

**Principles of Physical Metallurgy**  
**Prof. R. N. Ghosh**  
**Department of Metallurgical and Materials Engineering**  
**Indian Institute of Technology, Kharagpur**

**Lecture No. #26**  
**Common Binary Alloys**

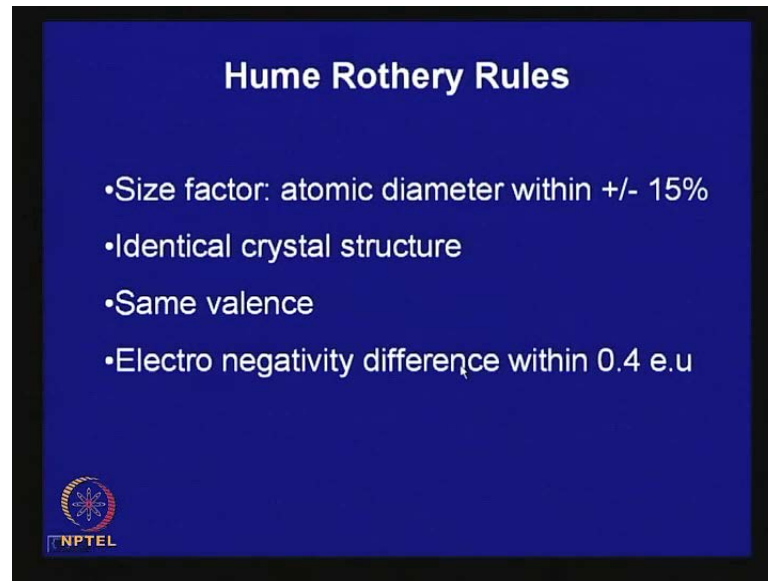
Good morning. Today, we shall talk about few common binary alloys. So far while discussing phase equilibria or phase diagram, we looked at mostly hypothetical metallic systems.

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Now, today first I think we will look at rules governing solubility in solid state. We will look at common isomorphous system, common binary eutectics, and we will see when we look at some of the phase diagrams, there are number of intermediate phases and compounds often we come across, and why do they come and do they follow some specific rules. And we will also in the process, we will learn about few common binary alloys, which are of commercial interest.

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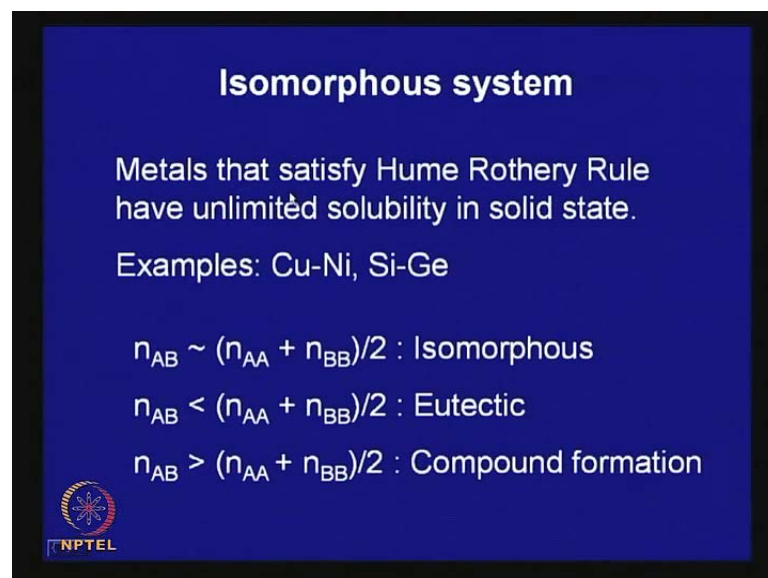
### Hume Rothery Rules

- Size factor: atomic diameter within +/- 15%
- Identical crystal structure
- Same valence
- Electro negativity difference within 0.4 e.u

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Now, the rules that govern the solubility limit is known as Hume Rothery rule. Now, the factors which are listed here; one of the most important factor is size factor. If the atomic diameters of two metals are within plus minus 15 percent, then we find that they have very large solubility. They can have provided few other conditions are made. Like one else, they must have identical crystal structure; they must have same valence. They must have nearly or a close electro negativity value that is within 0.4 and electro static units in that **polling** scale.

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### Isomorphous system

Metals that satisfy Hume Rothery Rule have unlimited solubility in solid state.

Examples: Cu-Ni, Si-Ge

$n_{AB} \sim (n_{AA} + n_{BB})/2$  : Isomorphous

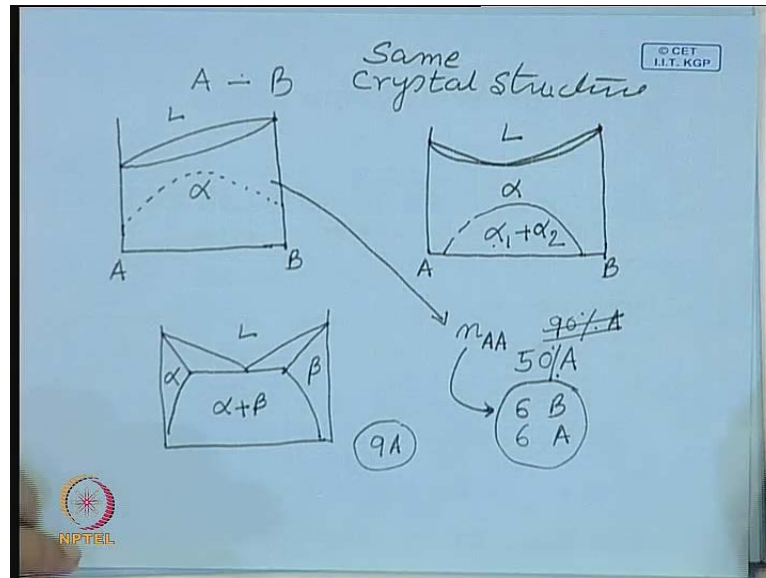
$n_{AB} < (n_{AA} + n_{BB})/2$  : Eutectic

$n_{AB} > (n_{AA} + n_{BB})/2$  : Compound formation

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And and we have seen that metals that satisfy that Hume Rothery rule; they have unlimited solubility in solid state. And some of the examples I think one we looked at is a copper-nickel alloy; another example is silicon-germanium. Now, what happens if here is deviation from non ideality?

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That means, if the size factor say suppose the two metals A and B **A and B**, they have same crystal structure; that is same crystal structure. But same case, where you have the atomic diameter are within plus minus 15 percent; you get this kind of a diagram. This is liquid; this is solid; this is alpha; you have unlimited solubility here. And in this case, the properties also we have seen they will vary like this; somewhere in between you will have the maximum strength. Now, what happens if the size is on slightly different? In that case, it starts we get deviation from ideality and this is like this. Say may be, it choose a minimum here; still it has solubility; say this is liquid and you also can have say this **and this** is alpha.

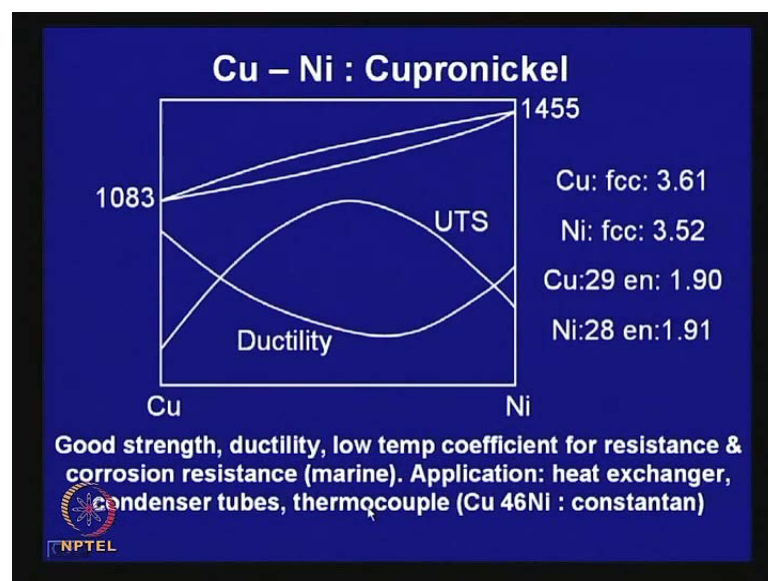
If the size factor differs little more, then **you have** we can have some amount of cluster formation and you may have this kind of visibility gap, alpha and alpha 2 forming. But both here alpha entire stage alpha 1 also has same crystal structure. If alpha 1 is FCC, alpha 2 is also FCC. Now, if this deviation goes on increasing, then what happens? Finally, you will end up with you take eutectic; say this is alpha; this is beta; this is liquid. Now, here what you have? If you look at that nearest neighbor; if it is an isomorphous system, that number of nearest neighbor is AA bond. Number of AA bond

will be equal to say, if the alloy contains say a 90 percent A. Or let us say more; somewhere in between let us say 50 percent A and 50 percent B.

