Phase Transformation in Materials
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Lecture – 08
Solid Solution Types

Students, we have discussed in the last class about the solid solutions and especially I have discuss about the regular solutions. Now in this lecture, as I am going to discuss about order solutions. So, it is better that.

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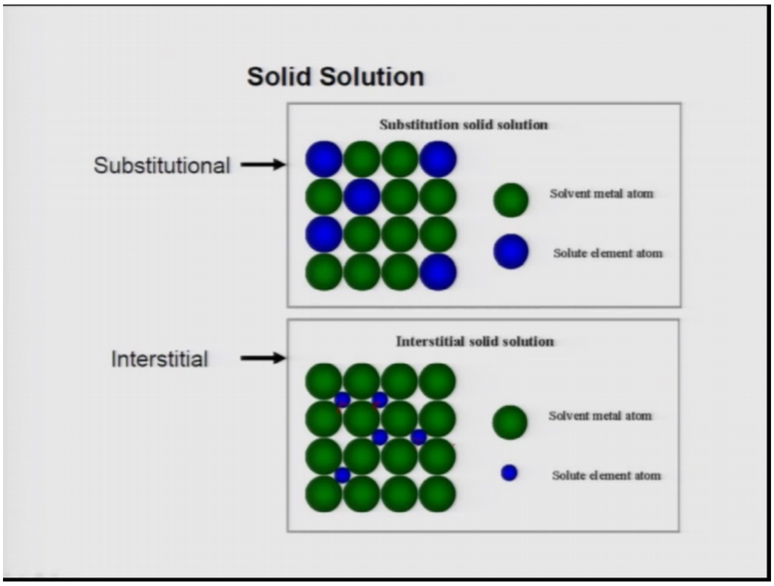

We start with a simple atomic scale picture of solid solutions as you know solid solutions actually can be of 2 types basically what we call as a substitutional solid solutions and interstitial solid solutions substitutional solid solution means we can replace the atoms of a lattice at sitting in a crystal structure by some other atoms.

Like here in the first case the green atoms are actually solvent atoms just like in a solution in liquid and the blue atoms are actually known as solvent atoms so; that means, initially all the atoms are occupied by the green and later on solve the atoms of a of blue type have replaced the green atoms. So, here actually you see there are five green atoms in a 2 dimensional lattice and remaining are the blue five blue atoms remaining are the green atoms.

So, a question is this direct replacement of atoms is known as substitutional solid solutions; that means, you are substituting the atoms of one type by other we can also have a situation in which we do not need to replace the atom sitting at the lattice positions, but we can actually accommodate solid atoms at the interstitial positions that is shown here the blue ones actually small size solute atoms; they are sitting at the interstitial positions here; you can see there are several ones are shown. So, this kind of solid solutions are very widely seen like steel even each carbon is actually added to the iron goes in to the interstitial solid solutions.

So, that is the normally that picture of solid solutions you can have only 2 types; now we can actually vary their level of complications and that is what we are going to discuss to show you a 3 dimensional crystal structure.

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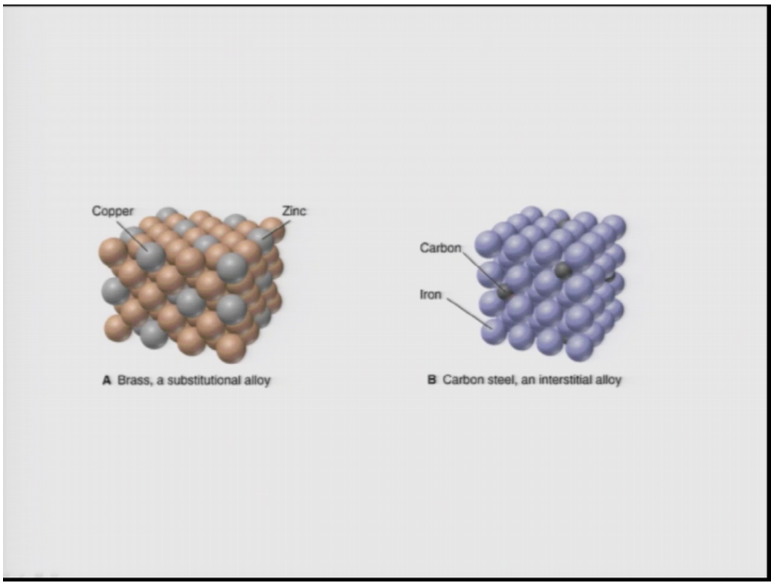

And the how atoms arrange this is a solid solutions of known as brass; brass consists of are copper and zinc and it can have different concentrations of zinc in copper, but you see here the zinc atoms which are actually grey there is; there if they are replaced some of these copper atoms which is showing as a yellow similarly on the right side I am showing a BCC structure of iron and carbon atoms are shown as a dark atoms small size they are sitting in interstitial positions.

