An Introduction to Materials: Nature and Properties
(Part 1: Structure of Materials)

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Lecture – 18
Solid Solutions and Alloys

We are again going to talk about Solid Solutions Alloys.

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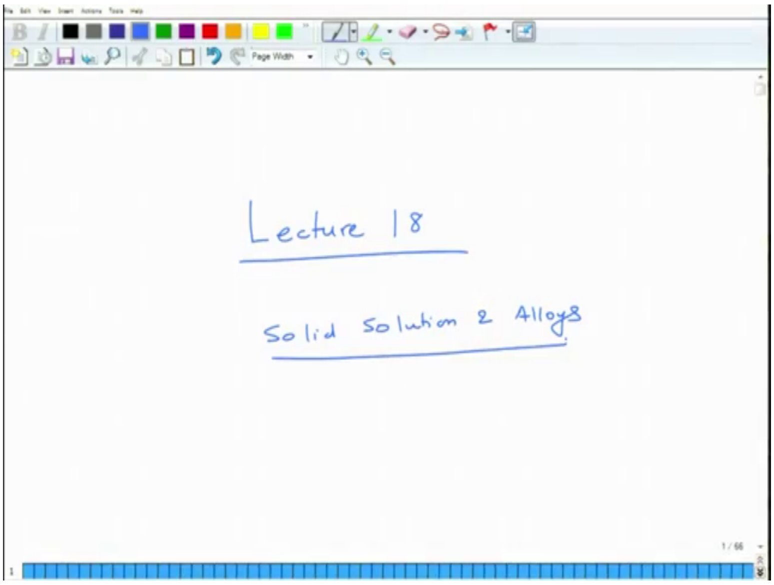

Lecture 18

Solid Solution & Alloys

In this lecture 18 continuing from where; we were in the last lecture. So, in the last lecture, we said that the when you put an impurity in a in a material, the impurity may go to either Substitution site or oc Interstitial site. if it goes to Substitution site makes a Substitution Solid Solution and if it go to goes to Interstitial site, it makes a Interstitial Solid Solution and that that where it goes is to determine by the size. So, there are some rules for Substitution Solid Solutions which were called as Hume Rothery Rules ok.

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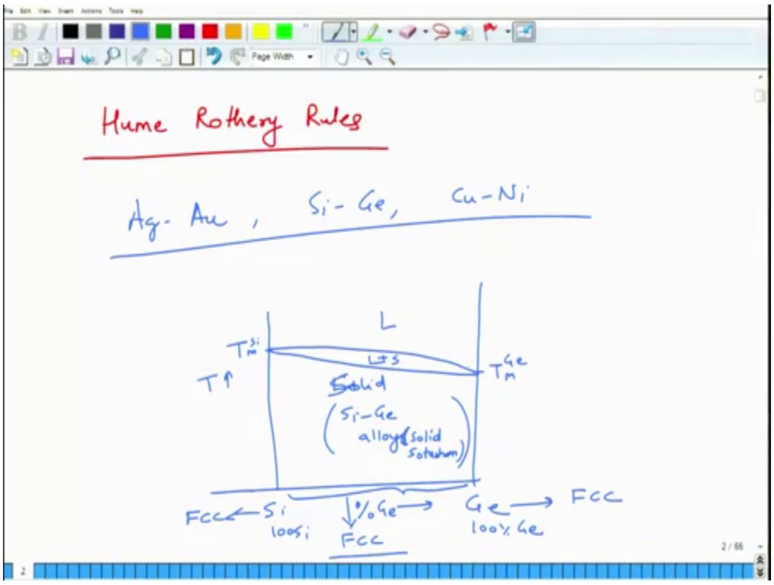

So, Hume Rothery Rules which said that depending upon the size difference; depending upon the valence difference. So, if you want to make a Substitutional Solid Solution, so, extensive soluble solid solubility is permitted only when the size difference is less than 15 percent and the valances are nearly similar or similar crystal structures are similar and electro negativity difference is very small. There are certain violations, but by and large the rules are followed.

So, the examples which we took were Gold-Silver, Silicon-Germanium and Copper-Nickel these are solid solutions basically. So, if you look at for example, what I mean basically here is, if you look at the phase diagram of Silicon-Germanium, so, this is composition excess percentage germanium from 100 percent Silicon to 100 percent Germanium. This is temperature axis ok. So, Silicon has a melting point let us say some T m Silicon, which is nearly 1400 degree centigrade, this is Germanium melting point T m Germanium and what they basically form is a structure which is all throughout the same structure. So, this is basically let us say it is a Silicon-Germanium alloy which is solid solution.

