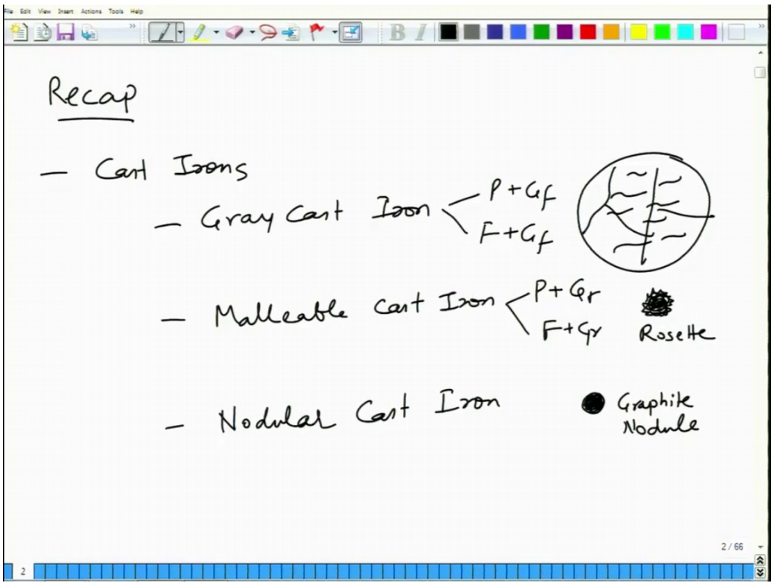
Phase Equilibria in Materials (Nature and Properties of Materials-II)
Prof. Ashish Garg
Department of Materials and Metallurgical Engineering
Indian Institute of Technology, Kanpur

Lecture - 30
Phase Diagrams for non-Ferrous Alloys

So, welcome to lecture number 30 of Phase Equilibria. So, we will just continue with the last part of Phase Diagrams of Alloys and make some common metals and alloys, before we get into some more aspects of phase diagrams of equilibria.

(Refer Slide Time: 00:30)



Recap

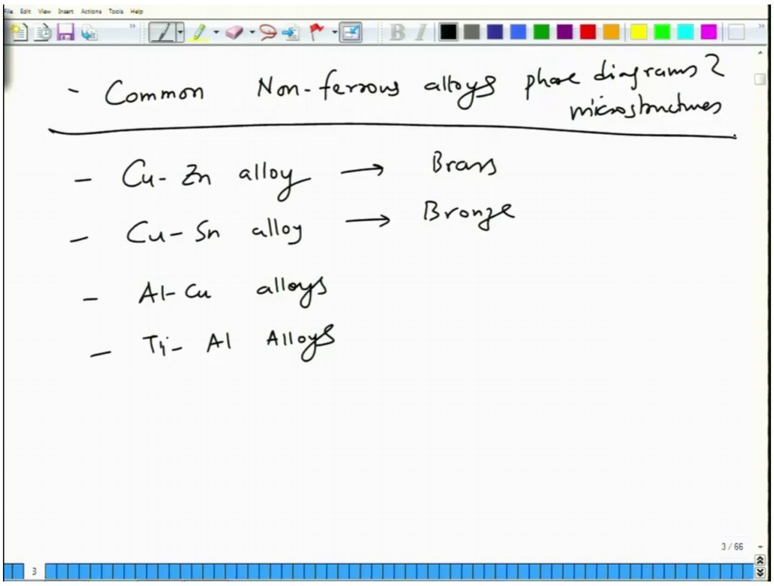
- Cast Irons
  - Gray Cast Iron < P+Gf / F+Gf
  - Malleable Cast Iron < P+Gr / F+Gr — Rosette
  - Nodular Cast Iron — Graphite Nodule

So, the first thing we do will do is to just recap. So, in the last lecture we discussed about cast irons. So, we discussed about gray cast iron, in which you can have pearlite or graphite flakes or ferrite and graphite flakes. These graphite flakes form as a result of higher carbon higher silicon content in gray cast iron which provides also high fluidity.

So, this is so, graphite flakes are present in this sort of flaky form, and they are present in this ferritic pearlitic matrix. The problem with these flakes is that they have sharp ends, as a result they reduce the ductility and tensile strength of the gray cast iron. And then second form of cast iron that we studied was malleable cast iron; which is derived from white cast iron is just that it is cooled slowly or in a moderate fashion. So, again you can have pearlite plus graphite rosettes or ferrite plus graphite rosettes.

So, instead of flakes you will have irregular nodules of graphite in the matrix of pearlite or ferrilite. They had better machine ability better strength has come to cast iron, and then we looked at nodular cast iron, which have some amount of calcium magnesium or cerium in there to improve the, to improve the properties and what they do is that basically they make the; so, in this the graphite is present in this sort of a regular rosettes. And here graphite is present in the form of nearly a nodule. So, this is graphite nodule and this is a rosette. So, they say basically irregular sort of. So, what we will do in this case?

(Refer Slide Time: 02:28)

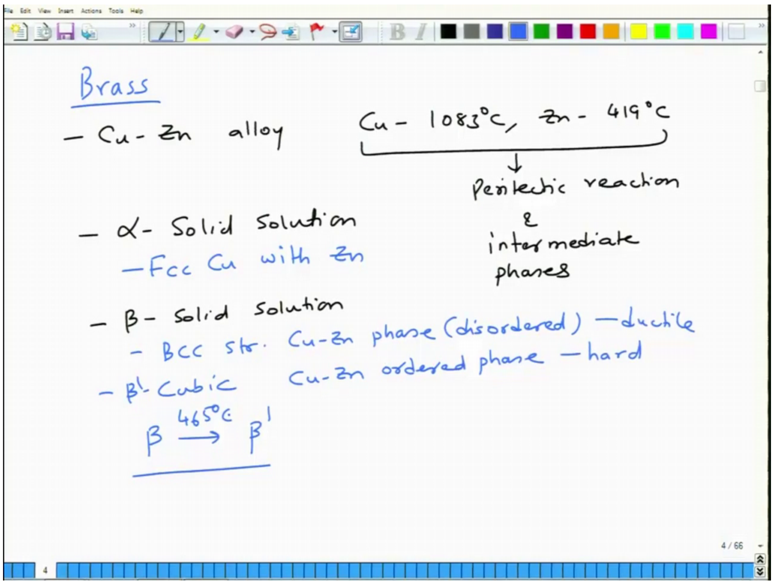


- Common Non-ferrous alloys phase diagrams & microstructures
- Cu-Zn alloy → Brass
- Cu-Sn alloy → Bronze
- Al-Cu alloys
- Ti-Al Alloys

In this lecture is that we will look at some common non ferrous alloys. And we will mainly look at copper zinc alloys; which is called as brass. We look at copper tin alloys which is called as bronze. So, depending upon composition you can have variety of bronzes will not get into types of bronzes. We will just look at the phase diagram and some of the reactions in that. And then you have then we have aluminum copper alloys.

