An Introduction to Materials: Nature and Properties
(Part 1: Structure of Materials)
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Lecture – 17
Solid Solutions Alloys

So, we start a new lecture today, lecture number 17, in this lecture, we will talk about Solid Solutions in the Metallic Context and Alloys which are formed by mixing one or two or more elements. So, let me just recap the initial the last lecture first.

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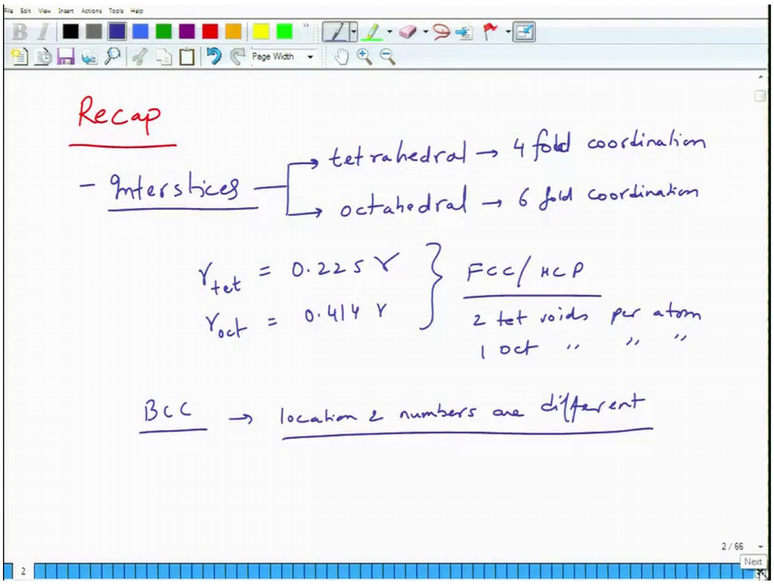

Recap

- Interstices → tetrahedral → 4 fold coordination
→ octahedral → 6 fold coordination

$r_{tet} = 0.225\ r$
$r_{oct} = 0.414\ r$
} FCC/HCP
2 tet voids per atom
1 oct " " "

BCC → location & numbers are different

So, in the last class, we learned about Interstices. Interstices are nothing but voids which are present in the crystal structures. And there are 2 types of voids that we are concerned about, one is tetrahedral and second is octahedral.

So, tetrahedral void is characterized by 4-fold coordination because it is a it is a body with the 4 corners. So, as a result the impurity that sits inside has 4 neighbors. Whereas, octahedral is 6-fold coordinated void and. If you have a regular tetrahedra and regular octahedron as, as is the case in case of FCC and HCP structures, then the size of an atom that can fit in tetrahedral in void is 0.225 of radius of the host atom. This is without distorting the tetrahedral void ok.

Similarly, r oct is 0.414 r. So, this is the maximum size of the atom that can fit in octahedral tetrahedral impurities without distorting the octahedral or tetrahedral. And this is in case of FCC or HCP. And in we also saw that in FCC HCP, you have 2 tetrahedral voids per atom and 1 octahedral void per atom. Things are different for BCC, you do not have a regular octahedral or tetrahedral, but you do have octahedral and tetrahedral voids and whose location and numbers are different.

So, this I showed you last time in a in a in a geometrical fashion. So, you were asked to count the numbers of octahedral and tetrahedral voids in BCC. So, I will leave it to you, that at that as home exercise; that is what is the location of tetrahedral octahedral voids in BCC structure? And what is there, what is their number? Ok.

And you can also calculate, what is the size of atom that can fit in there? You have to be a little careful there, because the sides of tetrahedral and octahedral are different, they are not regular. As a result, you need to look at the minimum size ok, the minimum side length. So, now in this lecture, we will talk about Solid Solutions.

