Advanced Metallurgical Thermodynamics Prof Dr B S Murty Department of Metallurgical And Material Engineering Indian Institute of Technology Madras Module-01 Lecture-27

Martensitic Transformations, Order-Disorder Transformation

(Refer Slide Time: 00:13)

Last class we were talking about martensitic transformation. We talked about the $($ ()) along a and b axis. This total is the actual martensitic transformation, so austenite to martensite transformation if you say it is a combination of these two. Depending on to what extend this process, second process can occur is going to decide what the c by a ratio is. Just after shear, c by a is 1.414 you have seen, and in principle it would like to come to 1.0, it is which is a B C C structure which is stable structure at room temperature. So, it would like to come from there to here depending on the carbon content present in the alloy, and depending on what is the extent of compression that can take place along C axis this would come towards this, if there is no carbon it would in principle be this. So this is what the whole structural is. Let us now look at the thermodynamic aspects where is the driving force is coming from.

(Refer Slide Time: 01:42)

We are already seen that at room temperature if I quench an austenite, if I take an austenite and then quench it the stable structure is B C C, am I right, at room temperature the stable structure is B C C. So austenite wants to transform to this B C C structure that means the F C C structure wants to transform to this B C C structure, that is the whole process, but in principle under normal conditions F C C can transform to B C C structure by a polymorphic transition involving what, what kind of a diffusion, short range diffusion. In principle F C C to B C C transformation can happen by short range diffusion, but because you are at a temperature where short range diffusion is not able to happen then you see a shear taking place. So, if I draw the free energy versus temperature diagram you would see a transformation something like this, at higher temperature it is the gamma that is stable, at lower temperature it is the martensite that is stable. Martensite in principle it could be a B C C martensite or a B C T martensite depending on the type of situation. So, there is a temperature which we call it as the T naught for this gamma to martensite, but actually the transformation never occurs at that temperature because the transformation needs some shear; you need a certain shear to occur inside the material, so that you would see the gamma transforms to martensite. If there is no shear gamma would not transform to martensite, and this shear for it to occur you need to provide certain driving force for the shear to occur.

As a result actually transformation occurs at a temperature below this at some temperature which is what we usually call it as M s temperature which is actually below the t naught. This is the extent of under cooling that you need from t naught to be able to have the transformation, and this m s temperature we all know is dependent on a number of factors one is carbon content, and the other alloying elements present and also the grain size for example, grain size can also control an M s. So, there are many factors which will shift this temperature to a lower temperature and alloyed transformation at the T naught. When do you have actually the transformation occurring very close to t naught, when the extent of shear that is required for the transformation is very very small.

In any particular system where the extent of shear that is required, the shear stresses that need to be provided for the shear to occur is very small then you can say that in principle M s comes close to T naught, otherwise you would always see some temperature which is below this T naught where the transformation occurs. This is where we need to understand the influence of stresses on martensitic transformation. We always say there is something called stress induced martensite, you heard of it, hard feel steels is one of the wonderful examples of it. You take an austenite and quench it and get the austenitic structure and deform it and you would see during this deformation this arsenate transforms to martensite. But the reason why you see arsenate transforming to martensite during deformation which is what we call it as deformation induced transform martensite and we even give temperature called M d temperature for that temperature where the martensitic transformation occurs during deformation, and usually this M d is always greater than M s. The reason is that whenever you deform a metal there is always shear stresses which come into the picture, whether you do tensile deformation or you do extrusion; you do wire drawing most of the processes excepting one deformation process which is called is static compression. For example if you have heard of hipping and sipping, if I do hipping for example, I have a isostatic hot compression or sipping cold is static compression. So, when you do isostatic compressing; that means you are not inducing any shear stresses inside the material, the moment you do not induce any shear stresses in the material the M s would actually go down. The moment, you have always some shear stresses which get induced into the material during deformation then you would see the M s will be higher than that .That basically means that you would see that the gamma transforms at a higher temperature to martensite rather than a lower temperature, the reason is whenever I apply stresses inside the material; shear stresses,

the gamma which is the parent phase will have a higher free energy when compared to the original gamma which is un deformed.

