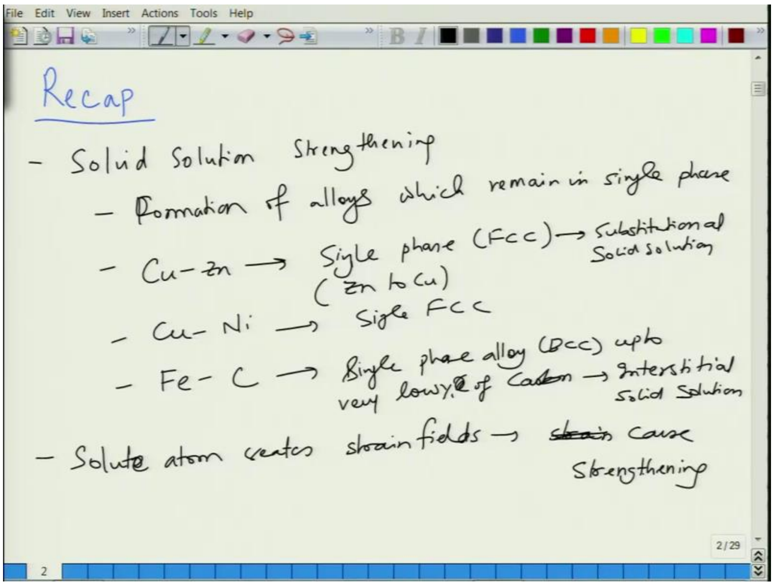
Project of Materials (Nature and Properties of Materials: III)
Professor. Ashish Garg
Department of Material Science & Engineering
Indian Institute of Technology, Kanpur
Lecture 33
Precipitation Hardening

So, welcome again to the new lecture of the course Properties of materials. So, let us just briefly recap the contents of last lecture.

(Refer Slide Time: 00:20)



Recap

- Solid Solution Strengthening
  - Formation of alloys which remain in single phase
  - Cu-Zn → Sigle phase (FCC) → Substitutional Solid Solution
    (Zn to Cu)
  - Cu-Ni → Sigle FCC
  - Fe-C → Single phase alloy (BCC) upto very low % of Carbon → Interstitial Solid Solution
- Solute atom creates strain fields → ~~strain~~ cause Strengthening

So, in the last lecture we talked about solid solution strengthening, so that this happens when you form formation, when you form alloys which remain in single phase. So, basically let us say, you have copper zinc. So, it remains single phase which means it remains single phase FCC when you add zinc to copper.

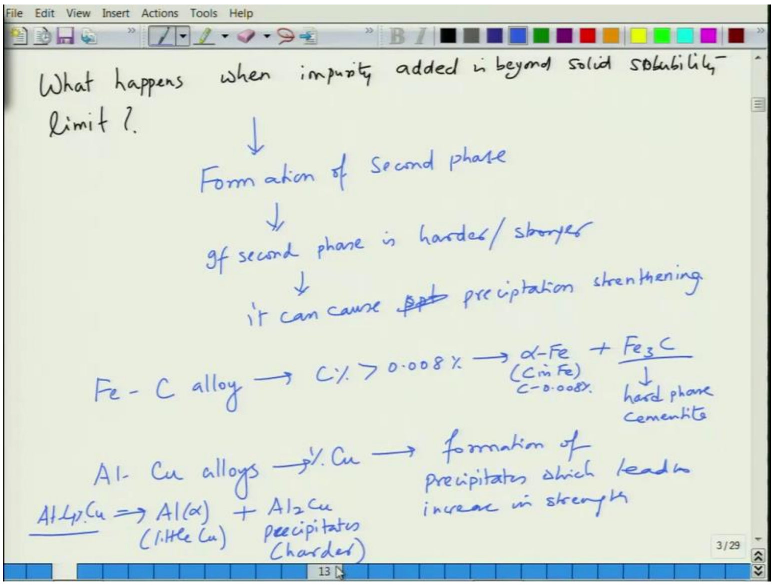
So, you do not add too much of zinc, you just add a little bit of zinc and this makes a substitutional solid solution. Because zinc and copper are similar in sizes. Substitutional solid solution. Similarly, you can have copper nickel, when you add nickel to copper, then also it makes a single phase FCC structure. It remains a solid solution throughout the whole composition range.

On the other hand, we can also form things like Fe-C which is iron carbon alloy, which is a you can remain single phase BCC alloy, up to very low percentage of carbon, very low percentage of carbon and here, it is a interstitial solid solution. So, basically as long as the alloy remains in single phase by addition of a little bit of impurity.

What you are doing is that, basically this solute atom creates strain fields and these strain fields cause which cause strengthening and this could be because of interaction of those strain field with dislocations or they are basically making the dislocation movement little bit more harder as result it leads to solid solution is strengthening.

So, basically in the early addition of impurity to an alloy, early stages of addition of an impurity to an alloy before a second phase of precipitate may form, what happens is solid solution is strengthening.

(Refer Slide Time: 02:46)



What happens when impurity added is beyond solid solubility limit?

↓

Formation of second phase

↓

If second phase is harder/stronger

↓

it can cause ~~ppt~~ precipitation strenthening

Fe - C alloy → C% > 0.008% → α-Fe (C in Fe) C-0.008% + Fe$_3$C ↓ hard phase cementite

Al- Cu alloys → % Cu → formation of precipitates which lead to increase in strength

Al 4% Cu ⇒ Al(α) (little Cu) + Al$_2$Cu precipitates (harder)