So, anyway there is a 2 d or 3 d; this is what actually observe in the solid solutions solid solutions are the phases which will see more in phase transformations because we will look at; we will see when you study about the solid state phase transformations how the solid solution phases will be transformed in to some other things; it will be clear to you then this how this concepts are important.

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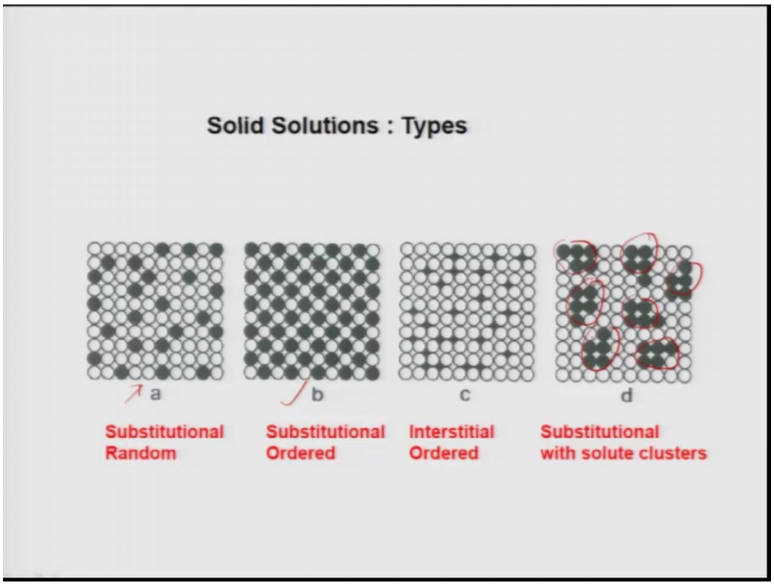

Now, as I told you solid solutions can be different types random ones that is what we discussed in the regular solution model are shown on the layered picture that is why the black atoms which are known as solute here sitting randomly in the or rather replace the white atoms randomly that is why they are called random solid solutions; we can also have order solid solutions; that means, the black atoms are now sitting at exact you know positions in the lattice you see here they are regularly sitting at different defined positions similarly for the white atoms. So, that is basically substitutional random and substitutional order type.

Now, you can also have interstitial order what is the meaning of interstitial order; that means, when interstitial atoms can actually sit specifically specific positions or specific industrial positions in the lattice that is what is shown here the black positions are actually interstitial positions where the atoms are sitting, but they are sitting only at fixed positions, they are not randomly sitting in the lattice that is why it is called interstitial order solid solutions there are many actually we will see some examples later, but there are many such solid solution exists in the literature.

Similarly, you can also have clusters in the substitutional solid solution cluster means the instead of black atoms which are solute sitting randomly in the lattice or in a in a definite defined positions in the lattice they can be cluster around certain positions like you can see here this is where the it is cluster this is also the several places the atoms are actually cluster around cluster means; they are sitting together they are not widely dispersed in the lattice positions so; that means, substitutional solid solution can be of 3 types random cluster type or order type; now depending on their nature, the free energy curves will change in fact, some of these.