A deformed gamma will always have a higher free energy, and if I use that Let's say, I use a different free energy curve for that now, this is called as a deformed gamma, gamma which is deformed will have a higher free energy than the normal gamma, and obviously you will see at some temperature it has to intersect either we have to make this or change the martensitic curve whatever it is. And if that is the case you would see another temperature, now the intersection has happened at a higher temperature, that means the T naught has shifted to a higher temperature, the austenite would transform to martensite at a higher temperature. If the T naught is shifted to a higher temperature then obviously the M s also will shift to a higher temperature.

So, you would see that the austenite deforms to, I mean transforms to martensite at a higher temperature which is what we call it as an M d temperature when you have deformed. But now how do I understand about the other aspect, if I subject austenite to a compression; isostatic compression, then the situation is different. Then the situation is, if you look at any time any material, if you subject it to a compression; that means you are trying to reduce the volume, you are compressing it. Whenever you are compressing it the phase that is always stable is a phase that occupies less volume. This is always the case for example, if you want a graphite to transform to a diamond you need to apply a compression, compression and also a higher temperature.

So, a high temperature and compression would make a graphite forms, and the higher the pressure that you apply the lower the temperature at which the diamond would form from graphite. So, the reason is the diamond is a much more close pack structure than graphite. So whenever, this is true even for any liquid to solid transformations, if you take a liquid to solid transformation, if you take a liquid which is trying to transform to solid and you apply a compression on the liquid, some kind of isostatic compression, you would see the phase that gets stabilized would be the phase which is always the can occupying lower volume; usually most of the cases solid occupies the lower volume, so solid become stable. Solid become stable means what should happen to the melting, it should increase.

So whenever you pressurize, it is basically clausius clapeyron, so if you go back to the clausius clapeyron, whenever I apply a vacuum you would see that because the pressure is reduced, at a reduced pressure you would see the melting point occurs at a lower temperature. Whenever I apply a pressure you will see the melting point will be higher, the solid melts at a higher temperature or the liquid does not solidify at the normal melting point but it will solidify at the higher temperature. So the melting point would go up when you apply the pressure except in cases where the solid occupies more volume then the liquid. So when the solid that is examples of like water to ice transformation, or say any other transformation, correct this is an important point. So, now if I look at in terms of stresses, any stress in principle should raise the free energy of a system, so that means the stresses would definitely raise the temperature of the free energy of gamma. But because of the fact that the martensite is more open structure than that of the gamma, the relative free energy changes will be such that the gamma free energy because of this pressure would actually go down with respect to the matensite when compare to what you have seen if there are no hydrostatic pressures.

So, there is definitely going to be some raise in the free energy of gamma because of the stresses that are there. But at the same time the second factor which contrasts that is the fact that the you are putting hydrostatic pressure, and then you would see if you simply look at the clausius clapeyron equations which says that d T by d P is delta V by delta S or delta S by delta V, delta V by delta S this and this. So if we look that, from that you would see that as the pressure increases; if both are positive, T Should increase, am I right. So, you would see or if one of them is negative you would see, in our case if you look at austenite to martensite, if you look at the transformation v of austenite, v of gamma should be equal to v of martensite minus v of gamma that should be is equal to positive. And if you look at the delta S part of it, so s of gamma and S of martensite, if you look at it which will be higher, gamma will be higher because it is a high temperature phase when compare to martensite, so this is higher. So, delta S will be negative now, S of martensite minus S of gamma that will be negative. So, one is positive another is negative, so this is going to be negative, the ratio. So, higher the pressure the temperature should be lower, and that is the case you would see that affect will coming into the picture, and as a result you would see this would have an overall impact of reducing the free energy of the free gamma in such a way that the T naught curve shifts to a lower temperature.

