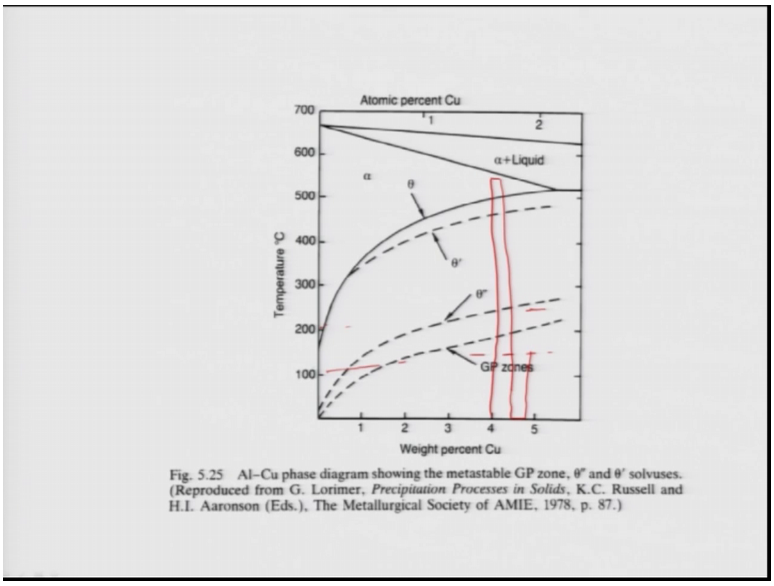
Phase Transformation in Materials

Prof. Krishanu Biswas
Department of Material Science & Engineering
Indian Institute of Technology, Kanpur

Lecture – 38
Age Hardening Alloy (cont.)

So, we are going to discuss about age hardening systems today. And trying to explain you how in aluminium copper alloys the phase transformations of precipitation formation and it is growth can control it is mechanical and physical properties. Basically we have discussed so far that aluminium copper, especially the aluminium reach copper alloys undergo precipitation harden able phase transformation. And here in this slide I am showing you a part of the phase diagram of aluminum copper.

(Refer Slide Time: 00:55)



As you see the phase diagram which involves alpha phase and the liquid plus alpha phase is shown. And on the top of which there are few dotted lines, and these dotted lines indicate the formation of the transient phrases during ageing treatment of aluminum copper alloys. The most important alloy is aluminum foo 8 percent copper which is known as (Refer Time: 01:25). And as you see here the typical phase transformation typical heat treatment cycle which leads to precipitation hardening is kind of like this. If I take a aluminum foo 8 percent copper alloy first thing we do is we heat this alloy to the single phase region. And because of this treatment which is known as annealing treatment, all the precipitates which are present in the alloy dissolves dissolve in the alpha phase, and then we form a single phase homogeneous alpha.

And that this is followed by quenching to room temperature. Just quenching means just take the alloy at a high temperature and put it into water directly. So therefore, there will be a change in the therefore, there will be change of rapid change of temperatures because of this treatment, and it will allow they all the copper atom present in the aluminum retained in a micro structure. And the next one which involves ageing is basically nothing but heating this alloy to a temperature between 150 to 200 degree celsius temperature.

So, 150 to 200 it tells us temperature, this is 100 I have 200. So, something around 130 to 190 degree celsius in the temperature range, these alloys which are quenched are given treatment for different time duration. And because of that precipitates form, and you have seen that precipitation formation is basically happens in a stage in a manner which is some sort given by these. First the GP zone forms. This is followed by theta double prime and theta prime and then finally, the equilibrium precipitate theta which has a composition of Cu 2 Al forms, that you have seen.

(Refer Slide Time: 03:25)

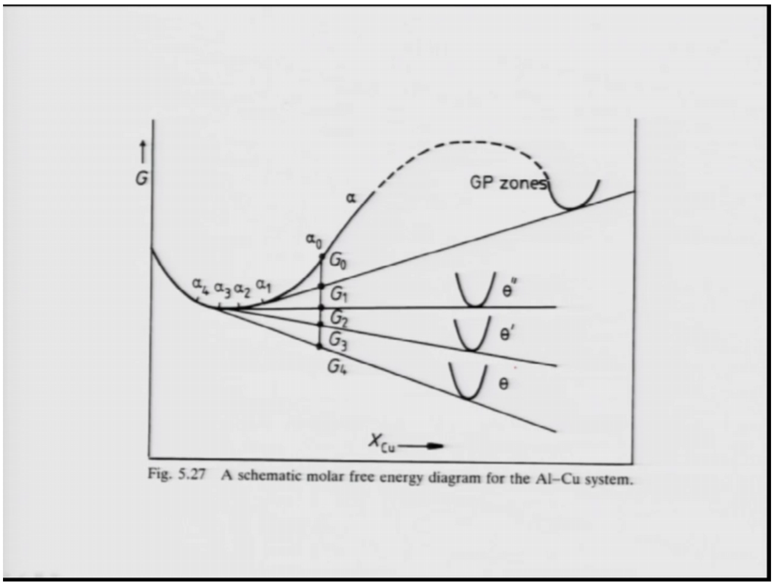


Fig. 5.27 A schematic molar free energy diagram for the Al–Cu system.