So, it is basically a Disordered Solid Solution; it is not an Ordered Solid Solution. So, at this temperature it is liquid between this it is liquid plus solid and here it is liquid plus sorry only solid and this solid is in the solid solution ok. So, at 0 percent Germanium, it has a structure which is FCC structure. At 100 percent Germanium, it has a structure which is 100 percent which is FCC and intermediate phases also have intermediate compositions also have FCC structure all throughout. It is happening within the same structure, same lattice it is just that some of the Silicones are being replaced by Germanium. If you move from Silicon side, if you move from Germanium side some of this Germanium atom are going to be replaced by Silicon. So, even at 50-50 it is 50 Germanium, 50 Silicon with each atom having a probability of being 50 percent Germanium or 50 percent Silicon each site occupancy.

So, this is a Disordered Solid Solution which shows extended Solid Solubility. So, this is true for Gold-Silver, this is true for Silicon-Germanium, this is true for Copper-Nickel.

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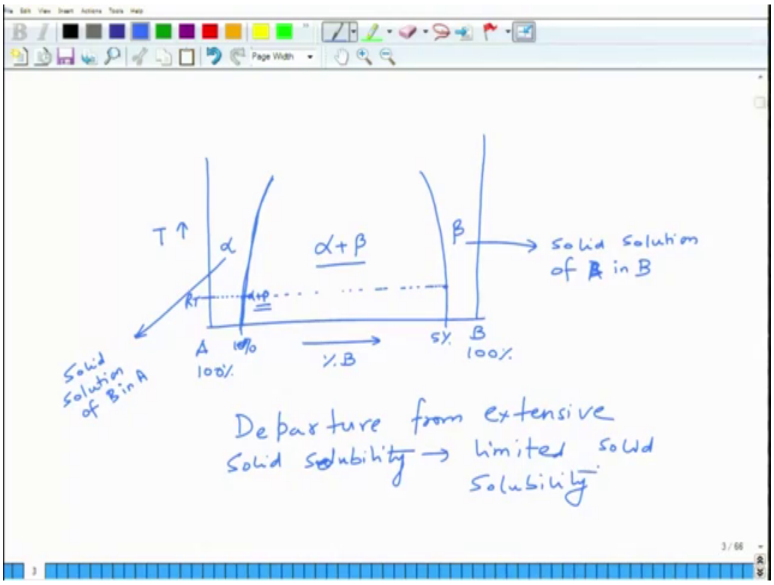

Departure from extensive Solid solubility → limited solid solubility

What happens in partial Solid solubility is slightly different. So, in partial Solid Solubility, I will not draw the complete phase diagram, but let us say you take an example of A and B, this is 100 percent A, this is 100 percent B and you go this is percentage B. And on the left side on though on the vertical axis, you have temperature. Now what happens in partial solve Solid Solubility is that, so, solid solubility typically increases as the temperature increases. So, this line determines up to which point in composition space the solid will dissolve. Similarly, on this side, you will have these boundaries. So, between this and this it will be let say alpha phase. Alpha phase is solid solution of B in A.

So, basically, it is A with some of the A atoms replaced by B. This is beta phase, this is basically solid solution of A in B. Essentially, it means it is nearly B with some atoms replaced by A and this is a Substitutional Solid Solution which is a Disordered Solid Solution; Disordered Substitutional Solid Solution. Between these 2 things, it gives a mixture of alpha and beta. This is one simple example, there are more complicated examples where some other phases may form and so on and so for, but this is one simple example of where solid solubility is limited.

Let us say, at this point it is 10 percent, at this point it is 5 percent or some other percentage. It increases as you increase the temperature, typically solid solubility increases as the temperature is increased. So, because the lattice dilates and there are other thermodynamic factors the competition between entropy and enthalpy eventually that determines what the solid solubility will be, but this boundary is the boundary beyond which you cannot add any more B to A, if you add any more B to A so, up to this point at a fixed temperature let us say this is room temperature. So, if you keep adding B to A, it will remain in the structure of A up to this point; beyond this point it will form beta phase.

