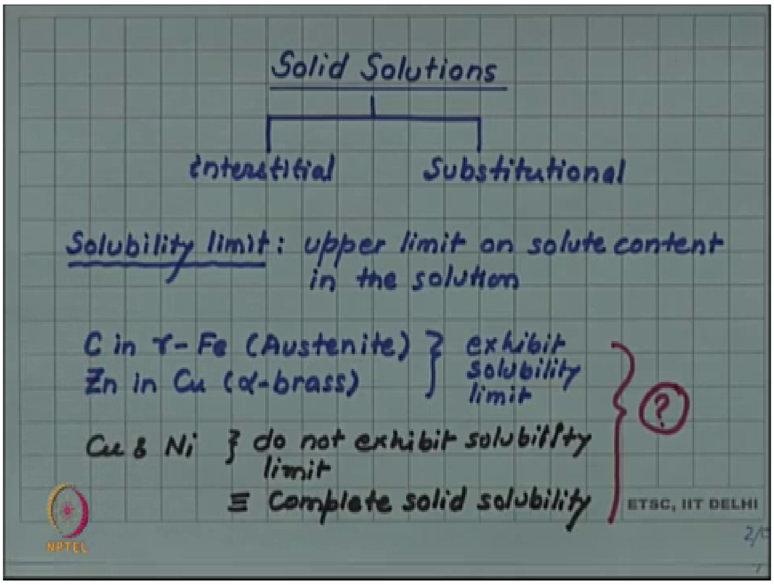
Introduction to Materials Science and Engineering

Prof. Rajesh Prasad
Department of Applied Mechanics
Indian Institute of Technology, Delhi

Lecture - 24
Hume-Rothery rules

Hello and welcome today we will discuss Hume-Rothery rules. These rules pertain to formation of continuous or complete solid solubility in solid solutions. So in the last lecture we were discussing solid solutions.

(Refer Slide Time: 00:33)



Solid Solutions

Interstitial   Substitutional

Solubility limit: upper limit on solute content in the solution

C in γ-Fe (Austenite) } exhibit solubility limit
Zn in Cu (α-brass)

Cu & Ni } do not exhibit solubility limit
≡ Complete solid solubility

?

ETSC, IIT DELHI

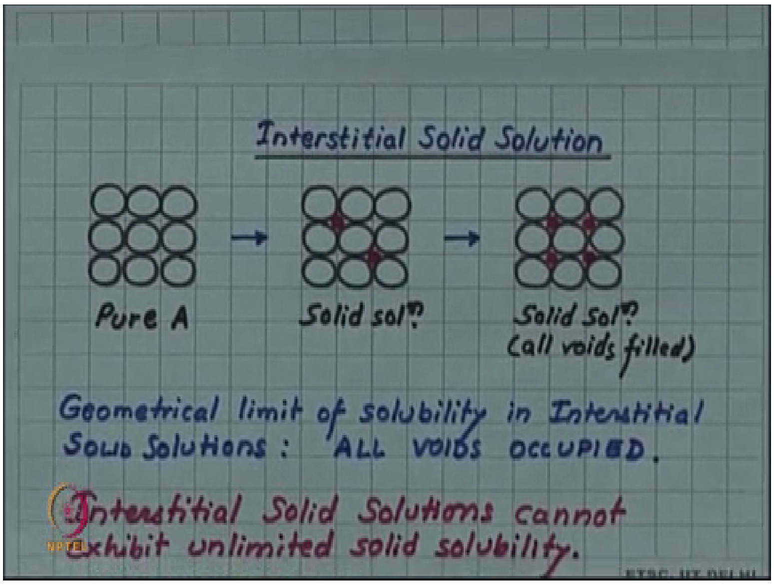
And we saw that we have 2 kinds of solid solutions interstitial solid solution and substitutional solid solutions, interstitial and substitutional. We also saw that in some solid solutions so let us see some solid solutions have solubility limit meaning that there is a maximum amount of solute there is a fixed maximum amount of solute which can be introduced into the solvent.

So, there is an upper limit on solute content in the solution. But we saw that there are 2 types of solutions some solutions show this upper limit. So, for example carbon in gamma iron which we call austenite or zinc in copper which we call alpha brass these solutions have a solubility limit that is only a maximum amount of carbon can go into gamma iron and a maximum amount of copper or zinc can go in each other maximum amount of zinc can go in copper so that is what is our alpha brass.