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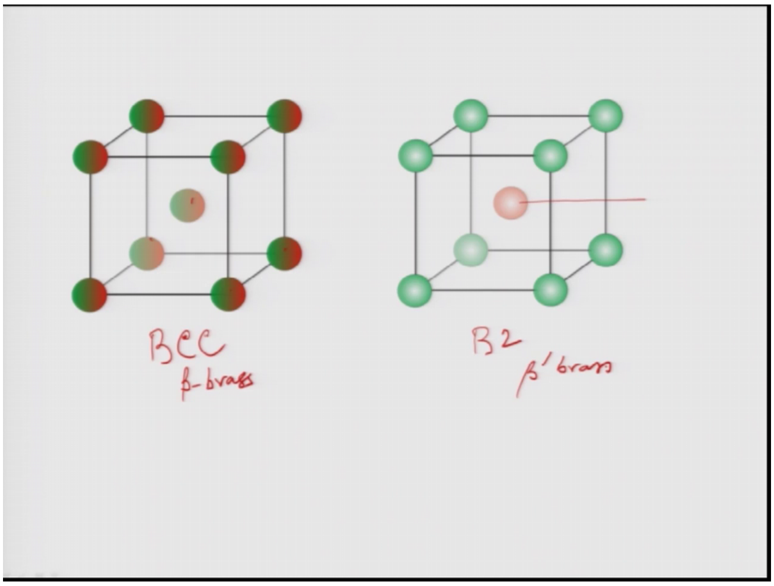

I will discuss in the lecture today to give in better idea of what is the kind of order disorder because ordering is very important for us see this is a BCC unit cell; why this a BCC cell because all the atoms actually; similar type sitting at the corners of the cube and the center of the cube there is no difference of type of atoms sitting at these positions.

On the other hand the moment; I put a pacific suppose pink color atoms in the body center positions, where are the corners of the cubes are occupied by the green atoms then it is called B 2 structure. The reason being is that you can have actually 2 different lattices here one lattice which is a simple cubic occupied by only the green atoms.

Other lattice which is also a simple cubic type in which these pink color atoms will be occupied so; that means, we can actually talk about 2 different lattices in the B 2 structures. On the other hand in the BCC structure it is a simple lattice that is the B body centered cubic because we do not differentiate type of atoms sitting at the coordinates or at the body centered, but here we are specifically allowing green atom sitting at the corner positions and the pink atom sitting at the you know centered positions. So, this is known as beta brass you know like I discussed or this is known as beta prime bus because this is order. So, this is the first type of ordering we actually normally observe bcc transforming into B 2 it is a order transformations.

Now, how this is this will happen and what are the thermodynamics and all this will discuss later part to make you clear that this is a task phase transformations by the way; now we can complicate more, but they are not complicated structures.

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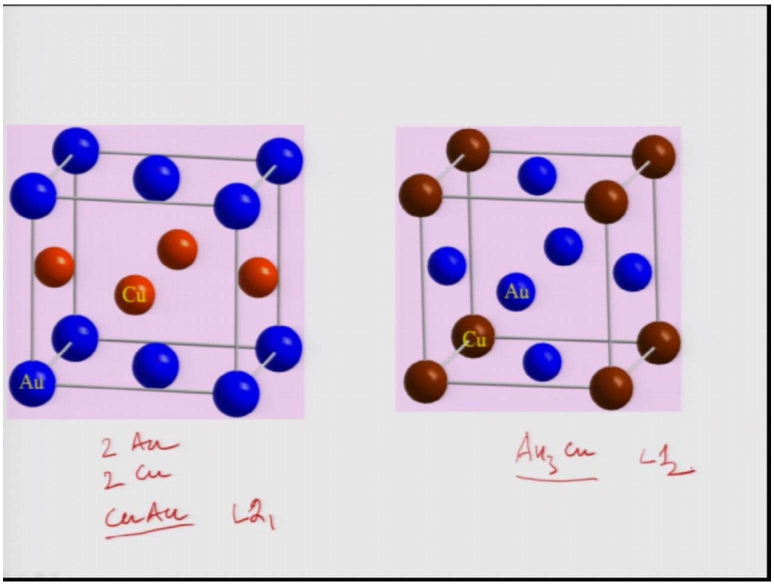

Let us look at silver copper; silver copper is a classic orderly surface transformation system you know copper atoms; if I allow; them this is a face centered cubic structure. Suppose if atoms are randomly sitting in the face centered cubic structure like copper and silver there is no specific type of atoms sitting at the different positions then we call it is FCC, but the moment copper atoms are only sitting at the 4 FCC positions and corner as well as 2 FCC positions, then it is called as order structure you know here if you look at carefully, there are 1, 2, 3, 4 copper atoms in unit cell, but these each copper atom is shared by 2 you know; 2 unit cells because they are sitting at the face centered positions. So, there are actually 2 copper atoms per unit cell effectively.

