Basics of Materials Engineering
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Lecture – 16
Defects in Crystalline Materials – 2 (Point Defects and Solid Solutions)

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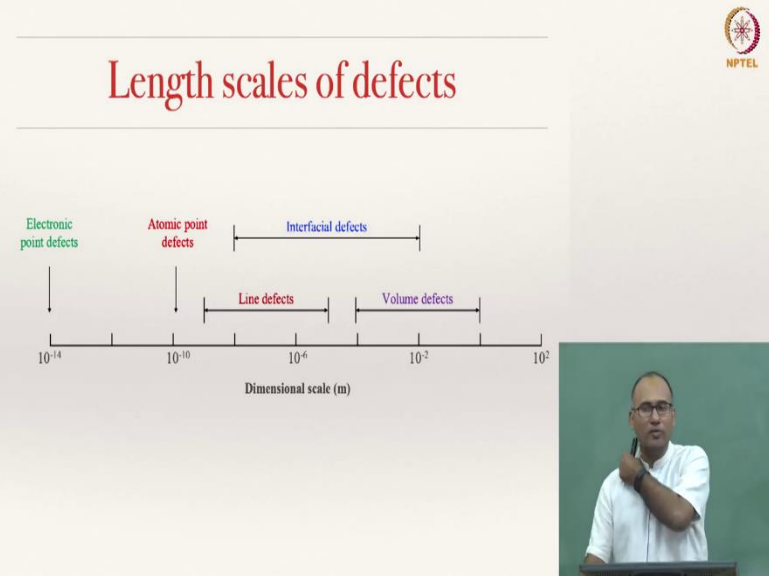

Length scales of defects

What are the different kinds of defects that we have discussed in the last class? Subatomic defects like -- where you need to have an electron and if the electron is not there in the material, then it becomes the defect for the atom.

That is the electronic point defects and then, atomic point defects; that means, the atom being present or not present, or the atom being present in a wrong position where it should not be. This is the zero-dimensional defect and we now said that there is going to be something called line defects. So, that is 1D defects and then, you have interfacial defects they are two-dimensional defects and then, volume defects which are three-dimensional defects.

What are the length scales? When we are talking about atomic point defects, we are working at the order of angstroms and when you are talking about line defects, you are talking at the scale of microns 10^{-6}m; couple of 10's of nanometers or 100's of nanometers to 10's of microns.

Interfacial defects, are having much higher length scale than the line defects. They can start from the micron scale to millimeter scale. Usually, volume defect can be observed with the naked eye whereas, line defects and interfacial defects are usually not observable with naked eye. You need to look under a microscope to actually identify the line defects and interfacial defects.

If you want to look at atomic point defects, you need to have a much more powerful microscope such as a transmission electron microscope. There you can see the individual defects, whether there is an atom sitting there or not. Nowadays, you can actually look at the material at that detail.

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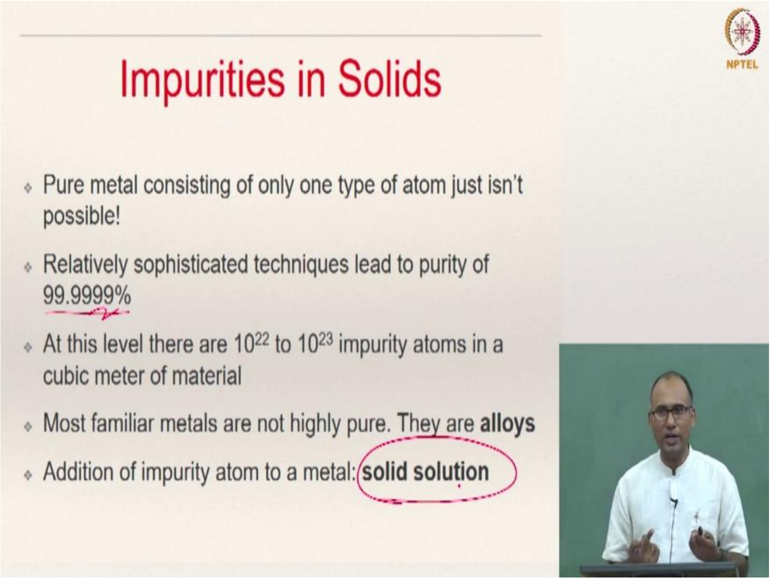

Impurities in Solids

- Pure metal consisting of only one type of atom just isn't possible!
- Relatively sophisticated techniques lead to purity of 99.9999%
- At this level there are 10^{22} to 10^{23} impurity atoms in a cubic meter of material
- Most familiar metals are not highly pure. They are **alloys**
- Addition of impurity atom to a metal: **solid solution**

Let us now look at the impurities in solids. As we have discussed, pure metals consisting of only one type of atom is just not possible. You will always have some impurities. I am not actually talking about equilibrium concentration of vacancies; I am actually talking about existence of some other material. Just iron is simply not possible, just copper is simply not possible.

