Phase Transformation in Materials
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Lecture – 36
Precipitation Hardenable Alloy

So, we started the discussion about the solid-solid phase transformations in the last class and I said you that we cannot discuss all the solid to solid phase transformation during this course, but we are going to choose few of them and discuss the first one which will discuss is basically precipitation hardenable alloys in which the precipitates forms from the solid solutions. As you know that this is a diffusional type phase transformation because atoms needs to move because of the diffusional gradient a compositional gradient and form precipitates.

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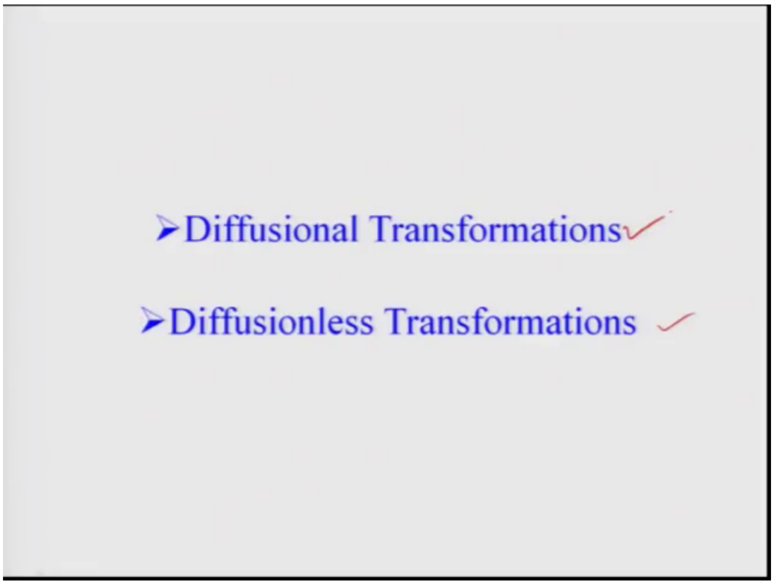

- Diffusional Transformations ✓
- Diffusionless Transformations ✓

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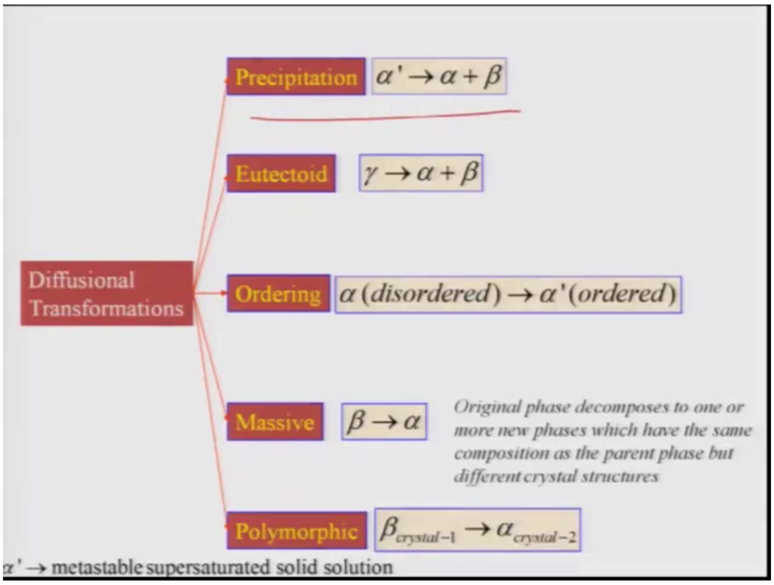

Diffusional Transformations

Precipitation $\alpha' \rightarrow \alpha + \beta$

Eutectoid $\gamma \rightarrow \alpha + \beta$

Ordering $\alpha\,(disordered) \rightarrow \alpha'\,(ordered)$

Massive $\beta \rightarrow \alpha$

Original phase decomposes to one or more new phases which have the same composition as the parent phase but different crystal structures

Polymorphic $\beta_{crystal-1} \rightarrow \alpha_{crystal-2}$

α' → metastable supersaturated solid solution

This also involves nucleation growth. So, we are going to discuss the first case that is the eutectoid transformation. So, that is these are the precipitation transformations.