So, two types of pressures, two types of stresses can lead to two different effects, one which is a compressive stress which is isostatic compression can lead to a lower M s if you apply, I mean nobody does this for a austenite, nobody has done, I mean except in case of powder metallurgy people have done, if you take a powders of let us say austenite and then do hipping of it; isostatic pressing is usually done only in powder metallurgy otherwise you do not use it in case of normal steels which are produced by casting root and then deformed to give whatever shape it is. You go through all other process such as rolling, folding, and other deformations, but you rarely use a kind of isostatic pressing, isostatic pressing is more in terms of powder metallurgy. So, in case you take iron or steel powders in the gamma state, and then do a hipping, and then you quench it and you compare with steel which is produced by a normal case you would see there martensite transformation occurs at a much lower temperature when compare to a normal speed.

So, only in such case you can actually confirm that under normal steels we do not need to use hipping at all. So, it is this is of more concern for powder metallurgy people, ok. So, in case you are dealing with powders and then doing hipping or sipping, and then trying to see whether I get matensitic transformation, you may say why I should bother about what temperature it should, it will transform. I need to bother about it because I need to know to what temperature I should bring it so that if I want to get hundred percent matensite, so M s itself is low, M f will also be low. So, for you to be able to get hundred percent matensite you need to go to much lower temperature, sometimes may be even sub zero, so that is an aspect which you need to understand. So, the pressure brings in this effect and that change the free energy, and as a result you would see the whole transformation changes. So this is another aspect which, regularly people do not talk about it, people always say deformation will lead to an increase in the martensitic temperature, temperature that deformation is only a deformation which induces shear. If there is no shear it is induced inside the material, and it is only a deformation which is just a compressive deformation, you would not be able to see that. I think with that we will close martensite, I think we have more or less talked everything about martensite including the crystallography aspect of it, I will not go too detail into the kinetics of it. yes yes thermodynamics will be similar accepting that you would see in some cases the shape memory effects particularly in the non-ferrous nickel titanium, and those are related to whether you have the martensite is a thermo elastic martensite, what is extent

of the the transformation strains that are involved. And also for example, I do not know whether you heard about it, why steel martensite is not a shape does not have a shape memory effect, you do not see shape shape memory affect in steel though there is a martensite transformation, Yes anything more. One of the primary criterions for a shape for a shape memory effect is that the transformation should be reversible austenite to martensite, and martensite to austenite should be reversible.

For example in a steel, typical steel when I start heating the martensite what happens, it starts tempering and then because of presence of carbon inside the carbon starts coming out in the form of carbides and you do not see martensite directly transforming back to an austenite, there are a number of intermediate phases that come into picture, isn't it. So, you unless you go back to a three temperature you would not actually get the austenite transformation. Where as in the non-ferrous nickel titanium and a number of other cases like copper base alloys these are all reversible transformations, there is no other phase involve and only when you have reversible transformation you will be able to see the shape shape memory effect, so that is another thing. Of course, as he mentioned about it the extent of strain is also important, you need to have a reasonably good amount of strain which can be able to be recovered during either heating or during deformation, we will not go into the details of it that is more of a kinetics and not really thermodynamics may be in some other consideration we see that. Now let us look at the other aspects, the other type of transmission which we have not covered so far is the order disorder.

(Refer Slide Time: 20:37)

Before we actually go into the thermodynamics let us look at how we recognize this order disorder transmission in a material. Whenever we say order and disorder, I think all of you are aware that when we talk about order there are two types of order in a material, we talk of structural order and we talk of chemical order. So, whenever I say this is an ordered material we are usually using the term chemical order, when I say structural order then a structural order it can be a crystal, it can be a glass or amorphous, or it can be even a third one which is a quasi crystal. These are the three types of the structural orders and the differentiation is, a crystal is one where you have both orientation symmetry and both rotational symmetry and translational symmetry, and this is where you do not have both, and this is where you have one of them, the rotational symmetry exits but the translational symmetry does not exist, that is how we talk about it.