Another and there are one silver. So, one gold atom coming from the corners because corners are shared by the 8 cubes and one coming from the face centered positions. So, there are 1 or 2. So, therefore, 2 1 plus 1 is 2 so; that means, there are 2 gold atoms and 2 copper atoms so; that means, this is say C u A u structure this is known as L 1, L 2 1 structure because atoms are actually occupying specifically pose face centered positions by the copper and corner atom plus 2 face centered positions by the gold. We can change the situation completely other way how; suppose, if I put corner atoms as a copper and all the face centered positions atom as a gold then I will have what is known as A u 3 C u structure very clear, there are 6 gold atoms in the lattice and as you know each gold atom is shared by 2 cells; there are actually 3 gold atoms, but there are only one copper atom effectively initial because these corners are shared by the 8 cubes. So, that is why it is called A u 3 C u structure this is actually known as L 1 2 structure or a structure.

So, you can clearly see by simply form a disordered structure we can build in order structures in a variety way away 1 is a B 2, then this L 1 2; L 2 1 different kind of structures can be created.

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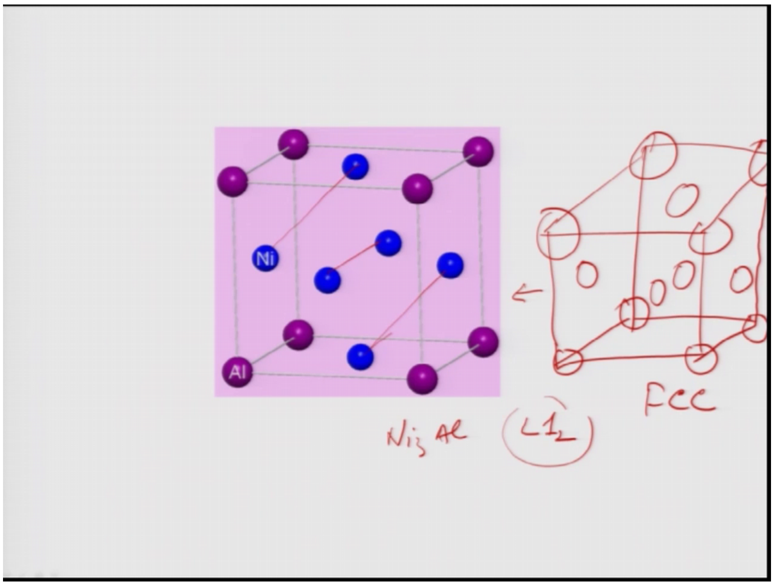

Now, there is another example, I will like to give which is the classical example known as N i 3 A L, this is also known as L 1 2 structure simple FCC unit cell, but this is no longer a FCC unit cell because atoms are pacifically occupying different positions as you see here aluminum atoms are sitting at the corners; that means, they are one aluminum atoms coming from the effectively coming from the unit cells, but there are 3 nickel atoms effectively confidential because nickel atoms are occupying the first center positions.

Now, this has 4 sub lattices specifically, one sub lattice is because of aluminum, then 3 sub lattices of nickel why 3 sub lattices because we can actually put 2 atoms 2 face centered atoms here like this and generate 1 sub lattice. Similarly you can actually have another 2 like this, I think, yeah, another 2 like that another 2 like this. So, by drawing a hole; many many unit cells, we can actually generate these sub lattices. So, pacifically speaking they are all row lower order structures or; that means, crystallographically and that is why actually ordered atomically.

So, by giving this examples it is evident to you that ordered structures basically come from simply putting the atoms in the pacific positions in a unit cell similar thing if I actually have a FCC unit cells like this, if I draw it here and put a random element of the nickel and nickel and aluminum atoms then what will happen it will be simply FCC unit cell, if I do not demarcate between the type of atom sitting at the corners and the face centered, then it becomes a FCC structure. So, FCC becomes L 1 2 when nickel atoms start sitting at the face centered position specifically and this is known as ordered disordered transitions and this is basically very important ordered transitions because this is used this material is used directly in the application like turbine engines or even in the jet engines.