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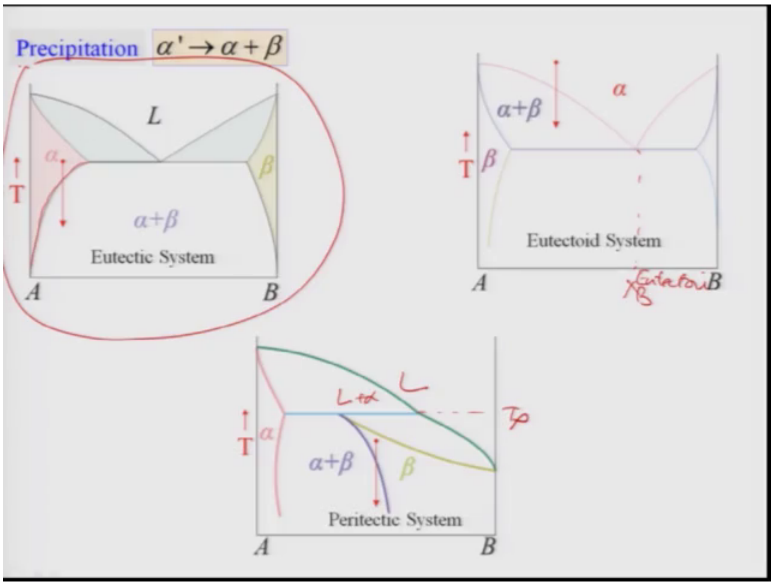

Precipitation $\alpha' \rightarrow \alpha + \beta$

Now, as you know as I shown you that there are different alloys which this kind of phase transformations are possible; the one which is more predominant is the first one; this is the case of aluminium copper alloy or aluminium copper silicon alloys and this is very widely used in the practical applications. So, we are going to spend most over time on these kinds of phase diagonal alloys.

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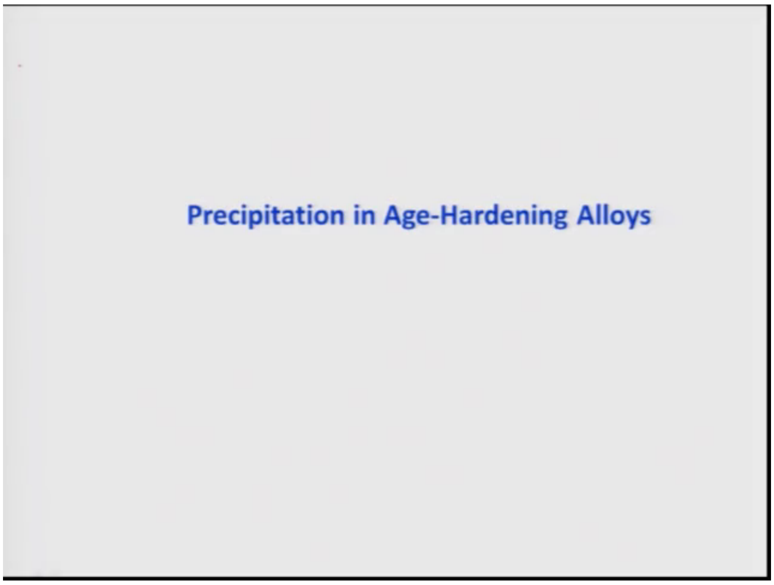

Precipitation in Age-Hardening Alloys

So, before actually I discuss in detail; let me just tell you that this is a very common phase transformation observed in many alloy systems; it is not only limited to aluminium copper.

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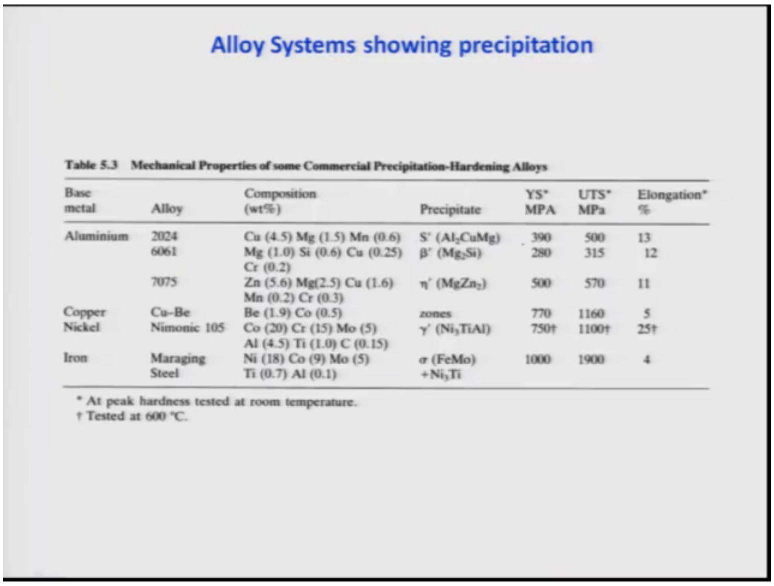