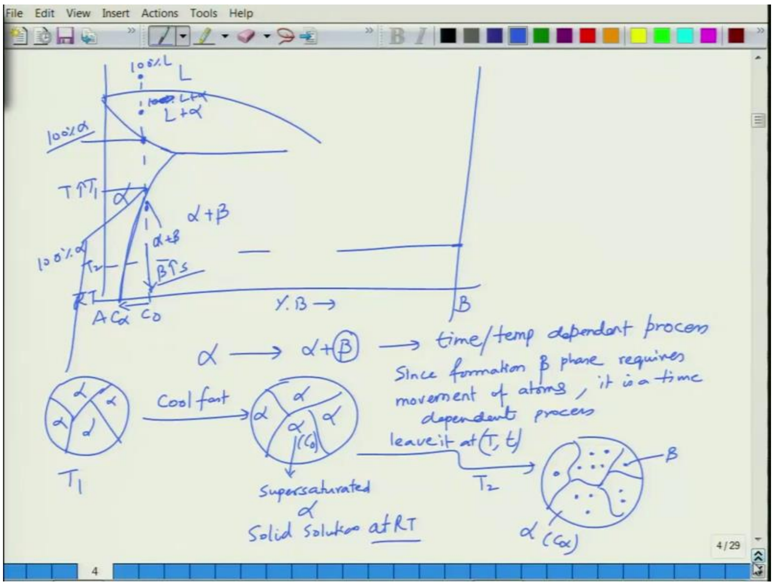
Now, when you add too much of impurity, when you add, what happens, when impurity added is beyond solid solubility limit. So, when you add more impurity what happens is that, it leads to formation of formation of second phase and if this second phase is harder, phase is harder or stronger, then it can cause a precipitation, precipitation strengthening. So, this is another way of strengthening that can happen.

So, essentially in iron-carbon alloys, let us say in iron-carbon alloys if you add. So, if carbon content is percentage carbon is more than 0.008 percent. Then what we form is, so we have alpha ferrite which is solid solution of carbon in iron. So, carbon in iron up to 0.008 percent. But then any extra carbon will lead to formation of cementite which is the second phase, which is a hard phase, cementite.

One of the one of the famous example is aluminium copper alloys. In this alloy, if you add more copper. So, let us say, when we have 4 percent copper, it leads to formation of precipitates which lead to increase in strength. So, basically what you will have is, aluminium alpha which has very little copper.

So, you can say a little copper. So, basically this is aluminium 4 percent copper alloy will have aluminium alpha with little copper plus Al2Cu precipitates which are harder and they cause the strengthening. But there is a whole sequence that happens in this process where that we will go.

(Refer Slide Time: 05:26)



$\alpha \longrightarrow \alpha + \boxed{\beta} \longrightarrow$ time/temp dependent process

Since formation β phase requires movement of atoms, it is a time dependent process

So, essentially what we are saying is that if you have a phase diagram like this, let us say this is the phase diagram and we just talk about it. So, this is the phase diagram, so let us say, this is liquid phase, this is liquid plus alpha phase, this is alpha phase and this is alpha plus beta phase.

So, let us say, you start from this composition, we start from this composition C naught. This is temperature, this is percentage B. Let us say, this is AB alloy. Start from this point, this is 100 percent liquid. At this point you will have 100 percent, liquid plus alpha some percentage. At this point you will have 100 percent alpha. So, basically this is 4 percent B in. So, C naught percent of B in A and it is a solid solution phase.

Up to this point, you have 100 percent alpha. But at this point you have alpha plus beta and as you going, keep going down, you can see the solid solubility of B in A goes down. So, this shifts to so. So, basically the amount of B that can be kept in A lattice goes down. As a result, you can see the beta content increases as you cool down. Now, this formation of from one phase to let say, alpha to alpha plus beta is a time dependent process.

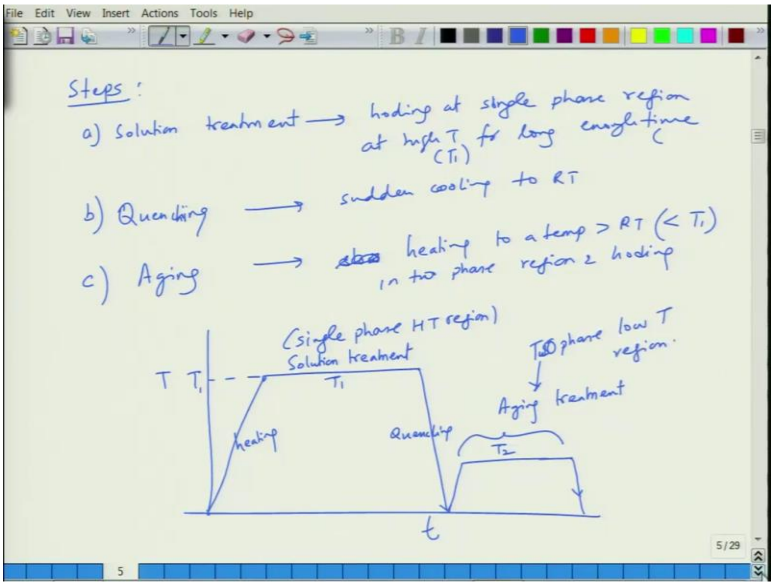
Time and temperature dependent process. So, what happens is that, at this point you will have a single phase alpha alloy. So, this is all alpha, somewhere around this point you will have essentially and if you, now what will happen is that, if you, if you cool it fast, then again it remains alpha. So, you will have alpha but this will be super saturated alpha. Because formation of beta requires some time because the amount of B that is present in alpha requires some time to come to of alpha because it is a diffusional process.

So, since formation of beta phase requires movement of atoms, it is a time dependent process. As a result, when you quench it, what we have alpha basically it is a super saturated solid solution. It is a super saturated solid solution. But if you leave it for some time, so if you leave it at certain temperature for certain time, then beta will slowly form in the matrix of alpha. So, now you will have alpha with solid solubility C alpha.

So, here it will be alpha with C naught, but at room temperature, it is a super saturated solution. This this is at temperature T1 and this is let us say room temperature. This is at T1, this is at room temperature. So, you heat it at a temperature T2 which is slightly higher than room temperature. Let us say, it is T2. So, beta will precipitate through the process of nucleation and growth.

Eventually, beta will form in alpha matrix and beta will have a composition corresponding to this end of the phase diagram. So, this is how it will happen. So, basically formation of precipitates, the time and temperature dependent process and this is what we can control the way it happens to create hardening in aluminium copper alloys especially. So, basically there are three steps to form precipitates.