So, as soon as you cross this point, it will start converting into alpha plus beta and this alpha plus beta will continue from to remain in existence until you reach this point. Proportion of alpha and beta will change which will be determined by Lever Rule, if you know the phase diagrams. The proportion of alpha and beta will change in this regime, but you will have 2 phase coexistence because the solid solubility of alpha and beta are limited. So, this is the limit of solid solubility of beta, this is the limit of solid solubility of alpha and this happens when you have departures from Hume Rothery Rules when the size differences are larger, when crystal structures are not similar, when valances are not similar and when electro new electro-negativity difference typically gives the information of compound, but these are the factors when. So, so this is you can say that the Departure from extensive Solid Solubility. So, this is the case of as we say limited Solid Solubility, is that clear yeah. So, this is what happens in most cases. So, as I said in case of Copper-Zinc you can have 35 percent Zinc in Copper. And in case of Zinc, you have 1 percent Copper in Zinc.

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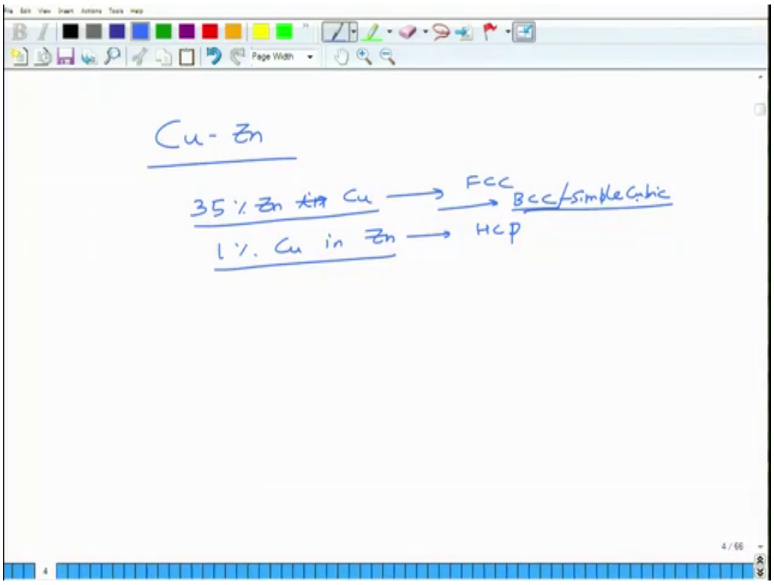

Cu- Zn

35% Zn [illegible] Cu → FCC → BCC/Simple Cubic

1%. Cu in Zn → HCP

So, you can see if; now you can correlate to the previous diagram that on the Copper side, the boundary can extend up to 35 percent, but on the Zinc side, it can extend only up to 1 percent and this is because Copper and Zinc have different structures, they have different valences. So, that is why and so, so, when you mix 2 elements sometimes as I said in Copper-Zinc example 50 percent, you have ordering.

So, in case of Copper-Zinc what happens is that, so, when you add 35 percent Zinc; it remains as FCC. When you are up to 1 percent; it remains as HCP. But in between as I said it starts forming other phases other phases which are different. So, for example, you had BCC fade in between or you had simple cubic phase in between depending up on the temperature. So, you no longer have FCC, HCP structured phases; you have some other phases. These phases are basically formed because Copper and Zinc tend to form secondary phases. So, especially at lower temperatures when you mix two elements they tend to arrange in themselves in ordering in ordered fashion. So, this is called as Ordering in alloys.

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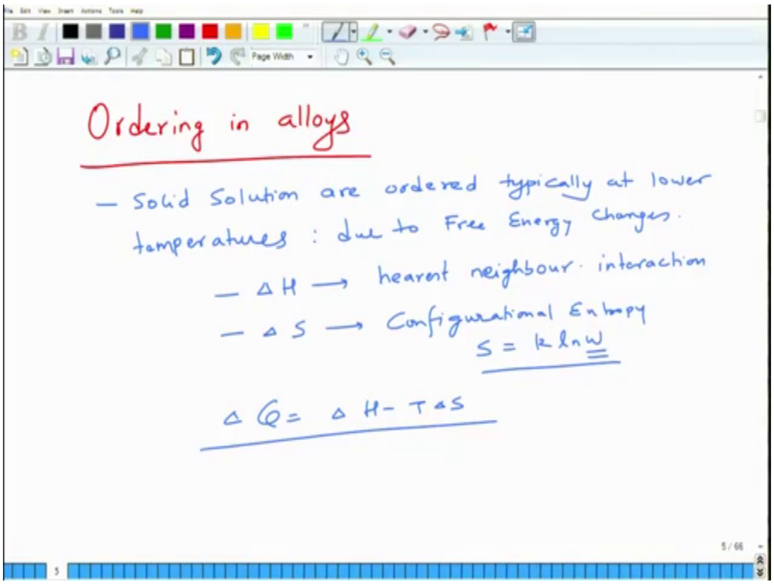