Alloy Systems showing precipitation

Table 5.3 Mechanical Properties of some Commercial Precipitation-Hardening Alloys

Base metal	Alloy	Composition (wt%)	Precipitate	YS* MPA	UTS* MPa	Elongation* %
Aluminium	2024	Cu (4.5) Mg (1.5) Mn (0.6)	S' (Al_2CuMg)	390	500	13
	6061	Mg (1.0) Si (0.6) Cu (0.25) Cr (0.2)	β' (Mg_2Si)	280	315	12
	7075	Zn (5.6) Mg(2.5) Cu (1.6) Mn (0.2) Cr (0.3)	η' ($MgZn_2$)	500	570	11
Copper	Cu–Be	Be (1.9) Co (0.5)	zones	770	1160	5
Nickel	Nimonic 105	Co (20) Cr (15) Mo (5) Al (4.5) Ti (1.0) C (0.15)	γ' (Ni_3TiAl)	750†	1100†	25†
Iron	Maraging Steel	Ni (18) Co (9) Mo (5) Ti (0.7) Al (0.1)	σ (FeMo) +Ni_3Ti	1000	1900	4

* At peak hardness tested at room temperature.
† Tested at 600 °C.

But many many alloy system; this is very common you give an alloy aluminium is of basically classic and these alloys are used in the alloy space industry the alloy which is named as 2024; this classification based on the certain aspects which I will not be able to discuss, but these alloys actually contents copper magnesium and manganese you see a copper content is about 4.5 weight percentage.

Then we also we also have alloys like 6061 or 7075; 6061, well in the 2024 basically the precipitated the phase is S prime as you see here is basically L 2 C u M g; normally in aluminium copper alloy, it is L 2 C u and that is known as theta, but in the when you are add little bit of manganese a little bit of magnesium not. So, manganese and magnesium both actually manganese will be about 0.6 percent magnesium will bit of 1.5 weight percentage the phase which forms as a precipitate basically S prime that has a composition of L 2 C u and little bit of magnesium present and it shows a very drastic change in the properties compare to aluminium; aluminium has yield strain about 60 MPa where has these alloy has addition about 400 GMPA.

That is like a you know huge increase similarly 6061 is again is an aluminium copper magnesium silicon alloy and because it has a magnesium; magnesium and silicon the precipitate is basically beta prime and this will be M G 2 S I type these also has a reasonably good properties, but not as good as the copper aluminium copper magnesium manganese and 7075 is basically a aluminium zinc alloy with a certain amount of coppers 1.6 weight percent magnesium 2.5 percent and rest like manganese and chromium.

So, these are actually 3 important aluminium alloys which. So, precipitation hardening behavior, but there are other alloys like copper beryllium which is used in the minds is contents about 2 percent to 8 percent of beryllium a little bit of cobalt normally forms zones. Basically, we will discuss about that it has very high increase of the mechanical properties and then you have nickel and iron alloys nickel alloys may basically mnemonic and it has cobalt chromium manganese sorry molybdenum aluminium titanium carbon little bit carbon and the precipitates we know that.

Precipitates are basically Ni3 Tl type, it can be N i 3 Ti L; N i 3 L type and this shows fascinating higher temperature properties. So, and finally, iron actually iron carbon alloys or something known as maraging steels they have huge amount of alloying elements nickel cobalt molly titanium aluminium it forms both sigma and Ni 3 Ti sigma is a hard a inter metallic f e a more type or f e shear type here and say f e mo and N i 3 T i both this precipitates leads to huge increase in the yield strain and as well as UTS and which you can see on the on the table.