(Refer Slide Time: 09:28)



Steps :

a) Solution treatment ⟶ holding at single phase region at high T (T₁) for long enough time

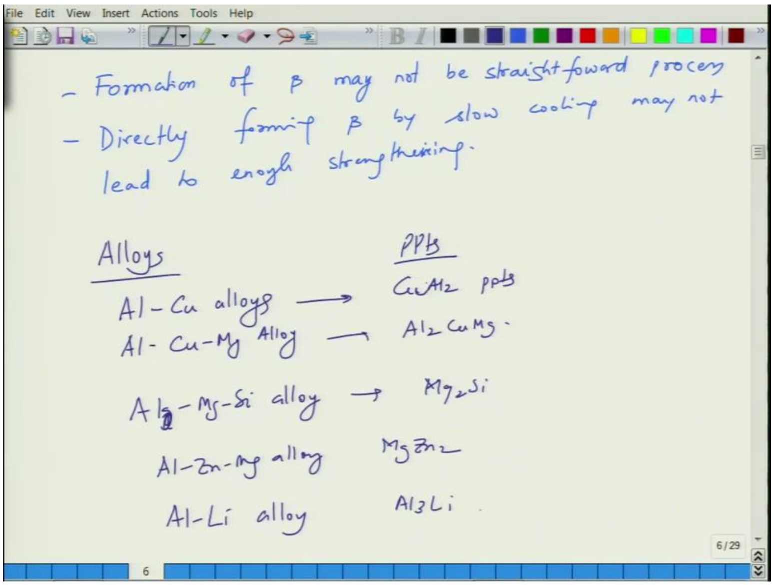
b) Quenching ⟶ sudden cooling to RT

c) Aging ⟶ ~~slow~~ heating to a temp > RT (< T₁) in two phase region & holding

So, steps are you can say one is, solution treatment which is basically holding at single phase region at high temperature for long enough time for all the impurity atoms to distribute themselves in the base matrix. Then, you do quenching. So, quenching is basically sudden cooling to room temperature. Let us say, and then we do a treatment call as aging, aging is basically slow, so basically heating to a temperature greater than room temperature but lower than let us say, if this was at T1, lower than T1.

In two phase region, and holding. So, essentially the plot is like this. If you say, time and temperature, you first heat it to a temperature T1 let say and then you hold it and then you quench it. So, this is solution treatment and then quenching. This is heating and then you heat it to slightly higher temperature. So, this is at T1, this is at T2, hold it and then again cool it. So, this is basically your, you can say, aging treatment. So, this is basically you can say single phase high temperature region and this is 2 phase low temperature region and why you have to do this is.

(Refer Slide Time: 11:40)



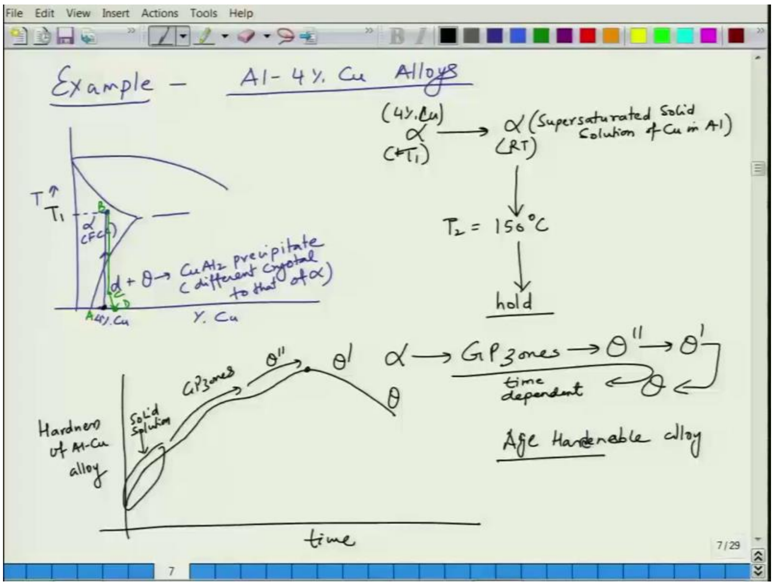
- Formation of β may not be straight-foward process
- Directly forming β by slow cooling may not lead to enough strengthening.

Alloys		PPts
Al – Cu alloys	→	$CuAl_2$ ppts
Al - Cu-Mg Alloy	→	Al_2CuMg.
Al-Mg-Si alloy	→	Mg_2Si
Al-Zn-Mg alloy		$MgZn_2$
Al-Li alloy		Al_3Li .

Because formation of beta may not be straight forward process and then directly forming beta by slow cooling may lead to enough strengthening. So, there are lot of the, lot of these alloys in which you do this kind of treatments. So, we have alloys which have such as aluminium copper alloys, you can have aluminium copper magnesium alloys in which, you know you form precipitates of basically CuAl2 precipitates.

So, basically CuAl2 precipitates are formed or you can have Al2CuMg precipitates in these, you can have Al-Mg-Si alloys which have Mg2Si precipitates. We can have aluminium zinc magnesium alloys which have MgZn2 precipitates. So, these are all precipitates. But this precipitate formation goes through a sequence of processes that we will see. Similarly, you can have aluminium lithium alloys such as Al3Li and so on and so forth.

(Refer Slide Time: 13:27)



So, one of the signature of these alloys is basically we take example of aluminium 4 percent copper alloys. So, what happens in this alloy is that, so again in this alloy, if you say temperature percent copper. So, the phase diagram is again. So, let us say, this is alpha phase, this is alpha plus theta phase and this theta is essentially CuAl2 precipitate. It has a different structure. So, different structure, different crystal structure to that of alpha. So, alpha is basically FCC structure.

This has different crystal structure probably orthorhombic structure. So, what we do is that, you take a alloy from a room temperature of 4 percent copper. You heat it to this temperature let us say high temperature here, somewhere here and then so, first is heat it and then you allow the solution treatment. Then you come back to a lower temperature, somewhere around here and then you hold it and then you cool it again.

So, you go from A to B to C and then you come to D. So, formation of theta precipitate goes through a series of steps. So, what happens is that, alpha when you cool it from let us say, T1 it becomes alpha to, at this point aging, let us say at RT, it is alpha but super saturated. Solid solution of copper and aluminium and this is 4 percent copper in aluminium.