So, there is an upper limit, but in some cases so another example is let us say copper and nickel this pair of element can be dissolved or can be mixed with each other in any ratio I can make solid solutions a starting from pure copper right up to pure nickel in any proportion so they do not exhibit any upper limit solubility do not exhibit solubility limit. or in other words it is also called that they form an extensive or complete solid solubility and Hume-Rothery rule.

And in today's this lecture we will address this question that why is this difference between these 2 kinds of solid solution that some have an upper limit on the solute exhibit solid solubility limit form so called saturated solid solution whereas, there is no such saturation if I am mixing copper and nickel I can do it in any amount.

(Refer Slide Time: 04:34)



Interstitial Solid Solution

Geometrical limit of solubility in Interstitial Solid Solutions : ALL VOIDS OCCUPIED.

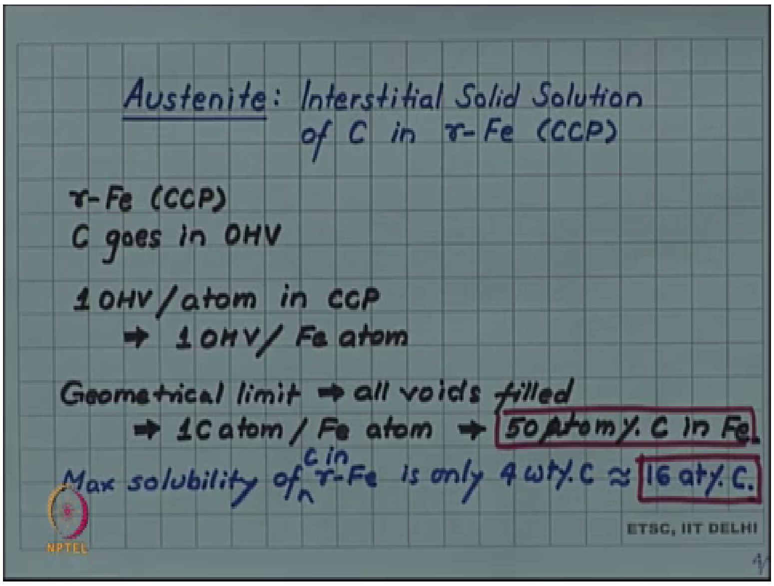
Interstitial Solid Solutions cannot exhibit unlimited solid solubility.

So, let us first look at 2 types of solid solution interstitial and substitutional. So, first let us look at the interstitial solid solution and let me start with this 2 dimensional cartoon example and let me call this pure A. So, the first diagram is representing pure A and now I want to make an interstitial solid solution by adding B to A and B of course, as we have seen in the previous lecture will go in the interstitial voids of A.

So, these are the location of interstitial void so I place one B here of course, there are other voids empty so I can put one more. Of course, I can continue this process and ultimately I will fill all the voids and once I have done that I have automatically found an upper saturation limit beyond this I cannot put any more solute. So, we can call this a solid solution call voids filled. This also solid solution, but only some voids are filled.

So, we can see that there is a geometrical upper limit once all voids are filled it cannot accept any more solute. So, these are called a geometrical limit of solubility. Solubility in interstitial solutions solution this happens when all voids are full. So obviously, interstitial solid solutions cannot show the kind of unlimited solute solubility which we were mentioning so we note that interstitial solid solutions cannot exhibit unlimited solid solubility. There has to be an upper limit when all voids are full the solution has to be saturated and nothing more can be done beyond that.

(Refer Slide Time: 08:12)



Austenite: Interstitial Solid Solution of C in γ-Fe (CCP)

γ-Fe (CCP)
C goes in OHV

1 OHV / atom in CCP
⇒ 1 OHV / Fe atom

Geometrical limit ⇒ all voids filled
⇒ 1 C atom / Fe atom ⇒ $\boxed{\text{50 atom\% C in Fe}}$

Max solubility of C in γ-Fe is only 4 wt% C ≈ $\boxed{\text{16 at\% C.}}$

ETSC, IIT DELHI

Let us look at real example that was a cartoon 2 D example. The real example of a solid solution of carbon in gamma iron this is austenite the name of this solid solution in particular is austenite and let us look at what is the real situation in this.