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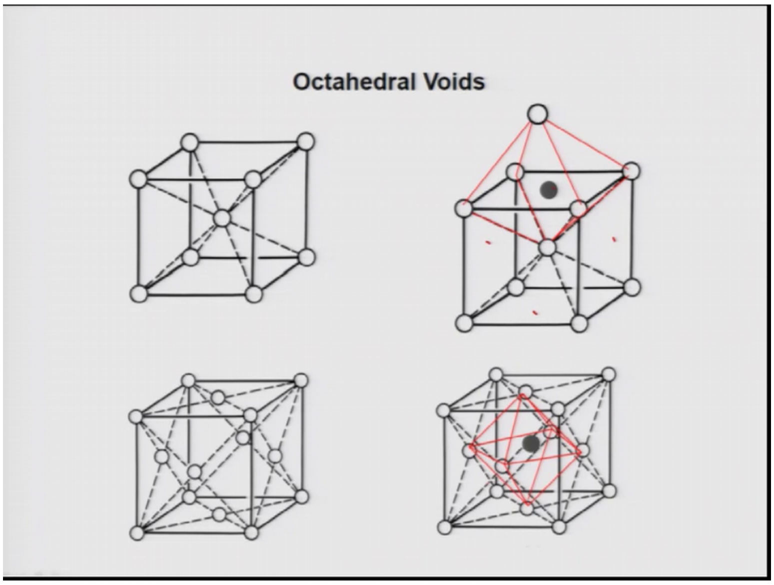

Now, giving this idea about order substantial order structures let me just tell you that how the interstitial solid solutions form normally interstitial solid solutions form by occupying the voids in the lattice. So, suppose this is the BCC unit cell that is of iron there are actually both octahedral and tetrahedral voids octahedral void is shown here you can see similarly in a FCC unit cell like this octahedral void is shown there. So, if I put a carbon atom there then carbon atoms can occupy in each of these you know phases they would be called the sitting at the octahedral voids.

Similarly, there are many FCC sorry many octahedral voids present in FCC structures. So, FCC is like gamma iron solid solutions of the FCC iron in and carbon.

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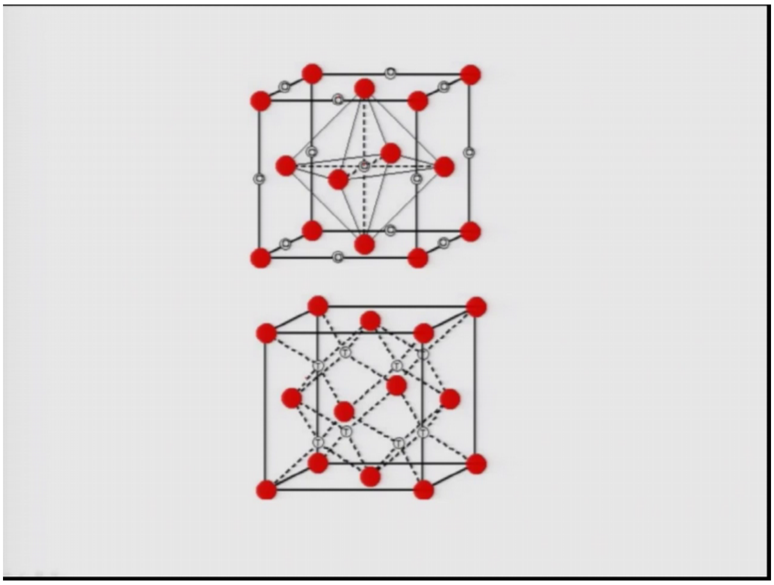

So, here I am showing you all the you know in the FCC crystal structure all the octahedral void positions you see here there is one at the center then there are sitting at the edges. So, there are many such. Similarly, I am showing you here the tetrahedral positions in the FCC unit cells, there are actually many; actually you can see 1, 2, 3, 4, 5, 6, 7, 8, octahedral tetrahedral voids presents there. So, there are empty number of voids presents in unit cells which can be filled up with this smaller size substantial this is the C C atoms and they can form different solid solutions you can have carbon sulfur nitrogen oxygen any kinds of things possible.