If you have extremely sophisticated methods to extract these materials, you can reach up to 99.9999 % of purity, right? Even when you buy gold, they will give you the purification number. If somebody says 99.9 % purity, that means, in 1 gram, 99.9 percent is gold and the rest maybe other materials, some impurities maybe there. So, at this 99.9999 percent purity level, you can have impurity atoms of $10^{22} - 10^{23}$in a cubic meter of material. You can have those many impurities.

Most of the metals that we are familiar with, that we are using in our engineering applications are not pure metals, rather they are alloys. For instance, steel is an alloy of iron and copper, bronze, etc. You may not use materials in their pure form. Even when you are making an ornament, you do not make an ornament with pure gold, right? What we add to gold? Think about it -- some of you do not know what you add to gold; so go back and check what your goldsmith adds to gold. It is not 100 % gold when you make an ornament.

When you add an impurity atom to your base material, you make a solution. A solution is nothing but a combination of the materials; you add one material to another material, and together they form a solution. If the state of the matter is solid, then it is called solid solution. If the state is liquid, then it is called liquid solution. In this class, we are going to talk about solid solutions. Solid solution does not mean that it has to be a liquid. If the state of the matter is solid, then you call this as solid solution.

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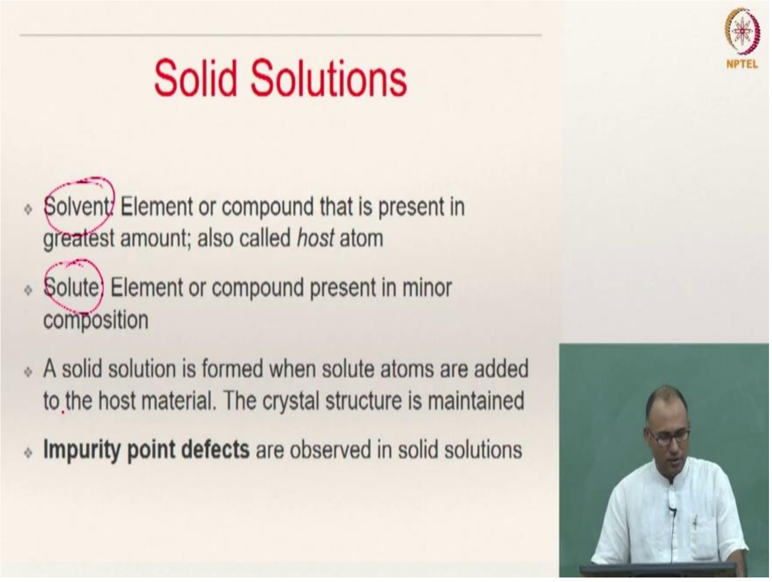

Solid Solutions

- Solvent: Element or compound that is present in greatest amount; also called *host* atom
- Solute: Element or compound present in minor composition
- A solid solution is formed when solute atoms are added to the host material. The crystal structure is maintained
- **Impurity point defects** are observed in solid solutions

When we are talking about solid solutions, you have a host and you have a guest. The host is called solvent. The element or compound that is present in the greatest amount is called solvent and it is also called host and the element that is added to this solvent is called solute or guest. Solvent is the one which is there in the maximum proportion and solute is the one which goes and sits there. So, you add the solute to solvent.

A solid solution is formed when solute atoms are added to the host material while maintaining the crystal structure. You observe these impurity point defects in solid solutions. Solid solution is actually something in which we intentionally add point defects.

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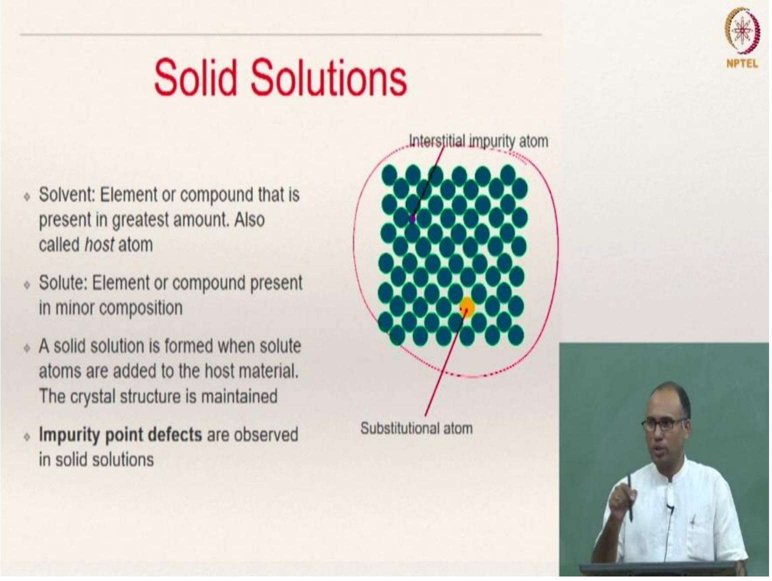

Solid Solutions

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- **Impurity point defects** are observed in solid solutions

Let us say this is a crystal lattice, the green ones are your crystal lattice and now you can see two different kinds of point defects. If a point defect is actually going and sitting in the interstitial location, then it is called interstitial impurity atom and if it is going and sitting in the substitutional position, it is substitutional impurity atom. We have discussed this previously when we were talking about different kinds of point defects.