So, phase diagram of volume copper alloys and then we will look at. So, basically we are looking at the phase diagrams and micro structures. And then we will look at some T i Al alloys. So, these are the 4 systems that we will look at from the perspective of non ferrous alloys. And these are all engineering alloys very useful alloys.

(Refer Slide Time: 03:40)



Brass

– Cu - Zn alloy

Cu – 1083°C, Zn – 419°C

$\downarrow$

Peritectic reaction
&
intermediate
phases

– α- Solid Solution
  – Fcc Cu with Zn

– β- Solid Solution
  – BCC str. Cu-Zn phase (disordered) – ductile

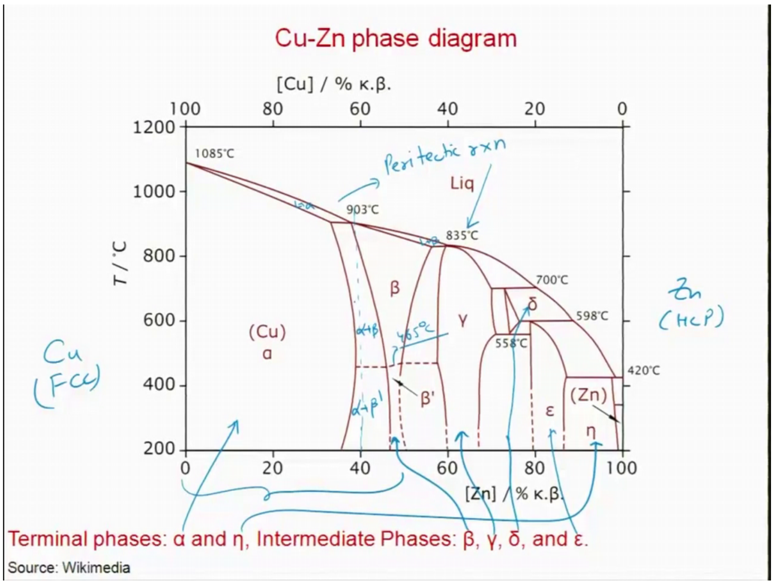
– β'- Cubic   Cu-Zn ordered phase – hard

$\beta \xrightarrow{465^\circ C} \beta'$

So, let us begin with brass, brass is basically you can say it is a copper zinc alloy. And here copper has a melting point of 1083-degree centigrade zinc has a melting point of 419 degree centigrade. As a result of large difference in the melting point the system has lot of peritectic reactions. So, as a result the phase diagram shows significant amount of peritectic reactions, and intermediate phases due to presence of white difference in the melting points. And they have different structures as well, copper as FCC zinc is HCP. So, as a result they have different crystal structure as well.

So, there are basically 3 compounds. First is first phase is the alpha solid solution; which is essentially you can say it is a FCC copper with some zinc, and then you have beta phase; which is essentially you can say BCC structured, Cu-Zn phase and disordered. Or it could be just Cu-Zn ordered phase, which is cubic ok. So, basically this there is a transition that happens in beta 2 beta prime, beta phase is a ductile phase, this beta prime phase which is cubic is the hard phase. So, beta 2 beta prime transition happens at 465 degree centigrade, when it undergoes a order disorder transformation. So, let us look at the phase diagram of brass first.

(Refer Slide Time: 05:46)



Terminal phases: α and η, Intermediate Phases: β, γ, δ, and ε.

Source: Wikimedia

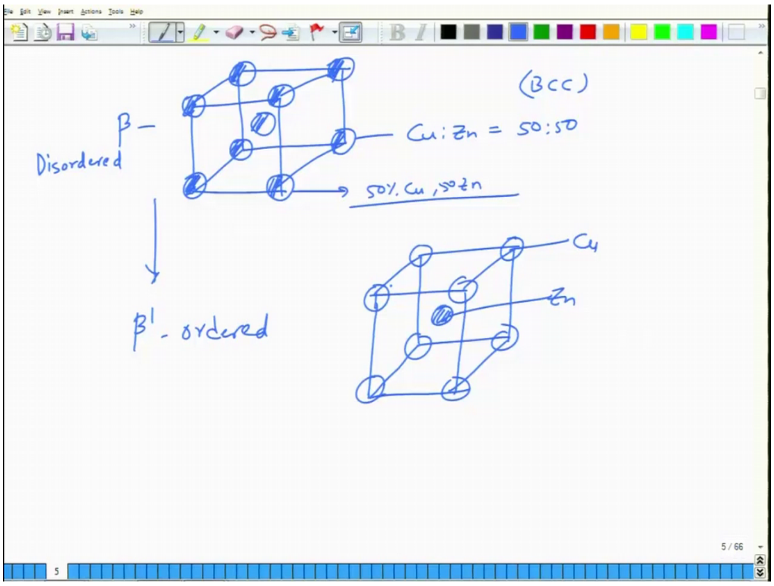
So, this is the phase diagram of graphs that you can have a look at. So, you have on the y axis melting point. So, 1080 roughly 10,83 25 degree centigrade is the melting point of copper 420 degree centigrade is the melting point of zinc. And there are a lot of phases, there are terminal phases alpha and eta terminal phases means terminal solid solutions. So, this is alpha, and the terminal another terminal phase is this eta which is zinc rich phase. Terminal solid solution means zinc rich or copper rich phase, and then we have intermediate phase phases. So, we have this beta here, and we have gamma phase field which is here, and then we have delta phase filled which is somewhere here, ok. And then we have eta phase which is here.

So, the quite a few phases in this phase diagram, because of sharp differences in melting point in a structure. So, we know that copper is FCC, and zinc on this side is HCP, and they have huge difference in the melting point; although, their atomic sizes may not be very different they have very closed to each other in periodic table. There is a peritectic reaction at 903 degree centigrade for zinc. So, this is at about slightly more than 40 percent of zinc. And this is first peritectic reaction that happens in brass.