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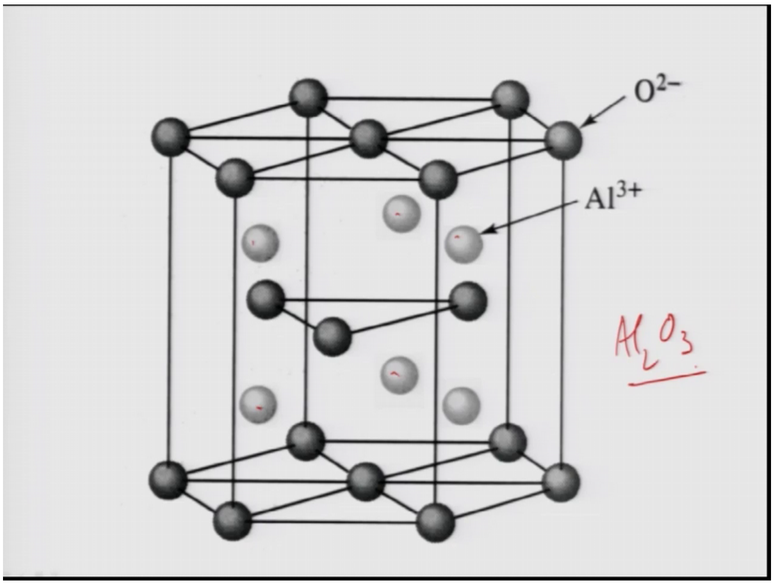

So, to give you an idea about the oxygen suppose this is hexagonal crystal structure of aluminum oxide you see here the oxygen atom goes in to the hexagonal structures hexagonal means this grey color atoms are oxygen sitting at the hexagonal lattice positions and our aluminum because smaller atoms, they actually go in to octahedral positions here and these are the octahedral positions of aluminum and that is why it become Al23 O3, Al2 O3 structure. So, this is gamma aluminum oxide by the way aluminum oxides are different crystal structures, but we can actually form this way different kinds of solid solutions whether it is a metal or ceramic it can be; it can be any types.

Now, up on giving you this idea; so, let me just go back and tell you. So, how do I deal with the free energy composition diagrams of these structures order structures as you see as you have seen the most of these order structures?

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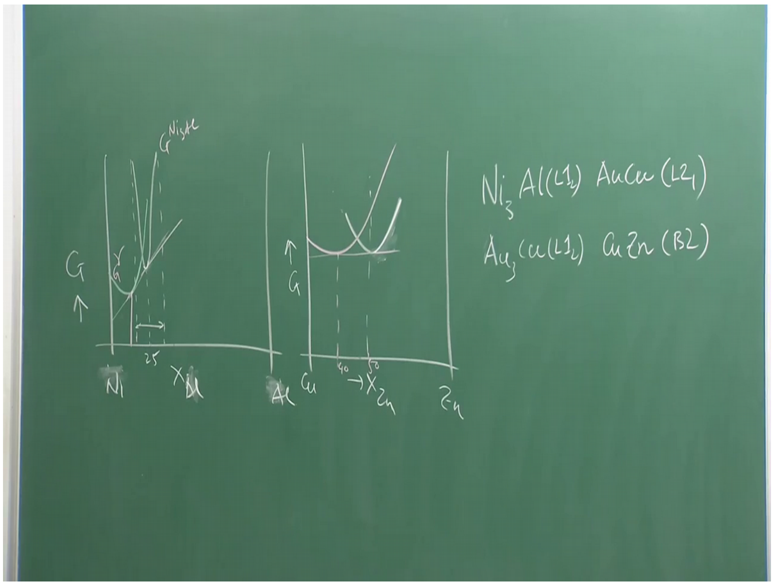

Now, I will go to the board and discuss most of the order structures actually are stoichiometric compounds like I told you about Ni3 Al which has a base specific compositions like 75 percent of nickel and 25 percent aluminum; that means, an (Refer Time: 14:38) must be 3 atoms of nickel and one atom of aluminum. Similarly I have told you about the Ao3 Cu structure; this is also a low in to structure or you can have A u C u structure this is it order tetragonal structure L 2 1 or you can have copper zinc which is a b 2 b 2 structure.

So, these are all different order structure, but if you see carefully they are they all has specific stoichiometry. So, what does it mean; that means, that they are stable only at fixed compositions, but fortunately in metallurgy all these compounds can accommodate little bit of compositional change, we are lucky enough that this happens; they are not actually specifically compounds, but there are crystals which are specifically lying compounds in the phase diagrams, but none of these are actually like if I; you know talk about A u C and A u Cc 3 3 C u both of them has a about 5 to 10 percent compositional differences by accommodated form.