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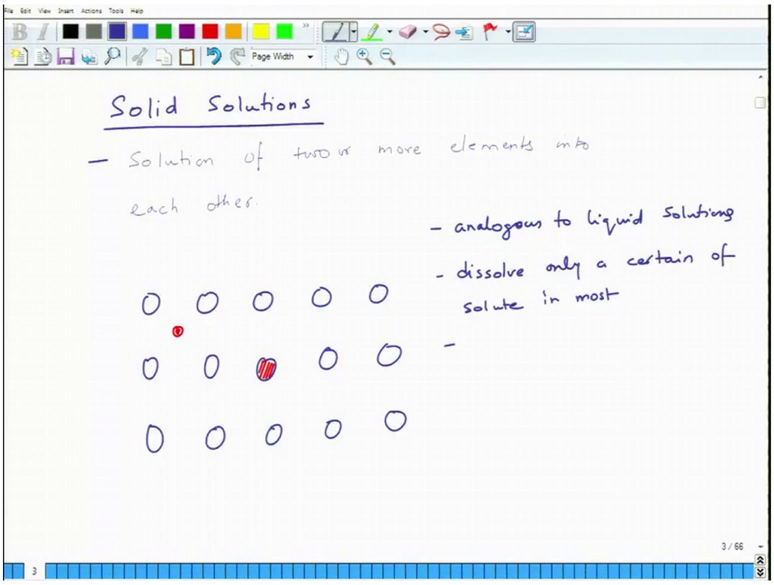

Solid Solutions

- Solution of two or more elements into each other.

- analogous to liquid Solutiong
- dissolve only a certain of solute in most
-

Solid solutions are just like liquid solutions. They are solution of 2 or more elements into, I think it is too small ok, solution of 2 or more atoms into each other. So, what basically what does it mean? So, you have a lattice of some structure, let us say some element or let me just first draw the 2-D diagram without getting into 3-D. So, so you have these atoms of host lattice ok. Now of course, this is looking very dilated, but it is not that dilated in a in reality. So, the impurity atom can go either here, a smaller impurity atom or the impurity atom can go here.

The question is how do you arrange, is there is there is there way in which they arranged? In some sense, although in some sense, Solid Solutions are just like liquid solutions and an analogous to such as, you know sugar in when you mix 2 liquids or sugar in water or salt in water. So, salt molecules dissolving in the water or sugar molecules dissolve in the water, but since water itself is amorphous structure or it does not have periodicity where atoms go it also of little consequence.

And water is generally loosely structured phase. As a result, the impurity atoms salt atoms or some other atoms have plenty of spaces to go into; however, you as you notice in case of salt as well and you put. So, there is a there is a saturation limit beyond with; excess salt does not dissolve into the liquid. You can see that the excess salt and just remains a solid within the water, because the empty spaces within the water phase are already filled. So, it is saturated.

So, then you go beyond the saturation. Similarly, with the sugar and anything else, same thing happens with solids as well. Solids also have only they can only dissolve only a certain amount of let us say solute solid. So, you have solute and you have solvent. So, solvent is the host phase and solute is the impurity phase. So, they can only dissolve a certain amount of solute in most cases ok.

There are some cases in which 2 elements can be put into each other with to either end and they still remain the same single phase. In solids, what happens is that since, atoms are periodically arranged. Sometimes you will see structures in which the impurity atoms also adopt structures which are ordered. And they give rise to structures which are ordered the structures are then disordered arrangement of solute in them.

So, there are various type of Solid Solutions, we will define them in now.

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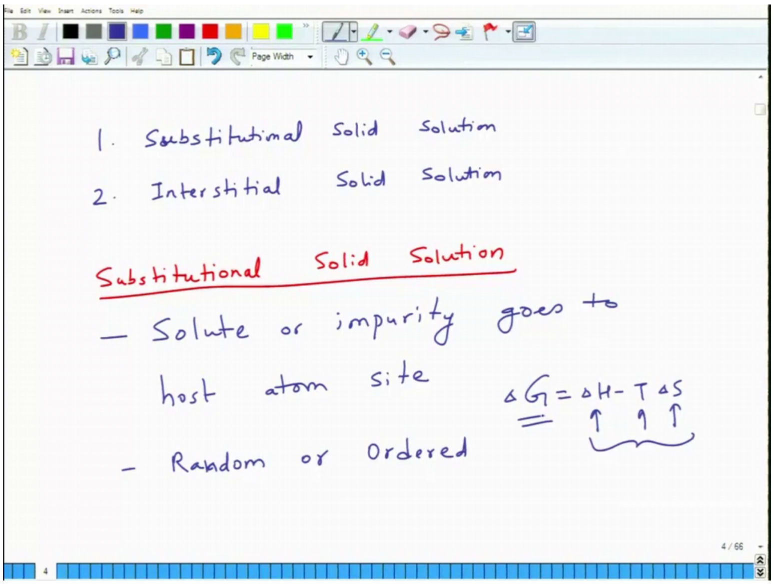

1. Substitutional Solid Solution
2. Interstitial Solid Solution

Substitutional Solid Solution

— Solute or impurity goes to host atom site

— Random or Ordered

$$\underline{\underline{\Delta G}} = \underbrace{\underset{\uparrow}{\Delta H} - \underset{\uparrow}{T} \underset{\uparrow}{\Delta S}}$$

So, first Solid Solution is called as a; Substitutional Solid Solution. And second Solid Solution is called as Interstitial Solid Solution. So, Substitutional Solid Solution basically means essentially means that the solute or you can say impurity atom goes to host atom site. So, it replaces it occupies the same site as the host atom.