And then so, it leads to formation of so, you have liquid plus alpha, this liquid plus alpha leads to formation of beta phase. Then you have another peritectic reaction at 835; where liquid plus beta result in the formation of gamma phase, and then you have another peritectic reaction, you have another reaction at 700 degree centigrade; which leads to formation of gamma phase, and then you have another reaction that leads to formation of eta phase

So, you have, you have lot of these phases which are present in this phase diagram, and sequence of sequential peritectic reactions in this phase diagram. The usefulness of copper zinc alloys is basically in compositions up to about 40 percent of copper. Beyond that copper zinc alloys are not very useful. But up to about 40 percent of copper, copper zinc alloys have high engine lot of engineering applications. So, let me for instance so, here for example, there is a transformation from beta to beta prime. This is at about 465 degree centigrade. And this beta phase of copper transforms to beta prime phase and alpha beta alloy of copper contain this beta prime phase, and this beta prime phase is a hard phase, and which is what provides strength to copper alpha beta allows.

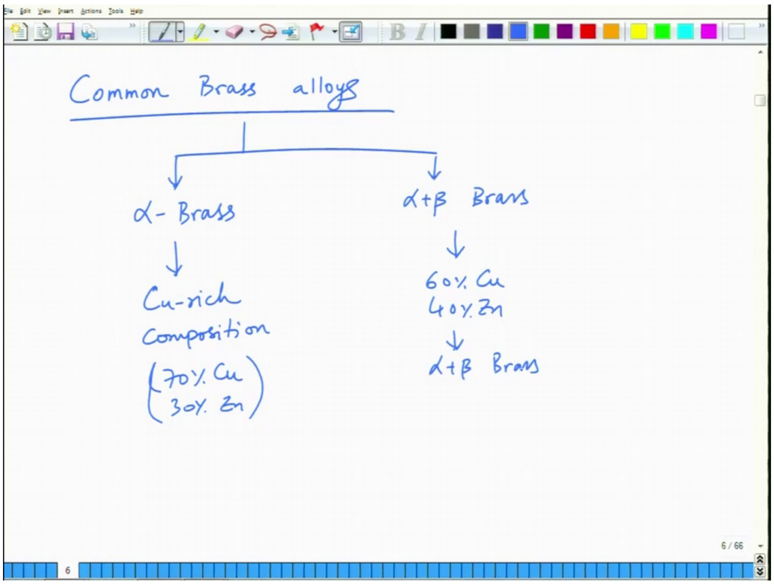
(Refer Slide Time: 08:53)



So, the beta phase is cubic based. So, this is beta phase in which this happens at 50 C u is to Z n 50-50. And for this phase you have each atom in disordered form is 50 percent copper and 50 percent zinc, which means there is a probability of equal probability of occupation of each of the sides. So, this is called a BCC structure. So, this is the disordered form. And it transforms to beta prime which is ordered phase; where Cu-Zn makes a cubic structure similar to BCC, but not BCC. So, this atom for example, could be copper and this atom could be zinc. Whereas, in this case 50 percent copper 50 percent zinc, right.

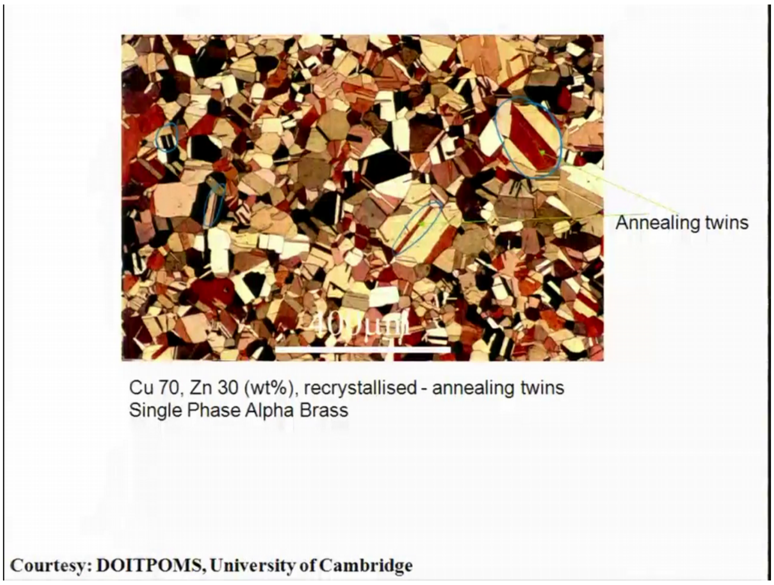
So, this is what is basically the transformation, that happens at about 50 percent copper 50 percent zinc. And this is what is evident in the phase diagram, it transforms from beta to beta prime phase from disorder to audit phase. So, there are 2 micro structures of brass which are very common.

(Refer Slide Time: 10:40)



Brass has so; one is alpha brass and second is alpha plus beta brass. So, alpha brass is basically you can say it is copper rich compositions, and beta brass is has a composition. So, for example, you can have 70 by 30 70 percent copper 30 percent zinc, this is all weight wise this is alpha brass ok. And the beta brass would be somewhere around let us say 60 percent copper, 40 percent zinc would be alpha plus beta brass, and they have very different microstructures ok. So, what you would see in alpha brass is; so, let me just go to yeah.

(Refer Slide Time: 11:45)



Annealing twins

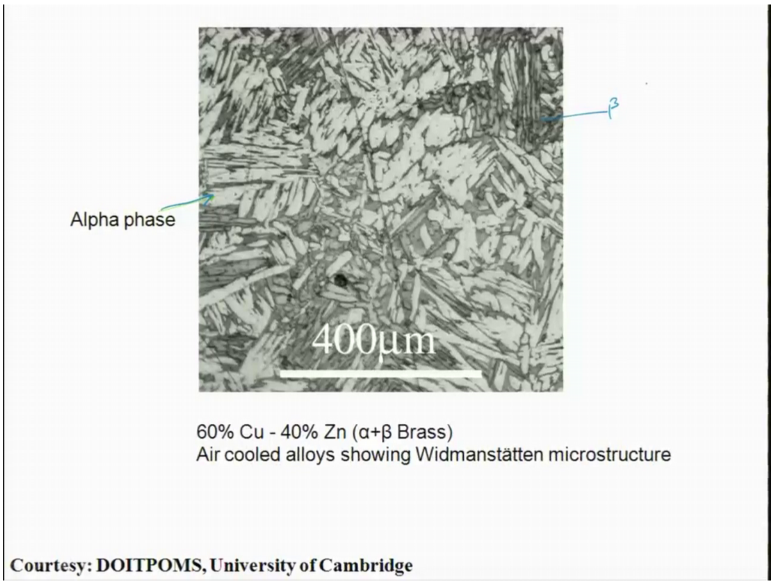
Cu 70, Zn 30 (wt%), recrystallised - annealing twins
Single Phase Alpha Brass

Courtesy: DOITPOMS, University of Cambridge

So, if I go to microstructure, this is the microstructure of copper 70 zinc 30 brass which has 30 percent of zinc 70 percent of copper weight percent. And basically, it is a recrystallization sample, it has lot of annealing twins, these twins form on 1 1 1 planes of copper and they are present like these facets within the grains we can see for example, this is a twin, this is a twin, you have lot of other twins. For example, this could be a twin so, any these are twins.