So, these things clearly shows that is precipitation hardening alloys are actually are the major class of alloys which are really use in the industry and that I have been talking about to you for the last you know cup. So, many lectures that where phase transformation is not only subject which is specifically dealing with basic aspects of the material science, but it has lot of applications oriented important aspects which needs to be understood now once so; that means, precipitation is a very common phenomenon in all these alloys and whatever I am going to discuss is basically going to give you a snapshot of the picture it is not possible to if discuss everything in the time frame we have.

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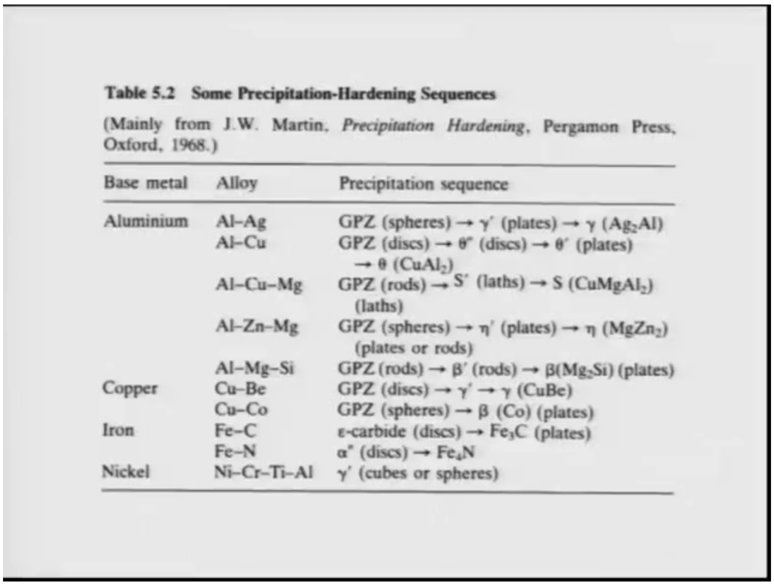

Table 5.2 Some Precipitation-Hardening Sequences

(Mainly from J.W. Martin, *Precipitation Hardening*, Pergamon Press, Oxford, 1968.)

Base metal	Alloy	Precipitation sequence
Aluminium	Al–Ag	GPZ (spheres) → γ' (plates) → γ (Ag_2Al)
	Al–Cu	GPZ (discs) → θ'' (discs) → θ' (plates) → θ ($CuAl_2$)
	Al–Cu–Mg	GPZ (rods) → S′ (laths) → S ($CuMgAl_2$) (laths)
	Al–Zn–Mg	GPZ (spheres) → η' (plates) → η ($MgZn_2$) (plates or rods)
	Al–Mg–Si	GPZ (rods) → β' (rods) → β(Mg_2Si) (plates)
Copper	Cu–Be	GPZ (discs) → γ' → γ (CuBe)
	Cu–Co	GPZ (spheres) → β (Co) (plates)
Iron	Fe–C	ε-carbide (discs) → Fe_3C (plates)
	Fe–N	α'' (discs) → Fe_4N
Nickel	Ni–Cr–Ti–Al	γ' (cubes or spheres)

As you know aluminium silver also form precipitates like GP zones; GP zone is the specific name which will discuss today then we have theta gamma prime and gamma which is basically G 2 L aluminium copper all of us must have some idea which will discuss in detail GP zone theta prime theta double prime theta prime and theta theta is nothing, but A L 2 C u. Then you can have aluminium copper magnesium aluminium zinc magnesium which I have discussed you can have aluminium magnesium silicon. So, like here beta beta eta a S or S prime copper as you say there zones or gamma phase and then other things like irons carbon iron iron nitrogen or even a nickel base alloys.

So, finally, they precipitation is happens it is sequence the creel cracks of the slide is the precipitation does not happen from super saturate solid solution is directly to the equilibrium phase when it happens in the sequence that is what actually the twinning of the properties in very possible by looking at simply heat treatment sequence are microstructures. So, as I said I am going to discuss more in general about aluminium copper alloys.

