding extra pressure to it or putting it under vacuum etcetera.

In general, there may be some special cases where that is also of interest, in general, that is not the case most of the factories that you are going to go industries, that you are going to go where you are making these metals, or metallic systems working with this metallic systems, the end use is at room temperature and atmospheric pressure.

So, the pressure is typically atmospheric where they are processing it, as well as where they are using it so, it is kept at one atmosphere. So, it is useful for us to have a phase diagram at one-atmosphere pressure. Temperature is critical because you can use the part at higher temperature, you can use the part at lower temperature many times this is happening and so, we are having greater focusing on the temperature.

If you go to systems used by chemical engineers or chemists, they are often working with liquids and gases. Their pressure is a very important parameter; you can change the system dramatically when your loop change by changing the pressure.

So, when you look at chemical engineering systems where they look at say some distillation process, they were working with crude oil and doing some various processes with respect to it, to get out the various fractions of the crude oil etcetera. So, temperature and pressure are both of interest then, for us, the pressure is typically set at one atmosphere, but at least we should keep that in mind.

So, this is called a phase diagram, it is also often called an equilibrium diagram, it is also sometimes called a constitutional diagram. This is a way in which you can pictorially represent the information that is conveyed to us by the thermodynamics of the process. So, I mean, but the most common term that is used is the phase diagram, that is what is typically commonly used.

So, what we will do in our next slide is we will simply magnify a H a region from this phase diagram. So, for example, I am sort of magnify this region of the phase diagram, just to tell you what is it that we can determine from this phase diagram. So, I am just going to magnify it so, that we can discuss that at the little greater detail.

And, particularly with respect to microstructure when I said what phases are present, what amounts of phases are present and so on relative amounts etcetera. This is something that is of interest and that we can look at. Also, in this context, we are often looking at this one temperature at a time as you come down in temperature.

So, it is convenient to look at the system at a given temperature. So, some temperature so, you will take some temperature here and you look at the system at this temperature. And, then later you would cool the system little further down, then you look at the system at this lower temperature.

So, each time we are looking at its temperature by temperature. So, at that time what is happening in the system is related to the horizontal line associated with that temperature and because it is at a constant temperature, it is referred to as an Isotherm, Isotherm and that line that horizontal line is also called a Tie line. So, we will just keep that in mind in our next slide, we will focus on that a little bit more and then you will get an idea of what we can do. So, we are just going to magnify this diagram a little bit and build on it from there.

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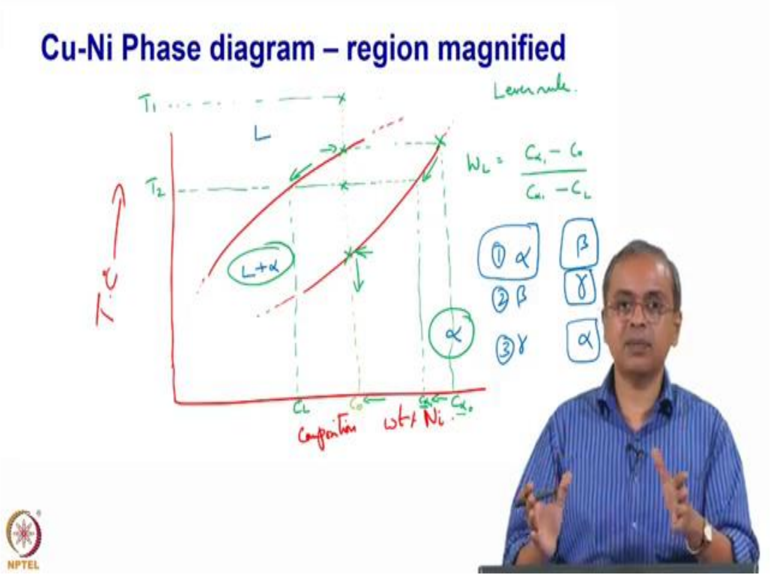

Cu-Ni Phase diagram – region magnified

So, we have temperature again on our y axis and we have composition on the x axis. Temperature in degree centigrade and composition, which is in this case weight % Nickel. And, we are looking at a magnified region of the phase diagram.

So, this is not a complete phase diagram, I am just going to draw a section of it. So, we just assume that this is dotted here. So, that it is headed somewhere and that is also dotted, it is headed somewhere. So, it is only a section of the phase diagram. So, now, we will assume that we have some composition C_0 and that is the composition that we are working with at a C_0, that is the composition we are working with and you begin to cool it, you take the system at a temperature T_1, this is the temperature T_1.

So, when you take the system to the temperature T_1 and keep in there and look for equilibrium, you will see that the entire system is in a liquid state. So, this is liquid here, we already mark that in the previous thing I will just mark it here this is liquid plus α and this is α so that is the idea here. And, when you are at T_1 it is all in liquid state. Once you drop below this temperature here and you stay above this temperature here. In this region of temperature from this point here to this point here as the temperature decreases, you will have the system in liquid plus α state.