When I say chemical order first and foremost is it is structurally ordered, and it can be chemically disordered or ordered, there is no possibility of looking at a structurally disordered material and look for a chemical order there. And similarly, again when I say chemical order we are again talking about long range chemical order, we are not talking about short range chemical order here. Short range chemical order and short range structural order will always be there in every material until you go beyond the **beyond** melting point, boiling point. When you are above the melting point you still have a short range order, you still have a short range structural order, if that is a chemically order there may be a short range chemical order also inside the material. But if you go beyond

the boiling point there you have a individual molecules and individual atoms, so you do not have a chemical order or neither structural order. So, whenever we are talking about an order; this material is ordered, we always talk about long range order, we do not talk about short range order that is what you people have to keep it in mind. And when I am saying the long range order, so it is not possible to have a structural disorder and a long range order, these two will not go together. You cannot have an amorphous alloy which is chemically ordered because it is already structurally disordered, so because it is structurally already disordered there cannot be a chemical order inside, chemical order we always look inside the unit cell. The moment you talk about the chemical order, that means how atoms are arranged inside the unit cell is what represent the chemical order.

If there is no unit cell there is no question of talking about how the atoms are arranged inside the unit cell, so as a result, because amorphous materials do not have a unit cell at all, so we will not talk about structural chemical order there. So, chemical order basically implies a structural order, so it is a subset of structurally ordered materials; that means it is a subset of crystals. So, chemical order or a chemical disorder is two sets inside structurally ordered materials. So if I consider, first of all that it is a crystalline that it has certain crystal structure then I talk about whether it is ordered or disordered, and this question of ordered or disordered comes into picture again for the structurally ordered materials only when you have more than one element inside the material. If you have pure metal we do not talk of a chemical order; obviously, so we have only one element means it is simply structurally ordered, that is it. You do not talk about chemical order; chemical order comes into picture only when we talk about alloys, more than one element.

When we have more than one element present then we talk of the chemical order, then we talk about how each element is arranged inside the unit cell if they are the randomly arranged. If there is no preferred sites for any one of the element we call it as chemically disordered, and such material are usually called as solid solutions or disordered compounds.

(Refer Slide Time: 26:20)

Solid Soluting
Disoland Compand

In fact, it is very difficult to differentiate between a solid solution and disordered compound. Both of them will have two elements if it is a binary alloy, two element which are which are randomly present inside the crystal structure, whatever may be the crystal structure. So, disordered compound is usually referred to as a solid solution. But excepting that, for example if I am talking about the nickel aluminum alloys, when I take compound such as N i three A l, N I three A l is a F C C based compound inter metallic with what we call it as $\frac{a}{a}$ to structure. So, here you have three atoms of nickel occupying the face centered positions, and the aluminum occupies the body corners, and now this becomes let us say disordered; that means inside the unit cell if you have hundred unit cells, in hundred unit cells you would have seventy five atoms of nickel, and you know twenty five atoms of, we should not take like that, when a in a hundred unit cells actually you have much more because every unit cell effectively have four lattice points, ok.

So, if I take let us say about twenty five unit cells with about hundred atoms, in this twenty five unit cells the nickel atoms will sit wherever they want to sit, the seventy five nickel atoms would sit wherever they want to sit, and the similarly the remaining twenty five atoms would sit wherever they want to sit. There is no preferred place for that, so that means out of the three face centered positions let us call them as half half half, I mean half half zero, zero half half, and half zero half. If we consider these three positions, one of them may be occupied by the aluminum, another may occupied by nickel. So there is no preference, you know sight for either nickel or aluminum, but the

structure is still F C C. The structure is still F C C excepting that aluminum and nickel are randomly sitting wherever they want and that is what a disordered compound is. And if you want to call it as solid solution also there is no problem in calling it as the solid solution excepting that there can be a solid solution of aluminum in nickel with about five percent of aluminum or ten percent of aluminum. You cannot call it as a disordered compound because it is not a compound at all, it is a solid solution of aluminum in nickel accepting that this particular thing if you want to call it as a solid solution this is the one which will have seventy five seventy five exactly.