So, lot of these sharp phases, these are twins form as a result of annealing, and this is a manifestation this is basically a single phase alpha. So, matrix is basically alpha and these are twins forming within the alpha phase itself. So, this is the typical microstructure of alpha brass. You can see the grain size is the order of about 50 to 100 microns. And this is one important alloy of copper zinc.

(Refer Slide Time: 12:41)



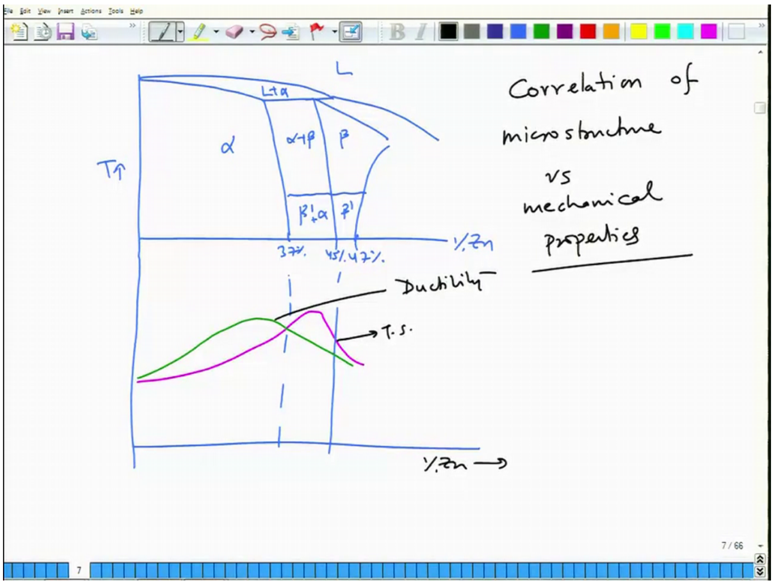
60% Cu - 40% Zn (α+β Brass)
Air cooled alloys showing Widmanstätten microstructure

Courtesy: DOITPOMS, University of Cambridge

Second alloy which has higher strength, that is in copper zinc is essentially, you can say alpha plus beta brass. And this alpha plus beta brass has it is a air cooled microstructure; which shows Widmanstatten kind of microstructure, in which alpha phase precipitates in the beta matrix. And so, if you look at the phase diagram for example, this is 60 40. So, if you go to phase diagram; 60, 40 would be somewhere here so, this is 40 percent 40 percent.

So, it should be 100 percent beta, but what happens is that some amount of alpha precipitates, and this is alpha plus beta prime. So, this is a 2 phase region in which this alloy is made. So, you start from single phase beta. So, this is single phase beta, and as you enter into 2 phase beta the alpha phase starts to precipitate out. And when you air cool it, you start forming this alpha phase these bright plates are of alpha, and these are interpenetrating plate kind of network needle kind of network of alpha and beta. So, this could be beta, and these are alpha phases. So, this is like a interpenetrating phase network of alpha and beta phases. So, this is alpha plus beta brass microstructure that you typically see.

(Refer Slide Time: 14:08)



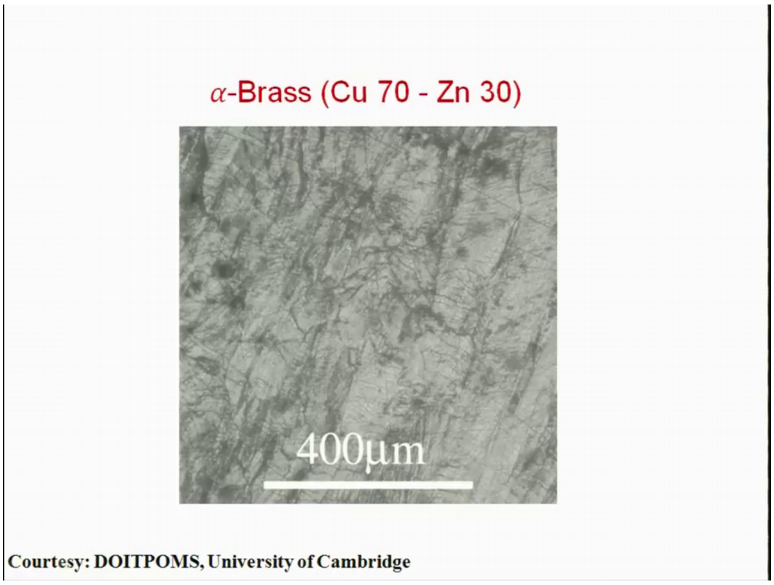
Correlation of microstructure vs mechanical properties

Now, in alpha in copper alloys so, as I said that so, if you draw the if you draw the useful part of the phase diagram. So, you have this peritectic reaction first one, right. And then you have let us say so, I am just zooming it up a little bit. So, this is another phase field. So, you have liquid, liquid plus alpha, this is alpha, this is alpha plus beta, and then you have beta phase field. So, beta phase field goes narrow somewhere here like this. And you have been transformation from to beta prime alpha plus. And this is about you know, 47 percent. And this is about 37 percent, and this edge is about 45 percent.

So, alpha and beta brasses lie between about 37 to 45 percent. So, when you plot the so, this is temperature and percentage zinc. When you plot within this range the tensile strength and ductility; so, between this 2 phase region so, if you plot tensile strength for example, the tensile strength achieves a maximum in this region. Whereas, ductility is has a maxima somewhere here. So, you can say this is tensile strength, this is ductility of brasses.

So, correlation of microstructure versus mechanical properties so, this is what you have in brasses. So, that is why the knowledge of phase diagram is important, because if you know what kind of phases are present you know beta phase is stronger and alpha phase. So, if you want if you want a strong brass, you go to alpha plus beta brass, if you want a softer brass then you go for alpha brass. Similarly, so, just like you have in you have an brass system in the so, this is again an image of alpha brass 70 30.