In that case, this AA bond if it is face centered cubic, the coordination number is 12. So, that means each A atom will be surrounded by 6 A atom and 6 B atom and 6 A atom; there is no preferential arrangement. Now, if this kind of clustering forms, then what will happen? What is happened is number of AA bond will increase; that means instead of say 6 A atom, it may have 9 A atom or even more surrounding an A atom. Similarly, each B atom may be 9 or 10 B atom surrounding it. So, that way a cluster forms and ultimately, it leads to a eutectic type of phase diagram and this is (Refer Slide Time: 02:09) what is shown over here. That condition for isomorphous system is that AB type of bond will be equal to the average of number AA plus N BB over 2.

So, this will exactly match with the atom fractions that nearest neighbor; that are number of AB type of bond will be that is given exactly by the atom fraction or the competition of the alloy. Now, when a eutectic forms, then what happens? The AA dot bond as like bonds will be more in number. So, that means AB type of bond will be less than what is expected from the composition. Then you get eutectic type of structure and in other case then we can also have a case, where number of AB bond is more than that given by the composition over here. In that case, there will be tendency to form compound and depending on the deviation extent of deviation, we can have different types of phase diagram. Now, we are look at few examples.

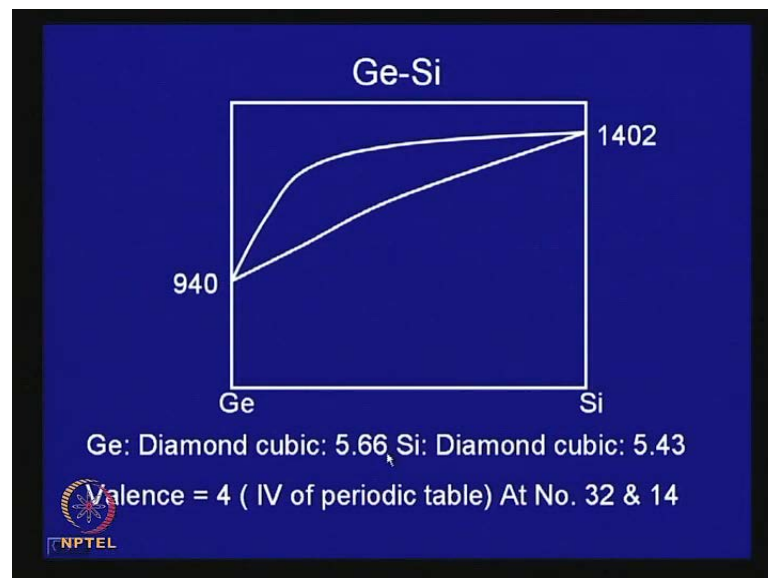
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Now, copper-nickel it forms an isomorphous system, it is soluble in all proportion in both liquid and solid state. And if you look at their crystal structure, both are face centered cubic. This is the atomic lattice parameter; 3.61 Angstrom, 3.52 Angstrom. So, the difference is not much. They are electro negativity; there you look at their atomic number; they are very close. So, therefore electro negativity is also very close. So, therefore they form an isomorphous system. This type of alloy is very common, one of the commonly used alloy. It has good strength, ductility, and in this alloy, this is how the tensile strength will vary.

And whenever tensile strength goes up, you will find the ductility of the material goes down. You will have **some** something like this and some of these common applications which are listed here. This material apart from strength and ductility combination, it has low temperature coefficient for resistance and it has good corrosion resistance. So, therefore it is used for the number of marine applications like heat exchanger, condenser tube and is also used as thermocouple, the copper constantan; that thermo couple that constantan is made up of copper 46 percent nickel.

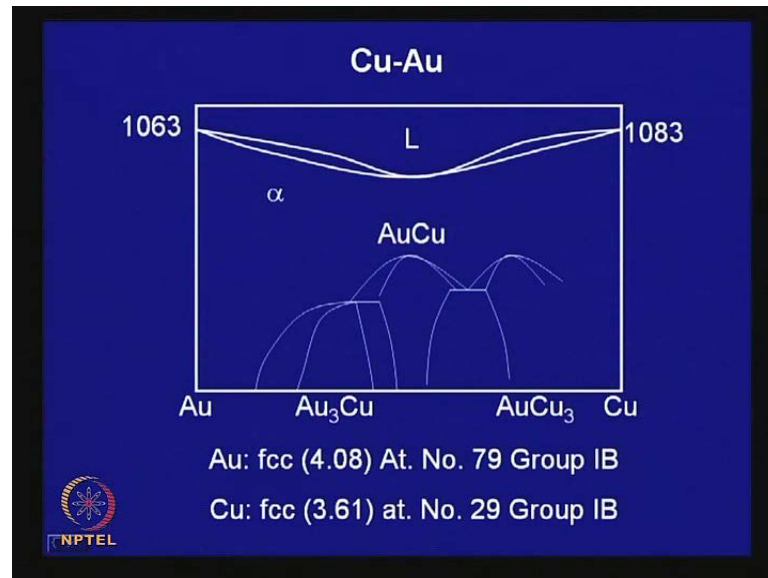
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Now, germanium-silicon also forms isomorphous system. So, these are the melting points; this as diagram is **mind you** is schematic and both germanium and silicon, they have diamond cubic structure. Look at their atomic **this look at their** lattice parameter; this is 5.66 Angstrom. One Angstrom means 10 to the power minus 8 centimeter minus 10 meter. So, diamond cubic structure is **5**.for the silicon, it has 5.43 Angstrom. Both

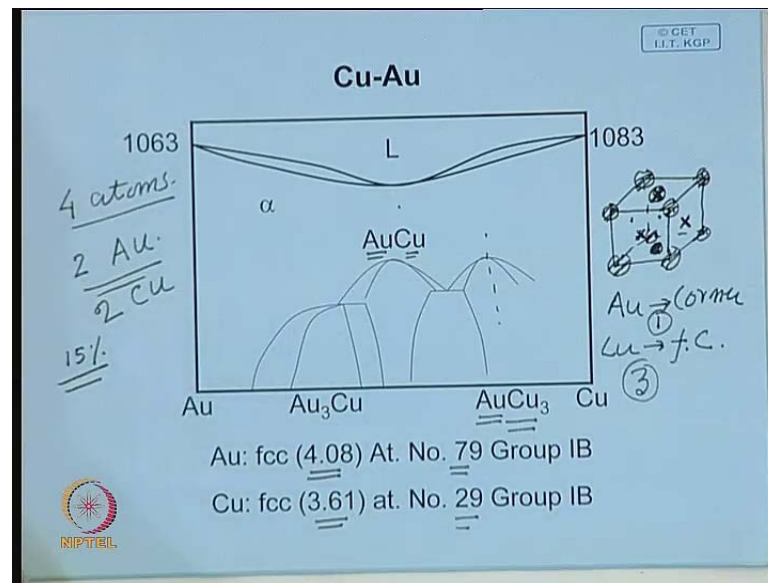
belong to group IV of the periodic table and their atomic numbers are 32, 14. And infact, their electro negativity is also not very much difference. So, that is why you get this kind of an unlimited solubility.

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Now, let us look at another case, where there is a slight deviation from in their size factor like copper-gold system **copper-gold system**. Say, high temperature; it has isomorphous system here. It shows a minimum somewhere in between and down below you will see there are now some changes. You **you** do see, when you go down at lower temperature, where the deviations effect shows up and here particularly look at the central region. So, here some kind of ordered structure formation is taking place; some kind of an ordering say **like atom** unlike atoms like gold-copper. Gold prefers to have more number of copper as its neighbor; say something like this here.

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So, therefore we see that in ordered structure, something develops and all this follows from because there is a deviation from ideality. If you look at their atomic lattice parameter, this is slight large; a little more difference is there. Look at their atomic number. There is a large difference in their atomic number. So, obviously their atomic diameter will be slightly different; I mean not will may not be within that 15 percent limit and here this kind of tendency shows up. Like here, this is the structure; both has face centered cubic structure. So, you have atoms; both have you have atoms at the corner of the cube and each of the face centered **each of the face centered**.