So, you would have the system liquid plus α state, you would have some amount of liquid, some amount of α. Once, you drop below this temperature the whole thing will be solid and it will all be α. So, this is how the system works. And, what happens is as you drop temperature from going from the liquid state, at the liquid state it is all uniformly at the composition C_0. Finally, when you are at α state also it is uniformly at the composition C_0.

If, you do it slowly, if you do this in an equilibrium process that is you are allowing everything to settle to it is lowest energy condition. Then, when you start, it will all be in a composition C_0, liquid of composition C_0, you will finally, reach FCC structure, which is which we will call α, because it is a solid solution. And, that solid solution will contain copper and nickel with exactly the same composition C_0, uniformly throughout that solid with some phi you my minor fluctuation, but in general, it be exactly the same.

If you do it equilibrium d in an equilibrium cooling process, if you do it non-equilibrium cooling process you will have fluctuations you will have regions which are higher than C_0 and composition, other regions which are lower in C_0 than C_0 and composition. So, you will have some variations like that. So, is not what we are immediately a H looking at. So, what happens as an equilibrium processes as you start cooling down you reach this temperature.

So, you have to draw a Tie line at that temperature just to understand what is going on, what happens is as you start cooling down, the liquid composition moves along this line. And the solid that is coming out of it moves along this line in the composition. So, the first solid that comes out actually has this composition here that is the first that is the composition of the solid that is first coming out.

So, I will call that $C\alpha$ and this is the at that time the composition of the liquid is C_0. At any other point so, that is let me they will keep that there, at any other temperature you will have these 2 compositions. So, this will be the $C\alpha$ at some other time and this will be a C liquid.

So, the point being the $C\alpha$ starts moving this way and eventually it reaches this C_0 that is how it happens. And, this Tie line helps you do that I figure out what is going on and what you need to understand is because it is an equilibrium process. Initially, you had a higher composition for $C\alpha$ as the liquid solidifies due to diffusion the composition of $C\alpha$ is shifting, that is the point you have to keep in mind, that there is a diffusional process that is happening, which helps enable the composition of the solid to become a uniform composition. Even though layer by layer it is coming with a slightly different composition.

So, it keeps on shifting and then you end up getting this composition C_0. And, so, this is how this phase diagram is used to understand what is happening. And at any given point in time, you can also find out the relative quantities of the different phases that are present. So, for example, if you want the at any at this temperature say T_1, this is T_2. At T_2, if I want to know how much liquid is there, versus how much solid is there, we use something called a lever rule or an inverse lever rule.

And, so, the weight fraction of liquid will be equal to $C\alpha$. So, I will call this α_1, and this is α_0 for example, so, see $(\alpha_1-C_0)/(C\alpha_1-C_{liquid})$. So, sort of weight weighted by the opposite side of that lever and that is why you have $(C\alpha_1-C_0)/(C\alpha_1-C_l)$, that gives you the weight fraction of liquid it is not very important that we should know this we should focus on this calculation at the moment.

But the point is this is how the phase diagram works. And, this is a very simplified phase diagram in typical systems you may have many more features in the phase diagram. Here, you simply have a liquid phase, liquid plus α phase, and an α phase. And, that is uniformly present for the entire composition. In many other systems, you have multiple phases that will show up at different temperatures at different compositions and so on.

And, all of that is calculated from thermodynamics and converted into a plot that looks like a diagram, which has composition was this temperature and that captures the thermodynamics of the system. So, that is the beauty of this thermodynamics and phase diagrams. And, it tells us what is possible in the system? And, that is what is important to us. It tells us what is possible with the system and what is the direction in which the system will move.

Now, if you look at what the thermodynamics has given us which is this phase diagram. The reason this is of interest to us from nanotechnology perspective is that when you go to the Nanoscale. If, you look at the phase diagram of the same system at the Nanoscale, versus the phase diagram of the same system at some other macroscopic scale.

What you will see is because of the Nanoscale, because the high energies that are due to some energy considerations at the Nanoscale which we will see. Some of the faces that were considered stable in that system, at when the system was having macro-scale grains, grains at a macro scale. Once, the system was having grains at micro-scale, amongst the faces that are present.

Like, I said here you simply had liquid plus α and α. You may have some other system where you are α phase, a β phase, and a γ phase. So, let us just say there is a hypothetical system, where I have α phase, β phase, and γ phase.

And, when you, in general, this is the most stable, this is the next most stable and this is the next most stable, in terms of stability.

So, normally if you take that particular system you will only see the α phase, but if you go to Nanoscale what will happen is it may you may find systems, wherein the Nanoscale this has been this order has been disturbed. And, suddenly you see β phase, γ phase, and then α phase, it can easily happen that way.

So, then what you will see is that for the Nanoscale system of the Nanoscale, sample of the exact same system, Nanoscale sample of the exact same system. Suddenly the β phase is what you see more easily, you see less of γ and you almost do not see α. Nothing else you have changed, you simply gone to small scale. And, that is how because of the small scale suddenly your expectation with respect to the phase diagram is suddenly changed.

