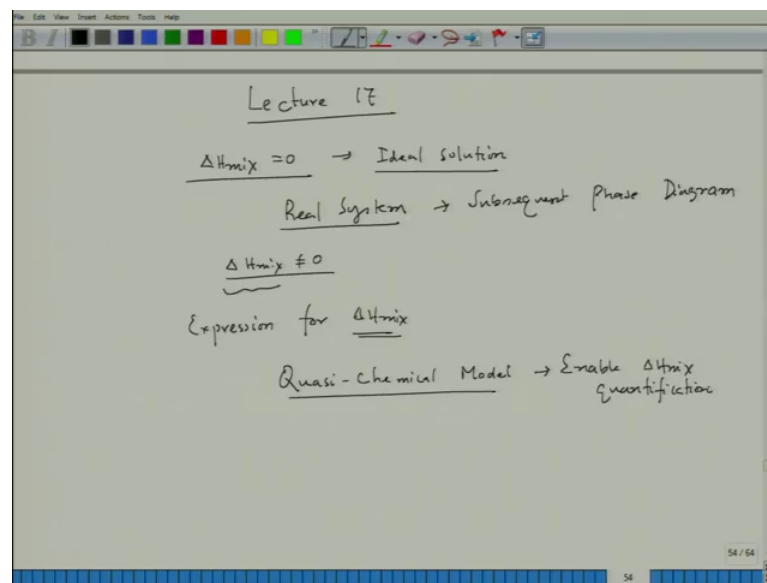


**Heat Treatment and Surface Hardening - II**  
**Prof. Kallol Mondal**  
**Prof. Sandeep Sangal**  
**Department of Material Science & Engineering**  
**Indian Institute of Technology, Kanpur**

**Lecture - 17**  
**Introduction to real solutions and expression of  $\Delta H_{mix}$  based on the**  
**Quasi-Chemical Model (QCM)**

Welcome to lecture number 17.

(Refer Slide Time: 00:18)

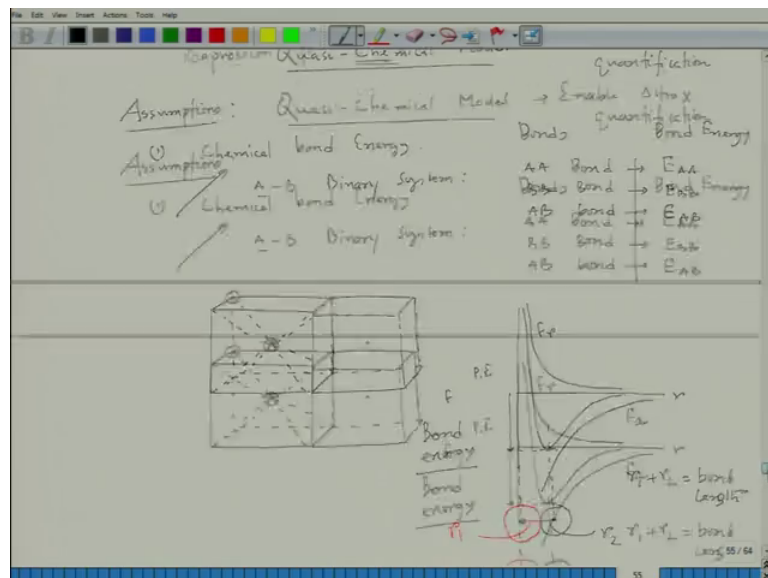


We have already seen that to the free energy determination for nucleation as well as for finding growth rate. One has to have a very clear idea on free energy composition diagram and subsequently the common tangent as well as tangent on the composition of the parent phase where from we are starting our transformation. Now whatever we have considered apart from that solid base transformation, in order to give an indication that how it is helpful to know free energy composition diagram and to find out free energy difference for nucleation in all the cases we have considered ideal solution, but situation may be different when we will not get ideal solution rather we would step into or real solution where we will not have this particular concept valid, because this particular concept is valid for ideal solution.