However, the manner in which it can do, that could be Random. So, it can randomly go anywhere or it could be ordered. So, this will be determined by various factors ok. So, for example, thermodynamics plays a important role, the entropy of entropy of substitution configuration entropy will play important role in determining where will go and temperature plays a very important role. So, it is a combination of enthalpy and entropy and temperature which will determine free energy of which structure will be minimum whether it will be. So, you know that G is equal to delta G is equal to delta H minus T delta S.

So, there is enthalpy of mixing, there is entropy of mixing and then there is a temperature term. These 3 terms together will determine whether the substitution will be random or whether the substitution will be ordered; Because in the end the free energy has to be minimized. So, I will not get into the details of free energy of mixing, but I will recommend you to go through any basic book on thermodynamics, such as Phase Transformations Porter Easterling and Materials. The first chapter of that book first, the second chapter of that book is very useful to understand mixing of 2 elements.

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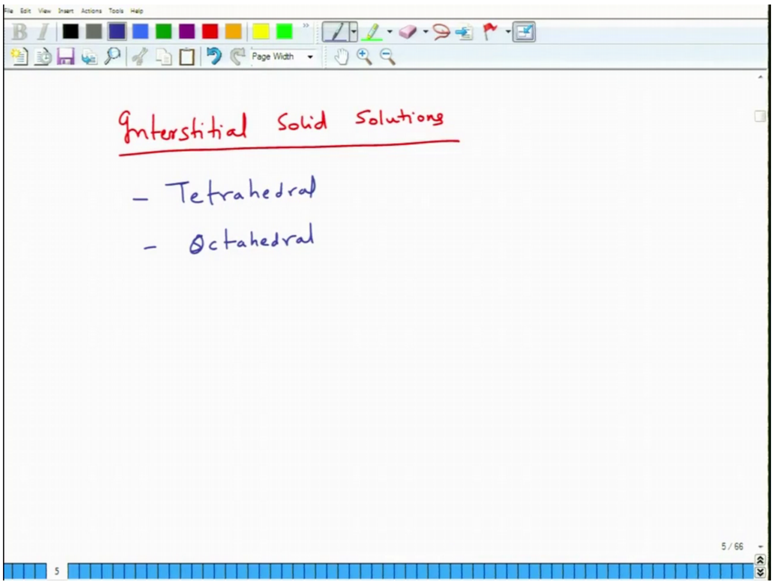
Interstitial Solid Solutions

- Tetrahedral
- Octahedral

So, and the second Solid Solution is Interstitial Solid Solutions. And again Interstitial Solid Solutions and this, the interstices may go to Tetrahedral site or Octahedral site. So, depending upon the size of the atom and the structure of the host phase whether it is FCC, BCC, HCP the impurity atom might decide to go to any of these sites. So, let me give you now some examples of the manner in which your Solid Solutions may form.

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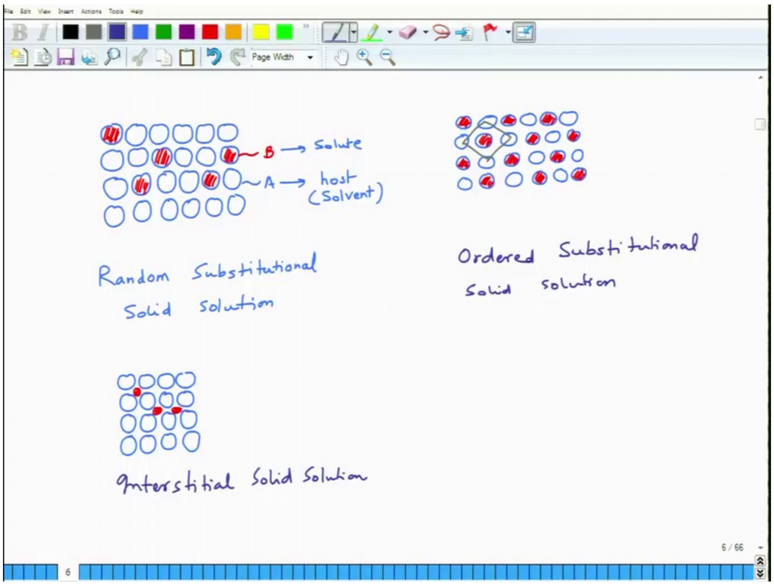