So, the composition would correspond to inter metallic composition, but the structure would correspond to a solid solution structure, clear. So, the composition will be exactly stoichiometric composition like seventy five twenty, but the structure will be a disordered structure; disordered chemically and ordered structurally, so that would the difference. So, there can be a numerous solid solutions with different different amounts of solute solute content, but the moment I say disordered compound the disordered compound will have a stoichiometry corresponding to that particular compound, so that would be the difference.

(Refer Slide Time: 30:25)

Now, if I want to look at how do I find out this extent of disorder when I take a N i three A l and make it disordered in principle, if I take a N i three A l and start heating and talk in terms of what is called order parameter, they refer to it as L which is a long range order parameter. Order parameter can change in two different ways, it can become like this or it can become like this, this is one and this is zero. What you mean by order parameter being one, that means the probability of finding a nickel atom let us say aluminum atom at the zero zero zero position; what are the positions here in F C C, zero zero zero, half half zero, zero half half, and half zero half. These are the four lattice points, am I right, and zero zero zero position is suppose to be aluminum in an ordered structure, these three are suppose to be the nickel positions. If the probability of finding aluminum at zero zero zero is point two five then we can say it is perfectly ordered, that is out of the twenty five percent of aluminum atoms inside the alloy all the twenty five percent of atoms are sitting at this, ok. So, that means if you look at probability of, if you call this as A site and you call this as B site, if all aluminum atoms are occupying A site then I call it as a perfectly ordered. If some of the nickel atoms are also occupied at the A site then it is not completely ordered, it is partially ordered and the disorder can be when the probability of finding aluminum at the A site is one then we call it as l as one; that means, all aluminum atoms are there at this. If you see partially aluminum is sitting there, and when you say that the probability of finding aluminum at this A site is point two five; if I call it as A site, if the probability p is one there, if the probability p is point two five then we will say l is zero. That means it is as if the total amount of aluminum is twenty percent, and the twenty percent is sitting everywhere, and twenty percent of the aluminum atoms are sitting here, that basically means it is as if there is no preferred site for aluminum. So, if you find the probability of aluminum atom sitting at the site as point two five then we say long range order is zero. So, this is how we can find out provided you know where the atoms are sitting. It is not easy to find out where the atoms are sitting, but there is an indirect way we can find out the long range order by looking at the x r d patterns. If you take a perfectly ordered structure N i three Al let us say which is perfectly ordered, which people have made let us say by some process and do an x r d of it, and then find out where; what is a basic difference between ordered structure and disordered structure if you do an x r d, you get extra spots or extra peaks which we call them as super lattice peaks; super lattice reflections.

(Refer Slide Time: 34:22)

In case of F C C what are the fundamental reflections, ' I am asking what are the reflections you are telling me what is A square plus k square plus l square, one one one, two zero zero, two two zero, three one one. What is the rule it follows, all should be unmixed, ok so that is how as she says this is A square plus k square plus l square is being three, four, eight, eleven, and twelve, twelve is two two two. These are what are called fundamental reflections; that means allowed reflections, and what are the super lattice reflections, these are I call them as fundamental, what are the super lattice reflections you can have one zero zero, you can have one one zero, you can have all others whatever is not possible. For example, you can have two one one, two one zero,

two one one, all of them which do not exist in this list. Each of them will have certain intensity depending on the structure factor associated with that reflection; every reflection would have a certain structure factor which we can calculate. And in principle if one has prepared a perfectly ordered thing in this p d f files, if you go you can take any one of the peak and find out what is the intensity of it.