So, if we get into the real system, and then subsequent phase diagram in order to understand that what are the phases that are possible at a particular temperature, if we operate the phase transformation at a constant pressure. Then we will be requiring the knowledge of phase diagram. And in case of real system where  $\Delta h_{mix}$  is not equal to 0 in most of the cases on that time the interrelation between  $\Delta h_{mix}$  with entropy of mixing would get us the proper knowledge of phase diagram. And the variation of phase diagram with temperature. So, let us get in to the  $\Delta h_{mix}$  part and we will try to find an expression for  $\Delta h_{mix}$ , which will enable us to get phase diagram in case of real system.

And subsequently, we would also get know what will be our free energy difference for nucleation of second phase. So, if we try to find out  $\Delta h_{mix}$ , we have to take help from quasi chemical approach, quasi chemical model. So, this is this will enable  $\Delta h_{mix}$  quantification. So, when you start with this quasi chemical model, it is based on some basic assumptions. So, assumptions are one is we will only consider the chemical bond energy.

(Refer Slide Time: 05:02)



Now, whenever we have any solution whether it is a solid solution solid alloy or on a liquid alloy or a liquid alloy, there will be interactions between the atoms. For example, if we consider A and B binary system. Then there could be formation of AA bond BB bond or AB bond.

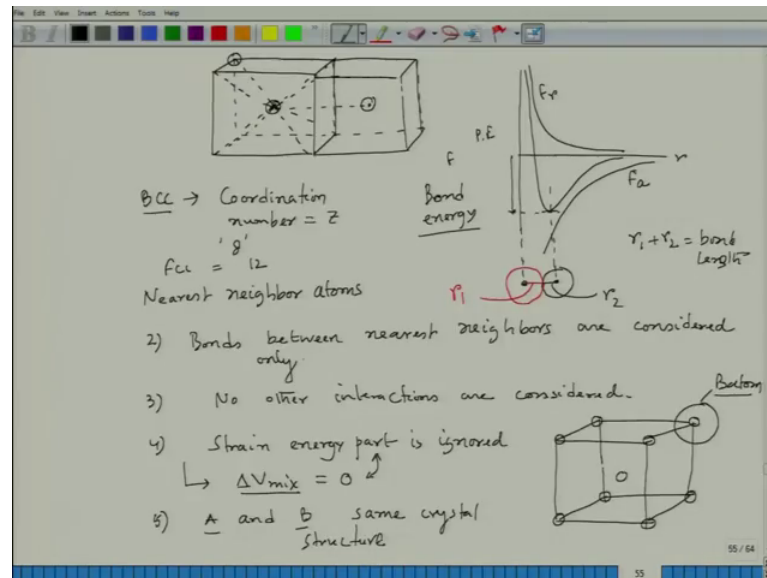
So, all 3 bonds can form in a solution. And each bond has got its own energy associated with it, we call it as  $E_{AA}$ ,  $E_{BB}$  and  $E_{AB}$ . So, this is bond energy and these are bonds. And every system has got its own structure. Let us say if we consider solid alloy formation, then even if it is AB type of solution there could be several probabilities

Now, let us consider one particular crystal. If we consider a simple BCC crystal so that place at the centre, there will be an atom. Then there will be bond formation with that atom with the surrounding atoms. And there will be side by another unit cell.

That would be there on its side. So, there will be side by another unit cell. Now there will be also the similar crystal structure will maintain no question is when I consider this particular situation we say that the bond formation between 2 atoms would always be there. And this bond will always consider the chemical bond energy and when we consider chemical bond energy as per classical situation. This is R distance if one atom is taken from infinite distance to another atom. Then I will get attraction force, this will be my attraction force which is  $F_A$  this is force part. And then as the atoms are close together very close together then the outer electrons will start interacting and then there will be repulsive forces also. So, the repulsive force would act like this.

So, this is  $F_R$ . And accordingly its potential energy would vary. So, if I consider potential energy, then the potential energy will be varying like this. And then this is the minimum potential energy, and this is my if I draw it. This is centre of one atom the centre of this is centre of another atom that. So, this is one atom and then if I try to draw with a red colour this is another. So, this is the  $R_1$  the radius of one atom. And this is the radius of another. So, bond length is  $R_1 + R_2$  is equal to bond length. And bond energy is this one, this is the bond energy. So, this is the bond energy. So, these energy will consider for our calculation.