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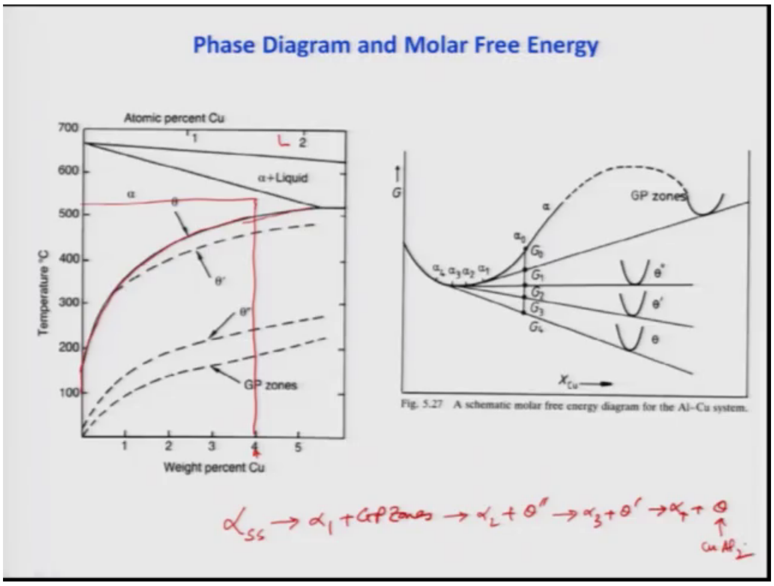

Phase Diagram and Molar Free Energy

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

$$\alpha_{ss} \rightarrow \alpha_1 + \text{GP Zones} \rightarrow \alpha_2 + \theta'' \rightarrow \alpha_3 + \theta' \rightarrow \alpha_4 + \underset{\underset{CuAl_2}{\uparrow}}{\theta}$$

Because that say classic alloy system which shows precipitation hardening and this is very important because all the theoretical backgrounds are basically based on the extensive study on this aluminium copper alloy.

The alloy which is important and widely used in the industries aluminium 48 percent copper alloy shown here; so, simply by adding 48 percent copper, we can actually change the mechanical properties of aluminium extensively as you know I have shown you the phase diagram aluminium copper phase diagram is basically very complex on the copper side aluminium side is not so complex; it has alpha phase and liquid and alpha is nothing, but a solid solutions of copper in aluminium, it has a FCC structure; the lattice parameter of 4.04 Armstrong. Aow as you know as I told you very nicely suppose if I draw a dot is a vertical line here at about 4 at weight percent of copper.

What is what is normally done in the age hardening; let us first discuss about that what is normally done is that this 4 percent weight percent copper aluminium alloy; that means, it has 48 percent copper and 96 percent of aluminium is heated at about 555 degree Celsius temperature in the temperature range and get for certain time. So, as you know copper which is basically a solid here will be dissolved nicely in the aluminium matrix and little form a FCC solid solution between copper and aluminium that is what is alpha phase. Now what is done is that from this temperature at about 550; this is quenched to let us say about room temperature quench into water normally.

Room temperature is about 30 degree Celsius. So, it is quenched. So, what will happen if it quenched the alpha phase remains because we did not provide enough time for the alpha phase 200 go transformation correct alpha phase will remain in the in the sample because it has been quench. Now once I take this quench sample this has basically quite a lot of copper and then what alpha phase suppose to have if you look at carefully I have shown you last class also if I quench a room temperature you should have basically alpha phase should not contained large amount of copper it should contented very very small amount of copper as you see here; this is the Solvus curve which is shown here Solvus is going down like this very rapid decrease.

So, at about say 100 degree Celsius temperature, copper solubility in aluminium is negligible small. So, because of that alpha phase will be is basically quenching to water will leave to super saturated alpha what is known as super saturated alpha. So, this supersaturated solid solution of alpha is not as stable phase thermodynamically because it has large amount of copper than it suppose to have. So, once a heat of 250 degree Celsius temperature; these supersaturated alpha transform and it is actually it transform many sequence basically of phases.

So, what actually happens super set alpha will transform to alpha 1 plus GP zones GP zones are actually the kind of a sheet of copper atoms sitting on the aluminium lattice on the 001 planes of aluminium FCC crystal structure. So, this is actually copper atom which is which is 2 layer or may be of 3 layers of the copper atoms sitting on the aluminium 10001 planes actually 001 planes that is the z axis planes. Now if you heat it up or keep it long time at 150 degree Celsius temperature for that again, this 2 transform into alpha plus theta double prime, we will discuss about this structure theta double prime later the finally, if you heat again and keep it at higher temperature for more time is become alpha 3 plus theta prime and finally, it will produce alpha 4 plus theta.

