Phase Diagrams in Materials Science Engineering Prof. Krishanu Biswas Department of Material Science and Engineering Indian Institute of Technology, Kanpur

Lecture - 18 Intermediate Phases

So, we are going to continue the same discussion this class also.

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In the last class, I just told you that there are three different types of intermediate phases exist in the binary phase diagrams, which normally forms by peritectic reactions, but there are other types other reaction also which can lead to formation of this intermediate phases. So but most of them actually forming by peritectic reaction that the reason what this whole thing into the peritectic reaction peritectic phase diagrams as a part of that. So, I told you that there are three types of intermediate phases; first one is valence type, second one is size factor and third one is the electron compounds.

So, first one is basically like a sodium chloride structure or calcium chloride structure, they are stabilized by the valence electrons. So, there is transfer of valence electron from outer shell to one and other atom and then the bonding happens. The second one which is stabilized by size factor for which I will show you some structure details in the slide but they are already called laves phases.

And there are three types of laves phases one is called Mg Cu 2 which are cubic structure, Mg Zn 2 which are hexagonal structure and Mg Ni 2 which are called hexagonal structure, again but double unit cell double the unit cell of hexagonal. It will be very clear to you when I show you the slides. And I show I give examples of those compounds third-one which we discussed in the last class, where we could not finish is the electron compounds they are called Hume Rothery phases because they are discovered by Hume Rothery. And these compounds are stabilized by e by a ratio where e is the number of valence electrons total number of valence in the compound and a is the total number of atoms in the compound.

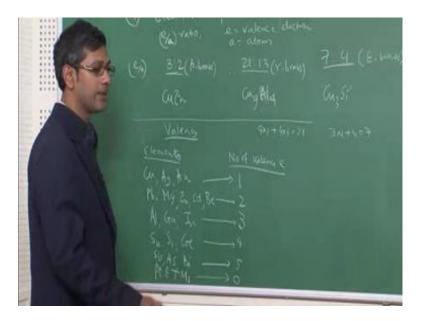
So, there are specifically 3 ratios only in which this compounds can form one is 3 is to 2; second one is 2 is to13; and third one is 7 is to 4 these all compound copper zinc phase diagrams. Specifically, 3 is to 2 is known as beta brass; 21 is to 13 is known as gamma brass structure; and this is known as epsilon brass structure 7 is to 4. And therefore, they do exist in the copper zinc phase diagram. Probably if you look at detail they are their composition that these are existing. So, beta brass as a bcc structure, bcc crystal structure; gamma brass is also bcc unit cell, and there is 52 atoms in the unit cell, large bcc unit cell. And this is hexagonal system or epsilon brass correct.

So, I have given you three examples Cu Zn - 3 is to 2 ratio electron by atom; Cu 9 Al 4 - 21 is to 13; and Cu 3 Si - 7 is to 4. Before actually we do this different kind of phase, let me just give you the valencies of different elements how do we are decided. So, valencies of different elements you need to know this is very important it is better you take it down when you are listening this lecture. So, let us suppose elements and number of valence electron correct number of valence electron, element or elements. Let us copper, silver and gold number of valence electron we considered to one; then for lead, magnesium, zinc, cadmium, and beryllium - 2; third one is aluminium, gallium and indium – 3; steel, silicon, germanium – four; antimony, arsenic, phosphorus, bismuth not phosphorus bismuth – 5. And last one is pt and transition metals 0; transition metals mean iron, cobalt, nickel, there is no without considered there is any valence electron.

So, this table you should remember you better take it down because you know you need to calculate defined ratios then we need this values that is what I wanted to give you at the beginning so that you do not forget. So, now, it is very easy copper and zinc as you see zinc exist somewhere, yes. So, copper -1, zinc -2; so for copper zinc, there are

three valence electrons; copper is 1 zinc is 2; and there are two atoms, so 3 is to 2. Copper and aluminium - 4 copper has one electron so 9 into 1 is nine 9 into 1 is 9 plus 4 into 3 is 12 so this is 21 and number of atom is 9 plus 4 - 13. So, here again copper silicon number of atoms are 3 plus 1 - 4, number of valence electron copper has 3 into 1 silicon has 47, 7 by 4 very easy, anybody can do these problems.

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Now, let us look into the different compounds after I give you the table different compounds different types of series of that and let me just remove these things to show you all the thing I will keep these table so that it helps you to understand.