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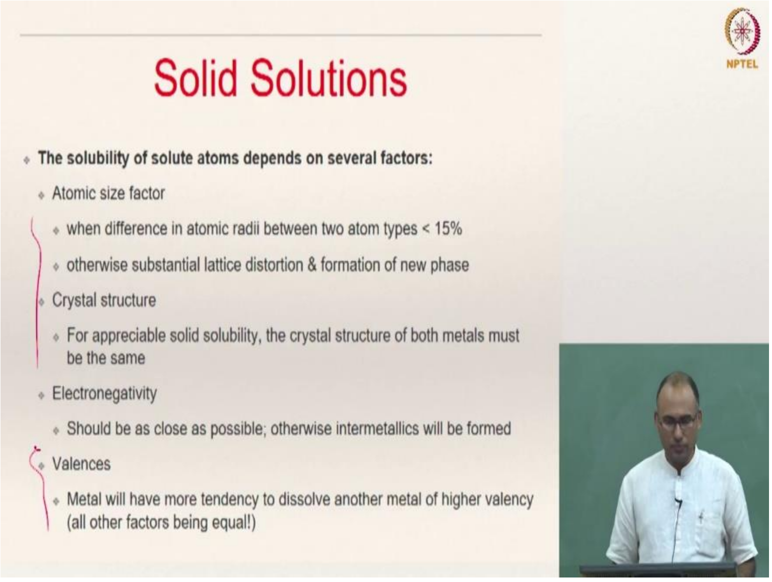

Solid Solutions

- **The solubility of solute atoms depends on several factors:**
  - Atomic size factor
    - when difference in atomic radii between two atom types < 15%
    - otherwise substantial lattice distortion & formation of new phase
  - Crystal structure
    - For appreciable solid solubility, the crystal structure of both metals must be the same
  - Electronegativity
    - Should be as close as possible; otherwise intermetallics will be formed
  - Valences
    - Metal will have more tendency to dissolve another metal of higher valency (all other factors being equal!)

How do you actually go about forming this solid solution? The solute atoms need to go and sit in solvent atmosphere; that means, there should be some amount of solubility for this solute atom in solvent atmosphere. Otherwise it cannot go and sit there.

This solubility depends on several factors. Firstly, the atom size factor; what is the difference between the atomic sizes? If you are forming an interstitial solid solution, meaning all your impurity atoms are actually going and sitting in the interstitial locations of your solvent cloud, such a solid solution is called interstitial solid solution.

If your solute atoms are going and sitting in the substitutional positions, they are going to substitute for your solvent atoms, then such a solid solution is called substitutional solid solution.

When do you form a substitutional solid solution or interstitial solid solution? That actually depends on several factors. One of the important factors is the atomic size factor. When the difference in the atomic radii sizes is less than 15%, only then you will be able to form substitutional solid solution, otherwise you will form interstitial solid solution or you will create lattice distortion.

For a good solid solubility, the solvent atom and solute atom should be having same crystal structure. If they have similar crystal structure, then the solubility is better. And their electronegativity values should be as close as possible. They should not have large difference in their electronegativity. The valences are also another important thing. Metals will have more tendency to dissolve another metal of higher valency. While all other factors being equal (the valences are not the primary thing), it will look to dissolve a metal which has higher valency than itself.

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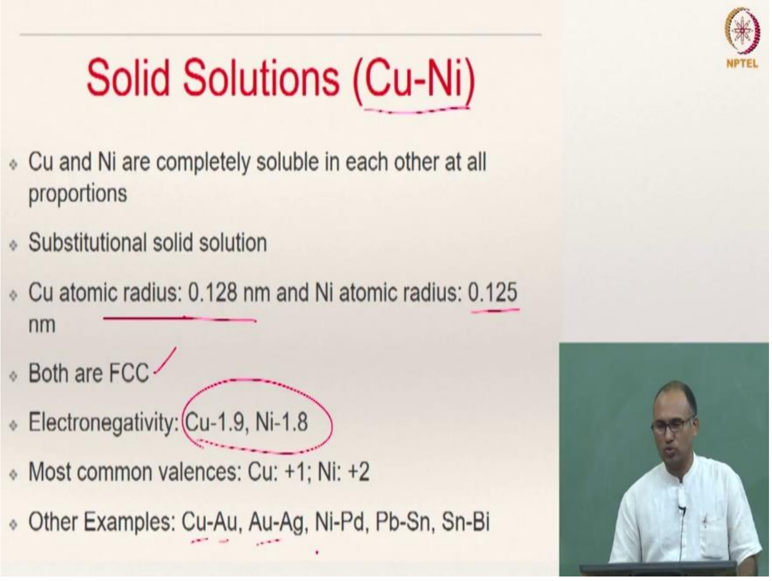

Solid Solutions (Cu-Ni)

- Cu and Ni are completely soluble in each other at all proportions
- Substitutional solid solution
- Cu atomic radius: 0.128 nm and Ni atomic radius: 0.125 nm
- Both are FCC
- Electronegativity: Cu-1.9, Ni-1.8
- Most common valences: Cu: +1; Ni: +2
- Other Examples: Cu-Au, Au-Ag, Ni-Pd, Pb-Sn, Sn-Bi

One very good example for a substitutional solid solution is copper-nickel system. Copper and nickel are completely soluble in each other at all proportions. If you take 90 percent copper 10 percent nickel and vice versa, they are completely soluble in each other, and it forms a substitutional solid solution. You can see why; the copper atom radius is 0.128 nm and nickel atom radius is 0.125 nm. They are very close to each other, that is why their solubility is high.