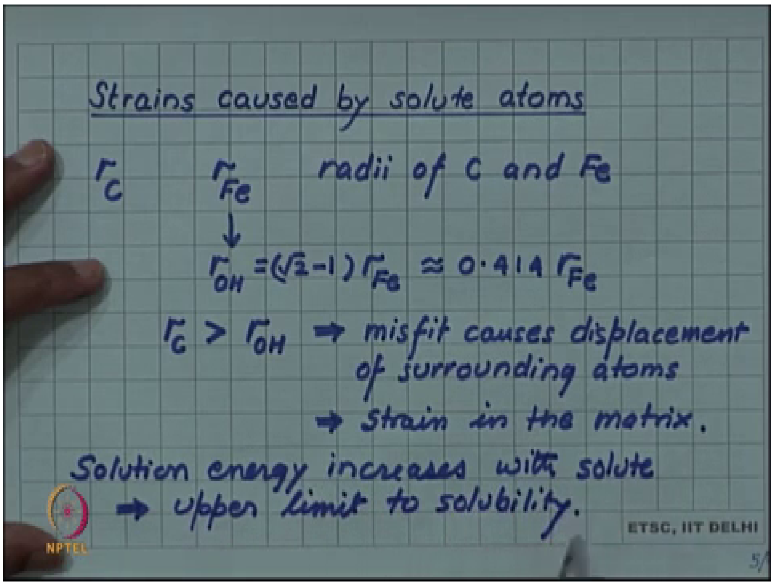
So, we have gamma iron which is CCP and carbon goes in octahedral void this is known from experiments that carbon goes in octahedral void. Now the question is how many octahedral voids are there in CCP of iron. We have done this exercise before and if you recall there is one octahedral void per atom in CCP.

So, this mean there is one octahedral void per iron atom in gamma, in CCP gamma iron there is one octahedral void per iron atom. And suppose in the geometrical limit we fill all these octahedral voids. All voids filled this will give us one carbon atom per iron atom which of course, in percentage you can see that this is a 50 percent, 50 atom percent, 50 atom percent carbon in iron so the 50 atom percent carbon in iron will be the upper geometrical limit in CCP iron you cannot put more than that.

In reality of course, you will see that this solubility is limited even further. So, if you look at a real case for the gamma iron we find that the maximum solubility actually is limited only to 4 weight percent maximum solubility of gamma iron of carbon in gamma iron is only about 4 weight percent and if you convert this into atomic percent you get this to be 16 atomic percent.

So although you had 50 atomic percent as the upper geometrical limit in reality it is only 16 atomic percent. So, the real limit the real upper limit experimentally observed upper limit is much much less than the geometrical limit so there may be other factor which might be controlling this solubility. So, what is that other factor?

(Refer Slide Time: 12:15)



Strains caused by solute atoms

r_C r_{Fe} radii of C and Fe

$\downarrow$

$r_{OH} = (\sqrt{2}-1)\, r_{Fe} \approx 0.414\, r_{Fe}$

$r_C > r_{OH}$ ⇒ misfit causes displacement of surrounding atoms

⇒ Strain in the matrix.

Solution energy increases with solute

⇒ upper limit to solubility.

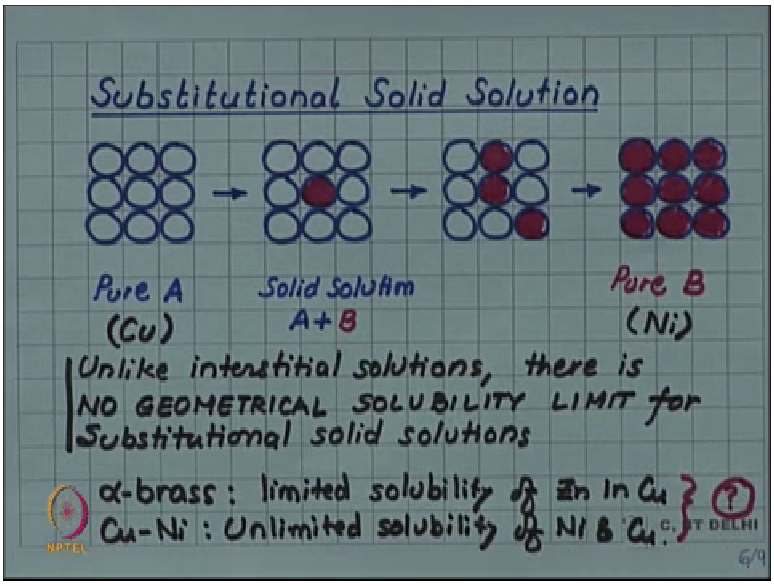
So, that other factor is a strain caused by the solute atoms. So, if we look at the size of the carbon atom, radius of the carbon atom carbon atom has to fit in the octahedral void. So, let us say that the carbon atom radius is r carbon and iron atom radius is r iron, this is the radii of carbon and iron.