Suppose, this is 75-25, so, you can actually start from 65 to about 85. Similarly copper can be changed like that. So, copper zinc actually has a large compositional change this is basically 50-50 percentage, copper 50 percent zinc, but in the central of the phase diagram of copper zinc will see that this has a range of composition in which the B 2 structure is stable

So, how do I show it in the in the you know free energy composition diagram suppose if I drop free energy composition diagrams of a compound which is as a very small range of solid solubility then it will be like this let us suppose this has a compositions of let us suppose this has a composition of 25 percent aluminum. So, this is aluminum this is nickel sorry this is nickel that is aluminum then otherwise it will pick up. So, this is 25 percent, but if you show clearly there is a range of composition it is stable this is these this is where we can vary the aluminum concentrations or nickel concentration by the way any of these are similar and till we can actually retain the order structure

But there are you know there are phases like I said in copper zinc; copper zinc has a large solid solubility and around 50 percent, suppose this is copper this is zinc and if I plot g and this is x z n this is x L x z n. So, you will find that it is its basically this is 50-50; you will find that it is stable in a large composition range. So, we can actually get a sallow shallow inverted parabola in the free energy composition diagram and, but the most important characteristic of these compounds or these phases are that they actually because they are stoichiometry.

So, they has they will be having free energies much lower than many cases than the solid solutions specific solid solutions it has not found. So, that is another advantage of another advantage of forming these compounds because they have a very in order structures. So, therefore, the entropic contribution is slow and because of that because atoms and in specific sides at the net and in the lattice sides. So, therefore, the entropy is low and what is important is the delta h because delta h is very high here why because compound formation leads to a lot of energy release and that is why the delta h is high, but delta s entropy change is not very high.

So, because of that many cases they have they will sit much I know above the solid solutions lines. So, like if I if I have to draw it very clear clearly they then I can see here these the FCCs solid solution which are nickel reach will be having much you know lower positions as compared to these now if I want to find out the solid stability conditions for that; obviously, then what I should do I should draw a tangent common tangent between them and that common tangent between them will tell you the solubility or the curves. So, you know the stability of these phases as you can clearly see here stability of these phases.

So, that is tells me that this is stable at twenty five percent, but this is also stable between this and this and this is stability of the compositions of the gamma solid solutions. So, this is g gamma and this is g N i 3 A l, similarly here as you know this is beta brass so; obviously, before that there will be alpha brass very clear alpha brass has accomplished large it is also; it is basically also a stoichiometry compound, but it has a large solid solubility limits and that is why this will be having because this is stable from 0 to 40 percent; this will be like this, then you can actually draw a common tangent and find out the stability change; this is 50 or this is will be 40 percent something like that.

So, that is the way actually we can actually think about discussing about these structures. So, difference between these and this diagram is that here because of shallow natures of the free energy composition diagrams, it is same as a solid solutions what I have discussed in the last class, but because of the you know stoichiometry of Ni 3 Al is you know specifically defined and their composition cannot be the very very much. So, that is why you have such a kind of construction.

Remember this all happens in the order compounds these are all very specific things second important thing you should understand these diagrams will also depend up on the you know order parameter what is order parameters is very clear that in these diagrams I have shown you in this diagram means here where is that let me go back it is very clear that when in a big suppose material large polymer material if pacifically in all the you know crystals the atoms of Ni goes to the face centered positions and atoms of aluminum goes to the corner positions then we have complete ordering; that means, all the sides which are to occupied by nickel are occupied by them only.

There is no change or occupations of nickel from their original sides to other sides or and vice versa all this sides which have to be occupied by the aluminum are occupied so; that means, it is order parameter is equal to one then we define, but reality it is not be the case reality will find there will be change over some sides will be occupied some pacific sides suppose for nickel like here if this out of this side is not occupied by nickel, but occupied by aluminum, then you call anti side effects, but this will lead to reduction of the order parameter and reduction of the order parameters is affected will be affected in the free energy composition diagram because the free energy reduce, you will change why because the moment will have anti sides entropy will change because you are then having little more randomness than a perfect order state in a perfect order states, it is completely random less, but the moment you bring in this anti side defects or some voids suppose some nickel positions are not occupied by aluminum or nickel atoms this remains of void then what will happen entropy of that system will be much higher than it completely order structures the moment you change the entropies the free energy curves position will change and the moment free energy curve position will change the stability will change this can be seen easily.