Random Substitutional Solid Solution

Ordered Substitutional Solid solution

Interstitial Solid Solution

So, for example, let me make a little closer structure. So, that it is close enough right ok. My impurity atom suppose if it goes. So, let us say if impurity atom is. So, in this case do you see any periodicity in random arrangement of ordered arrangement of impurity atom? So, this is let us say your B atom and this is your A atom. So, A is the host phase and B is the solute. In terms of chemistry, you call it as a Solvent phase host lattice. So, this is basically a Random Solid Solution, at Random Substitutional Solid Solution. Then you may have other example of. So, what I do now is, I oops there is one extra uh.

So, here, now you can see that your Solid Solution is random and you can actually construct a lattice here, but your lattice has changed now ok. Because if you remember your primitive, non primitive lattice concept, the lattice in this case is no longer a small blue square, rather it has become a the bigger this has become the lattice ok. So, this is called as your Ordered, Ordered Substitutional Solid Solution. This typically happens when the impurity concentration is a little larger.

So, random Solid Solutions form at lower concentrations typically and where it is within the solubility limit. And ordered substitutions or solutions typically form at higher concentrations and they form different phases altogether different structure altogether. So, I will show you some examples just a in just a minute. And the Interstitial example could be like this ok. So, your interstitial atom may go here for example, somewhere randomly. These are your interstitial sites. Now interstitial sites and reality may lead to distortion.

So, the atom may be slightly smaller or slightly bigger than the interstitial site. So, it may create tensile or compressive stresses depending upon what size it has. So, in real situations they do create stresses. Similarly, in sufficient solid solution they do create stresses because the size of the atom is not going to be exactly similar, there is got to be some difference. So, whether it is a difference of 1 percent, 5 percent and 10 percent, that will determine eventually whether Solid Solution will form or not.

But if the solution Solid Solution does form then there are stresses in the structure. So, this is called as your Interstitial Solid Solution. You can have ordering at the interstitial sites as well, you can have ordering at the interstitial sites. As we will see in case of for example, silicon carbide or zinc sulfide, but it typically happens in case of ironically or covalently bonded solids. In case of metallic solids, typically interstitial bonds Interstitial Solid Solutions are random in nature. So, render interstitial sites are randomly occupied, but we do have intermetallics, we do have ordered solid solutions in which you will have ordering of impurity at even at interstitial sites, but it is typically more common in compounds where covalent or ionic character is stronger.

So, the real examples of these two are for example.

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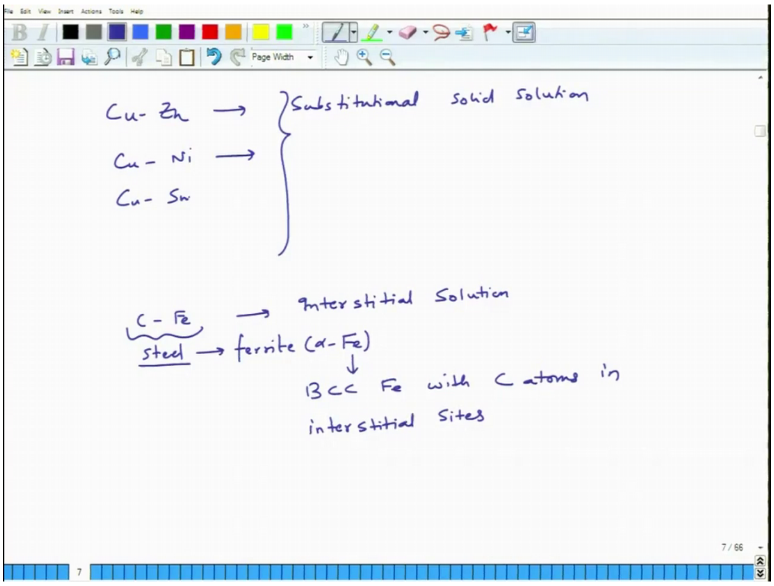