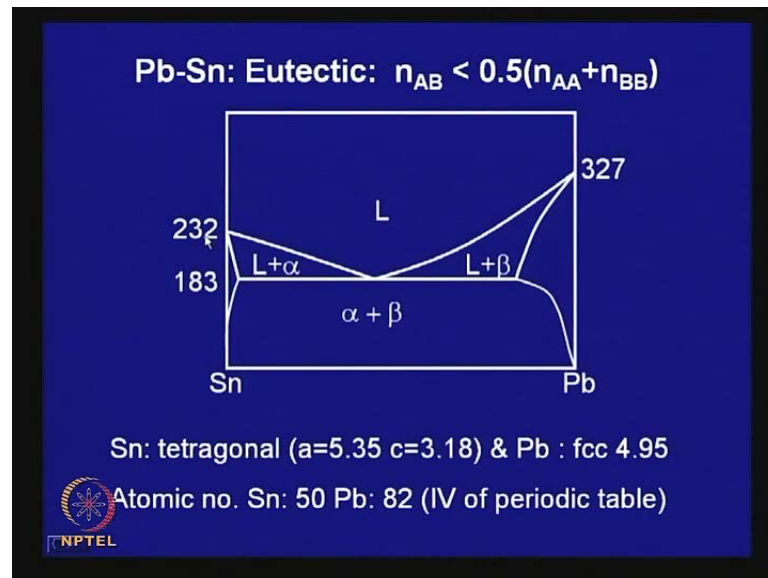
So, there are 6 phases. So, 6 face centered atoms and there are 8 corners atoms. Now, but these atom they do not belong solely to this unit cell and we know that face centered cubic structure. There are four atoms per unit cell and here when this kind of ordering takes place, what happens is gold and copper atom will occupy specific sides. Like here, **one atom will occupy** one of these will occupy each of these corner sides and these sides and that the base also. So, if you count, so there is one corner atom and one face centered atom. So, therefore two atoms is let us say is gold and let us say these **these** sides face centered that four face centered atom is the second atom copper.

So, this also is 2. So, they are in this ratio. Similarly, if you look at here; here also a similar kind of rearrangement takes place. Here, all gold atoms will occupy the corner atoms; corner sides. So, gold goes to corner side and copper atom face center side. So, there are 3 face center and 1 corner side. So, they are in ratio 3 is to 1, which represents



the composition. Likewise, there is a possibility you can have similar ordered structure here also. So, ordering in a way you can say thus this has a tendency to form a compound, where unlike bonds are more than the **normal** normally expected in a random solid solution.

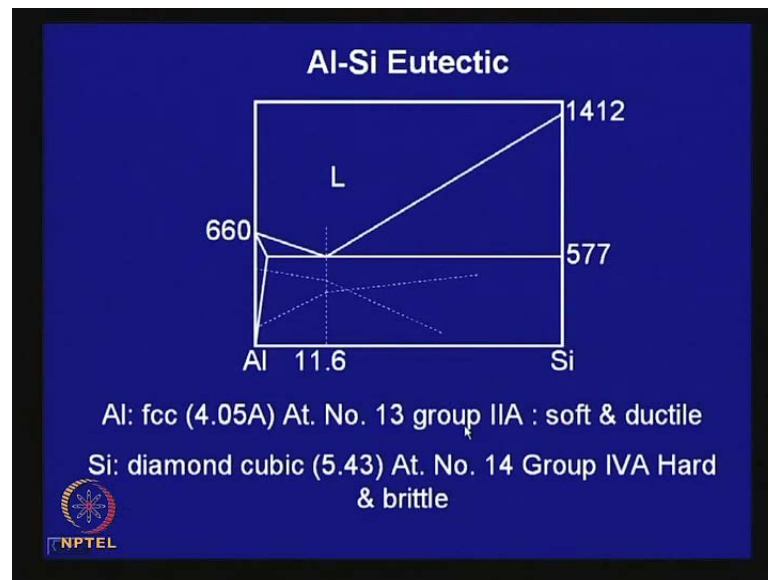
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Next, let us take up a case of a eutectic. So, this is lead-tin, which is a common alloy which is used as **(C)**. Because of its low melting point; because it forms eutectic, each of these metal they are low melting metal. Tin have a melting point 232; lead has 327 degree centigrade as melting point. Eutectic melts at 183 and the **(C)** composition is close to the eutectic composition. And here if you look at a crystal structure, why do you get an eutectic here? One is look at there is a difference in crystal structure. So, the unlimited solubility in solid state is ruled out; tedious tetragonal. This is the lattice parameter a; this is the lattice parameter c. Lead is face centered cubic; lattice parameter is 4.95 Angstrom. Atomic numbers, 50 and 82 and both belong to the same group of periodic table; group IV of the periodic table.



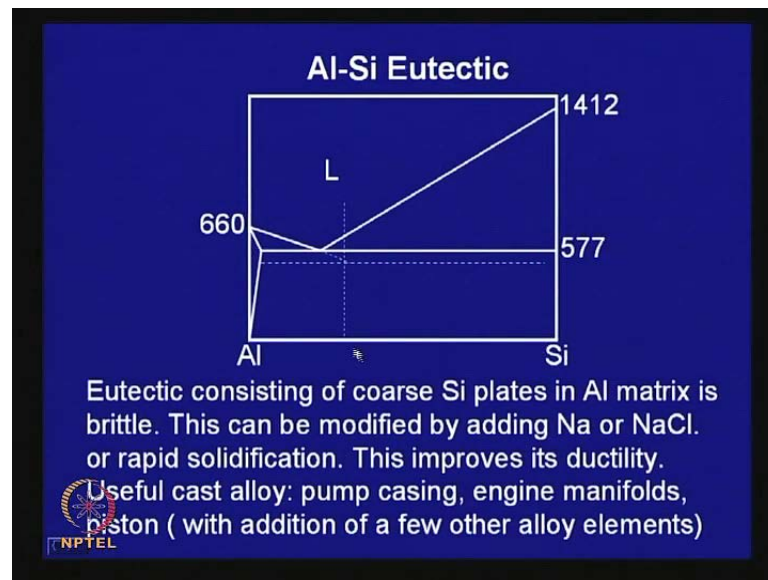
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Another common eutectic which is of commercial importance is aluminium-silicon. Aluminum-silicon is a good cast alloy and many of these components engine components are made of aluminium-silicon eutectic. So, look at this is an I mean not two scale; but in eutectic temperature is correct 577. This is the melting point of silicon; this is the melting point of aluminium. An eutectic composition is around 11 percent silicon; this 11 percent is a weight percent; atomic percent will be little different. Now, look at this crystal structure. They are different; this is face centered cubic.

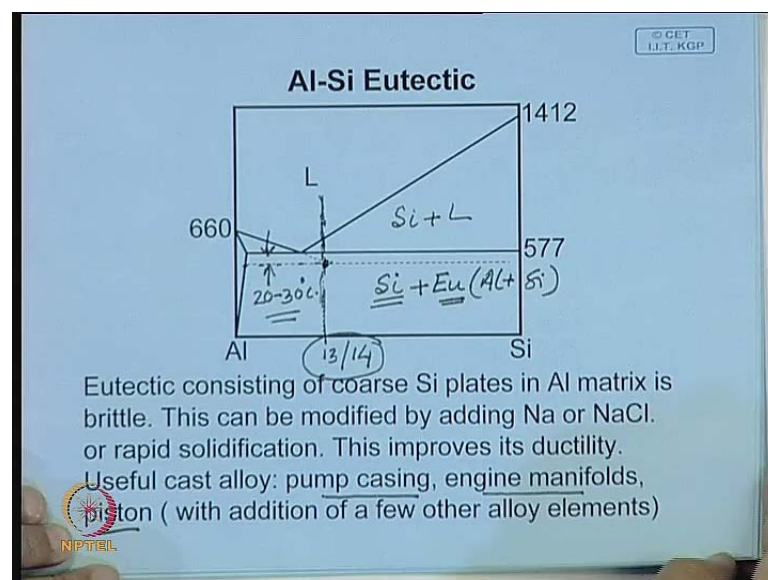
Its atomic number 13; it is a ah its valence is 3. So, I think it should be 3; group III element. Aluminium, this is soft and ductile; whereas, silicon is a cubic. Its lattice parameter is 5.43; atomic number 14; it is a group IV A element; it is hard and brittle. So, in the alloy if you have more amount of silicon, then it becomes brittle and it is not of much practical use. So, therefore if you want a good alloy (( )) good strength as well as ductility, then one may it could be you you modify this structure; such that, you can take in that eutectic can have more than what is predicted from a normal equilibrium diagram.