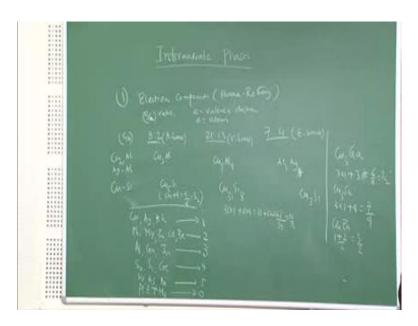
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And suppose I will tell you copper aluminium system and or silver aluminium, it exists. So, this is Cu 3 Al, we will calculate again Cu 9 Al 4, I have written already. And this is Ag 3 Al correct 3 plus 3 Ag 3 al Ag 3 Al 3 no, this is so what will happening 3 plus 12 is wrong, it should be different something is round here. So, it was Ag 3 Al was fine Al 3 Ag 3 plus 1 is 4, 3 plus 1 is 4, 7 is not coming, so it will be 3 yes 3 plus this is 4, so 3 plus 3 7 plus 7 correct. So, now, this is copper silicon Cu 5 Si Cu is 5, 5 into 1 and the 6, silicon is 4 so 5 plus 4 is 9, 9 and 6, 9 is to 6 is 3 is to 2. How 9 Cu has 5, 5 plus 1 4 9 and there are 6 atoms 9 by 6 is 3 by 2. So, you can clearly see that taking place.

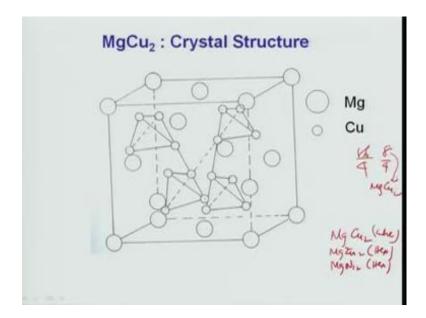
Now this one is Cu 31 is 31 into 1 plus 8 into 4 silicon has 4 so that means, 31 plus 32 - 63; and how many 39 atoms, 63 39 is 21 by 13 correct. Last one is Cu 3 Si this I have already discussed. Now for the last that is enough. So, these are all different examples of this valence compounds which forms by the reactions. It is very clear that this table is what is going to help you in calculating the ratios of different compounds correct. Let me just also give you some more examples.

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And like one example I will give you here is Cu 3 Ga Cu 3 Ga is fall under which one which category whether the 3 is to 1, 3 is to 2 21 is to 13 or 7 is to 4 let us see Cu has 1 valence electron so 3 into 1. Gallium has now many valence electron Ga 3, so 3 into 1 - 3, so 3 plus 3 is 6 and 4, atoms 3 by 2, it is a 3 by 2 compound very clearly you can see this will fall under beta brass. So, what about Cu 3 Sn, Cu 3 Sn is Cu is 1 so 1 3 into 1 Sn is how much Sn is 4 so 4 so 3 plus 4 is 7 and 4 7 by 4 such as say epsilon brass, so last one type. And then I have probably given Cu Zn this is Cu is 1 plus Zn is 2 therefore, it is 3 and number of atom is 2, 3 by 2.

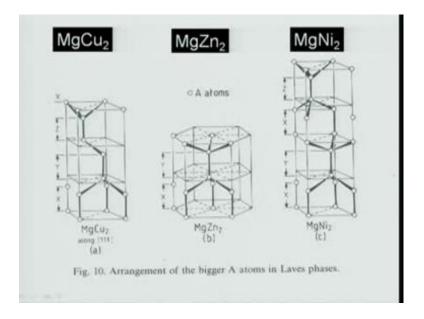
So, these 2 Cu 3 Ga and Cu 3 Zn they are different compositions. You can see one is 75 percent copper 25 percent gallium; other one 50-50 compositions,, but both of them are of same type see 3 is to 2 type; that means, they having bcc unit cell beta brass structure that is the major discovery of Hume-Rothery, that these compounds also they have different compositions of phase diagrams, they are coming at different positions in the phase diagrams but they are have similar crystal structure. And this crystal structures are the bcc or beta brass type. I hope for the this electron compounds, so let me just go back to the slides now, and let me show you interesting facts about size factor compounds.



I told you there are three different size factor compounds one is Mg Cu 2 type; and other one is mg so there are three types of (Refer Time: 11:39) Mg Cu 2 types which is cubic and Mg Zn 2 hexagonal; and third one is Mg Ni 2 again hexagonal. There are three types. So, first one let me see that I will show all of these are stabilized by size difference of the phase. The crystal structure Mg Cu 2 is shown in this slide, where Mg atoms are bigger atom, which are sitting at the corners of the cube also at the phase centres of the cube correct. This is phase centre cubic structure, but on the other hand copper atoms are sitting on the alternate tetrahedral voids, you know there are eight tetrahedral voids inside fcc unit cell.