And I told you that this can be explained using free energy composition diagram, such like this let us not go back into that it helps you to explain different in a equilibrium compositions between these transient phases GP zone. So, theta double prime and theta prime with the alpha. And this can be easily then described. To give an (Refer Time: 03:45) that you know this all You know that GP zone is nothing but a few layers of copper atom sitting on these one o o planes of aluminum alpha aluminum lattice.

(Refer Slide Time: 03:48)

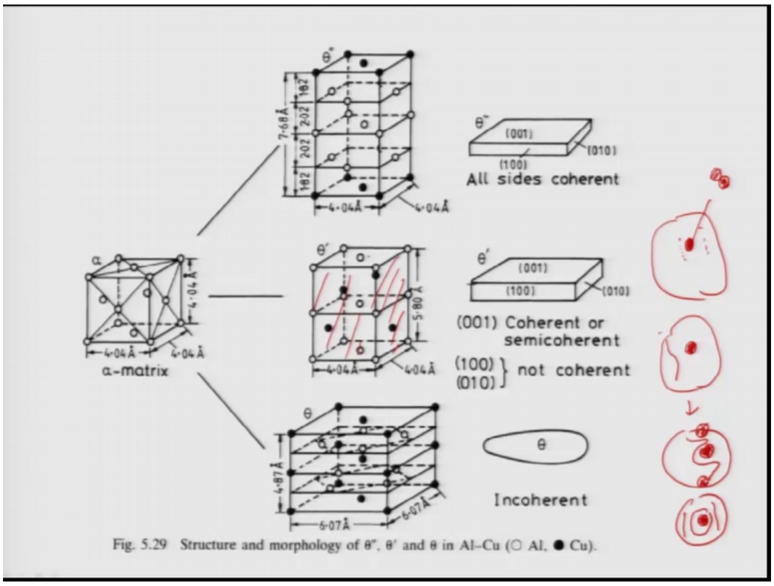
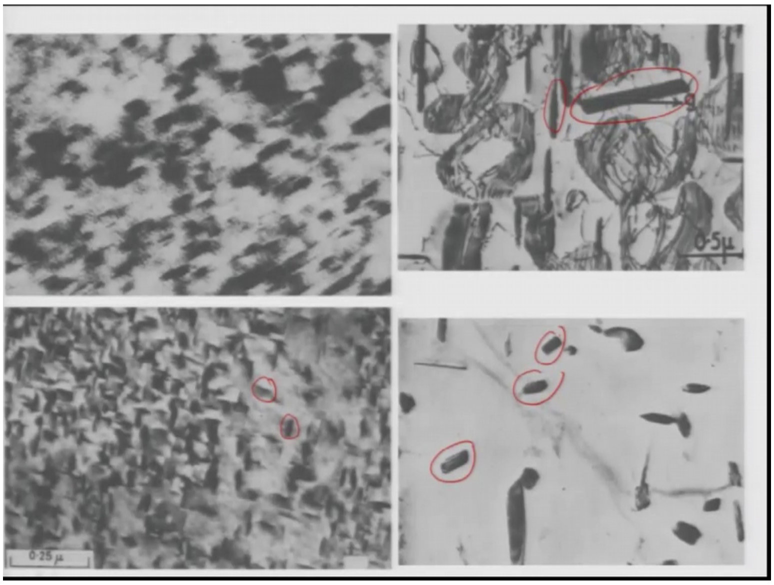


Fig. 5.29 Structure and morphology of θ'', θ' and θ in Al–Cu (○ Al, ● Cu).

And then theta double prime and theta prime is basically some sort of coherent structure along the different interfaces as described here, theta double prime has a coherency along all interfaces therefore, it retains low energy interfaces with the matrix theta double prime theta prime actually has coherent semi coherent along 1 0 0 1 planes, but non coherent on 1 o o or 0 0 0 1 0 planes. And on other hand theta which is equilibrium precipitated is some purely in coherent structure. So therefore, the transient phases actually help us produce different kind of interfaces between these phases and the matrix. This is what I told you also. And some of the micro structures which is shown you again shown me because it is helps you to understand.