And now we know that octahedral void will give you an accommodation for a maximum size so r octahedral which is root 2 minus one times the radius of atoms, in this case the iron atoms which is about 0.414 R iron.

So, the carbon atom has to fit into this void which can accommodate at most 41 percent of the radius of iron atom, but the actual size although carbon atom is smaller than iron atom, but it is larger than the void size and this misfit causes a strain, causes displacement of surrounding atoms which we say is a strain in the matrix.

So, as more and more solute dissolved more and more of this strain will come thus the strain energy of the system will increase this increasing strain energy is what causes an upper limit a physical upper limit of the solubility. Solution energy increases with solute and this finally, gives an upper limit to the solubility. Now, let us look at the substitutional solid solution.

(Refer Slide Time: 15:25)



Substitutional Solid Solution

Unlike interstitial solutions, there is NO GEOMETRICAL SOLUBILITY LIMIT for Substitutional solid solutions

α-brass : limited solubility of Zn in Cu
Cu-Ni : Unlimited solubility of Ni & Cu. } ?

So, in interstitial case we saw that there is a maximum upper geometrical limit which cannot be exceeded and in reality the real limit may be even less than the geometrical limit and usually it is much much less than the geometrical limit as we saw in the case of carbon in iron and that is because of the misfitting with the atoms do not fit exactly in the void and causes a strain. What is the situation in substitutional solution?

So, let us start with the substitutional solid solution again I have this cartoon diagram, where I start with this pure A, this is my pure A and then I start making solution by substituting now I am not putting the next atom in the void I am substituting A and it is a sum of A by B. So, let me substitute this central A by B so I have got a solid solution A plus B and I can increase amount of solute by substituting more where in the last figure I had already substituted for the central atom.

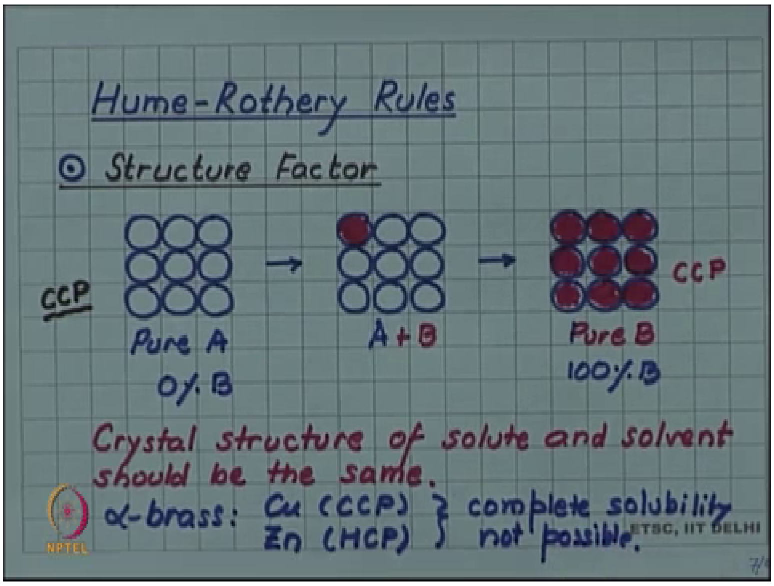
Let me substitute some more atoms so I have increased the concentration of B and if I continue this process if I substitute all of them at least there is no geometrical constraint one by one I can keep substituting all the A atoms by the B atoms so instead of pure A I get to pure B. So, unlike all voids filling leading to an upper geometrical limit there is no such geometrical limit in the substitutional solid solution I can at least in principle substitute all the atoms and get to pure B.

So, the conclusion is that unlike in interstitial solution there is no geometrical solubility limit for substitutional solutions so this is an important difference between interstitial and substitutional solid solution. And we have already seen an example that if we take this if I take A as copper and B as nickel.