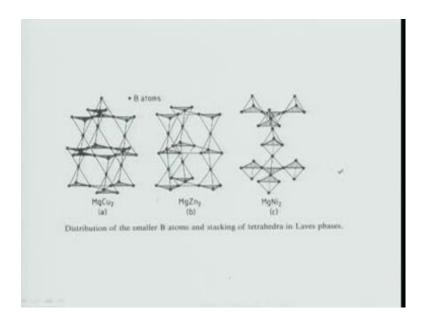
So, therefore, there are alternate tetrahedral voids, you see this is filled bottom one is not filled. They are bottom one is filled top one is not filled, similarly for these two. And these tetrahedrons are formed by copper. There are four atoms in each tetrahedron 1, 2, 1, 2, 3, 4 atoms in tetrahedron correct. So, how many atoms will be there, 4 into 4 - 16 atoms of copper. And how many atoms are present for the unit cell fcc unit cell of magnesium 8, how many 1 plus 3 4. But you have to understand that out of these 16 atoms 8 atoms are out of the outer the unit bcc cell other 8 are not that is why its 8 by 4 that is why its Mg 2 Mg Cu 2 Cu is 8 atoms and 4 atoms are magnesium. So, this is the first type of structure and there are many compounds like you know Ti b 2 (Refer Time: 13:34) they forms these compounds.

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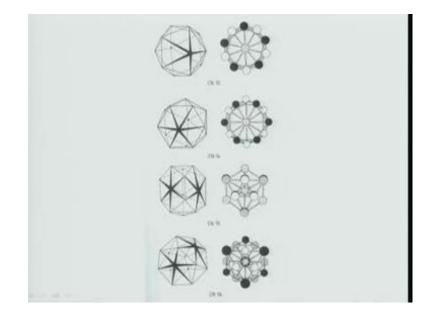
So, next one is Mg Zn 2, Mg Zn 2 actually basically forms such a kind of hexagonal structure and they also stabilized by tetrahedral atoms. And you can see here A atoms are the bigger atoms which are shown here B atoms will be shown in the next slide. While at the Mg Ni 2 is a same hexagonal structure only but unit cell is doubled instead of x plus y it is x plus 2 y x plus y plus z x plus y plus x plus z doubled, but z and y are same almost. So this is this.

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Now, let us discuss about this tetrahedral coordination you can see here for Mg Zn 2, Mg Ni 2 again tetrahedral coordinated zinc atoms as stabilized in this compound. Here tetrahedral coordinated copper atoms are stabilized in this crystal structure that is why it is called Mg Cu 2. Here tetrahedral coordinated zinc atoms are stabilized this structure here tetrahedral coordinated nickel atoms are stabilized this structure. So, this is therefore, these structures stabilized by stacking of tetrahedral in these structures.

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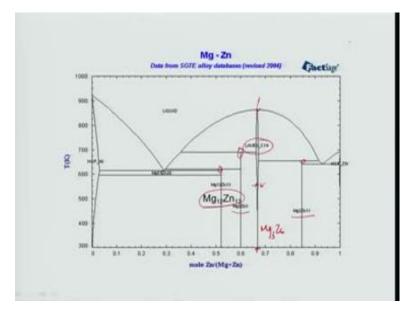


So, now I have shown you that there are different coordination, tetrahedral coordination, tetrahedral coordination, but they can have the coordination numbers obtain form this also is possible. So, there are different types of coordination possible that is what I am saying it is not only that you have 8 coordination and 12 coordination possible, you can have 14, 15, 16 coordination possible.

And they are known as (Refer Time: 15:17) phases which exist in different phase diagrams just to introduce you just I am showing it. This is CN 12 coordination number 12 which is same thing like fcc structure; fcc has coordination of 12 every atom is coordinated by twelve atoms. But if you have little bit distorted structure of that you can see here this is pentagonal surface, you can have a coordination number 14 or even more distortion lead to coordination number 15 central atom is coordinated here by 15 atoms. Or you can have 16 you can see correct. So, normally CN 13 does not exist CN 13 is for

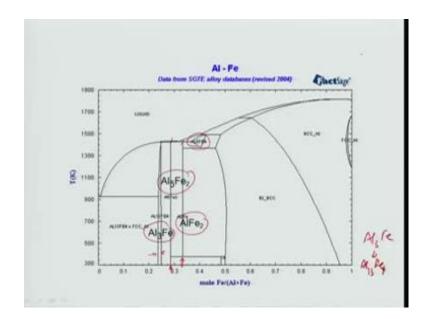
the (Refer Time: 15:59) structure which is part of this so that is what actually it does not exist.