Now, what you do is that, this alpha you heat it to let us say, 150 degree centigrade, T2 is 150 degree centigrade and then you sort of hold it and when you hold it, this alpha transforms to what we call as GP zones, then it transforms to what we call as theta prime, then it transforms to theta and then it transforms to theta, theta prime and then to theta.

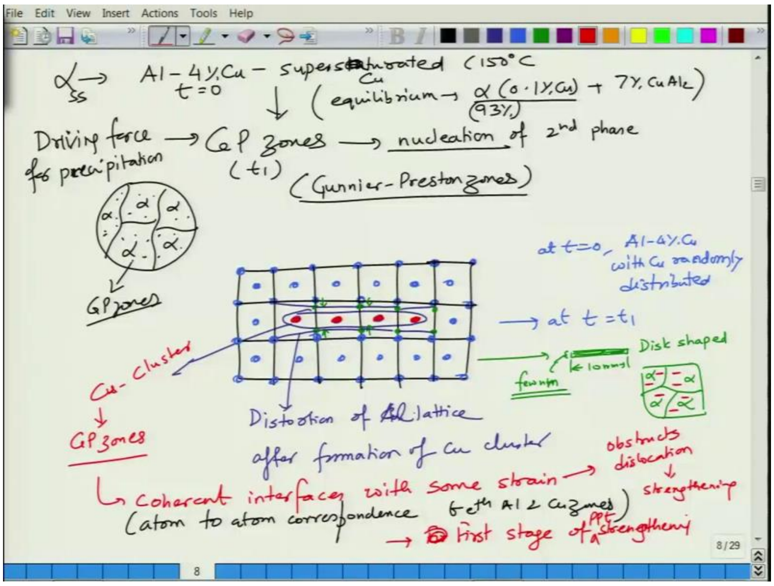
Now, so this is this happens as a function of time, time dependent. Now, this transformation is also related to we call as hardness of alloy as a function of time. So, it has a base hardness, so initial hardness and then it goes through a peak, goes through another peak and it goes to a situation like this.

So, when you form GP, so this is, initially this is what is what we call as solid solution hardening. So, you have some copper that will form solid solution. When you add more copper to it, formation of GP zones. So, this is where you form GP zones. So, GP zone is the first phase. We will come to the reasons later on.

The formation of GP zones increases the hardness significantly and then when formation of theta with double prime to theta prime happens, somewhere you have a maximization of hardness and when final theta phase forms, the hardness drops down.

So, this process is very important because if you do it at a temperature which is low enough. So the theta does not form, you get stuck somewhere between theta prime and theta double prime. Then you can maximise the hardness of aluminium alloys. These alloys are called as age hardenable alloys. Age hardenable means, as you age them, as you keep it at certain time at for certain time, at certain temperature, they become more and more harden and this is…

(Refer Slide Time: 17:51)



So, what is, what is basically GP zone? Let us say, let us say now what GP zone is? So, you have alpha which is alpha is, alpha SS let us say aluminium with 4 percent copper super saturated, saturated. Now if you hold it at a temperature let us say 150 degree centigrade, then this forms what we call as GP zones. What is GP zones basically? GP zones are nothing but.

So, this quenched alloy has 4 percent copper. It has large super saturation of copper. Equilibrium, equilibrium phase diagram says that alpha will have 0.1 percent copper and then you will have 7 percent of CuAl2 and this will be 93 percent. So, while at room temperature, copper can alpha can have only 0.1 percent. Copper remaining going to form CuAl2 precipitate. We are having an alloy with 4 percent. So, this copper is waiting to come out. But we have to provide it right condition.

So, as a result, what happens is that amount of copper that is present is about 40 times, 50 times higher. So, there is a large driving force for precipitation. So, driving force for precipitation and this leads to formation of GP zones which happens via process called as nucleation. Nucleation of second phase and this nucleation of second phase happens first via formation of GP zones.

So, what will happen is that, you have this alpha and you will have this GP zones forming various at various places. So, this is at time let us say T1, this is at T is equal to 0 let us say. So, these are GP zones. GP zone is nothing but called Guinier Preston zones. This is called after Guinier and Preston because they were the first to image or to visualise.

So, one cannot directly produce CuAl2 precipitate. So, what happens is that, let us say you have this aluminium matrix. In this aluminium matrix, we put atoms of aluminium. So and the copper atoms were randomly distributed. So, it was difficult to separate between the two atoms. So, you can say, so at t is equal to 0, it was aluminium 4 percent copper with copper randomly distributed.

So, you cannot make out which one is copper and which one is aluminium. Now, at t is equal to t1 when GP zones form, basically what happens is that, GP zones start forming in the form of let us say these middle ones are basically copper ones. So, some of the copper ones have moved out and as a result, it is sort of leads to distortion of the lattice. So, the distortion of the lattice causes the lattice to bend around. So, you can have some bending.

So, this this atom may move to let us say, this position, this atom may move to this position. So, there is a slighter shift, let us say and then new lattice may be like this. So, there is a bit of distortion of the lattice. So, this is basically a distortion of lattice, aluminium lattice after formation of copper clusters. So, what you have these, this is this thing called as copper cluster. So, these are nothing but here your, you can say, they become red, blue again.