So I have a real life example of 2 elements which do just this I can mix them in any proportion I can start with pure A and go to pure B making solutions of different concentrations and all those solutions are possible. So, A it is geometrically possible and there are examples of this also, but not all substitutional solution do this and we have example of this also we have already seen that in alpha brass there is a limited solubility of zinc in copper whereas, we saw in copper nickel we have unlimited solubility of nickel and copper.

So, this is the situation for interstitial solid solution unlimited solid solubility is not possible, for substitutional solid solution unlimited solid solubility is not ruled out by geometry but it is still physically some form unlimited solid solution copper and nickel being example and some do not. So, this was an important question and this is the question which Professor Hume-Rothery of Oxford University tried to address and we call them as Hume-Rothery rules.

(Refer Slide Time: 21:06)



Hume-Rothery Rules

⊙ Structure Factor

CCP

Pure A
0% B

→ A+B →

Pure B
100% B

CCP

Crystal structure of solute and solvent should be the same.

α-brass: Cu (CCP) } complete solubility
Zn (HCP) } not possible.

ETSC, IIT DELHI

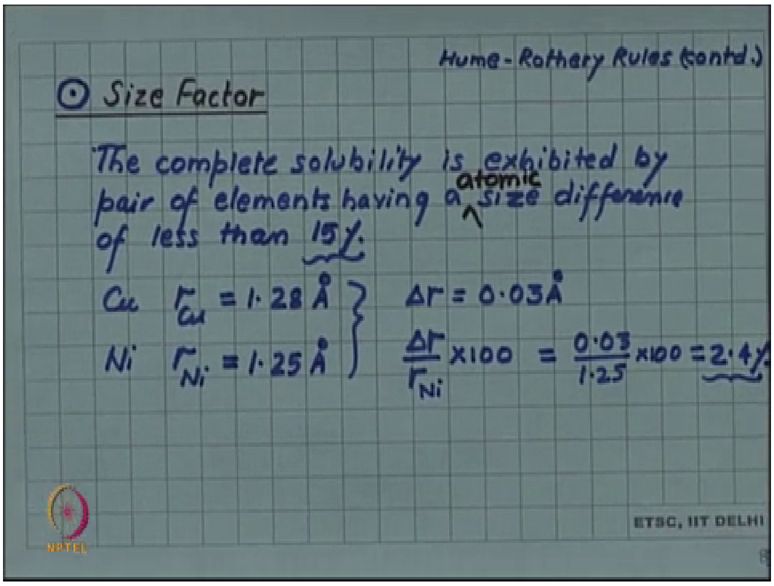
So, we now come to Hume-Rothery rules. These are empirical rule what professor Hume-Rothery did was to look at various substitutional solid solution and various factors related to them and try to correlate them with the solubility of those elements and based on that he found these empirical or experience based or experimental based rules.

So, these are not a strict rules they can be violated, but they do give us a guideline or guidance regarding the solubility limits. So, let us again start with our 2 dimensional cartoon example and we just saw that if we start with pure A, if I start with pure A and it starts substituting B for A so I start getting A plus B and if I substitute all of them I get pure B. So, in terms of composition I can go from 0 percent B to 100 percent B, if this is to happen so we start we were here 0 percent B which is pure A and this is 100 percent B which obviously is pure B.

So, from pure A we are going to pure B if we do this remember if we started with some crystal structure let us say the pure A is cubic close packed. So, on the cubic close packed sites I am replacing B for A one by one. So, the end result the pure B which I will get also has to be CCP. So, if we have complete solid solubility system like copper nickel, the 2 crystal structures have to be the same so the conclusion is crystal structure of solute and solvent in this case anyway distinction also is not immediately obvious because they can be mixed in any proportion. So, crystal structure of the 2 elements should be the same.

We saw that alpha brass does not form complete solid solubility. So, if we look at alpha brass again alpha brass we have copper, copper is CCP, but the other element is zinc which is HCP. So obviously, complete solid solubility is not possible because the structures are not the same so we will say structure factor is not favorable for solid solubility. Otherwise if I start replacing for copper 1 by 1 zinc then finally, I will end up with cubic close packed zinc but the zinc structure in hexagonal closed packed. So, complete solid solubility not possible.

(Refer Slide Time: 25:30)



Hume-Rothery Rules (contd.)

⊙ Size Factor

The complete solubility is exhibited by pair of elements having a atomic size difference of less than 15%.