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And this is where some tricks are played. If you add something additionally or if you cool rapidly, then it is possible to change that structure of the eutectic and this process is called modification. There are two ways modifications can be done. One is by adding something say like sodium or sodium chloride if you add to the melt, then the structure gets modified; say suppose if you look at this alloy composition, which is hyper eutectic.

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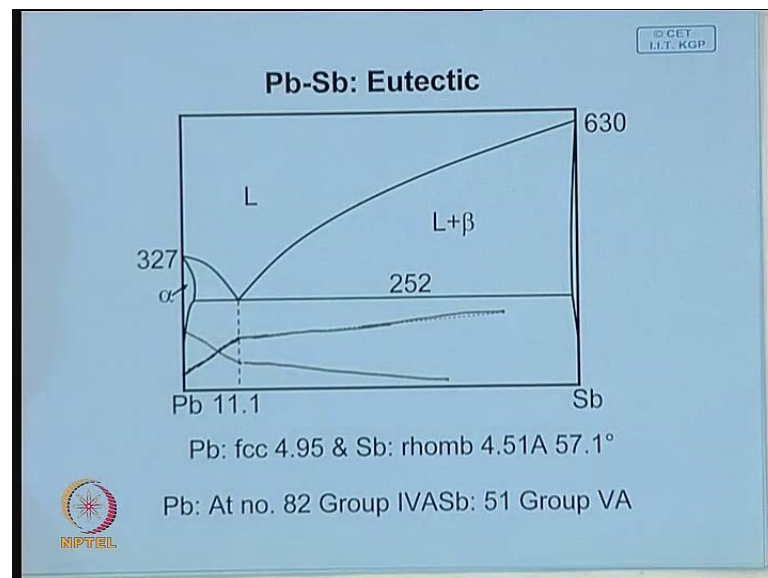


Say here may be around 13 or 14 percent silicon; this composition under equilibrium condition what you expect. It is a silicon plus liquid here. Here you have primary grains

of silicon which is brittle plus you will have eutectic, which is made up of aluminium plus silicon. Now, if you add sodium, then what happens? Its eutectic composition shifts to the right; the temperature also comes down here. So, its fluidity increases. So, it is more easy to cast and this drop may be about 20 to 30 degree centigrade and may drop by 20 to 30 degree centigrade.

And it can have more amount of silicon in the eutectic and silicon in eutectic they are relatively find. So, therefore its properties will be improved; strength will be improved; ductility will not be (( )) and it is a very useful cast alloy. Some of the components, which are made of aluminium-silicon; they are listed here and sometime few other alloying elements are also added to improve its properties. The modification is also possible by relatively faster cooling. If you cool it faster, then also the eutectic ratio eutectic will shift; so also the eutectic temperature comes down.

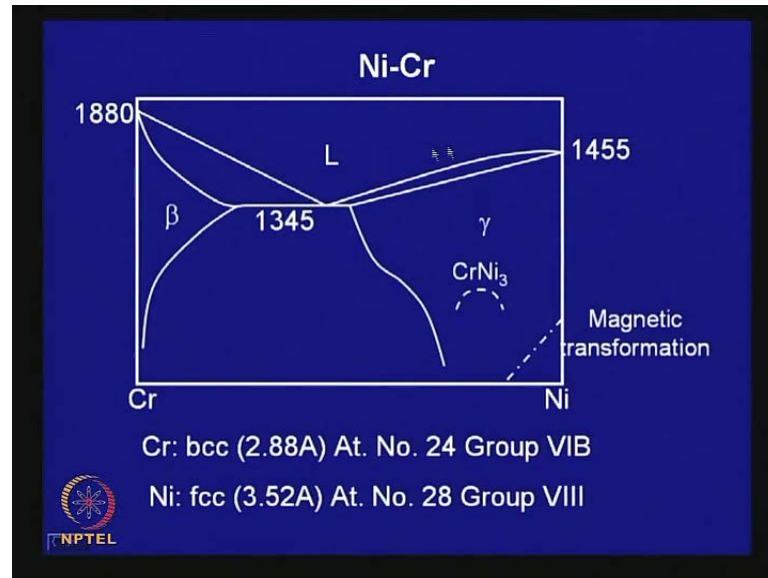
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So, this is another example of a lead-antimony eutectic. This also has the limited solubility and if you look at look at this lead, face centered cubic; antimony is the rhombohedra. And then lead atomic number is 82; antimony is 51 and they belong to different groups of periodic table and here also the properties will vary something like this. In most cases in cases, where the second element you know there are two ways these properties can vary. If say like here if eutectic is very fine, you may find the property improves; strength improves up to this. This part and antimony lead is relatively softer; antimony is brittle. So, therefore this part is strength although in increases, the

rate is not at the same level. Similarly, its ductility will also come down; the ductility say suppose it comes down like this.

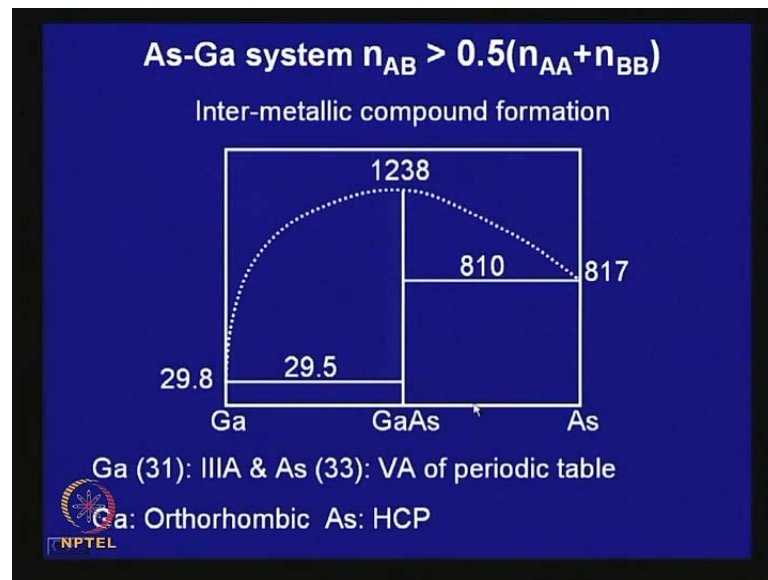
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Nickel-chromium is another good example. It is nichrome heating elements are made up of nickel-chromium around say somewhere 80 percent around this composition is the nichrome and it is a common heating element. Look at their crystal structure. They are different; their atomic numbers they are nearby chromium 24; nickel 28 and nickel is magnetic. So, here you have a Mc curie point. This **this** line represents the magnetic transformation temperature. **Nickel** pure nickel is ferro magnetic. But if you add chromium to it, that curie point comes down and this side, it is no longer magnetic. And infact, this fall... this is the basis alloy based on which super alloy, which are been used as gas turbine alloy have been developed.

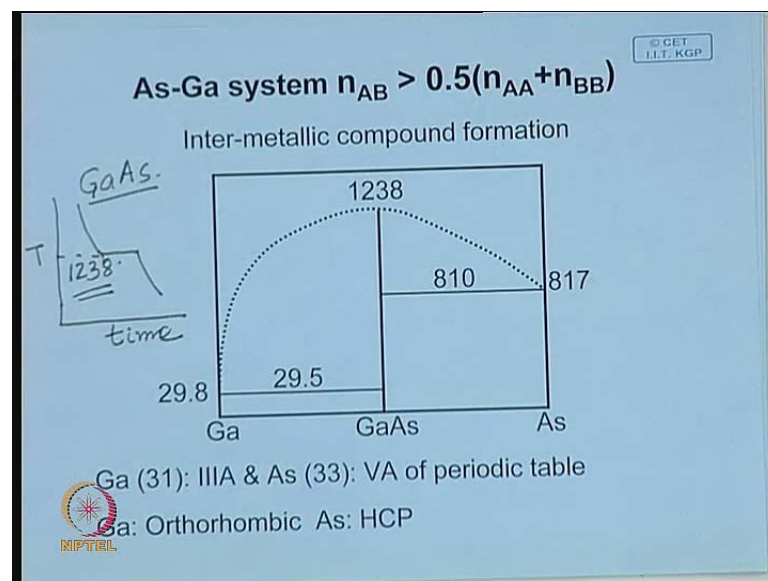
When gas turbine engine came up around the same time as a second world war, the best material that was available was austenitic stainless steel. And later on they found that, if you add that heating elements a little amount of aluminium, then its high temperature strength increases significantly. So, therefore life of this turbine **(( ))** made of out of these types of alloy. They last longer and performance of the engine also is better. So, therefore these form with this actually that large number of super alloy, which have been developed. They are actually based on nickel-chromium that nichrome alloy. The first generation of super alloy is called pneumatic.