Cu- Zn → } Substitutional Solid Solution

Cu - Ni →

Cu - Sn

$\underbrace{\text{C - Fe}}$ → Interstitial Solution

Steel → ferrite (α - Fe)

↓

BCC Fe with C atoms in interstitial Sites

Copper -Zinc is a example of Substitutional Solid Solution. Your Copper- Nickel is another example of Substitutional Solid Solution. Copper-Tin is also an al example of substitution solid solution. So, these are some examples of Substitutional Solid Solution. Your Interstitial Solid Solution says Carbon and Iron is a Interstitial Solid Solution. This is a very famous example of metallic alloy containing. So, this is basically steel right. Steel-steel has a ferrite phase which is alpha ferrite, alpha phase or rather let me call it alpha iron. Alpha iron is BCC structured phase and with BC BCC iron with carbon in become very complicated just.

So, it is basically BCC iron with carbon atoms in interstitial sites ok. These are some example of substitution. So, there are plenty of more examples in metallic systems; because most metals are impure, then even if you say it is 99.99 percent pure, I mean there is 0.1 percent impurity sitting there and that impurity may go to oc interstitial or substitution sites

So, let us just look at the example of Copper-Zinc alloy first.

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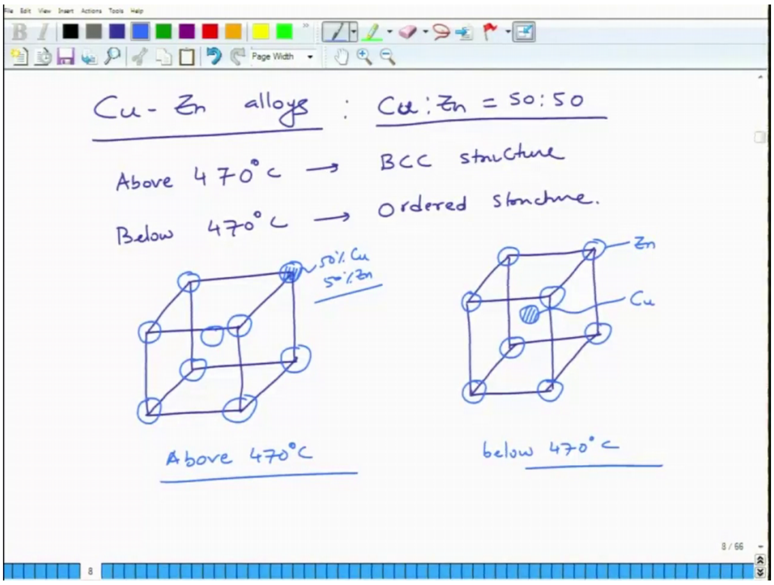

Cu - Zn alloys : Cu : Zn = 50 : 50

Above 470°C → BCC structure

Below 470°C → ordered structure.

Now, this is with the Cu2Zn ratio of 50 is to 50 ok. So, above 470 degree centigrade or so, it makes a BCC structure. You can see that the structure is not same as Copper or Zinc. It makes a BCC structure which is a disordered BCC structure. Below 470 degree centigrade, it makes a Ordered Structure. So, below 470 degree centigrade, it looks something like this. So, these are your atoms. You do not know which one is Copper and which one is Zinc.

So, there is a equal probability of. So, this is above, above 470 degree centigrade. So, it is possible that you know this atom will be Copper, some other will be Zinc, it is just that 50 percent of Copper, 50 percent are Zinc. So, each atom is characterized as 50 percent Copper and 50 percent Zinc. Because there is a equal probability of occupation of 2, 2 sites.

Ah. So, as a result, this is a disordered structure and it is a BCC structure; because each atom is 50 percent Copper, 50 percent Zinc. Below 470 degree centigrade what happens is that, there is a there is now, a specific preference for sites. So, this is Copper or Zinc whichever. This is Zinc. Here, it is it is here. So, you can see that Copper makes one sub lattice, Zinc makes another sub lattice and both of these sub lattices are cubic in nature, primitive cubic in nature.

So, these are 2 interpenetrating cubic lattices of Copper and Zinc into each other which are very ordered. So, this is below 470 degree centigrade and why this happens is that, if you look at this case where there is a random distribution of Copper and Zinc; there is no preference for Copper-Copper bonds or Copper- Zinc bonds or Zinc-Zinc bonds. Everybody is happy with everybody. Copper is copper is if it is if it is neighbor is Copper, Copper is also happy if it is neighbor is Zinc, Zinc is also with Copper being a neighbor or Zinc being a neighbor.