Cu $r_{Cu} = 1.28\,\text{Å}$

Ni $r_{Ni} = 1.25\,\text{Å}$

$\Delta r = 0.03\,\text{Å}$

$\frac{\Delta r}{r_{Ni}} \times 100 = \frac{0.03}{1.25} \times 100 = 2.4\%$

ETSC, IIT DELHI

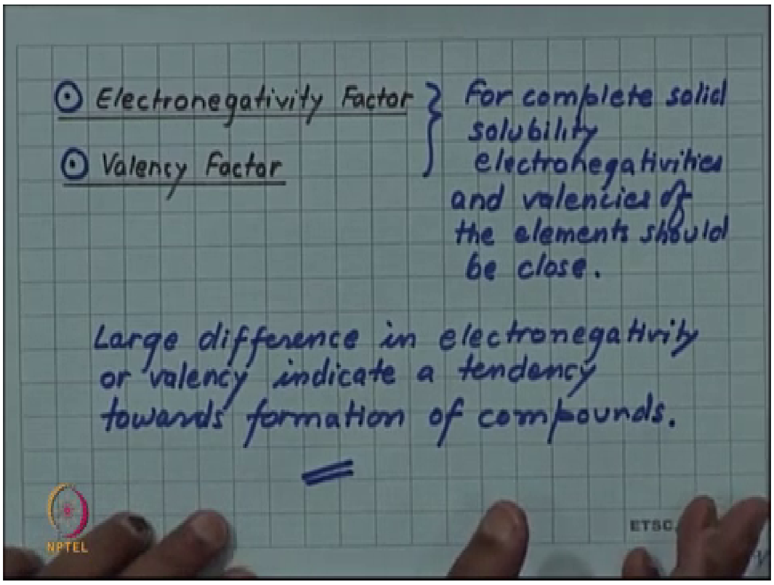
So, we now go to the next factor the size factor. Now structures may be same but it is still a complete solid solubility may not always be possible. So, there is another factor which is the size factor and we have already seen the effect of size in interstitial solid solution. The same effect of size comes here also that when 2 elements are widely different in size they will cause lot of a strain limiting the solubility. So, what Hume-Rothery found by a experimentally studying various systems so he found that complete solid solubility is exhibited by a pair of elements having a size difference well we should say we should call this atomic size difference we are having an atomic size difference of less than 15 percent. So, if the size difference is more than 15 percent it is less likely that they will form a complete solid solubility.

Let us go back to our example of copper and nickel. So, copper the radius of copper atom is 1.28 angstrom and the next element is nickel and the radius of nickel atom is 1.25

angstrom. So, we can see that the size difference delta r in this case is only 0.03 angstrom and if we try to find the percentage size difference this comes out to be about 2.4percent so you can see that 2.4 percent is much less than the 15 percent is specified by Hume-Rothery.

So, we expect that they should form a complete solid solution and in this case it is true also of course, these rules are provisional and it is not necessary that if the size difference is between 15 percent they have to form there are counter examples known, but this is the guideline for this kind of solid solutions.

(Refer Slide Time: 29:09)



- ⊙ Electronegativity Factor
- ⊙ Valency Factor

For complete solid solubility electronegativities and valencies of the elements should be close.

Large difference in electronegativity or valency indicate a tendency towards formation of compounds.

Finally 2 more rules are there and I am putting them together Electro-negativity factor and Valency factor. Again by experience Hume-Rothery found that for complete solid solubility electro-negativity. So let me write down for complete electro-negativity, electro-negativities and valancies of the elements should be close because what he found that if the difference is too large, if the electro-negativity difference or valency difference is too large so there is more likelihood of formation of compound rather than solid solutions.

Large difference in electro-negativity or valency indicate a tendency towards formation of compounds, so with this we complete this Hume-Rothery rules. So, we have now discussed a structure of metals, the close packed elements, the cubic close packed, hexagonal close packed and body centered cubic metals and then we also discussed the voids in those metals and then when the voids are filled we get solutions interstitial solutions and when atoms are substituted we get substitutional solid solution and then in today's class we discussed the difference between complete solid solubility and limited solid solubility and the pertaining Hume-Rothery rules.

So, with this more or less we have discussed the structure of metals and in the next video maybe we will take up the structure of carbon which is an inorganic material carbon and later on we will look at the structure of some non crystalline material.