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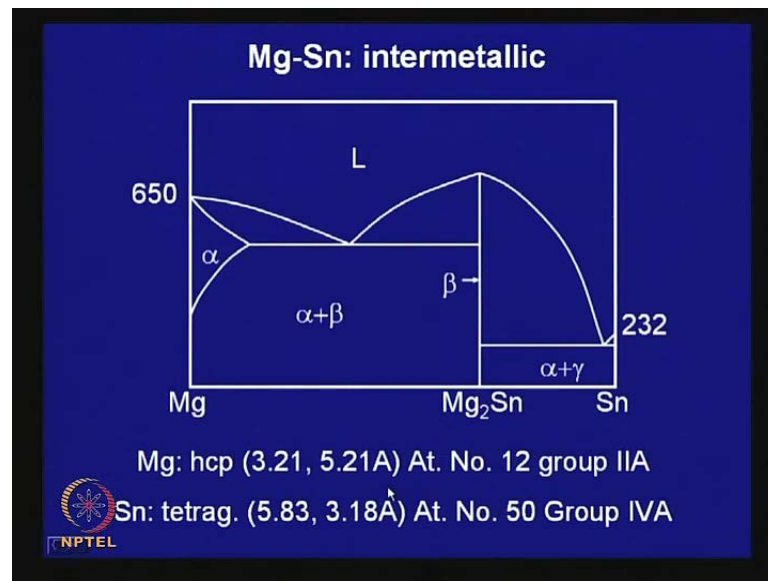
Now, here is an example of **s** case, where you have some intermediate phase forming. This is gallium; this is arsenic. We have gallium-arsenide. Look at their melting points. Gallium melts at around 30 degree centigrade; whereas, arsenic at **18000** around 817 degree centigrade. But look at this gallium-arsenide; melting point increases significantly and its behavior is exactly same as melting. If you **if you** plot it is a cooling curve or solidification curve, **it will be** freezing curve will be exactly same as that of a pure metal.

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Like gallium-arsenide is a pure metal **sorry** not a pure; something like gallium-arsenide is a compound. And if you will plot its cooling curve with time, it will follow and this kind. So, this temperature is 1238. It will appear as if its melting curve behavior is exactly similar to that of pure metal and their (Refer Slide Time: 24:58) crystal structure and which are listed here. Gallium is orthorhombic; arsenic is (( )) hexagonal close packed structure and gallium belongs to group III A; whereas, arsenic belongs to group V A.

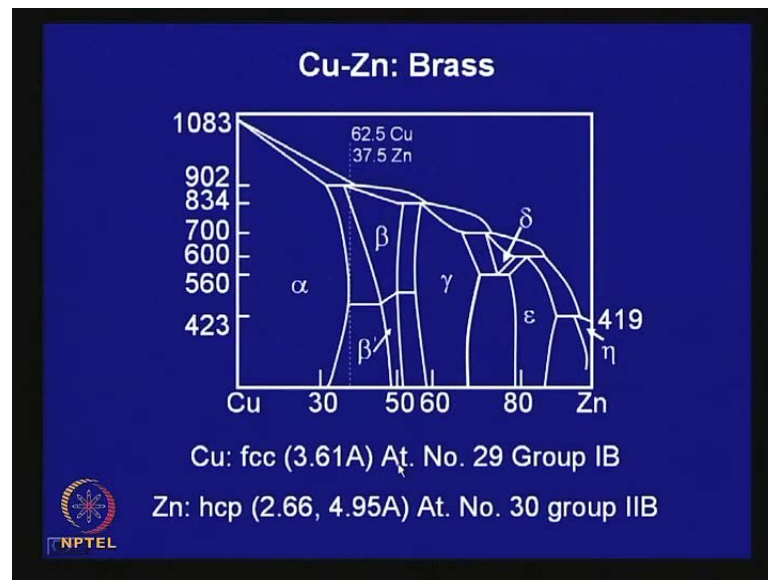
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Now, another example which is given here is magnesium-tin. It also forms the compound and this compound look at this; magnesium, Mg 2 Sn. So, Sn means tin belongs to group IV; its valence is 4. Mg belongs to group II and its valence is 2. So, therefore this compound it is something like a chemical compound. It is very close similar to a chemical compound that forms and this also has a **behavior** congruently melting behavior. So, that means its cooling curve will be exactly similar to that of this pure magnesium or pure tin.



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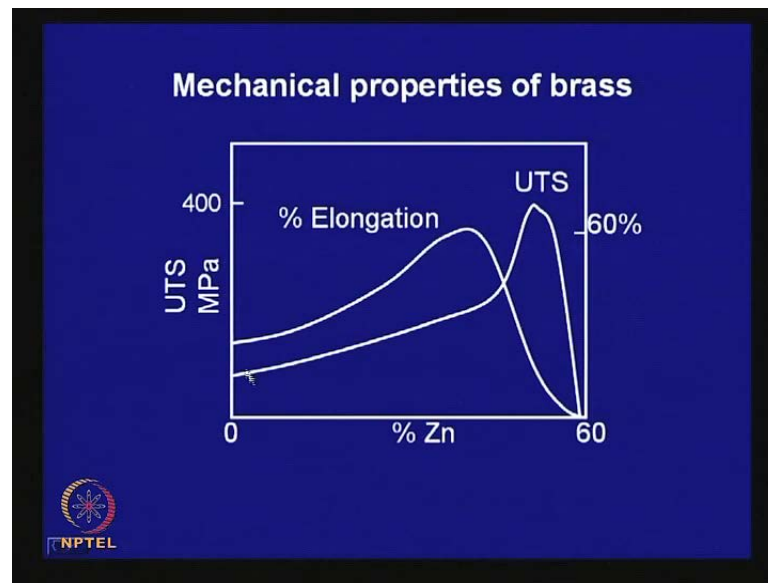


Now, let us look at a very common alloy, brass. This is amongst the first alloys, which have been used by mankind and both have if you alloy copper with zinc is melting point decreases. It will be easier to make and look at this diagram; apparently it looks rather complex. Now, copper it has a face centered cubic crystal structure. This is the lattice parameter 3.61; its atomic number is 29; it belongs to group I B. Zinc, it has hexagonal close packed structure. These are the lattice parameter; this is a; this is c; say atomic number 30; belongs to group II B; its valence is 2. So, what you find here? **you know** Its several intermediate phase like one here is a beta and here there is a beta prime.

So, if you cool below a particular temperature; that mean beta also has a composition somewhere close to around 50 atomic percent zinc. So, there are **so** copper and zinc atoms; they are present in 1 is to 1 ratio and its crystal structure is body centered cubic; alpha is face centered cubic. And when this ordering takes place, one of the atoms will occupy the corner side; another atom will occupy the body centered side. So, that is what ordering is in this particular case. You add more zinc, you get another intermediate phase gamma; you add even more, you get another intermediate phase which is called epsilon and ultimately, the terminals solid solution zinc rich solution, which is eta. So, you have several intermediate phases in between and amongst brass, the common brass which is used; which is known as alpha brass.