Firstly, they are close to each other and hence, they will only form a substitutional solid solution, because the interstitial sites are going to be smaller for them as the atom sizes are almost same. Both have FCC crystal structure and their electronegativity values are also very close (1.9 and 1.8), and hence, they form a very good substitutional solid solution with almost complete solubility, i.e., 100 % solubility in each other.

Other examples for substitutional solid solutions are copper-gold, gold-silver, nickel-palladium, lead-tin, tin-bismuth and so on.

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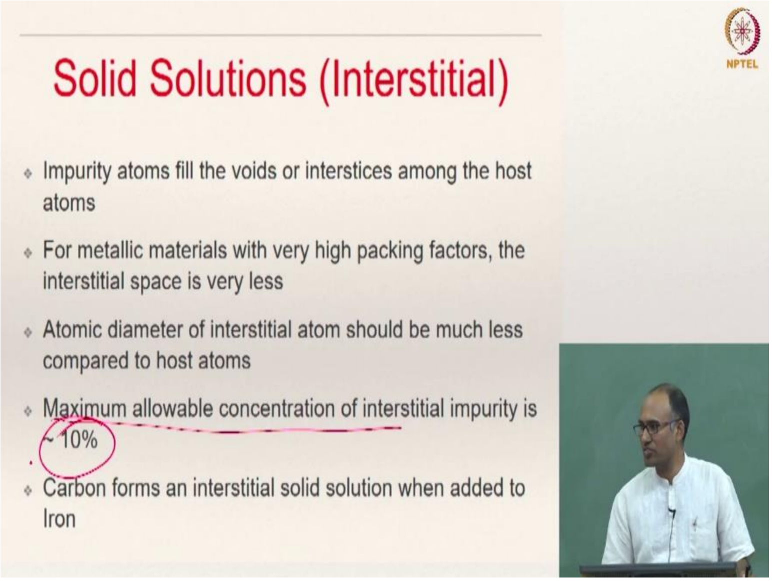

Solid Solutions (Interstitial)

- Impurity atoms fill the voids or interstices among the host atoms
- For metallic materials with very high packing factors, the interstitial space is very less
- Atomic diameter of interstitial atom should be much less compared to host atoms
- Maximum allowable concentration of interstitial impurity is ~ 10%
- Carbon forms an interstitial solid solution when added to Iron

What are the examples for interstitial solid solutions? When do you have interstitial solid solution? When the guest atom or the solute atom size is much smaller than the solvent cloud and then, it actually can go and sit in the interstitial positions. The impurity atoms fill the voids or interstices among the solvent cloud or host material.

When you have an interstitial solid solution, you cannot actually have complete solubility. Here, the maximum allowable concentration of an interstitial impurity in general is only about 10 percent. You cannot dissolve some material which will form an interstitial solid solution more than 10 percent concentration. For instance, carbon forms an interstitial solid solution with iron; so, steel is an interstitial solid solution of iron and carbon. The maximum solubility of carbon in iron is not more than 2 %.

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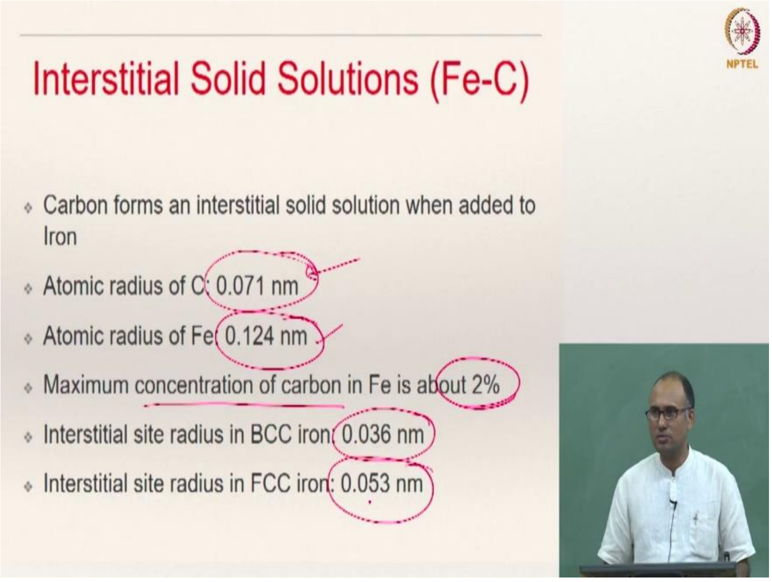

Interstitial Solid Solutions (Fe-C)

- Carbon forms an interstitial solid solution when added to Iron
- Atomic radius of C: 0.071 nm
- Atomic radius of Fe: 0.124 nm
- Maximum concentration of carbon in Fe is about 2%
- Interstitial site radius in BCC iron: 0.036 nm
- Interstitial site radius in FCC iron: 0.053 nm

You see that atomic radius of iron is 0.124 nm and carbon is much smaller 0.071 nm and that is the reason why it can go and sit in the interstitial locations. The maximum concentration of carbon in iron is about 2 percent.