Suppose if I have this curve let me just a little bit rewrite and tell you how it can happen suppose this curve goes down little bit suppose instead of these let me draw with a some other color, this is red color chalk suppose if the entropy increases and these goes down free energy is still lower now what will happen the common tangent will be little bit changed since he here the stability earlier stability was here some are there several decompositions and this one we although does not change much, but the decomposition stability is stable composition for the gamma phase which is FCC solid solutions on nickel has been decreased.

So, rather the reach range in which gamma plus Ni 3 Al is stable has increased. So, that is what happened in natural aspects naturally these are the situations are observed and surely these situations are very very you know observed because nickel aluminum has been studied extensively in the literature. So, by changing the order parameter basically we can do that how do I define the order parameters order parameter is defined like this.

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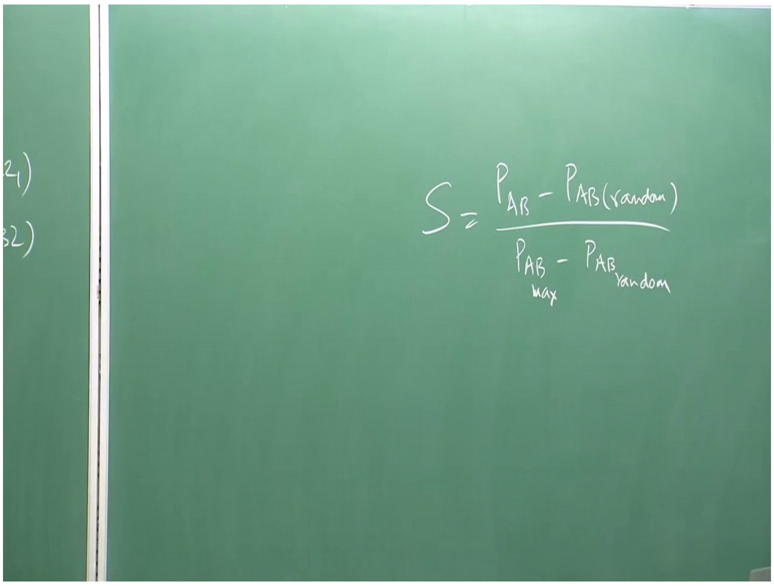

It is basically S is basically equal to P A B minus P A B random or something; let me just check random yes random minus P A B minus P A B; what is that complete order, no, no, this is maximum value minus random let me explain it this P A B at the top in the numerator the first one tells you the probability that all the sides how many sides are occupied by A or B atoms minus if it is complete random structure then; obviously, there is no pacific city of the occupations of the atoms in the lattice sides divided by if it is fully ordered structure suppose that denominator where is suppose P A B max means it is a fully order structure then what will happen every atom is sitting at the pacific positions minus random structure. So, these values much higher than this value.

So, that tells you the order parameter it can be actually change over to the compositions of the unit cells the composition of the lattices we can change over that that will do those are the pacific things will discuss later. So, in a very specific way, I will like to tell us that the order crystal structures are solid solution structures are ordered compounds they actually compound most; in some other cases, they are actually like composing; these is solid solutions; we have a large range of solid solubility of zinc and copper in beta and alpha phases or even gamma phases also in the copper zinc diagrams you have a little slightly different way of drawing these free energy composition diagrams and these diagrams will allow us to find out which very stable at what compositions at a particular temperature, fine.

So, in the next class, we will simply go ahead and discuss about some of the aspects of equilibrium in heterogeneous systems although we have discussed a few of these stuffs, but specifically we will go in to details as you see in the books if you go back to the books it tells you how we can actually get this free energy composition diagrams for different systems and that is what is very important to understand that you need to have a little bit idea about the phase diagrams because I will be drawing phase diagrams and so you the free energy composition; if free energy composition diagrams are different temperatures to show you how the free energy composition diagrams are important in terms of obtaining the phase stability will do that in the next class. So, hopefully we will be able to catch it up.

Thank you.