So basically take your material, find out what is the intensity of the one zero zero peak and take it as a ratio of a intensity with respect to the one one one peak which is the most intense fundamental for your sample, divided by I of the same peak for the standard and take the ratio of this, and square root of that is what is called the long range order parameter. The reason why we take square root is, the intensity is always square of structure factor, so square root of this is basically I am getting the structure factor with respect to my sample and the standard, standard is something which is a perfectly ordered. Anything you can choose any peak any fundamental peak and any super lattice peak, we choose usually the most intense super lattice fundamental peak, in F C C the most intense is always one one one.

You always know that for example in B C C the most intense has to be one one zero. As you go to the higher and higher theta the intensity goes down, if you have done x r d you will know this. And in addition only in certain cases you would see for example, two zero zero being more intense than one one one, when do you see that when there is a texture. If there is no texture inside the material then in principle two zero zero and all others will be smaller than one one one. So, this is how will, so we choose the most intense here and among these what is the most intense you can choose that and take the ratio of. So, you can choose any one them, in principle there are cases where you do not even choose one one one, when do you not choose one one one let us say, think of a hypothetical situation where I would not choose the one one one peak as the fundamental peak for finding out the long range order parameter. It is F C C, the face is F C C, and she says if it is not $F C C$ that is a trivial point. It is a still $F C C$, but I am not choosing one one one why, then when there is a second face inside the material. If you have some other face whose some some peak of it overlaps with one one one then obviously the intensity that you are looking at that peak is a combination of the intensity coming from the one one one peak of your ordered face plus some other peak of some other face unless you do what is called the deconvulation, and if they overlap is very good then you

cannot do deconvolution. If there is a small shift something like this then you can do decovulation, if the if the two peaks are not actually shifted at all, they are exactly falling one above other you cannot use that, then you should go to some other peak which does not overlap with any peak of the second face that can be any peak, so you have to start looking where. As long as it is a single face we choose the one one one, as long as we have more than one face we do not choose that, so anyway. So, this is all about how to recognize this is ordered or disordered, and how to calculate what is called the super lattice, I mean the long range order parameter.

(Refer Slide Time: 39:57)

Now, let us look at the thermodynamics of it. The moment we say it is ordered or disordered we can talk about the free energy of the ordered face, free energy of the disordered face. Free energy of the ordered phase is H minus T S, am I right, similarly I can also say here H minus T S where H of the ordered phase, S of the ordered phase, H of the disordered, S of the disordered. The moment I say this where I look at the ordered phase, the entropy is always a combination of two entropies; thermal and the configurational. The thermal entropy will always exist in any material at any given temperature excepting at the absolute zero, but the configurational entropy for an ordered structure is zero. In fact, if it is a perfectly ordered structure, if l equal to one then the S is zero because the number of ways of arranging atoms is one, what is S config, delta S config is $k \ln w$, where w is the number of ways of arranging atoms. If the number of ways of arrangements atom is one then that is zero, so, the configurational entropy is going to be zero.

So, in principle this particular term is going to be much smaller when compared to this term here. So, as a result if I now plot g versus t, and also look at these two; H of ordered and H of disordered. Whenever we talk of ordered structure a and b; when do you get an ordered structure, when omega is negative. Whenever omega is negative, whenever there is a strong attraction between a and b you get the ordered structure. So, that means H of the ordered structure is always more negative than H of the disordered structure. Disordered structure would not have the same bonding, so, as a result, so here you would see the ordered structure there is more attraction between a and b, so this is more negative than this, so this is less than that. And similarly if I look at S of ordered structure and S of disordered structure, S of ordered structure is also lower than the S of disordered, once I know these two I can actually talk about how the g verses changes with t. You would see two values of H, here H of the ordered will be lower, H of the disordered will be higher, and I will put it on this side to solve the problem. And if I look at how g changes as a function of temperature, g decreases with increase in temperature or increases with increase in temperature, decreases.