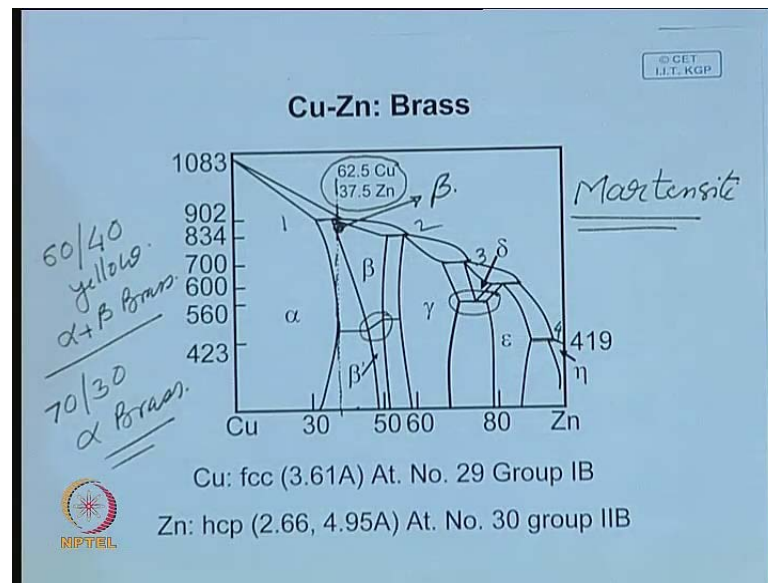


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And here **you know** if you look at the **properties** mechanical properties of brass, as you add zinc, you will find that UTS. It goes an increasing somewhere something like this and somewhere here it becomes maximum and then its drop down. And elongation ductility also increases up to a certain point and then it drops down and you get an optimum property around 30 percent of zinc. So, there the **30 percent** 70 copper 30 zinc is a common alpha brass and it has a several... It is also known as a cartridge brass, which is used for making cartridge **cartridges** and another important cast alloy is a 60/40 brass. 60/40 brass which will be if you look at the phase diagram, 40 percent zinc will be somewhere here.

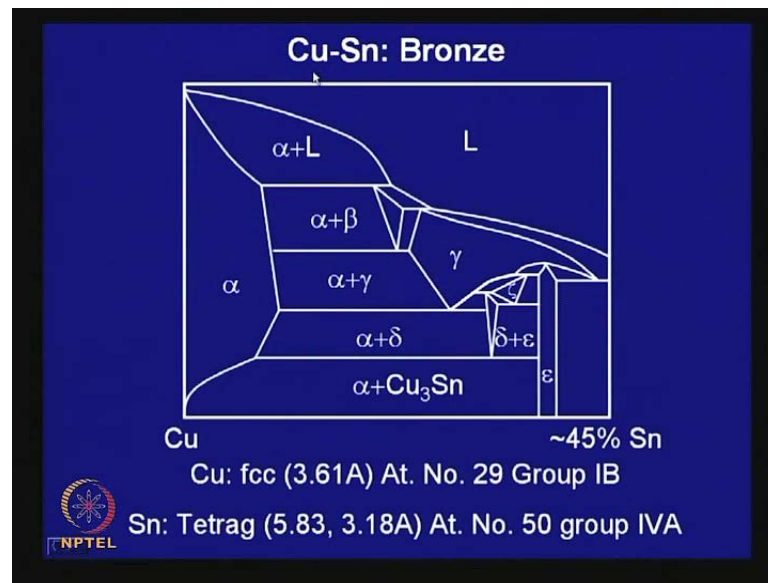
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So, where the structure will be 60/40 brass; it is yellow in color; color is yellow. It is called alpha beta brass and 70/30 brass, it is a single piece; it is called alpha brass. Now, this can be cold work; whereas this since it has 2 phases, it will be difficult to cold work. It can be worked; if you have to work it, you have to heat it to the beta range. So, this phase diagram also tells you not only about the micro structure, **it can** you can infer properties; you can find out the temperature range, where it can be worked. And one interesting alloy which is here which is shown by this line. This alloy **you know** if you heat it, here it is single phase; here it is beta.

But when you cool it slowly, here from some amount of alpha will precipitate out. Here sometime it will be mostly alpha and again beta starts precipitating out. But if you quench it rapidly, you do not allow this precipitate. Then you get a structure, where this high temperature thing is **(( ))** and we will later learn about it. This may not have commercial importance. But this is an alloy, where you have a transformation something when we talked about TTT diagram, time temperature transformation diagram. We talked about a phase called martensite; it forms without diffusion. So, here also you have a similar kind of transformation. If you heat this alloy to this range where it is totally beta, and then quench.

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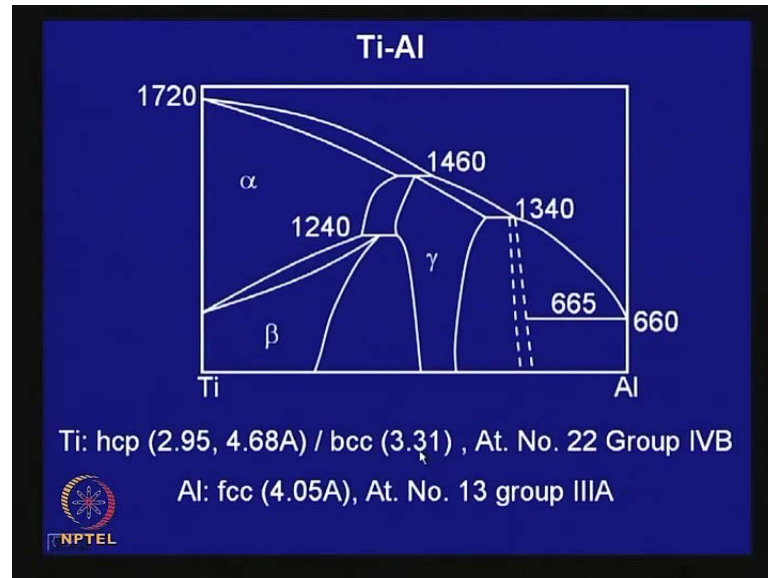


Another very common alloy is bronze; it is a copper-tin alloy. These also have been used in **sages** and the diagram look at it looks quite complicated. These schematically have represented. We have and gone up to the full range; you are plotted only up to 45 percent tin and look at the number of phases which appear and the number of peritectic. Say, if you look at the brass diagram; if you go back to the brass (Refer Slide Time: 30:50) diagram here; if you see that only have different peritectic reactions and one eutectoid reaction. You have 1, 2, 3, 4 peritectic reaction. Usually, you will find in phase diagram; if the two metals the melting point, they are widely different. There is a tendency to form peritectic type of systems and **and** this is an eutectoid system and you have an order disorder transformation here.

In case of this a bronze alloy; if you look at you have a peritectic over here, you have another peritectic here, and then again you have a eutectic here. And you have a eutectoid, you have peritectoid and it has another eutectoid here. So, you have multiple number of eutectoid and peritectic system and you have number of these phases. The primary solid solution is alpha, which is face centered cubic. Then you have beta, which exist only at high temperature; this is which region, where beta existing. Then you also have a gamma phase; this also exists at high temperature; but room temperature usually the most stable phase will be epsilon phase. The tin, if at all is present at room temperature, they will be present as Cu<sub>3</sub>Sn. But this type of precipitation reaction in

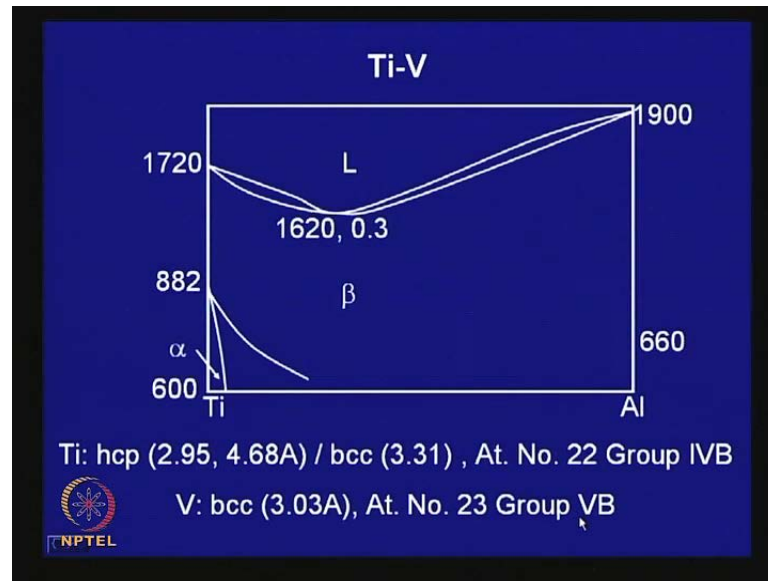
solid state is very slow and usually you here find instead of this, you may also find the delta phase retained at room temperature.

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Now, titanium is of is an alloy I mean which has a which has a great potential particularly for aerospace kind of application. There is lot of work which is going on in titanium and right now its commercial use is limited because of its cost. But it is expected that this cost will come down and titanium shows an allotropic transformation. At room temperature, it is hexagonal; it has a beta structure which is hexagonal which; these are the lattice parameter of their hcp. But, at high temperature it is bcc; so at high temperature, it will be more easier to work than at room temperature. And the intermediate phase also is there; that is the gamma phase and there may be some inter metallic here phase which is forming. And here if you look at this, this belongs to... Titanium belongs to group IV B; whereas, aluminium belongs to group III A.