(Refer Slide Time: 16:38)

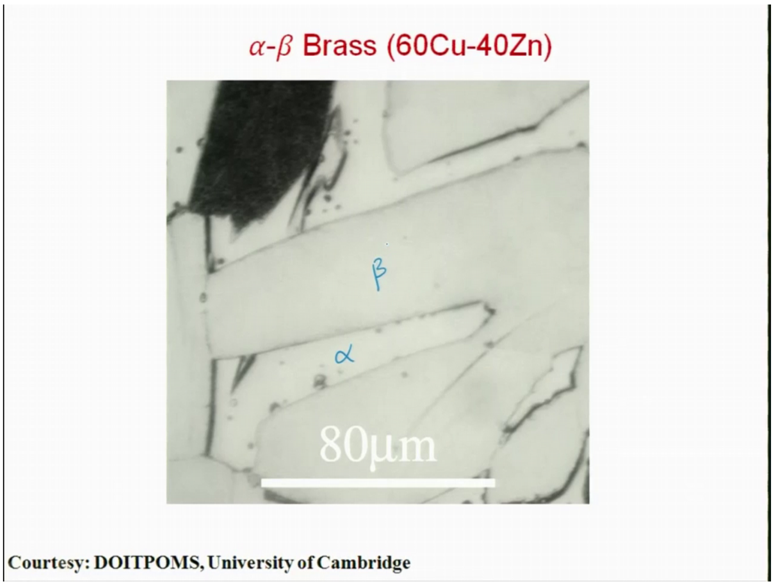


α-Brass (Cu 70 - Zn 30)

Courtesy: DOITPOMS, University of Cambridge

So, this is not recrystallized. So, this is recrystallize, this is not recrystallized as a result you do not see the annealing twins.

(Refer Slide Time: 16:52)

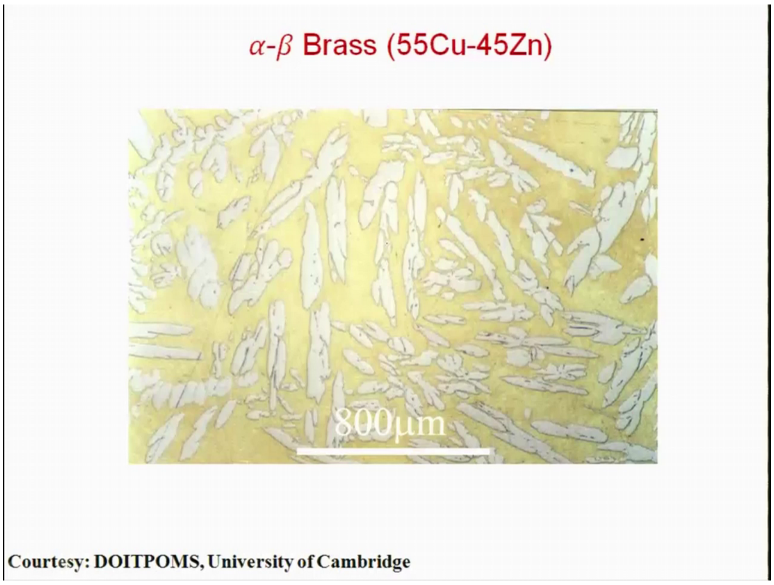


α-β Brass (60Cu-40Zn)

Courtesy: DOITPOMS, University of Cambridge

And this is another image of 60 40 zinc. So, you see these plates. So, one is of alpha another is of beta. So, it is a Widmanstatten kind of microstructure of alpha and beta.

(Refer Slide Time: 17:08)

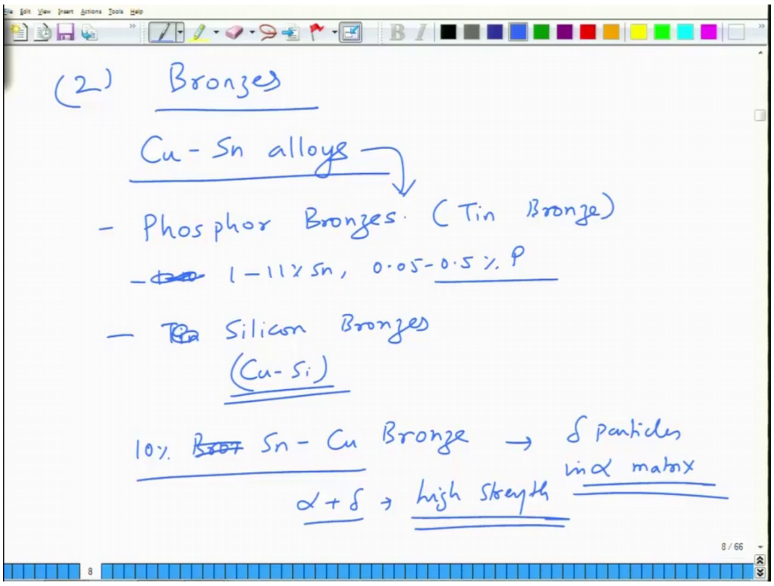


α-β Brass (55Cu-45Zn)

Courtesy: DOITPOMS, University of Cambridge

This is again alpha beta brass 55 45. So, you can see that this is beta matrix and you have alpha needles. Now second microstructure which is important in this series is, the copper tin phase diagram copper tin is called as bronzes.

(Refer Slide Time: 17:31)



(2) Bronzes

Cu - Sn alloys

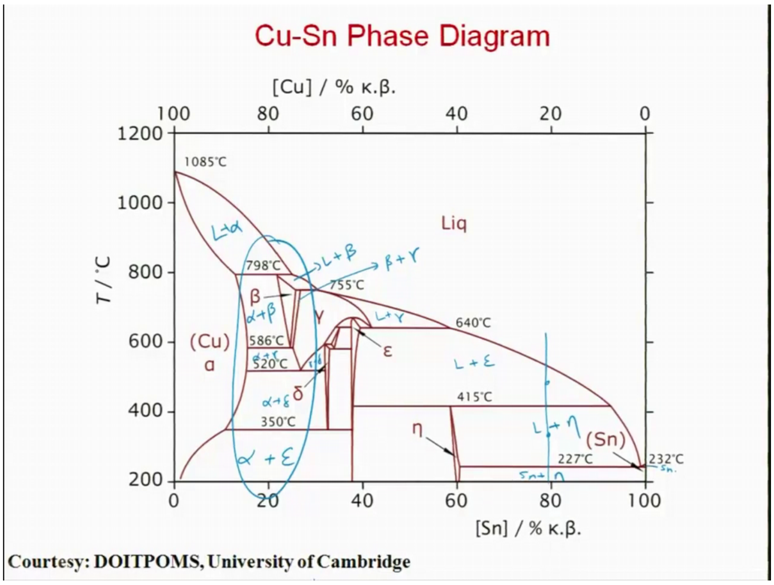
- Phosphor Bronzes. (Tin Bronze)
  - 1 – 11% Sn, 0.05 – 0.5 % P
- Silicon Bronzes
  (Cu - Si)

10% Sn - Cu Bronze → δ particles in α matrix

$\alpha + \delta$ → high Strength

So, we have second phase bronzers, bronzers are basically copper tin alloys. There are variety of bronzes for such as such as phosphor branches and variety of other bronzes ok. So, I will just go to the phase diagram first before we go to details.