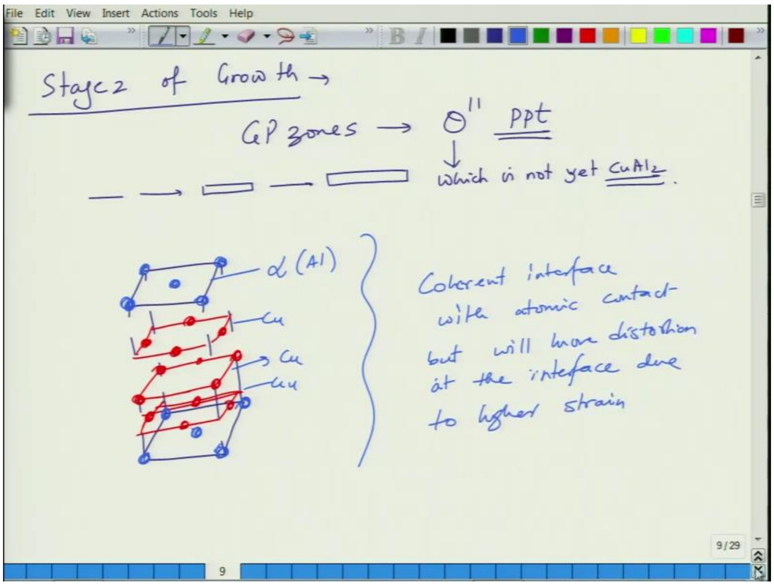
So, you can say, these are copper clusters and these clusters are called as basically you can say, the GP zones, GP zones. So, they do not break bonds. So, you can see there is a still atom to atom correspondence. So, they make a interface which is coherent interface with some strain. Coherent means, they need to they still have atom to atom correspondence which means you have atom to atom correspondence, correspondence between aluminium and copper zones. I will just wipe it little bit.

But since aluminium and copper have different lattice parameters as a result or different atomic sizes, they lead to some sort of strain. So, there is a strain at the interface which leads to formation of these coherent zones. So, as a result, this coherency strain basically obstructs dislocations as a result, you have some strengthening. So, this is you can say, the first. So, after solid solution strengthening, this is the first stage of strengthening, first stage of precipitation strengthening, first stage of precipitation strengthening.

So, these also can be explained in the forms of. So, if you have they generally precipitates at disk shaped. So, these precipitates at disk shaped, let us say. So, you can see these are disk shaped, very thin disk of let us say, thickness, the width of the order of about 10 nanometre and this will be maybe about a few nanometre, very thin disks. So, within the micro structure you may see them.

So, if you look at the micro structure you may have these alpha grain boundaries. So, these are all alpha and within this alpha, you may have these thin, thin, thin sort of GP zones. So, these are very thin disks. So, they lead to some sort of hardening and as they keep growing and they generally grow in only one direction.

(Refer Slide Time: 25:28)



Stage 2 of Growth →

GP zones → θ'' ppt

↓ which is not yet $CuAl_2$.

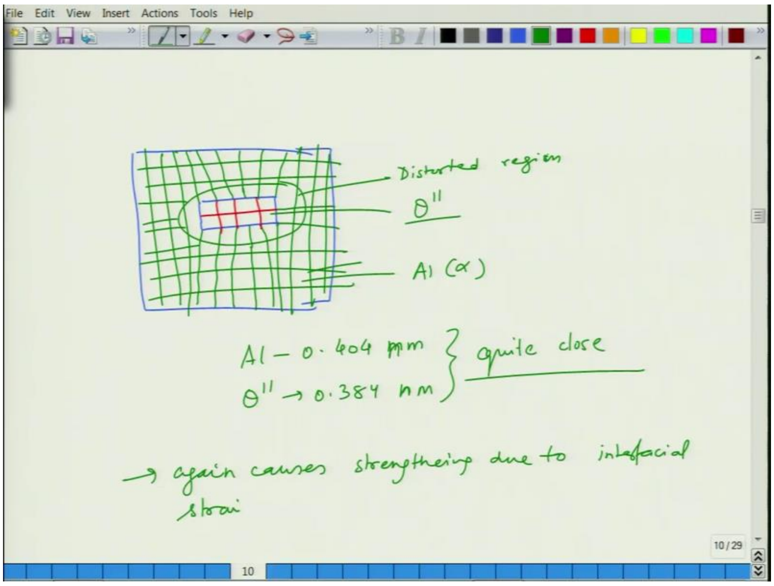
Coherent interface with atomic contact but will more distortion at the interface due to higher strain

So, stage 2 of growth will lead to formation of GP zones to what we call as theta double prime precipitate. So, because what happens is that, as they grow, the strain energy also increases and this sort of this limits the growth. So, as a result. So, these disks become little thicker with time. So, something like this they are growing.

Say eventually because there is a driving force for the growth to occur because more and more copper wants to come out. So, as a result, there is a growth. So, but you form what we call as theta prime which is not yet CuAl2 but reaching somewhere there. So, let us say, you have, so basically let us say, you have this aluminium and this another layer of aluminium, let us say, just drawing a schematic somewhere.

So, let us say, we have aluminium atoms like this and in between we are forming these zones of copper layers and let us say these copper atoms are and in, on top we have these aluminium again. So, this is basically we can say, alpha and or aluminium layer, this is copper, copper, copper. So, this is still forms coherent interface with atomic contact but with more distortion of, at the interface because of strain due to higher strain.

(Refer Slide Time: 28:06)



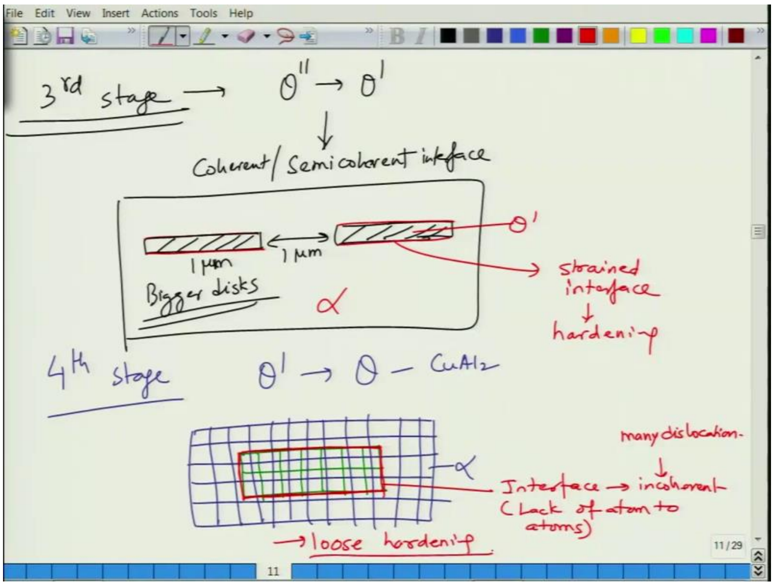
Al – 0.404 mm
θ'' → 0.384 nm } quite close

→ again causes strengthening due to interfacial strain

So, essentially it is going to look like if you have let us say you have a structure like this, in between we have a precipitate. So, precipitate has a lattice parameter which is similar to this, but your lattice has a parameter which is slightly different. So, lattice has let us say, so it will have may be one edge dislocations somewhere and this is basically much smaller in size, let us say as compared to the previous one. So, this is let us say, the distorted region. So, this is basically you can say distorted region.