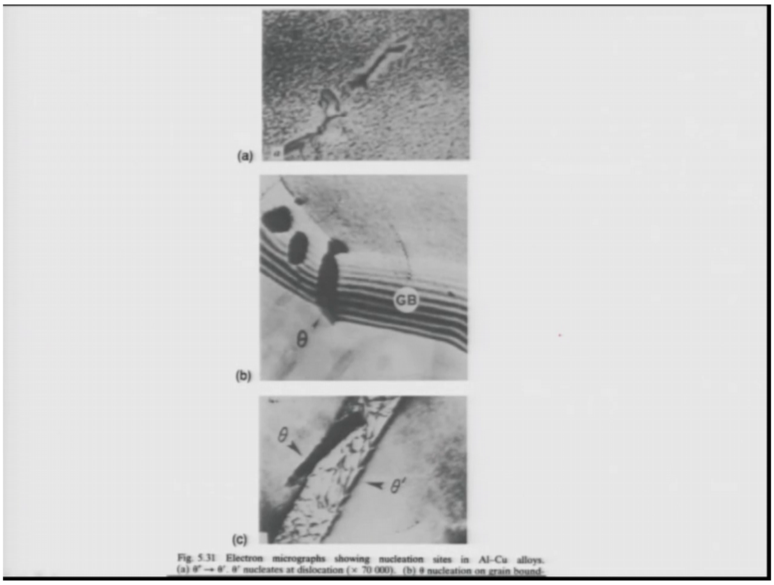
(Refer Slide Time: 04:43)



In GP zones as basically is nothing but a extra one or 2 layers of copper atoms on the aluminum on o planes. So therefore, they will lead to strain matrix which is shown here. Similarly theta double prime is also coherent along all interfaces only thing it can Lead to in a micro structure say such a kind of coherent strain, which you have discussed in our previous lectures.

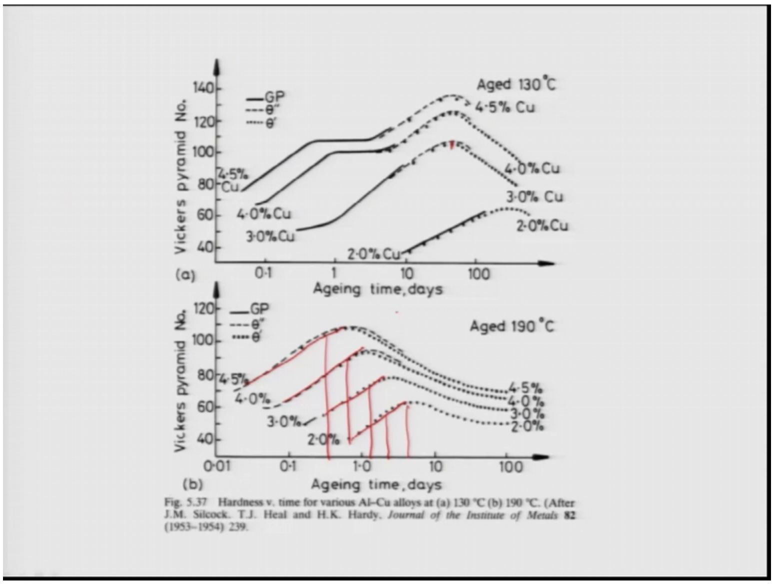
So, this will lead to a certain kind of a strain matrix, and this is what seen here these are the theta double prime precipitates. Theta prime precipitate which looks like a much bigger they are again elongated a long, and theta is basically a very well defined precipitates with no coherency along any of these interfaces. So, that is what is the truth. And in obviously, nucleation of these phases happens along the grain boundaries or the dislocations. And this can be used to alter the microstructure, as you see here the grain boundaries is present in which theta has precipitated.

(Refer Slide Time: 05:30)



Similarly, theta prime precipitated along a certain grain boundaries. So, it is possible to precipitate these nucleate these precipitates along the defects in the matrix.

(Refer Slide Time: 05:55)



Now, let us first discuss actually what happens that was recapitulation. What actually what happens when you heat treat this alloys during ageing treatments? I am showing you the plots which taken from these paper by silcock long back is in 1954. And this actually is very, very this tells you actually what actually happens in during ageing treatments.

Let us look at the top part of that. What is plotted here is the vickers hardness versus ageing time in terms of days, for different concentrations of these alloys. And the ageing treatment similarly the bottom figure is same thing. Only difference is that the ageing has been done at a high temperatures that about 900 degree 190 degree celsius temperature sorry. And so, let us first look at the top curve as you see here if you look at 28 percent copper alloy which is a very lean copper aluminum copper alloy. The ageing treatment at a at a lower temperature 130 degree celcius temperatures gives you a that takes lot of time to start the precipitation basically it takes about 10 days to start the precipitation.