(Refer Slide Time: 17:56)


Cu-Sn Phase Diagram

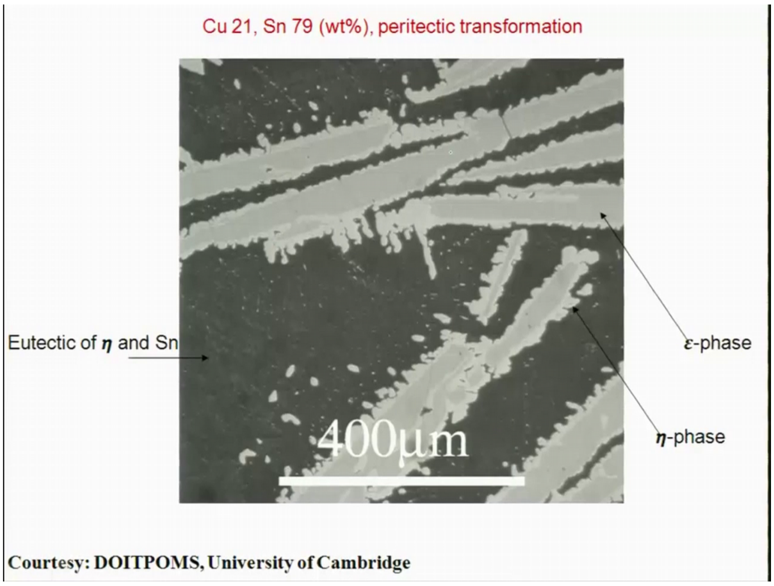
Courtesy: DOITPOMS, University of Cambridge

So, again in this phase diagram you can see that copper and tin have very vastly different melting points. As a result, they also have a lot of peritectic reaction. So, you have first peritectic reaction here at 798 degree centigrade, another one has 755 another one at 640, and then another one at 415 degree centigrade. And then you have a eutectic at about 232 to 227 degree centigrade. So, 415 up to 415 you have peritectic, and then you have a eutectic reaction.

So, again you can form the find the 2 phase fields. So, this is liquid plus alpha this is liquid plus beta, this is beta plus gamma, this is alpha plus beta. And then again you have delta phase field. So, you can have you can have gamma plus delta, you can have alpha plus gamma. So, this is alpha plus gamma, this is gamma plus delta. And then you have alpha plus delta, and then you have another phase field perhaps alpha plus this particular phase, eta phase. So, you have eta phase and so, you can label you keep on labeling. And this would be liquid plus gamma, and this would be liquid plus (Refer Time: 19:24) and this would be liquid plus eta. So, it also has a lot of phases, and these phases have different many of these phases of different mechanical properties.

So, as it is all bronzes also you do not you do not go to all the way to 100 percent tin. Typically, bronzes are less than about 10 percent or so, bronzes are so, general in general bronzes contain about 10 percent. So, if you 10 percent of tins, if you look at the phosphor bronze; a phosphor bronze contains about 1 to 11 percent 10 11 to 11 percent tin. And it contains some phosphorous about 0.05 to 0.5 percent phosphorus. Because phosphorus is represent in castings as a deoxidizer. So, as a result you have these fossil branches.

(Refer Slide Time: 20:17)



Cu 21, Sn 79 (wt%), peritectic transformation

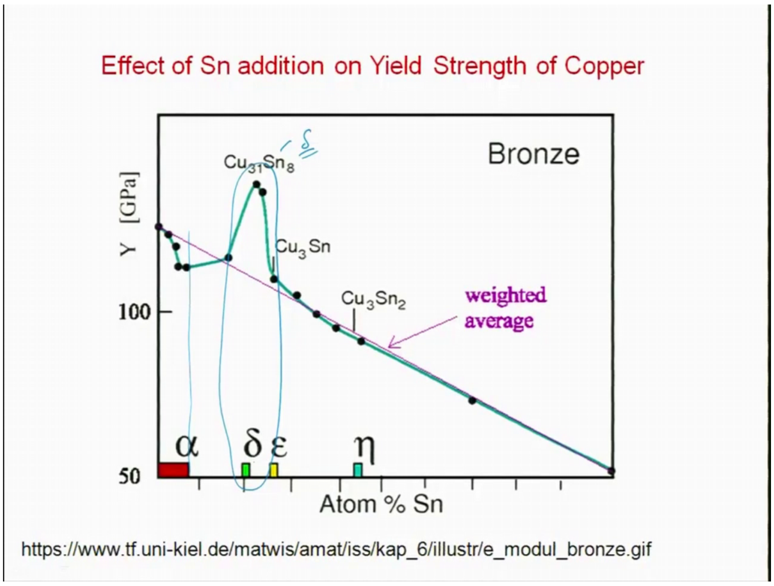
Courtesy: DOITPOMS, University of Cambridge

So, if you look at some of the micro structures or bronze. So, this is for example, copper 21, 10, 79 weight percent peritectic transformation, you have a microstructure which consists of you know you, so, you have a eutectic mixture of tin and eta phase, and then you have the first forming you have the you have the eta phase that forms. But this formation of new phase prevents the formation of the old phase that is epsilon phase.

So, a lot of epsilon phases is attained. If you go to phase diagram for example, this is 79 weight percent. So, we are standing somewhere here ok. So, ideally speaking you should have only so, this is your tin. And so, we must have Sn plus eta microstructure, but what we have is some epsilon retained, and now what happens is that as you start cooling. So, filing phase you will have liquid and silent region you will have formation of liquid and eta.

But there is no complete transformation, because the once the eta phase forms; the further growth or for the transformation of epsilon phase is stopped because of solid state diffusion. That has to occur across the eta phase as a result in the final microstructure you have eta epsilon phase that is retained. So, you see a microstructure which is eutectic of eta plus tin with needles of these with this eta phase and needles containing core of epsilon phase and periphery of eta phase. So, this happens because of non-equilibrium cooling. Because a complete waste transformation does not happens.