(Refer Slide Time: 10:24)



Similarly, the second assumption is, whenever we consider the bond formation between 2 atoms then we could see that for BCC we have a coordination number. And these coordination number we call it  $z$  in case of BCC, it is 8 in case of FCC it is 12. It means that the nearest neighbour atoms. And that time the bonds will be only between the nearest neighbour atoms. The interactions between atoms which are not nearest neighbour are not considered in this particular model. So, that place there will be another atom at the body centred in this case which is the body centred cubic. So, between these 2 atoms the interactions would definitely be there, but we will consider in our particular model construction. So, bonds between nearest neighbour are considered only.

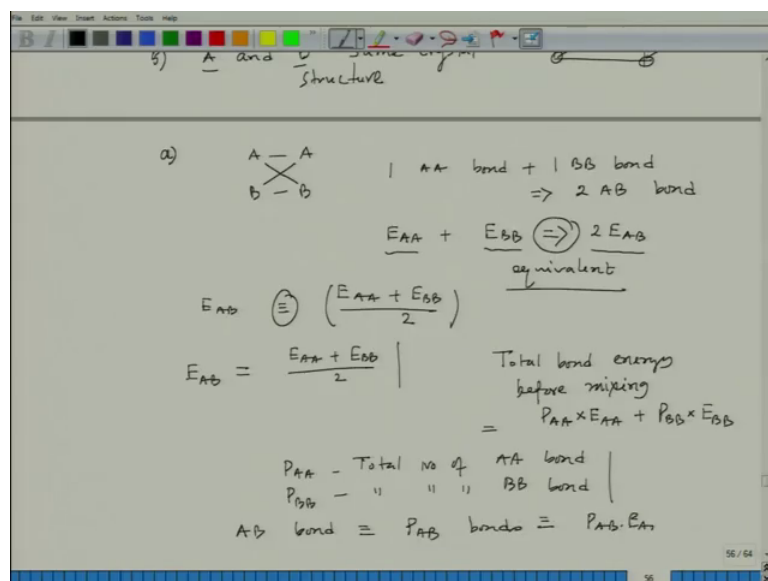
And interaction between atoms which are far away not nearest neighbour are not considered. The third assumption apart from bond energy and nearest neighbour bonds, no other interactions are considered. No other interactions there could be columbic interactions there could be violence bond interaction all sort of things will not be considered. So, no other interaction are considered. Now there could be another is one more assumption which is very modern assumption, whenever we have let us say your lattice of a particular pure atom let us say BCC, this is all a atom, let us say all the coorder and body centred positions are occupied by a atoms. Now if we consider a replacement of one co ordinary atom with a bigger B atom.

This is my B atom, which is much bigger than A atom then there would be volume dilation in the unit cell. And that volume dilation would introduce strain and whenever there is a strain there would be also associated with a strain energy, but in our model which is quasi chemical model, we will not consider the strain energy part. The strain energy part is ignored, and this also is associated with one particular concept. The concept called that  $\Delta v_{mix}$ ; that means, volume before and after solution formation from pure condition pure of pure A and pure B and then mixing and forming an alloy, we considered that molar volume would change as per the rule of mixtures; that means, molar volume of pure A and pure B would be just added up as per the molar fractions of A and B.

So, the effectively we do not get any change in volume. So, this is considered as 0. So, which is almost corroborating each other; that means, if there is no volume change we would not get any volume dilation and effectively we are not getting any strain energy part. And there is one more assumption we will consider which is A and B, those are 2 elements they have same crystal structure this would help us to divide the expression for  $\Delta h_{mix}$  on these 5 assumptions we are going to derive the expression for  $\Delta h_{mix}$ .

Now, some of those considerations important considerations, while deriving  $\Delta h_{mix}$  are one is.

(Refer Slide Time: 16:24)



Let us say AA bond and B B, bond if we consider and let us say one AA bond is breaking and one BB bond is breaking actually we are getting 2 AB bonds. So, one AA bond plus 1 BB bond is leading to 2 AB bond.