Basically that is the time in which GP zones forms. Then slowing hardness increases and it takes about couple of takes about 200 days to get a optimum hardness. So, that is the problem using a low ageing temperature. If you say low ageing temperature kinetics of formation of these precipitates is very low. It is little bit improves if you increase the concentration of copper because copper is what is leading the formation of precipitates starting form GP zones to theta double prime and theta prime, but you see it takes quite a out of time about they know 50 days to reach a peak hardness.

The peak hardness means the hardness actually hardness actually starts with the very low value initially that increases, and reaches a maximum and then again decreases. This is the typical hardness curve ageing curves which I have already discussed in the last lecture. So, the peak hardness means the temperature or time at which the hardness is actually mean the maximum bulb as you see here if this ageing is done at.

About 130 degree celcius temperature the time required to achieve peak hardness for alloys with 3 to 4.5 percent copper alloy does not change, it remains same. On the other hand if we age at 990 degree celcius temperature, which is above 60 degree higher than these the peak, hardness time required to achieve peak hardness is of very low. It can be obtained even less than one day of heat treatment just about something like 6 to 7 hours is enough.

Not only that even for the very lean copper alloys like 2 atom percent 2 8 percent copper alloys it requires about 7 to 8 days to achieve the peak hardness level. So that means, what the ageing temperature has a propound role in defining or in leading to the formation of this precipitates. And it can actually lead to very you know interesting aspects in the actual production. Because when you are preparing this alloys for this actually when you are doing the heat treatment of this alloys for different components, important aspect is reduce a time.

But you know if you want to reduce the time quite a bit by increasing temperature very high, it leads to coarsening of the precipitous very rapidly. That is also a problem. So therefore, the optimum temperatures of heat treatment for the most of these alloys ageing is something 150 to 170 degree celsius temperature. So, 190 is actually little on higher side, 130 is on the lower side. So, these particular view graphs tells you that these heat treatment or ageing treatment must be done with the optimum less temperature. And remember these points which is shown here the points are basically for theta prime, because this tells you the what kind of precipitates this form.

Surprisingly if you look at the lean alloys, just after you know GP zone it directly goes into theta prime as you see here. But on the another hand for the little preacher alloys it 4 or more than 4 percent copper alloys, and 3 actually 3 and more than 3, 3 weight percent copper alloys. The sequence is all just like what we see in the real micro structural length scale that is GP zone followed by theta double prime and theta. And obviously, at a very high temperature or very high time theta will precipitate that is what is not shown here.

But that is not actually desirable because theta has in coherent micro structure interfaces with the alpha. So therefore, the hardness decreases further. So, why such a curve why such a kind of behavior you observe. First of all you know GP zones are basically what they are actually copper layer sitting on the aluminum planes, I mean telling you again and again. So, this copper layers actually start blocking the dislocation motion, but because they are only few layers of copper atoms the hardening is not very high hardening is basically coming from the coherency strain which is generated in the matrix. So therefore, the hardness increase because GP zone formation is start very high but.

The moment the theta prime or theta double prime actually start forming the hardness increases very rapidly. The reason is very simple theta double prime as you see here in the previous plots theta double prime is this structure it has a tetragonal structure built in automatically with a and b same 4.04 hamstrung, but c is about 6 point 7.68 hamstrung. And it consists of alternate 2 layers of copper on the both sides of the 0 0 1 planes of aluminum in side you have aluminum layers. You see here the this round they these open circles are basically aluminum and the closed one is copper.

So, basically it develops 2 layers of copper on the both sides of the aluminum. And these layers of copper actually leads to distortion of these lad lattice or rather the increase of the c axis of the lattice and gives you the theta double prime tetragonal lattice. So but very interestingly although these forms like kind of structure all the interfaces whether it is 0 0 1 1 0 0 or 0 1 0; that means, all the all the you know faces of this tetragonal unit cell remains coherent with the aluminum lattice aluminum is shown here. And these coherency is basically gives the increase of hardness more.

Because as a dislocation moves from the alpha to the precipitated theta double prime there is this strain or this basically the between the precipitated on the matrix this is there is a stress developed because of this coherency strain and this stress actually block the dislocations to move inter side these precipitates. Because as we know if a precipitate is present in the matrix like this and a dislocation is to be is to move you know like that a dislocation is present somewhere there it just pass through it, and if the matrix and the precipitated has a coherence micro structure.