Iron can occur in two forms, right? You have alpha iron and?

Student: Gamma.

Gamma iron, right? Alpha iron is BCC while gamma iron is FCC. It will have two different crystal structures. It changes its phase depending on the temperature and composition.

If you look at BCC material iron lattice, you will see that the interstitial site radius is 0.036 nm by knowing the radius of iron and if it is FCC, then you have 0.053 nm.

Please note that the carbon is actually going and sitting in the interstitial site, but the size of carbon atom is actually larger than any of these two. When carbon goes and sits, it disturbs the crystal lattice locally. It will create local distortions and hence, the energy of the crystal might change because of the local distortion.

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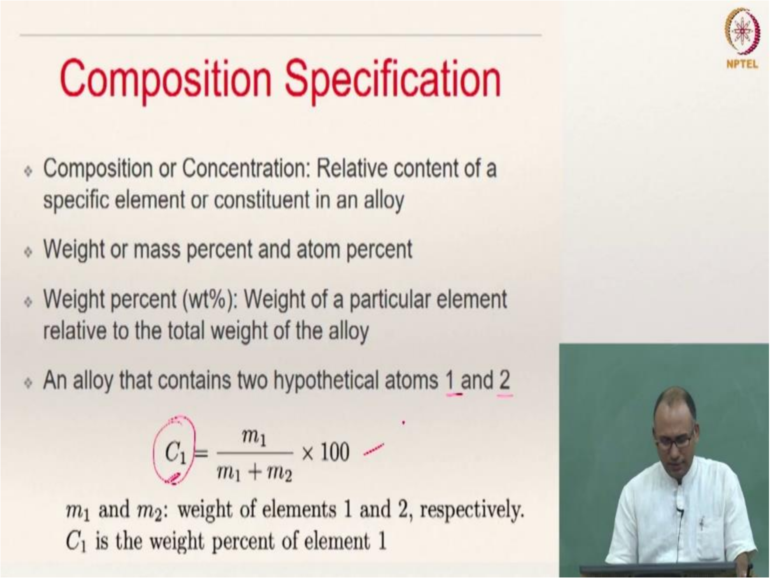

Composition Specification

- Composition or Concentration: Relative content of a specific element or constituent in an alloy
- Weight or mass percent and atom percent
- Weight percent (wt%): Weight of a particular element relative to the total weight of the alloy
- An alloy that contains two hypothetical atoms 1 and 2

$$C_1 = \frac{m_1}{m_1 + m_2} \times 100$$

m_1 and m_2: weight of elements 1 and 2, respectively.
C_1 is the weight percent of element 1

Student: (Refer Time: 13: 48).

We will discuss about it when we are talking about phase diagram. At this point of time, I am not discussing that, but we will discuss when we are talking about phase diagram.

The question is why does iron change its crystal structure when you go from one temperature to another temperature or composition? Iron is called alpha iron at low temperatures and gamma iron has little high temperatures and again at much higher temperature, it becomes delta iron (BCC). We will discuss why it changes crystal structure maybe towards the second end of this course.

How do we specify the composition or concentration of a solid solution? The relative content of a specific element or a constituent in an alloy is called the composition. You can describe this composition as weight percentage or atom percentage. What is the meaning of weight percentage? The weight of a particular element relative to the total weight of the alloy. What is the atom percentage? Instead of weight, you only talk about the number of atoms; the fraction of number of atoms, then it is called the atom percentage. We will see the definition in a moment.

Suppose you have a binary alloy. What you mean by binary alloy? You have only two elements, one solute and one solvent. If you have a binary alloy made of atoms 1 and 2, the composition in weight percentage can be defined $\frac{m_1}{m_1+m_2} \times 100$; that is the regular definition that you have studied.

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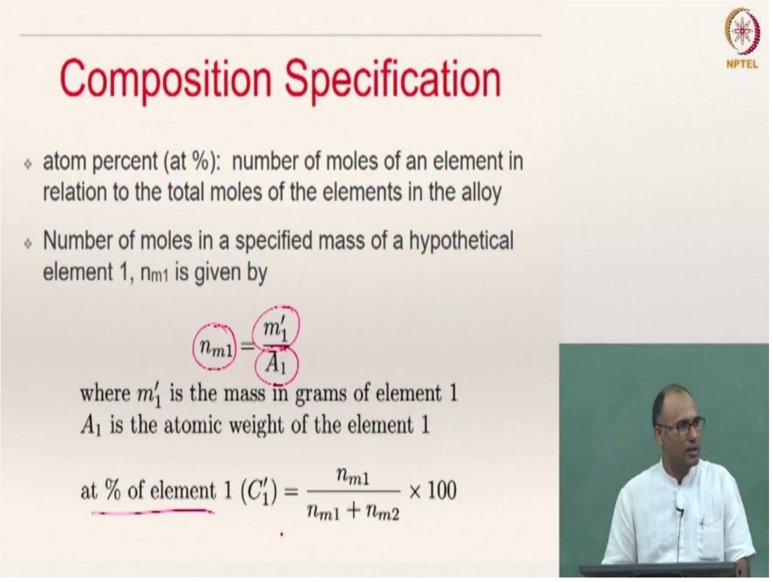