So, this would be your, if you can draw the lattice completely, this would be your aluminium that is, alpha. This would be theta double prime. So, it is pretty much coherent, fully coherent and so lattice parameter of aluminium is 0.404 nanometre and for theta double prime, the lattice parameter is 0.384 nanometre not millimetre and they are quite close. So, as a result, they still maintain a coherent or a sort of semi coherent strain interface. So, this again causes strengthening due to interfacial strain.

(Refer Slide Time: 29:55)



3rd stage → θ'' → θ'

↓

Coherent / Semicoherent interface

1 μm ⟷ 1 μm

Bigger disks

α

θ'

strained interface → hardening

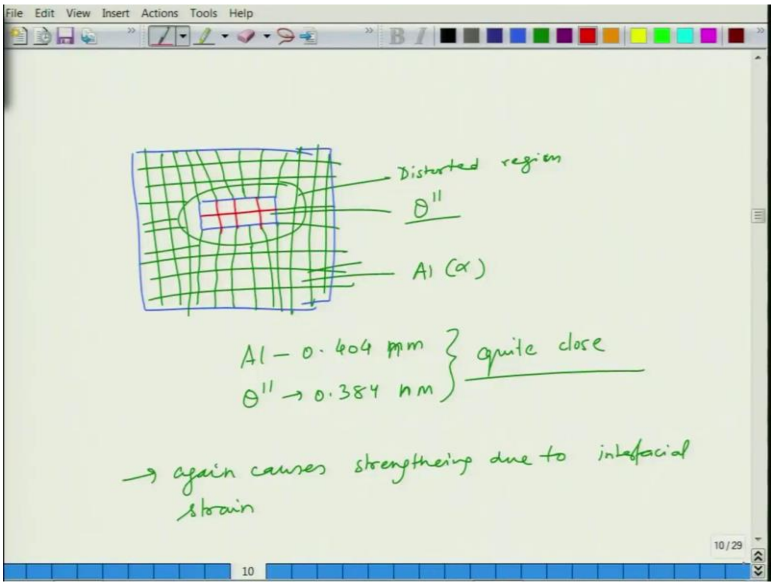
4th stage θ' → θ – CuAl2

α

many dislocation

Interface → incoherent (Lack of atom to atoms)

→ loose hardening



Distorted region

θ''

Al (α)

Al – 0.404 nm
θ'' → 0.384 nm } quite close

→ again causes strengthening due to interfacial strain

The third stage is basically you can say, third stage is where we have theta double prime changes to theta prime. So, when it changes to theta prime which is basically the some more copper is precipitated out. It is not yet CuAl2, but what it forms is a, is a sort of semi coherent, coherent and semi between coherent and semi coherent interface. So, the disks have grown. So, the disks will be of the order of 1 micron and the distance between these disks will also be of the order of 1 micron.

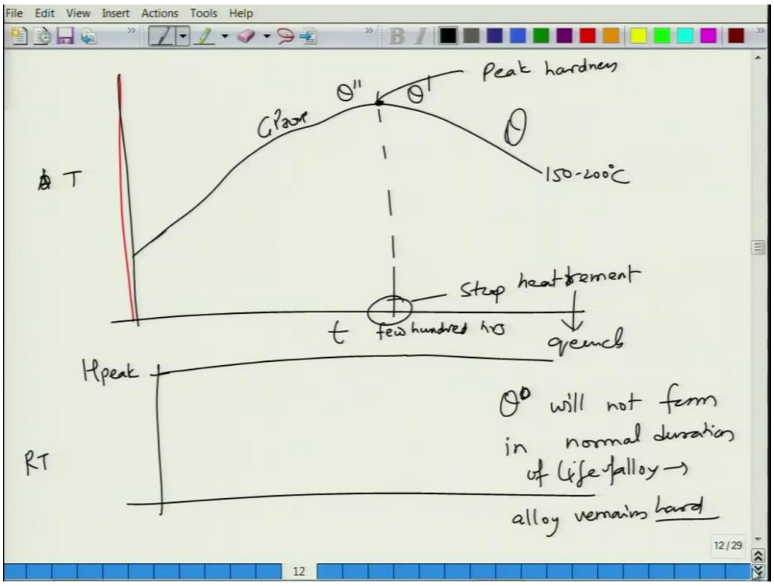
So, these are bigger disks you can say. So, there is, so if you now put, so this is in, so this is the precipitate, this is alpha, this is theta prime. So, interface will be still be strained interface. So, this is a strained interface. So, this is again strained interface leading to hardening. Now, the fourth stage will be formation of, so this theta prime will convert to theta that is, CuAl2.

So, what will happen is that, in that case. So, let us this is my aluminium matrix. So, this is alpha matrix.

In this now, I create phase which is like this, which has a lattice parameter something like this. So, we can see that this interface now, this interface becomes. So, forget about the what the blue ones inside but this interface is, in coherent. Because lack of atom to atom contact and this basically happens because of necessity to relieve the strain. Because as you keep growing GP zones into theta prime to theta, theta double prime to theta prime, the interfacial strain increases.

The interfacial increase strain increases. So, as a result, so surface energy decreases but interfacial strain increases. So, to decrease that interfacial strains, you will have to then nucleate more and more dislocations. So, as a result, you will lose this interfacial contact or atom to atom contact all together and what you form is a incoherent interface with lot of many dislocations and that is where you will lose hardening. So, that is why, now this is, this all this process is a temperature dependent process.