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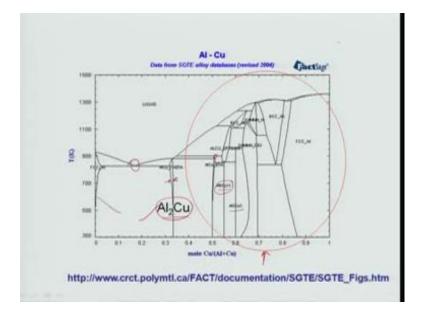
And I also would like to tell you that this compounds which I showed you in the earlier other than this they are very useful correct like Mg 12 Zn 13 this is a very it forms eutectic with alpha, this eutectic forms with alpha this is like (Refer Time: 16:26) like structure.

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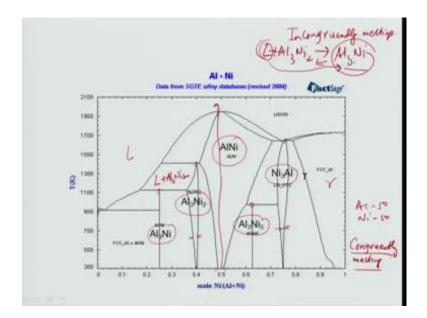
And now yes now this one sorry, this one Al 3 Fe, they are always used in the intermetallic compounds in the high temperature applications Al 5 Fe 2 Al 3 Fe widely used.

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I told you that Al 2 Cu eutectic this eutectic is very classical eutectic were many many alloy system that and aluminium copper is duralumin is a material used for the (Refer Time: 16:59) application and in that this eutectic exist and then you have and aluminium nickel is a classic system in which all of them are used.

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Al Ni has a very high melting temperature; it can be used. And then Al 3 Ni 5 or sorry Ni 3 Al or Al 3 Ni they both are used for many applications especially Ni 3 Al is used in the turbine blade applications. So, with this, I have given you that the phases which forms by the peritectic reactions. And I told you that there are phases which exist in the phase diagram which does not forms the peritectic reactions which forms by congruent melting. Let me just explain that congruent melting stuff. Now I just take this diagram to explain you. Congruent melting means when a compound melts its composition does not change when it become liquid.

Let us take examples of Al Ni and it has 50-50, 50 percent nickel 50 percent aluminium. So, when it melts directly to the liquid the composition of the liquid exactly same as the solid and that is why it is called congruently melting compound. It forms directly from the liquid with same composition of a liquid. So, this congruently melting compound exists in many, many phase diagrams. This is one such there is another one I shown you here aluminium silver where is that this aluminium silver Ag Mg it also forms by congruent melting you can see this is forms directly. So, this compound melt it will become liquid will have same compositions correct.

By on the other hands things which are forming by peritectic reactions let us apply this one Mg or let us simply use the aluminium nickel system that is much easier here. Let us suppose this one Al 3 Ni, it forms Al 3 Ni is forming by this is phase full of liquid it is a liquid plus Al 3 Ni 2, therefore, Al liquid plus alpha sorry liquid plus Al 3 Ni 2 reacting peritectically to form Al 3 Ni. So, now, if heat this one so that means, if I see the reverse reaction by heat this Al 3 Ni what will happen you will have this solid will form another solid of different compositions Al 3 Ni compositions and the liquid. So, therefore, liquid will never has the compositions the compositions will have the solid, and these are called incongruent element compound incongruently melting compound these are called.

So, thus there are two types of this intermediate phases as for the melting is concerned; one for the congruent melting like Al 3 Ni which directly melt in liquid without change in compositions, and there are compounds which melts by peritectically, when it is heated up. So, therefore, liquid has different compositions than the solid at the (Refer Time: 20:20). Peritectic phase as these compositions liquid has completely different compositions than this; together another solid phase forming and they are called

incongruent melting compounds. So, with this, I have completed all the important parts of intermediate phases.

In the next lecture, I am going to talk about monotectic phase diagrams. And you know monotectic and syntectic are the phases diagrams which are distinctly different forms what you have seen so far. And before actually we do that I will show you few experiments where liquid phase immersibility is demonstrated and then I will go ahead with monotectic reaction.

Thank you.