So, there is no preference for any particular kind of neighbor. In this case, below 470 degree centigrade, Copper prefers to have Zinc as a neighbor and Zinc prefers to have Copper as a neighbor; because this changes the enthalpy. Enthalpy is depending upon the number of nearest neighbors, ty type of nearest neighbors.

So, this is determined by thermodynamics, what will be stable. So, this is a disordered this is a Disordered Solid Solution, this is the Ordered Solid Solution. In Disordered Solid Solution, you cannot pinpoint and say this is Copper atom or this is Zinc atom [FL].There is a probability ok, but in case of ordered structure, you can make a difference. And this is very clearly seen in X-ray diffraction pattern.

When you do the X-ray diffraction analysis as I will show you later, X ray diffraction will show you a pattern for disordered structure same as a BCC material which is very different for a cubic structure; primitive cubic which is for ordered copper. Because here, you will see 2 super lattices one of Copper, one of Zinc. So, they will have their own effect on the it is X ray diffraction.

So, now the question that arises is so.

Student: Sir, can we have this disorders structure at room temperature?

Of course yeah, you can have a disordered structure room temperature. Any dilute solid solutions are disordered. This is at very high disorder concentration this is 50 50, but if you have let us say 1percent Zinc in Copper or for example, Copper-Nickel very good example, Copper-Nickel all the way it is FCC. So, you cannot distinguish which is Copper which is Nickel. So, Copper-Nickel for example, is like this.

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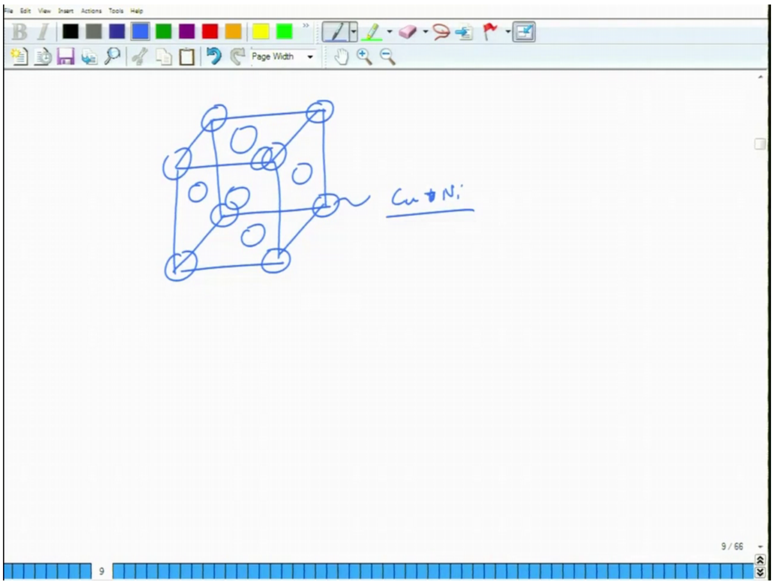

Copper is FCC right.

So, at any concentration, each atom is mixture of Copper and Nickel. The probability of each site being occupied by Copper and Nickel is determined by their fraction. So, if it is Copper-Nickel 50 by 50, each atom is copper 50 percent Copper 50 percent Nickel. I mean it is not realistically it will be either Copper or Nickel, but probability wise it is 50 percent Copper, 50 percent Nickel. If it is 25 percent Copper, 75 percent Nickel, it will be 25 percent Copper, 75 percent (Refer Time: 24:38). So, there is a; so, this is the Disordered Solid Solution which remains FCC even at room temperature. No matter what the fraction of two elements is ok.

So, let me; so, these Solid Solutions when you make the solutions, solutions are called as basically Alloys.