Ordering in alloys

- Solid Solution are ordered typically at lower temperatures : due to Free Energy changes.
  - $\Delta H \longrightarrow$ hearent neighbour interaction
  - $\Delta S \longrightarrow$ Configurational Entropy
    $S = k \ln W$

$\Delta G = \Delta H - T\Delta S$

So, as I said at lower temperature, it had a ordered structure ok. So, this ordering in alloys is it happens in Solid Solutions typically at lower temperatures: due to free energy changes and this is mainly determined by delta H which is dependent upon the nearest neighbor. Enthalpy is determined by the nearest neighbor interactions because it is enthalpy is a manifestation of bond strength and bond strength is a manifestation of nearest neighbor. What is the configuration? Copper-Zinc bond will have different bond energy, Zinc-Zinc bond will have different bond energy, Copper-Copper bond will have different bond energy. So, delta H and then you will have delta S which is predominantly Configurational Entropy which is given as delta. So, s you know is given as k l n w where w is the number of ways in which arrange 2 atoms.

So, when you mix A and B, you can arrange A and B number of different ways. So, find out. So, you calculate various permutation combinations, then you calculate the configuration entropy. So, you then, so, after that you do delta G is equal to delta H minus T delta S. So, at a fixed temperature workout what is free energy and at a given temperature whether you will have a disordered structure ordered structure will be determined by minimization of free energy at a given temperature.

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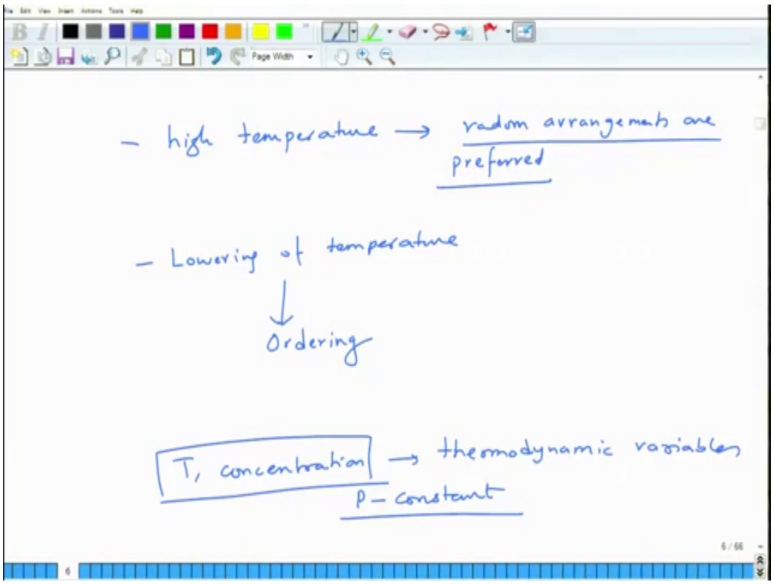

- high temperature → random arrangements are preferred

- Lowering of temperature

↓

Ordering

$\boxed{T, \text{concentration}}$ → thermodynamic variables

P – constant

Usually at high temperatures random arrangements are preferred typically. And lowering of temperature leads to leads to ordering which is mainly determined by lowering off Enthalpy. Enthalpy is lowered as a result your ordering takes place. It can also (Refer Time: 12:52) function of concentrate, it is also there func it is also a function of concentration not every concentration will give you ordered alloys that is also true.

But typically, we talk in the context of fixed compositions. So, we take a composition and then we see whether it is ordered or not at a given temperature, but yeI mean not every composition is ordered. So, it is also so, so. So, thermodynamic variables are thermodynamic variables are temperature concentration. So, these are thermodynamic variables. Of course, pressure is also thermodynamic variables, but in most metallurgical processes pressure in these kinds of processes at least pressure is kept as a constant ok. So, yes temperature and concentration both are variable. Here, we were talking about fix fixed composition, but of course, if you change the composition, you will have to change the whole thing all together in that and you may find that there is something else which is happening there.