(Refer Slide Time: 21:50)



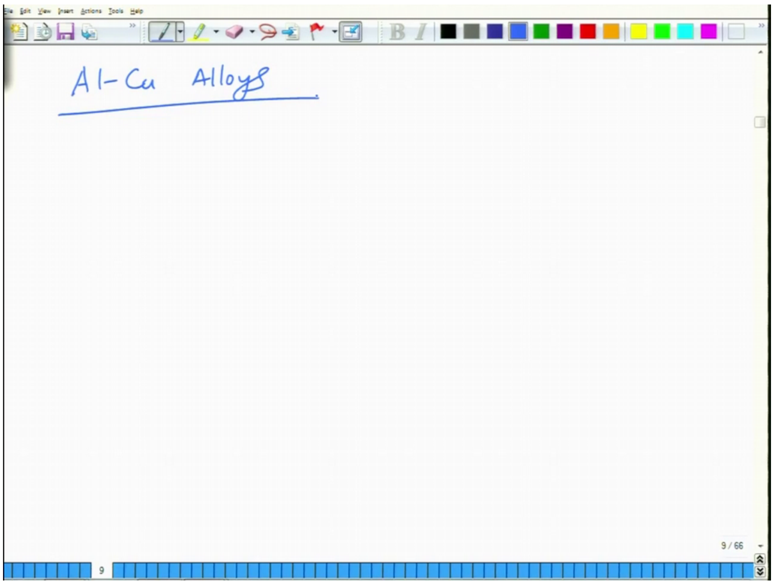
Effect of Sn addition on Yield Strength of Copper

https://www.tf.uni-kiel.de/matwis/amat/iss/kap_6/illustr/e_modul_bronze.gif

And if you look at the effect of strength, effect of tin addition on the strength of copper. So, as we keep adding tin to the to copper. So, at about so, you can see the first one is alpha phase, the alpha phase strength is somewhere here. So, tin addition to copper leads to decrease in the strength, but then you have a spike in the strength at this composition where you form this these delta and eta phases Cu 3 Sn 8 and C u 3. So, Cu 31 Sn 8, sorry, C u 31 Sn 8 not C u 3; is the delta phase that leads to formation of inter metallic compounds within the matrix and it gives rise to strengthen these tin alloys.

And then you have other phases like epsilon C u 3 Sn eta C u 3 Sn 2 and so on and so forth. So, you can see that, if you want high strength, you are you have to be around roughly around 20 percent of 10 to 20 percent of tin. So, you can see that within this you have to be somewhere here to achieve high strength in the. So, this region is what is the important region for bronzes. So, you have lot of bronzes that that are present in case of. So, you have 10 bronzes, you have silicon bronzes. So, you have so, we have lot of bronzes, we have phosphor bronze, we have tin bronze. So, this is basically tin bronze is the phosphor bronze. And then we have silicon bronze silicon bronze is basically contain it is a so, basically you can say it is a copper silicon alloy, ok. So, copper tin alloy is this tin bronze and the silicon bronze is copper silicon alloy.

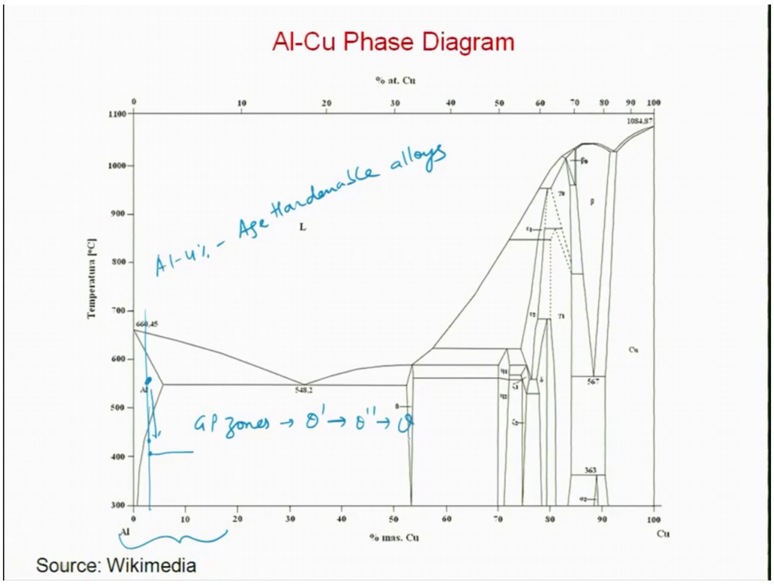
(Refer Slide Time: 24:57)



Al-Cu Alloys

So, a variety of these structures, and basically in this let us say 10 percent bronze alloy 10 percent tin copper bronze shows essentially then delta you can say particles in alpha matrix. So, if you have alpha and delta mixture as I showed you that as you add as you add 10 the delta phase as high strength. So, if you have delta phase present in the alpha matrix it provides strengthening. So, high strength is obtained when you have this mixture of alpha and delta and this leads to high strength in tin bronze. So, this is about the bronzes, and then we look at you can say aluminum copper alloys, again very useful engineering alloys aluminum copper alloys.

(Refer Slide Time: 25:06)



Al-Cu Phase Diagram

Al-4% - Age Hardenable alloys

GP zones → θ' → θ'' → θ

Source: Wikimedia

So, what you have in this? It is a very complex diagram aluminum copper diagram. So, you again have you know beginning the beginning up to about 50 percent you have this eutectic phase diagram, after that you have a series of peritectic reactions. Because again you can see aluminum as a melting point of 660 degree centigrade, and then it has melting point of 1084 degree centigrade 1085-degree centigrade copper.

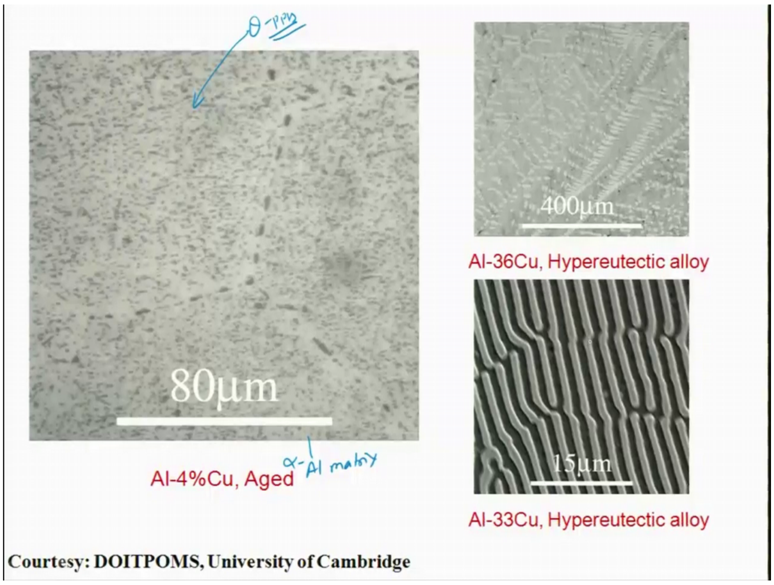
So, system is quite complex it has a lot of intermetallic phases, but this is what is the useful portion of the alloy aluminum copper aluminum some copper is about 4 5 percent coppers the useful part. So, essentially what you do is that you take about 4 percent copper, start from liquid phase and then go down all the way.