(Refer Slide Time: 33:09)

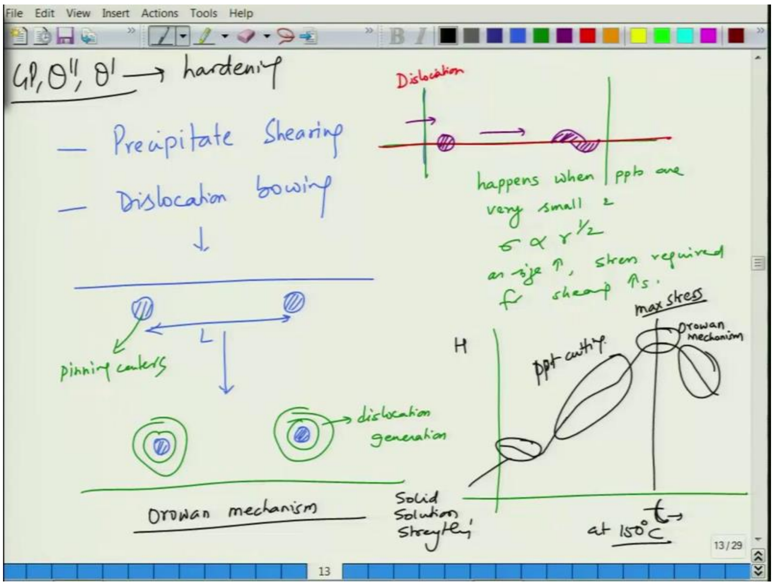


So, when you do when you do age hardening of aluminium alloy. So, this is temperature versus time. So, you do it at such a temperature, so that this is achieved after a very long time. So, let say few 100 hours. So, about 150-200 degree centigrade and this is where your theta double prime to theta prime transition occurs.

This is GP zones and then you stop here. So, you stop heat treatment and then quench. So, you quench at this point. So, you go to peak hardness, so this is peak hardness. Quench at that point, you do not want to go to theta regime. So, when you quench at that point, you go to room temperature. So, at room temperature, you will start with. So, now if you look at room temperature, you will start at let us say, this is Hp, peak hardness and this hardness remains constant because theta prime does not form easily at room temperature.

So, theta prime, theta will not form in normal duration of life of alloy. So, alloy remains hard because the kinetics of precipitate formation is very small. So, these basically precipitates form these precipitate formation of these precipitates leads to hardening.

(Refer Slide Time: 34:47)



$GP, \theta'', \theta' \rightarrow$ hardening

- Precipitate Shearing
- Dislocation bowing

happens when ppts are very small

$\sigma \propto r^{1/2}$

as size ↑, stress required for shearing ↑s.

So, basically we have said that theta double prime, GP zone, theta double prime and theta prime lead to hardening. Now, how does this occur? There are two mechanisms through which hardening occurs. One is the precipitate shearing and second is dislocation bowing. So, in the precipitate shearing what happens is that, when you have a dislocation and let us say this is, this is dislocation line, you have a slip plane.

So, this is dislocation and you have the precipitate let us say, here this is a precipitate and you apply stress to it, it comes to a situation where precipitate gets sheared in such a fashion as the dislocation passes through it. This happens when the precipitates are very small. When the precipitates are very small, they have a continuous slip plane with the matrix as a result, dislocation can always find a slip plane through the precipitatant passes.

So, this happens when precipitates are very small and this is stress increases as r to the power half. So, as size increases, the stress required for shearing increases. Second phenomena is, at the same time when these precipitates start growing, then second thing happen is when these precipitates become bigger with larger separation between them.

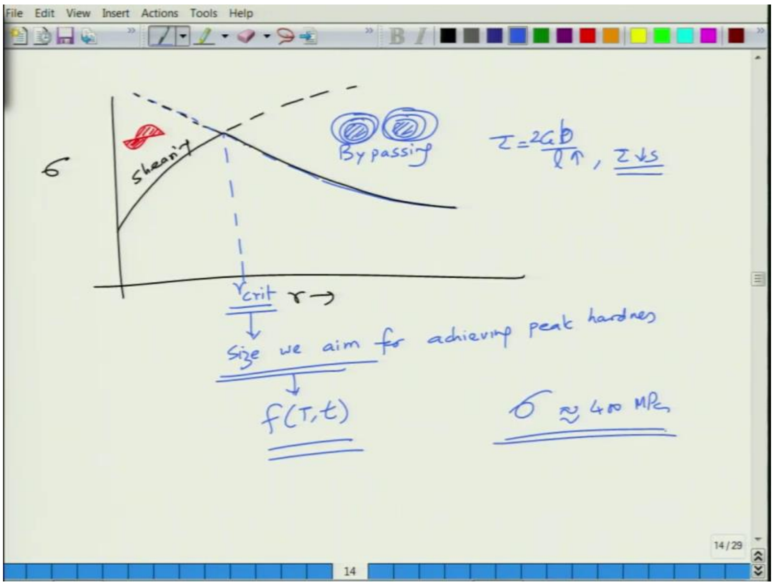
Let us say, L. Then the dislocation line when it approaches them and as it leaves them, these act as pinning centres. So, these act as pinning centres. So, basically then the dislocation when it goes pass them, it leaves these loops of dislocations around. So, basically this leads to dislocation generation which will again lead to strengthening. So, as a result, there is a, there is a curve which one can draw for hardness.

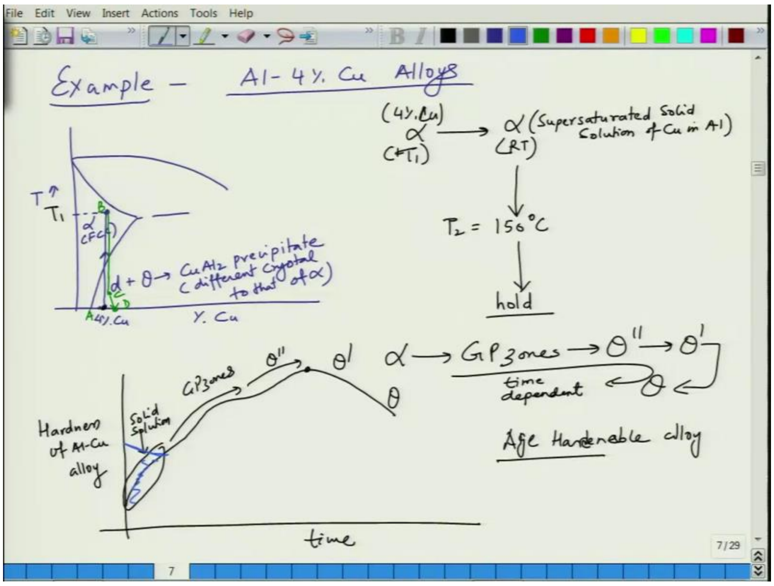
You have solid solution strengthening to begin with and then you have this GP zone, then you have theta theta double prime and so on and so forth. So, in the beginning what happens is that. So, this earlier stage is essentially solid solution strengthening. So, this is let us say hardness H and this is time at let us say, 150 degree centigrade and then initially you have formation of GP zones.