Composition Specification

- atom percent (at %): number of moles of an element in relation to the total moles of the elements in the alloy
- Number of moles in a specified mass of a hypothetical element 1, n_{m1} is given by

$$n_{m1} = \frac{m'_1}{A_1}$$

where m'_1 is the mass in grams of element 1

A_1 is the atomic weight of the element 1

$$\text{at \% of element 1 } (C'_1) = \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100$$

If you want to define atom percentage; number of moles of an element in relation to the total moles of the elements in the alloy. So, number of moles can be defined as mass of that particular species divided by the atomic weight of that particular species and hence, atom percentage can be defined as number of moles of atom type 1 divided by the total number moles, i.e., $\frac{n_{m1}}{n_{m1}+n_{m2}} \times 100$.

You can actually express the composition either in weight percentage or in atom percentage. When you look at these composition diagrams, you will either have weight percentage or atom percentage, sometimes you will have both of them. If you draw the diagram, on the bottom *x* axis you will have weight percentage, on the top *x* axis you will have atom percentage. You can read the diagram either in terms of weight percentage or atom percentage.

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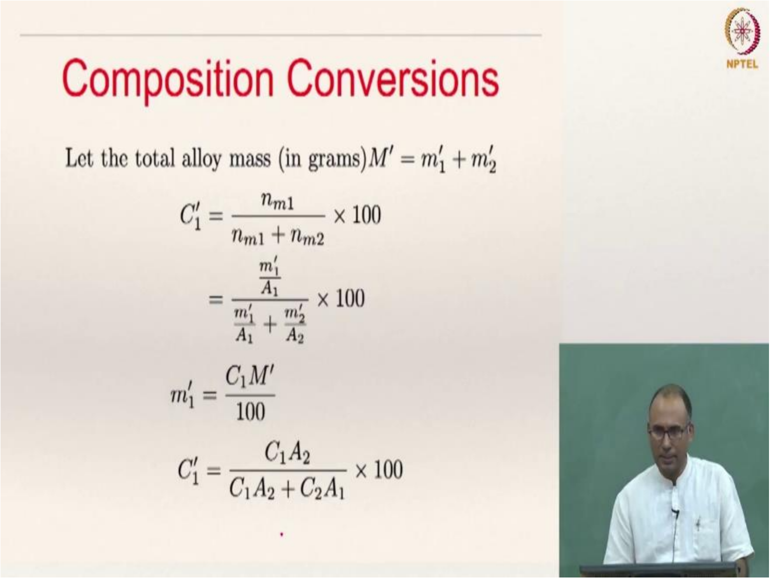

Composition Conversions

Let the total alloy mass (in grams) $M' = m'_1 + m'_2$

$$C'_1 = \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100$$

$$= \frac{\frac{m'_1}{A_1}}{\frac{m'_1}{A_1} + \frac{m'_2}{A_2}} \times 100$$

$$m'_1 = \frac{C_1 M'}{100}$$

$$C'_1 = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100$$

I am not going to discuss these derivations, but you should be able to convert from one to the other by knowing the atomic weights of these materials. So up to here I am not going through; we will do that through tutorials, but the slides are there so, you can go through the slides.

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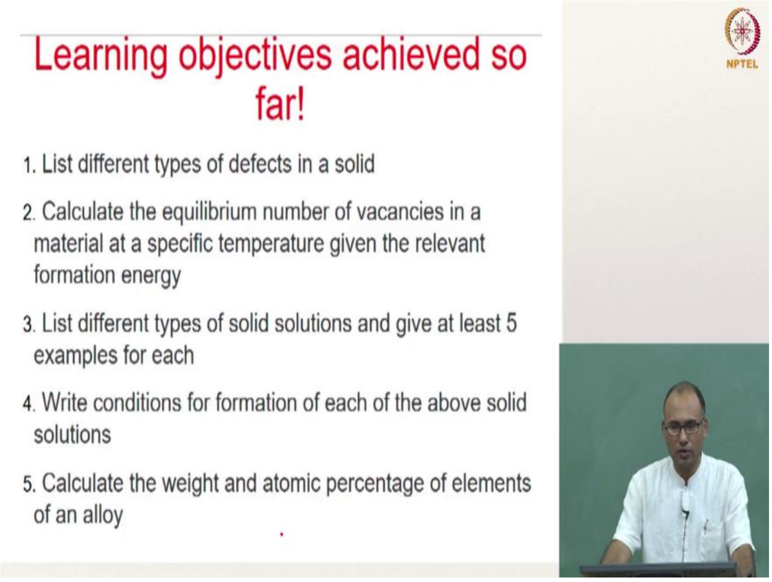

Learning objectives achieved so far!