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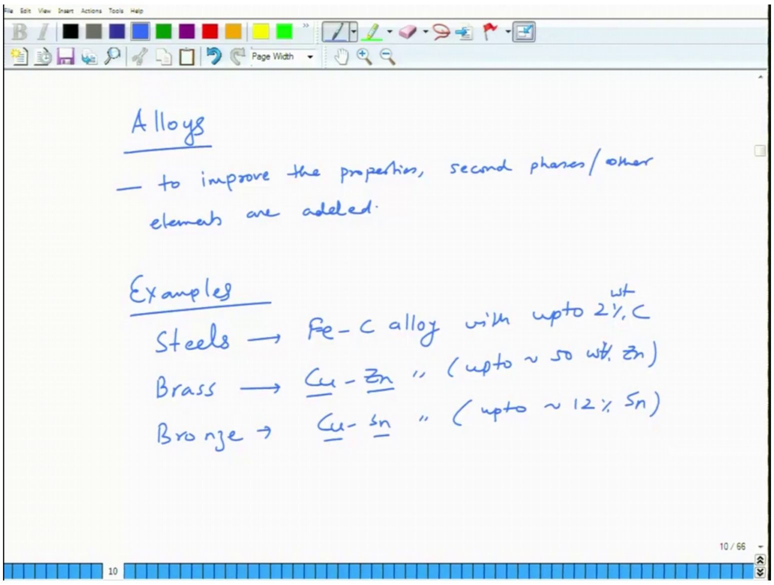

Alloys

— to improve the properties, second phases/other elements are added.

Examples

Steels → Fe-C alloy with upto $2\overset{wt}{\%}C$

Brass → $\underline{Cu}-\underline{Zn}$ " (upto ~ 50 wt% Zn)

Bronze → $\underline{Cu}-\underline{Sn}$ " (upto ~ 12% Sn)

And the atoms are put in intentionally to improve the properties, second phases are or other elements are added ok. So, it is intentional in many cases. In some cases of course, it is unintentional because we cannot remove the impurity, but in most cases that is intentional for example. So, examples are Steel which is Iron-Carbon alloys with upto 2 percent Carbon ok. Then, you have Brass, Brass is Copper-Zinc alloy upto about 50 weight percent Zinc. This is again 2 weight percent.

And then, you have Bronze which is Copper-Tin alloy which has upto about 12 weight percent ok. Now, here one thing that is interesting is copper has a structure which is FCC, Zinc has which is if HPC, Copper again has FCC, here Tin has HCP or which is it depending upon, but it is HCP.

So the question is what is the structure that the eventual alloy are going to take place, are there any guidelines? Ok. So, there are certain guidelines which are called as Hume Rothery Rules ok.

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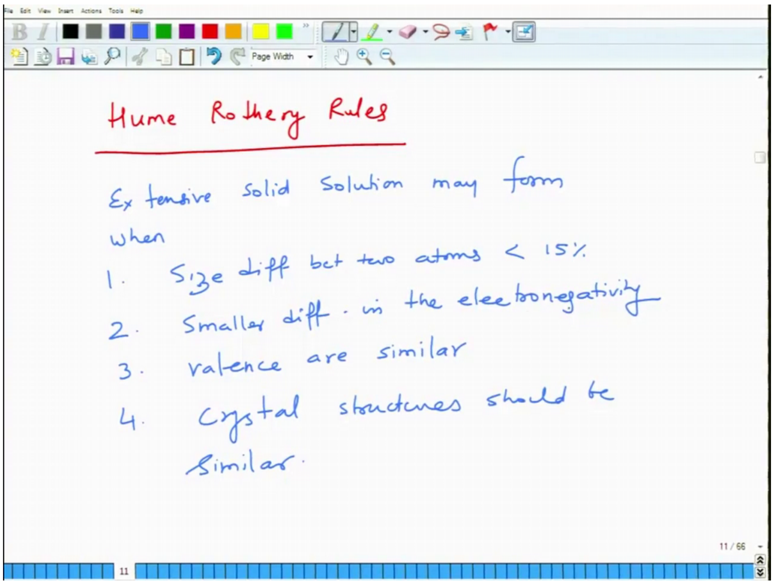

Hume Rothery Rules

Extensive solid Solution may form when

1. Size diff bet two atoms $< 15\%$
2. Smaller diff. in the electronegativity
3. valence are similar
4. crystal structures should be similar.

Now, it is say that Extensive Solid Solubility occurs may form when, number 1, the size difference between two atoms is less than 15 percent. Number 2, there should be smaller difference in the electro negativity which means they should not be very far apart in the Periodic Table, otherwise they will make ionic bond. So, there should be smaller difference in the electronegativity. Third is their valences are similar. Now, these are not exactly rules these are guidelines because there are violations which are there, but by and large they are followed in most metallic systems.

So, and fourth is the crystal structures should be similar. So, when the valences are valances are not similar than the variance of. So, element with higher valence is likely to resolve in the element of lower valence. That is typically the norm. And if electronegativity difference is large, then instead of making alloy, it tends to make a in compound ordered compound.