So, there are. So, Order alloys in incase of alloys Metallic alloys they are often called as Intermetallics.

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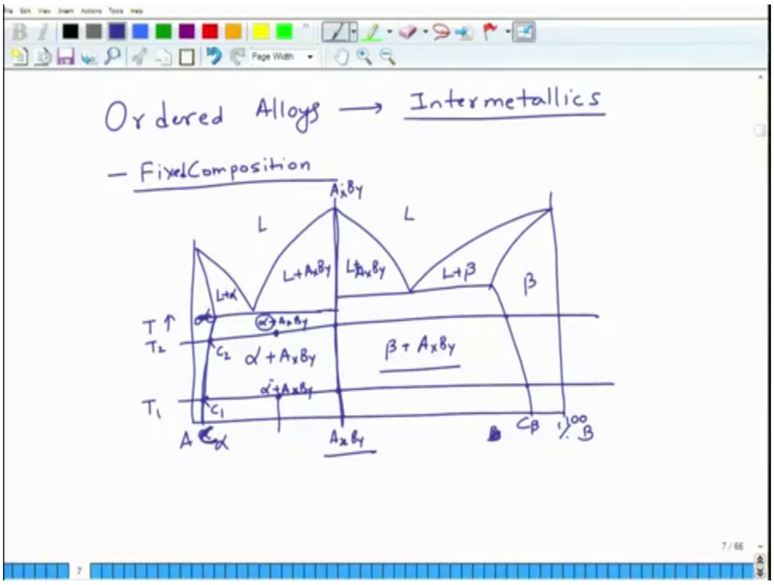

These Intermetallics are strange compounds because they have very Fixed Composition. If you go slightly away from the composition, they will decompose into something else or they or they will be present in a two-phase mixture where this particular compound will be present or something else. So, let me draw a phase diagram for example, A B let us say, let me see if I can; this is temperature. So, this is on this side you have. So, this is alpha phase, this is beta phase, this is liquid this is liquid the temperatures may vary. So, this is liquid plus alpha. This is a compound which is let us say A, B compound or A x B y compound which is enter metallic compound. So, this is liquid plus A x B y, this is again liquid plus A x B y and this is liquid plus beta, on this side you have alpha plus A x B y, here you have beta plus A x B y. So, you can see that at this particular composition which is let us say A x B y, you have a fixed composition. If you are standing at this composition, you are in 2 phase regime where you have alpha plus A x B y, you can see that the solid solubility of alpha is changing as a function of composite temperature. The solid solubility is moving towards right as you increase the temperature. Similarly, solid solubility or beta phase also it is not drawn very neatly let me just probably draw it little neatly. So, this will be 100 percent B and this is the this is let us say alpha C; C alpha, this is let us say C beta ok.

So, solid solubility is increasing has increase the temperature of alpha solid solubility is increasing of beta has increase the temperature towards the left this is beta phase. So, as you so, at this temperature, if you compare these 2 temperatures at T 1 and T 2, at T 2 alpha has more amount of B than at T 1 right. Similarly, at T 2 beta has more amount of a then at T 1 is a right, but you can see A x B y, this remains vertical. The composition of A x B y does not change, it is a line compound. It remain fixated. When you are some other composition, you have alpha plus A x B y alpha of this composition A x B y of this composition, but composition of A x B y will remain same if you were for example, at this temperature. So, if you keep the composition fixed, go to this temperature. At this temperature again you have alpha plus A x B y, but composition of alpha has changed according to this composition. So, at this temperature, alpha had a composition of C 1, at this composition, alpha has a composition of C 2, but A x B y has same composition all throughout. This is a line compound which means it has a fixed composition and it forms at only at that particular composition.

So, in 2 fertilize, you will see at a composition. You will have 2 phases, one of may one of them may be line compound for example, Cementite as we see in Steel. Cementite is a fixed composition thing ok. So, in Steel that is a very good example actually.