Only way is the dislocation can pass through it by cutting through; that means, it can it has to create 2 new interfaces. If it has to move here this precipitate which is shown here will be cut into 2 pieces. And that is what happens and because of these you know cutting methods precipitate size is precipitate small; obviously, for the theta double prime. And so, because of these 2 new interfaces analytics. So, work done is pretty high. And that is why this dislocation motion is inhered.

But on the other hand as theta prime forms or phase transformation higher time or may be at higher temperatures whichever is true, theta prime is going to be forming. And theta prime has also tetragonal lattice structure, but difference is that theta prime atomic elements is different. As you see here the 2 layers 0 0 1 on the top and the bottom actually they consist of aluminum atoms. On the other hand the central layer is also aluminum atoms, and form this from this copper atom present in the different corners or the phases of these tetragonal lattice.

So, because of that the this phase loses it is coherency along you know 1 0 0 or 0 0 1 planes; that means, coherency along these 1 0 0 planes are this ones this sets this are they

1 0 0, and 0 0 1 planes are this ones. So, they lose the coherency, only coherency maintain is on the aluminum positions aluminum sorry, on the top and bottom planes. So, because of that now dislocation has 2 choices. Either it can cut through this precipitate or it can form a loop, around it by the dislocation move it can form a loop around it when it passes through; obviously, dislocation will come like this and then slowly bend it and then once you bends it can basically form a loop like this. So, finally, it will lead behind this is the precipitates let me tell you. So, this is let us first denote this part ok.

So, this is the precipitate and it comes close to the precipitated then it bends, and then finally, it loose behind a loop and then it moves ahead. So, because of that because it creates a loop around the dislocation this is known as all ones mechanism. Because of that the new dislocation which is come again will be subjected to a stress fields generated by the loop.

So, more number of dislocations passes to more loops should be forming at around the precipitates, and the stress field generated will be higher. And that is gives you strength, but remember this depends on the distance between these precipitate present. Even the precipitates has to be you know in a particular separation. Otherwise these kind of bowing of dislocation leading formation of a loop will not happen. So, that is why the precipitate size must be little bigger as compared to theta double prime. Theta on the other hand is basically completely in coherent structure. So, only way dislocation can pass through is loops blinking around it. And they will be; obviously, bigger in size.

Because the growth will happen at higher temperature time. So, because of that the material loses strength slowly. And that is why these hardness slowly drops up. So, that is the main reason why you see such a kind of such a kind of ageing curves in the micro structure or in the real heat treatment. So therefore, if I want to create a good material which is be applicable for the various potential applications. So, we need to have a combinations of good hardness in the ductility. That is only possible when you have on this side of a curve, on the rising side of a curve. That is what I am showing you here in all the cases. So, if the heat treatment is done such a way that the temperature and time is selected properly, then we can be you know hardness can be you know on the increasing side of these hardness plots. And then we can achieve a good combination of this strength and ductility.

That is what is actually done? So, the selection of these heat treatment temperature and time has to be judiciously done. Otherwise alloys will not be applicable in real applications. That is very important aspect which you must be remember. You know there are other things which you would also remember. You have to understand that this precipitates which are forming they forming basically or nucleating on the gain boundaries or on the internal dislocations presents, near the gain boundaries So, less within the grains.

So, we can actually improve the ageing efficiency or the ability of the alloy to age with nicely by doing 2 different approaches. One which is very routinely done is that after suctioning treatment and followed by quenching the alloy can be given a deformation plastic deformation. So, I simple rolling it or giving a forging treatment. But doing that we create large number dislocations or different structure in the alloy in the in the in the sample. And then if you this was this is followed by ageing treatment; that means, this you know deformation is given prior to the ageing treatment deformation lead to dislocation and different structure, then if the ageing defects will allow the nucleation of these precipitates very easily.

So therefore, one of the ways to achieve faster ageing and better distribution of the precipitates in the micro structure is given a prior plastic deformation to the prior to the ageing treatment. Other way is to use what is known as double ageing treatment. Double ageing treatment means we can actually have ageing treatment done at a lower temperature something like 120 degree celsius here, and this will only lead to formation of GP zones. Large number of GP zones will form, because other precipitates will not form at the temperature. GP zones will be preferentially forming across the whole micro structure all that was the whole sample.