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And titanium-vanadium is another alloy. I think usually it is customary. If I go back the previous one (Refer Slide Time: 35:36) you change this. High temperature phase is usually beta; the low temperature we call it close packed is alpha. So, you make this change here. This high temperature we will... ofcourse, this is custom which we will follow. It does not matter. I mean what whatever you write; but what it means is a low temperature phase, which is close packed. Usually (( )) represent it as alpha and high temperature, the bcc phase as beta. So and here it is correctly represented.

And if you look at their crystal structure, because crystal structure is different; it cannot have unlimited solubility at all temperatures. So, here that allotropic transformation takes place; this portion is beta; this is the terminal solid solution portion alpha. So, vanadium you can say it stabilizes beta at lower temperature. If you want to bring down the hot working temperature, you may have to add an element like vanadium. There are many similar other elements also, which will stabilize that beta phase and this is the typical diagram of a titanium-vanadium alloy.

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**Intermediate phases**

1. Electrochemical compound:  
 $Mg_2(Pb, Sn, Ge, Si)$   
 $Mg_3(Bi, Sb, As)_2$
2. Size factor compound:  $Fe_3C$
3. Electron compound:  $CuZn$ ,  
 $Cu_9Al_4$ ,  $CuZn_3$

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And infact, you can go on like this; there is no end to it and this hand books give you the phase diagram. Metal hand books gives you the phase diagram of different metals and infact, there are now computer data bases like FACTSAGE, you can go to their site.

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Binary phase Diagram

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There are thermodynamic database in many cases and it gives you. **you know** if you log on to their site, you can get **any phase diagram** any binary phase diagram; the list of binary phase diagram, you can get from this and this thermodynamic database. This is a thermodynamic database and wherever these are experimental data not available, it will

refer to thermodynamic databases and construct the phase diagram. (Refer Slide Time: 38:23) Now, what we have seen now that when you have a real system, you do get several **you know** the intermediate phases and these intermediate phases, they have some specific crystal structures also. Now, let us look at what are these intermediate phases little more critically.

(Refer Slide Time: 39:43)

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### Intermediate phases

1. Electrochemical compound:  
 $Mg_2(Pb, Sn, Ge, Si)$   
 $Mg_3(Bi, Sb, As)_2$
2. Size factor compound:  $Fe_3C$
3. Electron compound:  $CuZn$ ,  
 $Cu_9Al_4$ ,  $CuZn_3$

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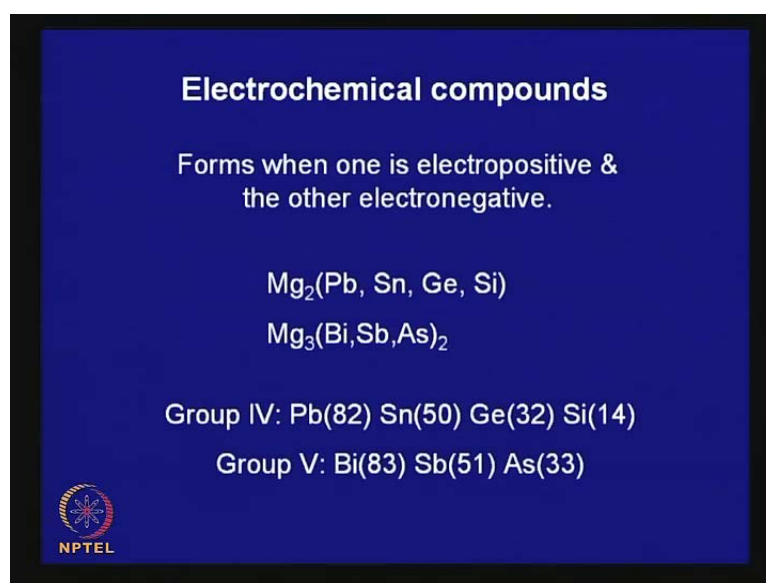
That intermediate phases can we put in to 3 groups. One is an electro chemical compound like a chemical compound formation it takes place; that is like whenever they **they** belong to different groups in the periodic table, then there it may be a tendency. If they are further apart, there may be tendency to form a compound like magnesium here. Magnesium belongs to group II; whereas these elements lead, tin, germanium, silicon they are group IV and they form a compound. And this is **you know** it is in proportion to their valence;  $Mg_2Si$  or  $Mg_2Pb$  it is like a chemical compound.

Similarly, magnesium arsenide  $Mg_3As_2$ . Arsenic belongs to group V; so its valence is 3; so it forms  $Mg_3As_2$ . Similarly, bismuth, antimony can also form a similar compound. And we also talked about a solid solution, where the solute element goes to the interstitial sites like carbon and this also is depends on the size factor. When there is a large difference say something like say 40 percent or so large difference in their atomic sizes, that means carbon atom is so small; that it can be accommodated within the interstitial sites of iron lattice. In that case, there is a possibility that compounds may form and like Cementite, which is  $Fe_3C$ .



This is called size factor compound. This is not necessarily guided by their valence. So, therefore their derive a different names, size factor compound and likewise, you have another type of intermediate phases which are called electron compound; copper zinc, copper aluminium alloy Cu<sub>9</sub>Al<sub>4</sub> or Cu<sub>3</sub>Zn. So, look at **you know** although we have been they **they** do not come in that order of that valence; there is not **(( ))**. So, this is not necessarily we cannot say that this is an electro chemical bond that is forming. So, this belongs to yet another class of intermediate phase.

(Refer Slide Time: 42:27)




**Electrochemical compounds**

Forms when one is electropositive & the other electronegative.

Mg<sub>2</sub>(Pb, Sn, Ge, Si)  
Mg<sub>3</sub>(Bi, Sb, As)<sub>2</sub>

Group IV: Pb(82) Sn(50) Ge(32) Si(14)  
Group V: Bi(83) Sb(51) As(33)

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And now these look at this electro chemical compound. It forms, when one is electro positive and the other is electro negative and we get these examples that Mg<sub>2</sub> any of these; similarly, Mg<sub>3</sub> and any of these belonging to group V elements. So and these are listed; these are the atomic number and their group are listed. Now, if you go if these atoms are smaller, we have seen that bond formation; bonds are stronger, when this atom size decreases. In that case, atom can come closer. Therefore, this bond Mg<sub>2</sub>Si; this bond will be much stronger than that in Mg<sub>2</sub>Pb. So, therefore what we expect? The stronger bond, higher is the melting point and which is shown here.

(Refer Slide Time: 43:20)

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### Electrochemical compounds

Forms when one is electropositive & the other electronegative.

$Mg_2(Pb, Sn, Ge, Si)$   
 $Mg_3(Bi, Sb, As)_2$

Group IV: Pb(82) Sn(50) Ge(32) Si(14)  
Group V: Bi(83) Sb(51) As(33)

Handwritten notes:  
 $Mg_2Pb$   $\xrightarrow{550^\circ}$   
 $Mg_2Sn$   $\xrightarrow{778}$   
 $Mg_2Si$   $\xrightarrow{1085}$

If you look at their melting point, this increases as you go up the group; that is silicon  $Mg_2Si$  has the highest melting point; but  $Mg_2Pb$  has the lowest melting point.

(Refer Slide Time: 43:42)

### Size factor compounds

$0.41 < (r_{\text{interstitial}} / r_{\text{metal}}) < 0.59$

Smaller atom can be accommodated within the interstitial gaps:  $MX$  or  $M_2X$  :examples – carbides & nitrides of Ti, Zr, Hf, V, Nb, Ta

$(r_{\text{interstitial}} / r_{\text{metal}}) > 0.59$

More lattice distortion resulting more complex crystal structure: example  $Fe_3C$

Now, size factor compound is actually formation is primarily guided by the atomic sizes.