1. List different types of defects in a solid
2. Calculate the equilibrium number of vacancies in a material at a specific temperature given the relevant formation energy
3. List different types of solid solutions and give at least 5 examples for each
4. Write conditions for formation of each of the above solid solutions
5. Calculate the weight and atomic percentage of elements of an alloy

that is about point defects. So, what did we learn so far? Now, can we list different types of defects in a solid?

Student: (Refer Time: 17:29).

Can we calculate the equilibrium concentration of vacancies in a material at a specific temperature, given the relevant formation energy? We can calculate. Can we derive the expression for equilibrium concentration of vacancies? Can we list different types of solid solutions? Today we have looked at substitutional solid solutions and interstitial solid solutions, and can we give at least 5 different examples for each?

We have already given 5 examples for substitutional solid solutions copper-gold, gold-silver. And I have given you one example for interstitial solid solutions, but you should be able to go back and find out what are the other materials which form interstitial solid solutions -- other alloys that you are familiar with are actually interstitial solid solutions.

What are the conditions for the formation of either a substitutional solid solution or an interstitial solid solution? We have looked at the atomic size factor, electronegativity, valency and crystal structure. Based on that you can actually decide whether a particular system is more probable to form a substitutional solid solution or an interstitial solid solution. We should be able to calculate weight and atomic percentage of elements of an alloy. If you know the volume fractions, then you should be able to calculate weight and atom percentage. That is what we have looked at so far.

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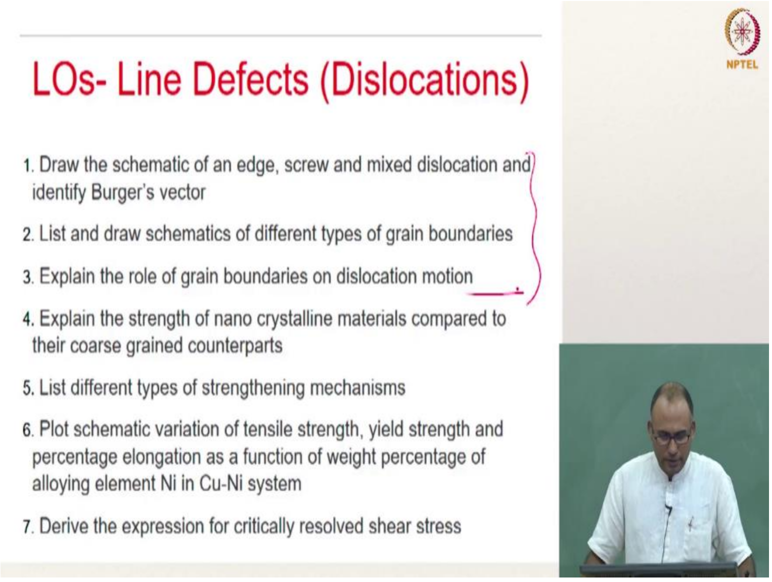

LOs- Line Defects (Dislocations)

1. Draw the schematic of an edge, screw and mixed dislocation and identify Burger's vector
2. List and draw schematics of different types of grain boundaries
3. Explain the role of grain boundaries on dislocation motion
4. Explain the strength of nano crystalline materials compared to their coarse grained counterparts
5. List different types of strengthening mechanisms
6. Plot schematic variation of tensile strength, yield strength and percentage elongation as a function of weight percentage of alloying element Ni in Cu-Ni system
7. Derive the expression for critically resolved shear stress

We have looked at zero-dimensional defects. Now, we need to focus our attention on line defects or one-dimensional defects. These line defects are also called dislocations.

Let us see what are the concepts that we are going to learn in this module. First of all, you should be able to draw a schematic of an edge, screw and mixed dislocation and identify Burger's vector. We should be able to list different kinds of grain boundaries and draw schematics of these grain boundaries. And explain the role of grain boundaries on dislocation motion.

And can we explain with the knowledge gained until here to swhy a nano crystalline material is much stronger than the coarse grain counterparts. Nano crystalline copper is stronger polycrystalline copper. Why is that? Will we able to explain that? And what are the different types of strengthening mechanisms? What do we mean by strengthening? We will discuss. We should able to list different types of strengthening mechanisms.

And plot the schematic variation of these mechanical properties as a function of weight percentage of alloying elements. We have just now seen that you have substitutional solid solution and interstitial solid solutions, and depending on the composition, how your mechanical properties change. And finally, you should be able to derive the expression for critically resolved shear stress to talk about plastic deformation in a material.