Then this sample can be again taken to higher temperature like something 170 to 175 degree celsius temperature and kept there for some time. As a GP zones as homogeneously form in the microstructure at because the lower ageing temperatures in the first stage, this will allow the formation of the precipitation of the precipitates like theta double prime and theta easily on the GP zones. So, by using either a plastic deformation prior to the ageing treatment or by using a double. So, double stage ageing treatment we can actually improve the mechanical properties of these alloys expensively. And these are all routinely done in the actual practices. Actually all the alloys which is used for the aero plane body is normally heat treated or ageing treatment is done after the plastic deformation, just to increase the nucleation density of these precipitates in a micro structure.

(Refer Slide Time: 19:56)

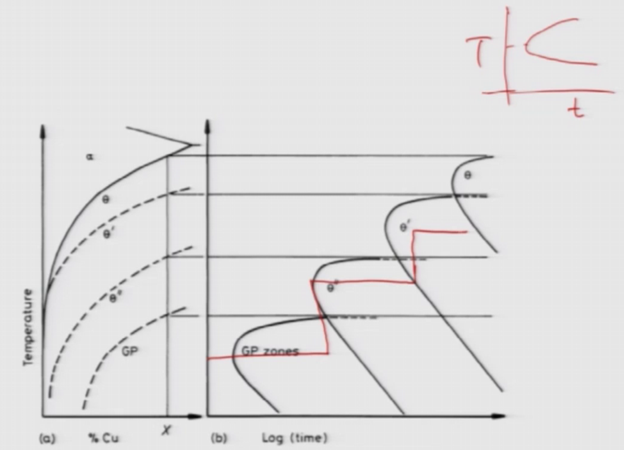


Fig. 5.32 (a) Metastable solvus lines in Al–Cu (schematic). (b) Time for start of precipitation at different temperatures for alloy X in (a).

Another important aspect which I already discussed let me tell you again.

Using these kinetics of the heat treatment or ageing treatment, one can actually generate something like a time temperature transformation curves. Although it is not truly T-T-T curve, but it can be. So, here as you see here this is the phase diagram, which is shown alpha and theta. And these are these dotted lines which corresponding to the different transient precipitous GP zone theta double prime and theta prime.

Now we can we can have something like a nucleation and growth kinetics built in into that and these curves are obtained like that; obviously, these looks like a Johnson mehl equation which is available for the steels, why? Because any if you look at any transformations the transformation rate depends on if I plot time as the temperature versus time transportation will be maximum, at some intermediate temperatures at higher temperature it will be a lower. And lower temperature it will be lower. This is mainly because at higher temperatures the driving force available is low. So therefore, nucleation growth it is a low.

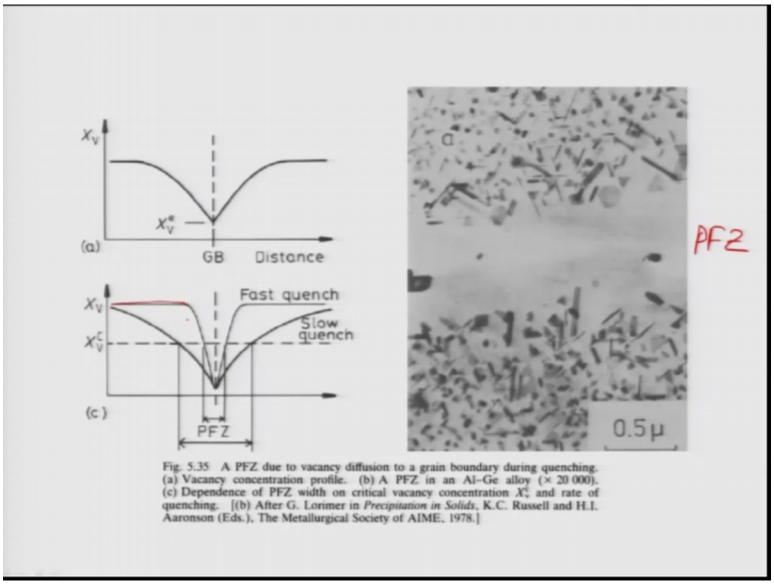
But lower temperatures nucleation driving force will be higher, but because diffusion is slow. So therefore, growth will be slow in the precipitation hard able or diffusional transformation by the way. So, that is why you always see is see separate curve. So, if the intermediate temperature some had between that both the optimum value of nucleation rate and growth rate can be achieved. Because diffusion as well as driving force both has to be optimally chosen. And that is why all this curves such a c separate nature. And GP zones because it forms at the lower temperature.

So therefore, they will reach they will be starting at a lower time scale a lower temperature both followed by theta double prime theta and prime and theta. So, this curves allows you to select the heat treatment cycles right. You can clearly see this is the time log this is temperature. So, if I simply do a double heat treatment first I can simply allow this things to happen like that. So therefore, a lot of large number of GP zones will form in the micro structure.