So, now the question is the rate at which decreases are going to be different for both of them. One of them which is having higher entropy will have a steeper slope, so you would see the the disordered structure would go like this, the ordered structure would go like this because the S which is the slope of it. So this is the S of the order, this is the S of the disorder. At any given temperature if I look at the entropy you would see that the disordered structure should have a steeper slope when compared to the ordered structure. If that in the case you would see at some temperature these two will intersect, and that is what we call it as T C, what we call it as a critical temperature T C beyond which you would see the the disordered structure will be more stable than the ordered structure, and you would see an ordered structure transforms to a disordered structure. It is almost like a liquid solid transformation that we have seen earlier; exactly similar to that you would see this happening, ok.

So, you'll only thing is then there are two ways in which it can decrease, that is what we call it as first ordered and second ordered transitions. It is one where the order parameter remains almost one up to the T C and suddenly at T C it changes to zero, this is something like first order transition where you have sudden change in the phase structure at a particular temperature. There is a discontinuity, so the solid **become** remains a solid up to a melting, suddenly at a melting it becomes liquid, it is not that the extent of disorder in the solid keeps on increasing and at the melting the the it becomes liquid, it is not a continuous transformation it is a discontinues transformation. Whereas there are certain order disordered transitions which are continuous where the order parameter continuously increases changes with T C and finally becomes zero at T C, this is what a second ordered transition is; this is what a first ordered transition is. These are what are called continuous transformations, it is more of mechanism of ordered disordered, let us not much bother too much about it, but as far as the thermodynamics are concerned is concerned we can talk about this. And obviously once I know this, at the transformation temperature I can equate these two, am I right.

So once I equate it, H naught minus T into S naught is equal to H d minus T into S d. So, in principle I can talk about T which is T C should be equal to H naught minus H d divided by, if I take it this side it will be S naught, so S not minus S d, am I right, no \overline{no} no this you bring it this side, this you take it that side, S d minus S naught will be, why this is negative this becomes positive. So, T into S naught this is right this is right so you can see that this is what it is. And as a result this difference which is nothing but related to the omega, so larger the is called the interaction parameter between a and b the more negative the interaction parameter is, the higher will be the T C. So, the ordered disordered transition temperature would be higher if this difference is higher. If I treat disordered structure as that where the interaction parameter is zero because in principle you can take it as ideal solution it is disordered structure a and b, there is no preference they are all sitting everywhere. So, I can call a disorder structure almost like a solution which always will have the interaction parameter as close to zero, and that is what we say isomorphism kind of phase diagrams you get when a interaction parameter is zero where liquid gives gives a solid which is a disordered or chemically disordered; structurally ordered of course but it is chemically disordered. So, H d basically is close to zero; H of the disordered, whereas H naught is decided by the omega, the larger the omega and this is negative and this is also negative, so, negative negative goes off, so finally you will get a positive number for T C, is it not?

So, this H naught is more negative than this, so this is why this is negative number and this is also this is less than this, so this is also a negative number. So, ultimately you get a positive value for the T C, and the value of the T C is again going to be decided by this to a large extent than this because S of the disorder does not depend on anything, it does not depend on what is a and b it is simply configuration entropy. If I am taking fifty fifty lets say copper zinc, it has a certain value, if I am taking N I three Al let say seventy five twenty five, it has certain value of configuration entropy. It does not depend on whether it is nickel or aluminum or copper or zinc, configuration entropy does not depend on that.

So, you can see it is this omega which decides it, that is why in certain compounds the transformation occurs at a lower temperature, in certain compounds transformation does not occur until you reach the melting point. In copper zinc four hundered and fifty is where it transforms, whereas in Ni three Al it transforms, **transforms** the order disorder transitions occurs at the melting point. When the solid is actually melting then the disorder takes place, chemical disorder, so structural disorder and chemical disorder occur together in such a material, so this kind of things needs to be understood, so everything is related to this.

We will stop now.