And, therefore, what you actually get in the system is different. And, then if you go back to what we said, you have thermodynamics it results in equilibrium, which gives you a certain microstructure and you get some properties. Now, since the face and the microstructure itself is what phases are present and how they are distributed.

And, now suddenly you see that the phases that are going to be present are actually different because you have gone to the Nanoscale because it has altered the relative impact of some terms in the thermodynamic equation. And, suddenly a face that was less stable in the macro scale is now more stable at the Nanoscale.

And, therefore, the microstructure of that system is suddenly different. If the microstructure is different, you can almost I mean you can be almost assured that very likely the properties of the system are going to be different. And, that is how the Nanoscale has an impact. And, this is very important, because at the end of the day we want materials with interesting properties, interesting ranges of properties.

So, whereas, previously when you were working with this material in the macroscale, you were limited to a certain range of properties. Now, suddenly because you have gone to the Nanoscale and different phases are becoming available at the Nanoscale, you are getting a completely new set of properties and that is how the Nanomaterial is becoming interesting to you. The same composition is giving you completely different properties by going to the Nanoscale.

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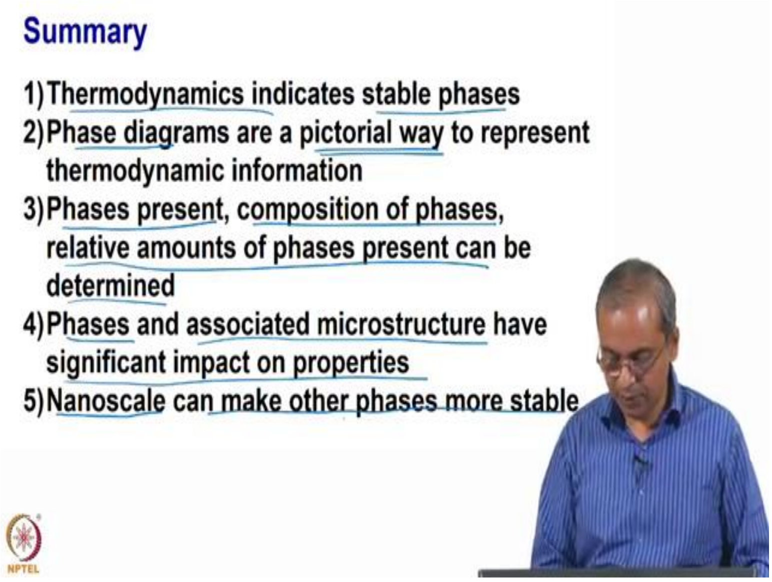

Summary

1) Thermodynamics indicates stable phases
2) Phase diagrams are a pictorial way to represent thermodynamic information
3) Phases present, composition of phases, relative amounts of phases present can be determined
4) Phases and associated microstructure have significant impact on properties
5) Nanoscale can make other phases more stable

So, in summary, thermodynamics indicates to us, what stable phases are going to be present. What are the phases that are going to be stable in the system is what thermodynamics indicates to us? Phase diagrams are a pictorial way of representing the thermodynamic information.

It tells us what is the information that is there in the system and what is possible in the system, and it presents it in a way through, which we can actually look at a range of possibilities in the system. And, in each case you can gauge for yourself. What is the system going to give us as a microstructure or at least what is the high probability that the system will give us a certain type of microstructure, or what phases will be present, that is what you will get from the phase diagram?

It helps us tell it tells us what phases are present it will tell us what is the composition of the face; we saw that it tells us the liquid composition it told us the α composition.

So, it tells you what phases are present, whether it is only liquid phase or is its liquid plus α or is its α phase. It, tells you what is the composition if it is liquid plus α, it tells you, what is the composition of the liquid, what is the composition of α. It tells you the relative amounts of the phases present, that also we can calculate. We can actually look at that system and you can say that this is the weight fraction of liquid phase that will be present that is the weight fraction of the α phase that will be present.

And, we also saw that the phases and associated microstructure. Have a very significant impact on the properties. And, that is something that is the key or the crux of all of material science, the end of the day we want properties, because there is some induced which needs those properties, needs material with those properties. And, that is the fundamental, driving theme behind material science or we could come up with interesting properties and then somebody finds a use for it.

So, that could also happen, but generally, this is what is the idea here. And, we also noted that when you go to the Nanoscale because it can impact thermodynamics of the system by accentuating certain aspects of the thermodynamic relationships much more than in the macro scale, you can actually change the relative stability of different phases. And, therefore, you can make other phases more stable which is very important, you can make other phases more stable, therefore, you can get a microstructure which you would not otherwise expect in the system.

And, with that, you can completely change the properties and therefore, you can change the utility of the system. So, this is the impact of Nanoscale on thermodynamics and phase diagram and such and how it impacts the end use that we can put into.

Thank you.