Then I can hit it up little high temperature and keep it there long time. So, it will allow me to form large number of theta double prime on the existing GP zones. And that is why it can be done. In fact, in many of these actual practices sometime people given even 3 stage heat treatment heat it up and keep it there also. So, you can actually have commissions of GP zones theta double prime and theta prime forming in the micro structure and give you the optimum value of the hardness.

So, such a kind of generate you know T-T-T curves or transformation temperature curves, can allow you to basically select your heat treatment cycles very nicely. So, that is the important part. And another important thing which is I saw discuss is that as you know this is this is important Because of the heat treatment cycle which you do.

(Refer Slide Time: 22:43)



Remember that the first thing we do in the heat treatment cycle is solutionzing at higher temperature. Something like about 500 to 550 degree celsius for the aluminum copper alloys.

Because of this solutionizing temp temperature all these precipitate theta prime get dissolved into the alpha matrix. And at high temperature; obviously, this is done. So therefore, there will be large number of vacancies created high temperature. As we know the equilibrium number of vacancy depends on the temperature in a particular material. So, higher temperature there will be large number of vacancies created, and they will be remain as a equilibrium defects. Now as a part of the heat treatment these high temperature solutionaized treatment is always followed by quenching at room temperature. So, as we quench a room temperature all the precipitate all these sorry all these vacancies which are form will be quenched in the micro structures.

Now these vacancies which are quenching from the high temperature to low temperature has a preferential role or very important role to play. Because this vacancies can then coheres and form vacancy loop and they can also form dislocations. They can lead to crossly of this dislocations because of the availability of these things.

But most important thing They can allow it to happen is the diffusion of the copper atoms. Because diffusion normally happens in the subsequent (Refer Time: 24:08) solutions by vacancy movement. So, at the vacancies are actually present in large number during ageing treatments this allows us to you know diffusion to have faster.

That is one important aspect. As I told you diffusion has a sink dislocation will act as a sink for the diffusion, because sorry for the for these vacancies, vacancies will form a loop and this can be again lead to formation of dislocations.

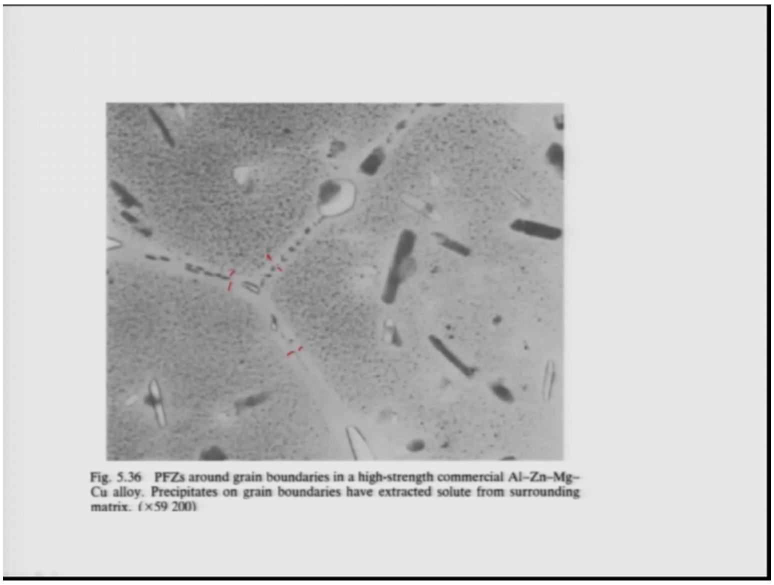
There is a another very important sink in the micro structure for the for these deficiencies, that is for the grain boundaries. Grain boundaries are basically have that structure if you look at it. And because of that this deficiencies can slowly moving to the grain boundaries and get you know sunk by the grain boundaries. So therefore, if I plot the distribution of fraction of the vacancies as a function of distance Between the 2 grains.

As you see here that the grain boundaries that vacancy concentration equilibrium concentration is very basically very low. So therefore, these vacancies which will be you know present at the gain boundaries will not allow the precipitates to form. Because for the precipitates form we need certain minimum amount of copper atoms. Because GP zones actually noting but the copper layers present on the aluminum alpha aluminum FCC lattice.

So, because of that the precipitates grain boundaries will be precipitation free. And these zones are called precipitation free zones or PFZ in the literature. This is widely seen; obviously, quenching rate has also a role, if you quench very fast as you see here if you quench very fast, you create you retain certain amount of vacancies inside the grain, but at the bend boundaries there is rapid drop defiance concentration. That is because grain boundaries access sink for the vacancies.