Now, if we consider energy wise. So, 1 E AA bond plus 1 EBB bond, actually leading to 2 AB here remember these are not equal these are equivalent; so equivalent bonds. So, 1 AB, 1 2 AB bonds are forming from 1 A bond, and 1 BB bond. And that is what energy wise 2 AB bond is equivalent to 2the bond energy total bond energy after forming of formation of AB bond, which re coming from one bond of AA and one bond of bb and that is what this situation is arriving at. So, I can consider that would be having some relation with e AA plus EBB by 2.

Because these are equivalent, I m saying equivalent may not be same because I am getting to AB bonds from one bond each of AA and BB. Now there could be situation like be could be equal to e AA plus EBB by 2 and if that situation arises. Then we have initially complete a pure A and pure B and it means pure AA bond and pure BB bond. So, the total bond energy before mixing would be simply total bond energy before mixing could be equal to p a p is basically nothing, but number of AA bond into e AA plus p BB into EBB and p AA and p BB total number of e a bond and.

Similarly, this is total number of BB bond and after mixing, I get AB bond equivalent to let us say P AB bonds, this is the total number of bonds equivalent to according to this particular format AB into AB. And the time we are considering that the entire AA and BB bond are breaking down forming complete AB bods. So, there is no trace of AB AA or BB bonds in the final solution that time. If this particular concept exists, then I could see to the energy before mixing and after mixing there is no change in energy. So, I would be able to mix A and B completely and that 2 randomly.

So, it would yield random solution.

(Refer Slide Time: 21:36)

$$E_{AB} = \frac{E_{AA} + E_{BB}}{2}$$
 Random Solution | Total bond energy before mixing  

$$= P_{AA} \times E_{AA} + P_{BB} \times E_{BB}$$

$P_{AA}$  - Total no of AA bond  
 $P_{BB}$  - " " " " BB bond  
 $AA \text{ bond} \equiv P_{AA} \text{ bonds} \equiv \frac{P_{AA} \cdot E_{AA}}{2}$

$\checkmark E_{AB} < \frac{E_{AA} + E_{BB}}{2}$  → Short range order  
 $\Rightarrow <<$  → Compound.

---

$E_{AB} > \frac{E_{AA} + E_{BB}}{2}$  → cluster of AA or BB regions  
 $>>$  → AA rich side.  
 BB rich side

Now if I see another aspect which is  $E_{AB}$  less than  $e_{AA}$  plus  $E_{BB}$  by 2; that means, after mixing I could see that the system energy would go down. So; that means, if a system energy goes down because is less than that this particular volume. So, AB one formation would be preferred no this could be a small negative or this would be large negative; that means, this value is smaller neget small negative or large negative compared to this particular added value. I would get 2 different situations. If it is smaller negative that case, I would get short range order. And if it is largely negative I would get compound.

Now, on the other hand side, if  $E_{AB}$  greater than  $e_{AA}$  plus  $E_{BB}$  by 2. Then if I break this AA and BB bonds and form AB bonds, actually I am increasing the system energy which may will not be preferred by the system. So, that case I would end getting 2 more situations. One is if this is slightly greater than this particular added value or highly greater than this particular added value, then I would get 2 situations in one case I would always like to have a small cluster of AA or BB region, and if it is largely positive compared to this value largely greater than this particular value. So, that case we would get AA rich side and BB rich side we call it phase separation phase separation.

So, now we would see that this particular value this particular parameter, if we considered as small  $e$  is very important very crucial. If it is less than 0, if it is equal to 0 or greater than 0 I would get these many situations if it is less than 0.

I would get short range order or compound formation if it is equal random solution if it is greater than 0, I would get clustering up AA and BB regions or phase separation a rich side and B rich side. So, we would try to relate this  $e$  with coordination number, which is  $z$  as well as composition of A and B. And this composition of A and B means  $x_A$  and  $x_B$ .

So, in our next lecture we will try to relate this energy difference with composition of A and B in that alloy or the solution, and coordination number. And then we will see that how  $\Delta s_{mix}$   $\Delta h_{mix}$  varies with the composition change with the composition change.

Let us stop here. We will continue in our next lecture where we will address this and this.

Thanks.