So, depending upon how you cool and at what temperature you heat treat, you can make very strong alloys. So, these are aluminum 4 percent copper for example, are you can say age hardenable alloy. And this hardness comes because of theta precipitates. You can see these theta precipitates, if theta precipitates also go through formation of variety of stages. So, you start from GP zones which goes to theta prime to theta double prime and then to theta.

So, we do not want to form the final phase theta, we want to stop somewhere at theta double prime. So, what you do is that you take a composition solutionize it in this range, and then cool it to lower temperature, and then hold it at certain temperature here. So, that you can form the precipitates and then again cool it so, that you stop the phase transformation kinetics completely.

So, again the knowledge of diagram is important where you want to be and at what temperature you want to solutionize at what temperature you want to cool to achieve the phase transformation. So, this is again a very important material aluminum copper alloys which is useful for.

(Refer Slide Time: 26:55)



Al-4%Cu, Aged

Al-36Cu, Hypereutectic alloy

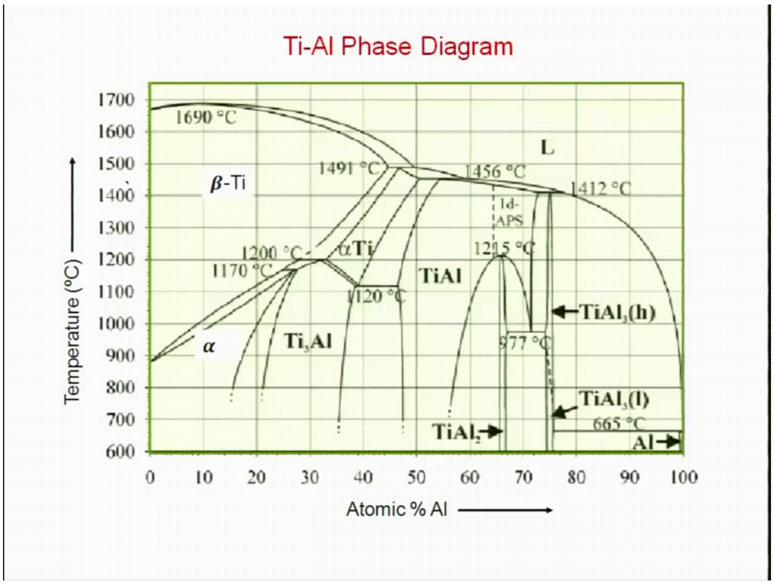
Al-33Cu, Hypereutectic alloy

Courtesy: DOITPOMS, University of Cambridge

So, this is for instance the few microstructure. So, this is aluminum 4 percent copper aged. You can see precipitates of theta phase between the aluminum matrix. So, these black ones are the precipitates of this is aluminum matrix. Alpha basically, and then you have these theta precipitates, it could be theta prime or theta double prime.

We can have higher compositional alloy for example, a hypereutectic and hypereutectic alloys. So, they look like you know alpha aluminum plus eutectic mixture. So, this eutectic looks like this. So, you have these again parallel plates of 2 phases growing and eutectic mixture.

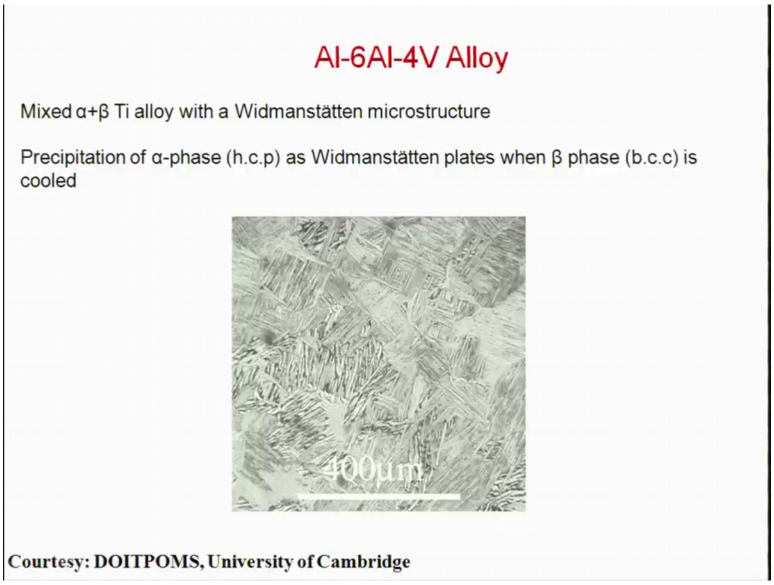
(Refer Slide Time: 27:38)



Ti-Al Phase Diagram

Similarly, you have finally, you have titanium aluminium phase diagram; which has again lot of complex reactions, because titanium is a high melting point material aluminum is a low melting point material again it has complex phases. The 2 most important phases are alpha phase and beta phase in titanium. And they form lot of intermetallics like Ti-Al, Ti-Al, Ti-Al 2 which are very hard phases. So, you can engineer titanium alloys by knowledge of this phase diagram.

(Refer Slide Time: 28:05)



Al-6Al-4V Alloy

Mixed α+β Ti alloy with a Widmanstätten microstructure

Precipitation of α-phase (h.c.p) as Widmanstätten plates when β phase (b.c.c) is cooled

Courtesy: DOITPOMS, University of Cambridge

So, for instance if you have this alpha beta mix titanium alloy, which has so, alpha phase as a hexagonal closed path structure beta phases b c c structure and make sure these 2 provides good properties in alpha plus beta alloys. So, these are titanium aluminum 6 aluminum, sorry, titanium 6 aluminum 4 vanadium alloys. So, 6 percent aluminum 4 percent vanadium, and this kind of microstructure is again alpha beta interpenetrating microstructure called as Widmanstatten microstructure.

So, again they are useful alloys from the engineering perspective. So, these are some microstructure that we wanted to look at from the perspective of phase diagrams of non ferrous alloys. So, what we have learned is about various non ferrous alloys phase diagram; such as brass, bronze, aluminum alloys and titanium alloys. In the next lecture now what we will do is that, we will look at the methods to determine the phase diagram binary phase diagrams followed by in subsequent lectures about the ternary phase diagrams.

So, thank you very much.