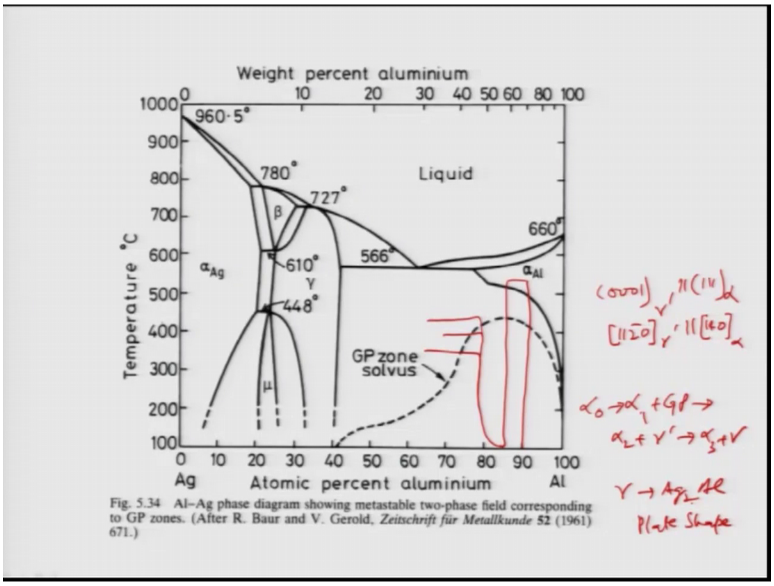
Vacancies will go and you know get lost in the in the grain boundaries. So there will be reduction of the vacancies concentration with grain boundaries. And because of that; obviously, the copper atoms cannot form these GP zones and precipitations not possible. This is widely observed in the microstructure, like this one You see here.

(Refer Slide Time: 26:18)



This is the, this are the 3 you know grain boundaries or 3 grains meeting at a point. So, near the grain boundary there is hit precipitation free zone present, which is widely observe in the aluminum copper aluminum zinc magnesium copper alloy. And this precipitates here actually also theta GP zone and theta double prime ok.

(Refer Slide Time: 26:41)



So, in the last at the end of these last portion of the these part of a precipitation hardening, let me just tell you aluminum copper is not only the one alloy which undergo precipitation hard enable precipitation hardening. But there are many others one of the important one is silver aluminum, which I mentioned in the last class.

Silver aluminum also forms 2 phases, as you see here what are the phases it forms this is alpha phase this is aluminum leach silver concentration something like about maximum is about 80 percent, eutectic temperature. And then you have a you know equilibrium between gamma and the alpha. Gamma is actually hexagonal structure here, and because of that gamma is hexagonal structure and because of that these alloys also undergo precipitate harden able hardening.

And the way things happen is this again I have let me not discuss the whole thing alpha 0 which is super saturate solutions it must forms alpha 1 plus GP zone then it becomes alpha 2 plus theta gamma prime. And then alpha 3 plus gamma and gamma prime and gamma both are hexagonal structure on the other hand alpha has a FCC structure. So therefore, the only orientation relationship which is possible which can lead to coherency between these precipitates gamma prime or gamma.

Basically gamma prime is such a kind of things that 0 0 1 plane of gamma prime must be parallel with 1 1 1 plane of alpha similarly 1 0 1 1 toward 0 direction of gamma prime must be parallel with one 1 0 direction of alpha. So, that is the that is coherent that will allows to have the coherency between the precipitates and the matrix phase. And it is seen to be specifically observe. Only problems is that because of the silver which is expend expensive material this alloys are not used so much. But as you see here this alloys can be used actually little higher temperature than the aluminum copper alloys, because these this all was which is shown here can actually go up to 550 degree celsius temperature. So, treatments will remain same again you take any alloy hit it up to this stalwart temperature.

Above the stalwart temperature then followed by quenching, and then one can do heat treatment at different temperature at the here or little higher or little higher depends on whatever. So, that is this routine way of doing the things. Here again the basically the precipitates final gamma of a precipitates is Ag 2 Al, and they are actually plates a (Refer Time: 29:23) they looks like a plate aluminum into cu and (Refer Time: 29:92) varies almost similar ok.

So, let me stop here for the this part of this portion of this lecture. In the so therefore, precipitation hardening is basically important an important class of alloys. And these phase transformations are to be nicely known to all of us. Because they becomes very important class of alloys. And there are many such I have only taken the example of aluminum copper to explain you the different aspects of the precipitation hardening. And I have given you here the (Refer Time: 30:01) some examples from aluminum silver alloys.

So, in the lecture we are going to start with another diffusional transformation that is known as eutectoid transformation.