It could be it is called as Inter Metallic, it is called as a Line Compound or something like that it is much. It looks like as if it is ionic compound, but it is like a it has a higher high ionic or covalent character than metallic bonding because the large difference in the electronegativity it is called as an Inter Metallic Compound or Line Compound.

So, these are certain guidelines which are to be followed when you form the structures. Deviations typically lead to lower solid solubility. If you have deviations from these rules they lead to lower solid solubility which means you cannot dissolve a large amount of impurity in the host phase, if there is a large size difference, if there is a large valence differences, there is a large change in the crystal structure because you know they are not compatible with each other as such.

So, let me give you some examples.

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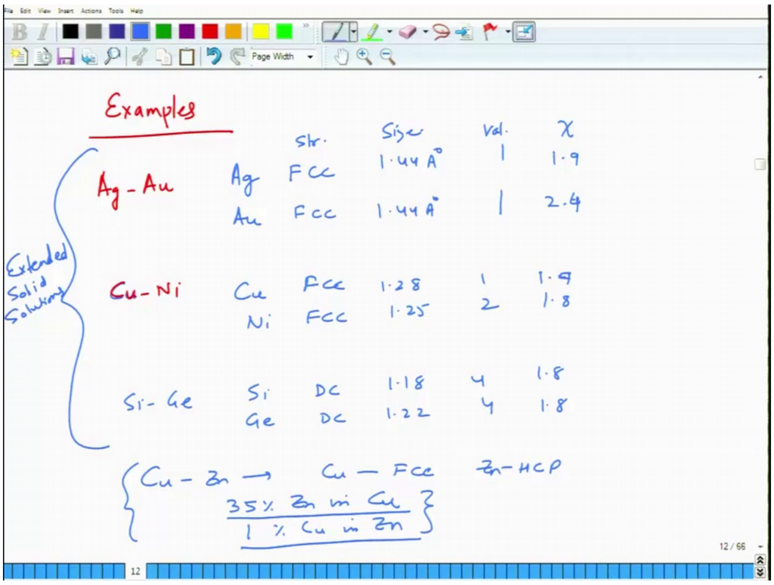

Examples

Extended Solid Solutions

		Str.	Size	Val.	χ
Ag - Au	Ag	FCC	1.44 Å	1	1.9
	Au	FCC	1.44 Å	1	2.4
Cu - Ni	Cu	FCC	1.28	1	1.9
	Ni	FCC	1.25	2	1.8
Si - Ge	Si	DC	1.18	4	1.8
	Ge	DC	1.22	4	1.8

Cu - Zn → Cu — FCC Zn - HCP

35% Zn in Cu

1 % Cu in Zn

For the first example, let us say Silver-Gold. So, we can see that Silver here has FCC structure, Gold has again FCC structure, Silver has a radius of 1.44 angstrom, gold has a radius of 1.44 angstrom, it has a valence of 1, it has electro negative 19, it has electro negativity of 2.4 this. So, this is electro negativity, this is valence, this is size, this is structure. And they make a Solid Solution which is extensive Extended Solid Solution.

Similarly, Copper-Nickel, I was tolling to talking about the Copper-Nickel system. And the reason for that is Copper is FCC, Nickel is FCC, Copper has a radius of 1.28, Nickel has a radius of 1.25 ray, their valence is a not similar by the way, Copper could be plus 1, electro negativities are fairly identical and they make Extended Solid Solutions all the way from Copper to Nickel.

And then Silicon-Germanium is another system which is very well known system. So, Silicon Germanium both are diamond cubic. I will come to diamond cubic structure later on I have ex, but this is like this is a basically FCC lattice Silicon this is 1.22, radius, this is 1.18, valence is 4 for both of them, electro negativity is same, they make the Extended Solid Solution ok.

On the other hand, when you make Cu-Zn, Copper is FCC, Zinc is HCP. As a result of solid solubility is limited, you can only put 35 percent Zinc in Copper. And nearly 1 percent Copper in Zinc without making a second phase ok. So, these are Extended Solid Solutions spanning from pure Copper to pure Nickel or pure Gold to pure Silver or pure Silicon to pure Germanium. And this is a Partial Solid Solution.

It makes a Solid Solution up to 35 Zinc on the copper side. And it makes a Solid Solution only up to 1 percent Copper on the Zinc side. If you are between these two ranges, then they make second phases which are not solid which may or may not be solid solutions, but there are different phases ok because it cannot accommodate more Zinc or more Copper in it.