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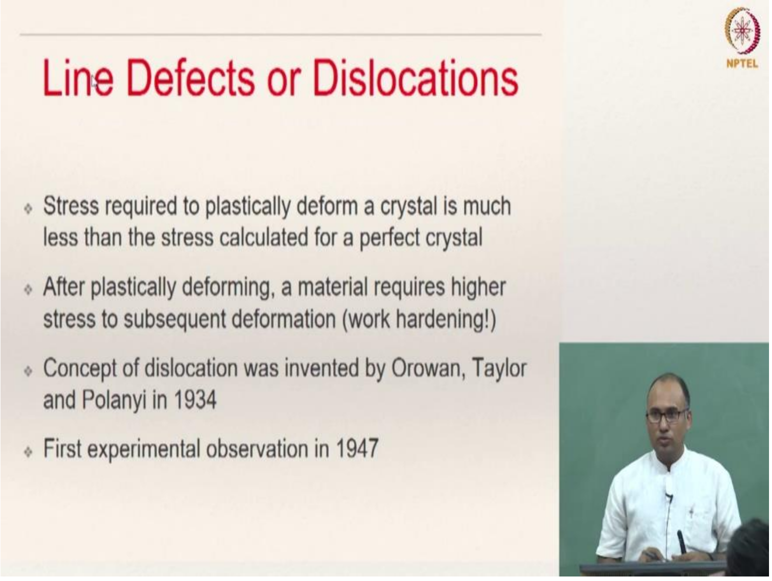

Line Defects or Dislocations

- Stress required to plastically deform a crystal is much less than the stress calculated for a perfect crystal
- After plastically deforming, a material requires higher stress to subsequent deformation (work hardening!)
- Concept of dislocation was invented by Orowan, Taylor and Polanyi in 1934
- First experimental observation in 1947

I will just introduce you to the concept of the line defects and then, we will stop, so that we can again start the same point tomorrow.

As we have discussed in yesterday’s class as well as in today’s class, the stress required to plastically deform a crystal is much less than the stress calculated for a perfect crystal. The theoretical shear strength we have calculated, turns out to be much larger than the real shear strength of the material so, the shear strength -- the reason why we call that represents the plastic deformation is basically because one atom which is in contact with a set of atoms is actually going away from this atom so that means, the neighbors of this atom are changing.

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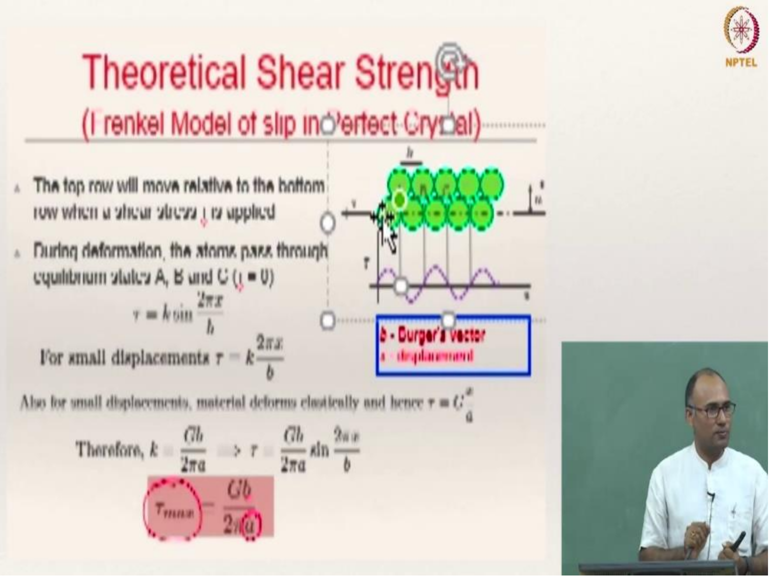

Theoretical Shear Strength

(Frenkel Model of slip in Perfect Crystal)

- The top row will move relative to the bottom row when a shear stress τ is applied
- During deformation, the atoms pass through equilibrium states A, B and C (τ = 0)

$$\tau = k \sin \frac{2\pi x}{b}$$

For small displacements $\tau = k\frac{2\pi x}{b}$

Also for small displacements, material deforms elastically and hence $\tau = G\frac{x}{a}$

Therefore, $k = \frac{Gb}{2\pi a} \Rightarrow \tau = \frac{Gb}{2\pi a}\sin\frac{2\pi x}{b}$

$$\tau_{max} = \frac{Gb}{2\pi a}$$

b - Burger's vector

x - displacement

If you remember this picture for instance, this atom A here -- when it moves, when you are applying the shear stress, this atom A is actually in contact with this first atom here, but when you are applying shear stress the atom A actually move to the position B. And then, its neighbor is changed; that means, there is a breakage of bond and that means, once you remove the shear stress there, it will never be able to come back to its original configuration and that is what we call plastic deformation. Plastic deformation is non-reversible whereas elastic deformation is reversible.

When you are applying an external load to a material, first you stretch the bonds before you break them. Before breaking them if you remove the load, then the elastic bond is retained and hence, it will come back to its original configuration. That is the reason why within the elastic regime when you remove the load, the material comes back to its original configuration.

But when you are going past that area, then you are actually breaking the bond here. Once you break the bond, energy is dissipated and then, after that if you remove the load, it cannot come back because that energy is dissipated in terms of heat and bond is broken. It is an irreversible process. That is what we call plastic deformation.

The stress required to plastically deform a crystal, the theoretical shear strength in other words is actually much larger than the real strength of the material and it turns out that if you impart plastic deformation to a material, the further deformation requires higher stress; that means, after plastically deforming a material, the material requires higher stress to subsequent deformation and that is what is called work hardening. We will talk about why such a thing happens.

These dislocations are actually nothing but line defects and how do they look like and how do they move in a crystal is something that we will look in the next week.