(Refer Slide Time: 43:57)

The slide is titled "Size factor compounds" and contains the following text:

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**Size factor compounds**

$0.41 < (r_{\text{interstitial}} / r_{\text{metal}}) < 0.59$

NaCl. Smaller atom can be accommodated within the interstitial gaps:  $\text{MX}$  or  $\text{M}_2\text{X}$  :examples – carbides & nitrides of Ti, Zr, Hf, V, Nb, Ta

$(r_{\text{interstitial}} / r_{\text{metal}}) > 0.59$

More lattice distortion resulting more complex crystal structure: example  $\text{Fe}_3\text{C}$

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And here what is important is the ratio of the atomic diameter or atomic radius like radius of this interstitial atom, radius of the metal atom. If this ratio is between 0.41 to this, you have the tendency to form a compound. If it is even I mean this ratio is less than this, then it is present as a solid solution. Its crystal structure is the crystal structure of the period metal. But if it is in this range, then there is a tendency to form a compound and this compound has interesting crystal combination either  $\text{MX}$ ; M is metal and X is the interstitial element in to X. So, like this and some examples are carbides and nitrides of titanium carbide, zirconium carbide, hafnium carbide or hafnium nitride, vanadium nitride, vanadium carbide. And these are some of these examples, where this type of the structure founds and here the crystal structure is little simple.

It is appears **you know** you may find the crystal structure will be very much similar to the crystal structure that you get in sodium chloride. So, in case of  $\text{MX}$  say one will be occupying that means sodium position; another will occupy the chlorine position. So, this type of structure is rather simple. But with nitrides, the structure nitrides are simpler than carbides and here particularly... But if you look at cementite; here if you look at their atomic diameter or atomic radius, this is greater than this. So, therefore in this particular case, there is more lattice distortion; that means carbon atom is larger than the nitrogen atom. So, when carbon goes in to iron lattice, it produces a larger distortion; then it results in a more complex crystal structure. (No audio from 46:16 to 46:26)

(Refer Slide Time: 46:29)

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**Laves phase:  $AB_2$**

Forms when atomic size difference is about 20-30%.  
Each A atom has 12 B & 4 A atoms as its neighbor &  
each B atom has 6 A & 6 B atoms as its neighbor.  
Average co-ordination number is 13.33 (greater than  
that of a close packed structure). (12)

$AB_2$ .

Crystal structure:  $MgCu_2$  (cubic)  
 $MgNi_2$  (hexagonal)


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Another type of intermediate phase you often talk about; it forms is called laves phase. This forms when also this is also we can say, size factor compound. This forms when the atomic size difference is around 20 to 30 percent and it has an interesting structure say  $AB_2$  type of structure, where **you know** each A atom has... If you look at this, each A atom has 12 B as its neighbor and 4 A atom as its neighbor and each B atom has 6 A and 6 B atom as its neighbor. And therefore, average coordination number; in that case, each A atom has 16 neighbor; each B atom has 12 number. So, average coordination number is 13.33, which is greater than that of a close packed structure.

In the close packed structure like face centered cubic are hexagonal, the maximum coordination number that you can have is 12 and here it is possible because you have atoms of two different diameter. So, therefore the coordination number here can be... I mean it is possible in such cases; coordination number to be greater than 12. And then common crystal structures which has listed here is one is the Mg Cu 2 type of group; that is here also you can say this is an  $AB_2$  type of structure, laves phase. And this is based on a cubic lattice; whereas this is based on a hexagonal lattice. Mg Ni 2, this is another group which is based on a hexagonal lattice.

(Refer Slide Time: 48:39)

$\beta$ brass ( $e/a = 3/2$ )	$\gamma$ brass ( $e/a = 21/13$ )	$\epsilon$ brass ( $e/a = 7/4$ )
CuZn	Cu <sub>5</sub> Zn <sub>8</sub>	CuZn <sub>3</sub>
Cu <sub>3</sub> Al	Cu <sub>9</sub> Al <sub>4</sub>	Cu <sub>3</sub> Sn
Cu <sub>5</sub> Sn	Cu <sub>31</sub> Sn <sub>8</sub>	Cu <sub>3</sub> Si
NiAl	Fe <sub>5</sub> Zn <sub>21</sub>	Ag <sub>5</sub> Al <sub>3</sub>



Now apart from this, we also talked about electron compound. What are they? And this denote **these** they **they** do not follow that rule of that valence like Cu Zn. **You know** usually, this has the valence 1; zinc has valence 2 and this; but they have a... and what people have found and what has been found out? These types of compounds form at particular ratios of electron to atom ratio and which you can possible to calculate; say suppose you consider copper and zinc.


(Refer Slide Time: 49:24)

Electron compounds

Cu Zn  
1 2  $e=3$   $a=2$   $e/a = \frac{3}{2}$

CuZn BCC  $\beta$  Brass.

NiAl  $e/a = \frac{3}{2}$

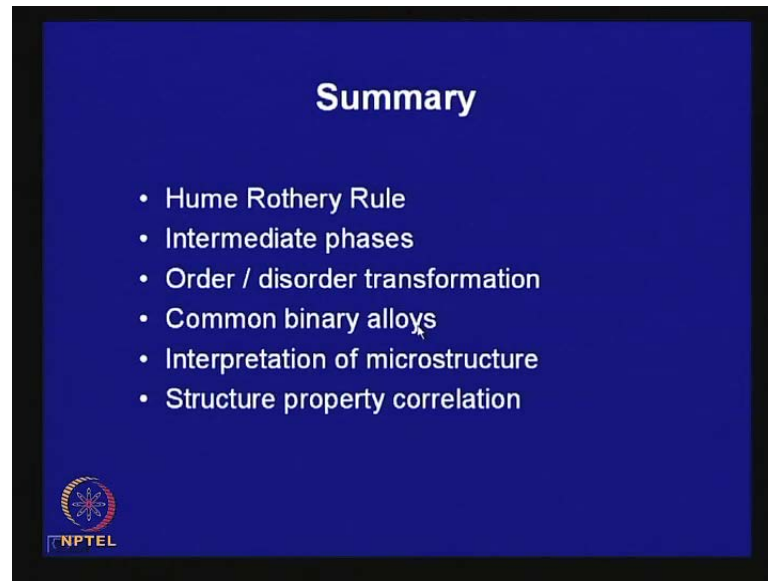


Now, zinc can give 2 electron; copper can give 1 electron. So, total number of electron is 3. Number of electron is 3 and number of atom is 2; so the ratio here e by a ratio is 3 over 2. So, it has been found in several cases wherever this kind of relationship is I mean this kind of electron to atom ratio is attained, you get a crystal structure which is very similar to copper-zinc crystal structure, which is bcc **bcc** crystal structure or we can say this is called beta brass. Structure is same as beta brass and there are examples (Refer Slide Time: 48:39) several examples which are given here. Cu Zn, Cu 3 Al here that valence of aluminium is 3; this is 3 plus 1; you have 4; 3 plus 1; 3 copper atom; so 3 electron and 1.

So, 4 atom and you have 3 plus 3 6; 6 electrons; so 6 by 4; it comes out to be 3 by 2. Look up this case; you can do the similar calculation; you can check here. Here also, the electron to atom ratio will be 3 by 2. Now, when you where you have compound formation like this with transition element like nickel-aluminium. Here when you calculate e by a ratio, you assume that transition elements the valence is 0. So, in that case you have 3 electrons; this is 0; but this gives 3 electron. So, total electron is 3 and number of atom is 2. So, this is 3 by 2. In the same way, (Refer Slide Time: 48:39) you find that gamma brass type of structure **gamma brass type of structure**. Gamma brass is **C** 5 Zn 8.

If you calculate electron to atom ratio, it will come out to be 21 over 13 and you get similar ratio in several other cases. They all belong to the class called gamma brass type of structure and this you get in a particular electron to atom ratio. Likewise, you have another called epsilon brass type of structure; this is e by a ratio is 7 by **3**. Some of these examples, which are given over here and here also, when you calculate iron is a **an iron** **is an** transition elements, its valence will be taken as 0. So, when you calculate this, this is zinc is 21; valence is 21 as number of atom is 21 and each zinc can give you 2 electrons. So, you have 42 electrons and total number of atom is 21 plus 5 26. Therefore, the ratio comes out to be 42 by 26, which is same as 21 to 13.

(Refer Slide Time: 53:09)



So, therefore whatever we have seen today is we looked at some common binary alloys, and we also looked at the rules that govern the solid solubility limit, we talked about Hume Rothery rule. We have seen that when we looked at several phase diagrams, in many cases number of intermediate phase formation takes place, we looked at their structures. We also talked about order disorder transformation, and we looked at few common commercial binary alloys. We also and these alloys some cases we looked at the interpretation of micro structure, and structure property correlation. So, with these we finish this topic, and next class we will begin a new chapter. **Thank you very much.**