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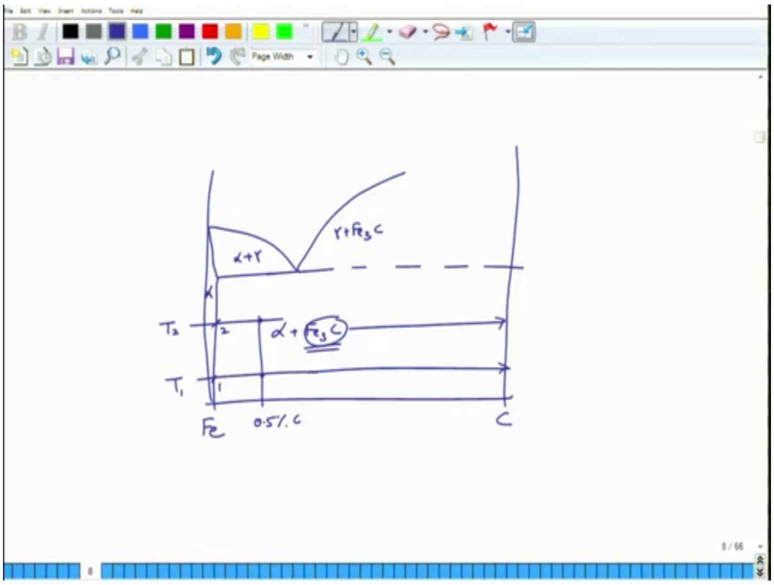

So, if I draw the phase diagram of Steel, this is Iron, this is Carbon. So, Steel has a eutectoid reaction. I will only draw the low temperature reaction ok. I will just draw them. So, this is alpha, this is alpha plus gamma and this is gamma plus Fe 3 C and this is alpha plus Fe 3 C. Fe 3 C Cementite whose composition is given by this line, it is a fixed composition.

So, Fe 3 C as you changes the temperature. So, if I am at let us say 0.5 percent Carbon-Steel at temperature T 1 and a temperature T 2, I have alpha and Fe 3 C in both cases, but here alpha has a different composition which is this, here alpha has a different composition which is this. So, this is number 1, this is number 2, but Fe 3 C has same composition which is determined by this vertical line which is Fe 3 C. It is a line compound, it is composition cannot change because composition is 3 Iron 1 Copper 1 Carbon 3 is to 1 ratio has to be maintained. So, this is the Line Compound or a Inter Metallic Compound ok.

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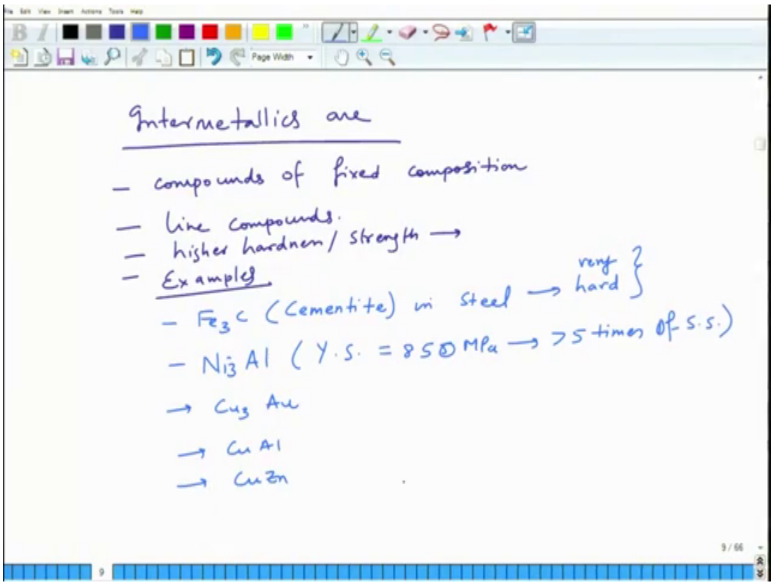

Intermetallics are

- compounds of fixed composition
- line compounds.
- higher hardness / strength →
- Examples
  - Fe_3C (Cementite) in Steel → very hard }
  - Ni_3Al (Y.S. = 850 MPa → >5 times of S.S.)
  - → Cu_3Au
  - → CuAl
  - → CuZn