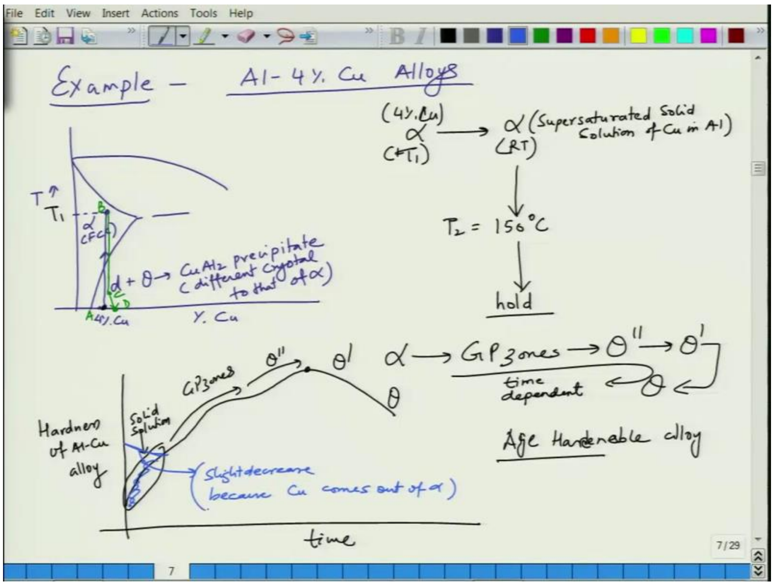
So, what we have is the hardness which causes the cutting mechanism takes place in this case and so in this case, what we will have is basically the dislocation cutting precipitate cutting mechanism will dominate and then here you will have, you will have Orowan mechanism. So, this is also called as Orowan mechanism of dislocation going and somewhere between them when you have a critical size, where the stress is maximised, you will have hardness like this. So, this is maximum stress point.

So, there is a critical size below which precipitates are sheared because the stress required for shearing s lower and after that the stress required for bowing is lower because precipitates have grown in size, their separation is increased. As a result, the stress required to bow is lower as compared to shear. So, as a result, there is a critical stress.

(Refer Slide Time: 38:54)







So, when you look at the, now the shear stress variation, so sigma as a function of precipitate radius. So, this is the let us say shearing part. So, this curve is basically we can say is the, this is bypassing curve and this shearing. So, in this case, the precipitates is going to be sheared and here the dislocation is going to be, precipitate is going to be and you will have these kind of precipitates.

So, when the size becomes increased, size becomes size becomes more then the separation also increases as a result. Because tau is equal to Gb over l, to Gb over l. So, as l increases, the tau decreases. Hence it can bow easily at lower when they are very close to each other, then this stress is very high, but the stress required for shearing is lower.

So, there is a critical size at which you achieve a maximum stress that is required that is r critical. So, this is the size that we are, we aim for achieving peak hardness and this is the function of time and temperature. So, this what happens in precipitation hardening. Basically precipitation of hard precipitates in aluminium alloys goes through a sequence of nucleation and growth mechanisms.

So, first let us say an aluminium alloy, the copper clusters from what we call as GP zones which have a coherent interface with the matrix and they lead two sudden strain at the interface as these because more and more copper wants to come out of aluminium as you, as you hold the alloy for longer time, these GP zones, grow into theta double prime and theta prime precipitates which are also coherent or semi coherent with the matrix.

They again contain lot of interfacial strain as a result they again cause more strengthening and strengthening is because of balance between shearing and by passing and the peak hardness is achieved when you have this balance exact, when you are at critical size when, when, when shearing and by passing are balanced again each other, giving rise to maximum strengthening and then as you, as theta, theta prime convert to theta, they became really very large and then precipitate start then, then the dislocation starts bowing around them as a result, the strengthening is lost.

So, these age hardenable alloys or precipitation strengthening alloys are those alloys in which you want to form the precipitates of optimum size. So, that you achieve maximum strengthening and this happens after solid solution of strengthening is already happened. So, initially you can see there is a drop in the strength because the copper comes out. So, as a result, I think earlier I increased. In the earlier plot, so this would be actually like this.

This is not right, it should be slight decrease. So, because of slight decrease, because copper comes out of alpha. So, this is what basically precipitation strengthening is. Now, what we have covered up to this point is, all the strengthening mechanisms which means strain hardening which is because of deformation, then grain size hardening which is because of creation of more and more grain boundaries that is by doing the, making the grain size smaller which leads to obstacle (())(42:45) dislocation motion.

Third is solution strengthening which is by putting some impurities. But the remain in solid solution and they create strain field which lead to destruction, dislocation obstruction and then formation of precipitates fine precipitates of size that is optimum which leads to maximum strengthening and this leads to really, really hard alloys, especially in case of let us say aluminium copper alloys you get very high level of strengthening.

You can have strengths of the order of the shear stress that you may achieve is about 400 mega Pascal. So, In fact, sigma could as high as 400 MPa in these alloys and corresponding the hardness can also be very high. So, this is where we will stop now. So, we have covered the mechanical, property aspect of materials. Looking at elastic properties, the plastic properties and the finally strengthening mechanism. From the next lecture onwards we will start the electrical properties of materials, the basic introduction to specially metals and semiconductor. Thank you very much.