So, basically Intermetallics are compounds of fixed composition. Typically they do not have any variation in the composition and they are called as Line Compounds. The examples are first one is Fe 3 C or Cementite in Steel. A lot of times you have this Ni 3 Al Nickel Aluminum system, Ni 3 Al is very and lot of and another thing is that these line compounds are very strong. They have very highest, they have much higher strength, higher hardness and strength over host Lattices. So, for example, in case of Ni 3 Al, Ni 3 Al has a yield strength which is of the order of 850 MPa. This is nearly 5 times more than of Stainless Steel S.S. And every means, if you if you look at the composition Aluminum the soft alloy. Nickel has a strength which is of the order of Iron-Steel, but Ni 3 al the line compound is very strong. Similarly, Cementite and Steel is extremely hard, it is very hard very hard. That is why we prefer high Carbon Steels for application which require high hardness and this high hardness comes from Cementite. And similarly, you have things like Cu 3 Au. These precipitates they form in Copper-Gold systems and they again give rise to high hardness.

So, Copper-Gold similarly there are a lot of other systems, you have things like Cu Al, I showed you Cu Zn. So, all of these Intermetallics or fixed composition they have high hardness and then, so, for example, Ni 3 Al, Ni 3 Al again.

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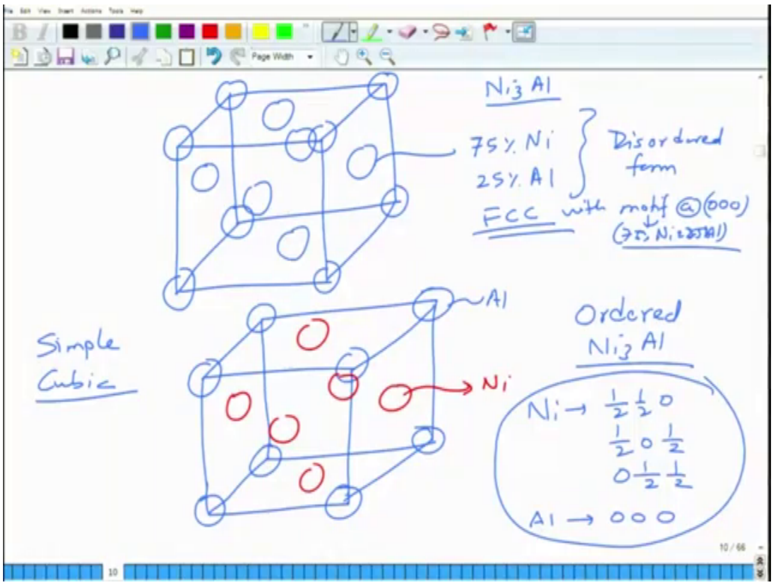

So, Ni 3 Al when it is disordered, then this is Nickel is FCC, Iron is FCC, Aluminum is FCC. So, when it is disordered, then each atom can be considered as 75 percent Nickel and 25 Aluminum in disordered form. This is Ni 3 Al. When it is ordered, then it is different. In case of ordering, this is Nickels sorry this is let me draw all the 6 atoms this is Order structure. So, here what is this? Nickel and this becomes, so, this is ordered Ni 3 Al where Nickel goes to half, half, 0; half, 0, half and Aluminum goes to 0, 0, 0. So, this is a FCC Lattice. And what is that is what Lattice is this?

FCC Lattice with motif at 0, 0, 0 and this motif is basically 70 percent Nickel and 20 percent Aluminum. In this case, it is Simple Cubic right and Simple Cubic with 4 atom motif. So, this is the motif, 4 atom motif. And this Ni 3 Al is very useful because it is used in super alloys as strengthening to strengthen the super alloys. Nickel based alloys are super alloys and this if you add some Aluminum to Nickel, they form Ni 3 Al precipitates and these precipitates provide resistance to dislocation motion and they make the Nickel-Aluminum alloys and Nickel alloys stronger for high temperature applications.

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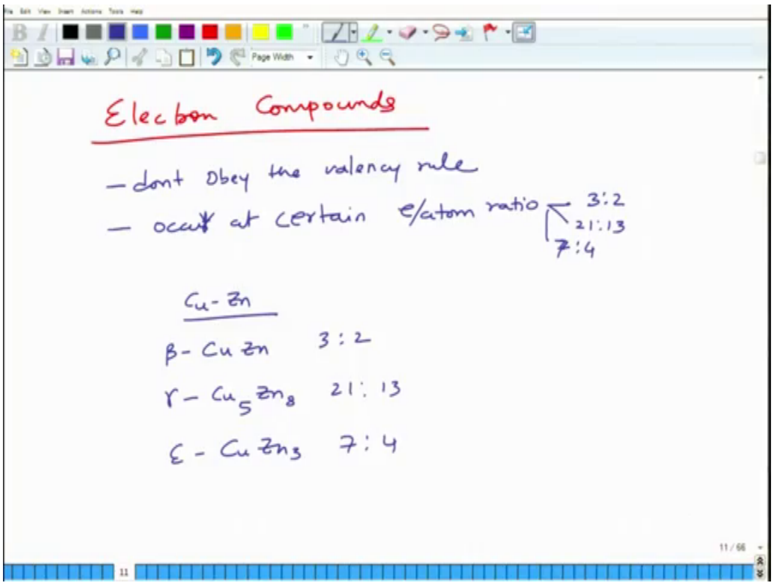

Electron Compounds

- dont Obey the valency rule
- occur at certain e/atom ratio ← 3:2, 21:13, 7:4

Cu-Zn

β- Cu Zn 3 : 2

γ- $Cu_5 Zn_8$ 21 : 13

ε- $Cu Zn_3$ 7 : 4

Then, there is another category; last category I will say is called as Electron Compounds. These are the compounds which do not obey the rule of valency. So, do not obey the valency rule. They occur at certain electron to atom ratio and these ratios are typically 3:2, 21:13 and 7:4. And they are formed in same system for example, Cu-Zn. Cu-Zn could be beta Cu-Zn, Cu 3 Zn 2, gamma Cu Zn Cu 5 Zn 8 sorry this is not Cu 3 Zn 2, this is Cu Zn; because valence is Copper has 1 valence and Zinc has 2 valence which was valence is electrons are 3 atoms are 2. Here, 5 into 1, 8 into 2 will make it 21, atoms are 13. And then third one is epsilon Cu Zn 3 which has 7:4. So, this is 3:2, this is 21:13 and this is 7:4. So, these are called as Electron Compounds. So, what basically we have looked at is various type of compounds Line Compounds, Electron Compounds, Solid Solutions, how they follow Hume Rothery Rule and why Solid Solutions form and what are the guidelines.

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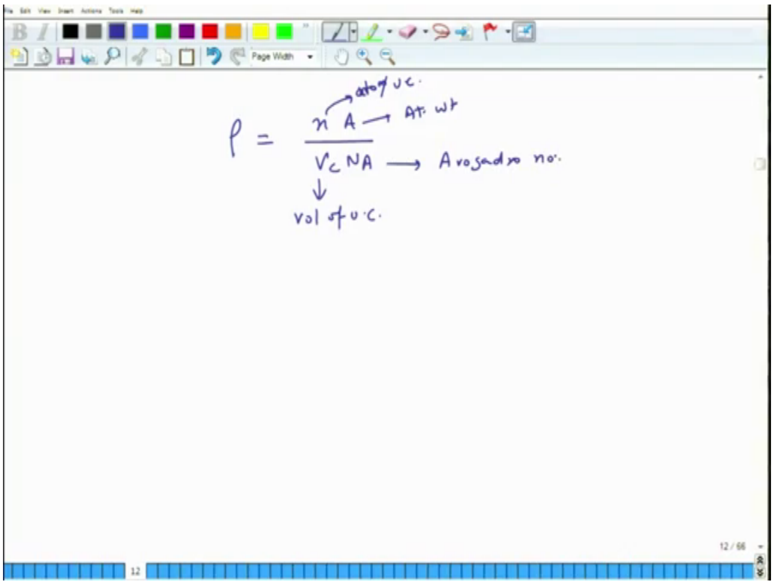

$$\rho = \frac{\overset{\text{atom/u.c.}}{n}\; A \rightarrow \text{At. wt}}{\underset{\text{vol of u.c.}}{V_c}\; N_A \longrightarrow \text{Avogadro no.}}$$

Finally, if you want to calculate the theoretical density of a material, it is given as n A divided by V c N A, where n is the number of atoms per unit cell, this is atomic weight, V c is the volume of unit cell and N A is the Avogadro number, that this by this, you can determine the atomic density of the density of metals ok. So, this completes our Metals and Alloys chapter. And we will in the next class start the Covalent of and Ionic Solids.

Thank you.