Theta is nothing, but at a composition of C u L 2. So, actually see here these alpha 2 alpha 1, alpha 2, alpha, alpha 4, there actually same alpha, but different concentrations of copper why because as this is phases form this is a GP zone theta double prime theta prime and finally, theta which is a basically co incoherent precipitates having a body center tetragon structure. It takes out the excess copper which is there in the super saturate alpha solid solution is remember carefully we have quench the sample from higher temperature to room temperature and retain huge amount of copper in the crystals in the in the sample and this copper which is present in the alpha phase is not a; cannot stay there longer because it is a meta stable phase because of that it will come out actually heat it up a give surface and time for the diffusion happen because you need to provide temperature and time for the diffusion of copper are comes in the sample.

And this gives the formation of these precipitates now one can actually discuss in a detail manner that is what I have shown you here as you seen that this different phases like GP zone theta double prime theta prime and all these things what are they let us look at the empire clearly first.

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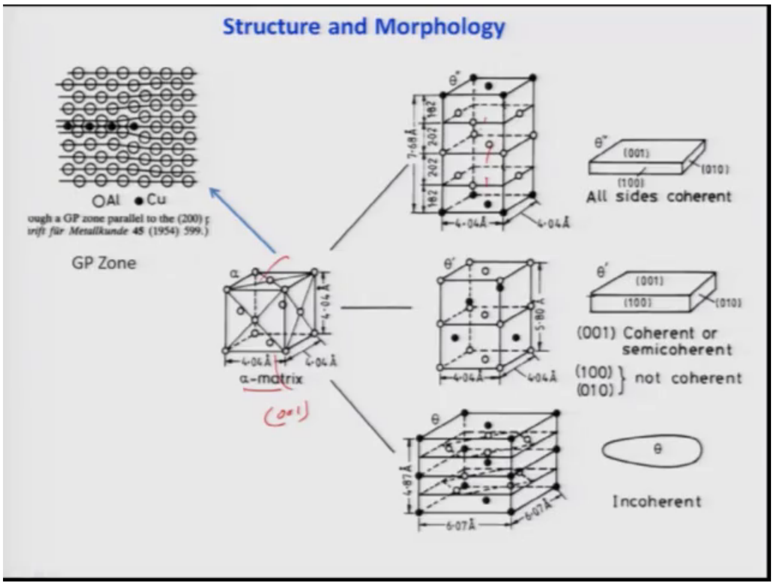
Structure and Morphology

ough a GP zone parallel to the (200) p
rift für Metallkunde 45 (1954) 599.)

As you said GP zone is nothing a specific copper atoms sitting alone 001 planes of aluminium what is this let us look at first aluminium matrix, this is the alpha matrix you see it is nothing, but a FCC aluminium basically start FCC aluminium anymore because as it is lot of copper inside it. So, therefore, all the atoms which I am showing here as this blobs; they are shown as aluminium every in the books also, but they all of them may not aluminium, there will be some of a atoms will be copper and it has a lattice parameter of our 4.04 Armstrong.

Now, if you see carefully, this is nothing, but a segregation of the copper atoms along certain planes and these planes are happens to be these planes that is 001 planes of the aluminium alpha crystal and they actually from actually some layers may be 2 layers or 3 layers that is what is shown here you see these are the copper atom sitting as a layer and because of that because of that it forms very very you know dist not very dist distorted structure in the lattice and therefore, these are actually known as zones. In fact, this was discovered by Guinier and Preston simultaneously while analyzing the x-ray diffraction patterns of these alloys.

The x ray diffraction pattern shows tricks in the in the patterns and looking at the tricks they concluded that such a kind of zones actually form during the first able precipitation of aluminium copper alloys and that is why this is named by their name G; GP zones G for Guinier; P for Preston now what happens this is the first. So, alpha transformed to GP zone or alpha super saturated transform to GP zone first. Now once if you keep it for long time, then it will first transform to theta double prime we will discuss later how why it has it was from GP zones and theta double prime and theta and theta prime and theta first let us look at crystal structures of that.

As you see here it is shown theta double prime is shown like a you know it has again a is about 4.04 armstrong and c is about 6.7.6 in a armstrong basically. So, importantly it is basically the 001 planes actually remain almost similar you see here FCC only in between we have alter layers of aluminium you see here this is aluminium this is aluminium ;this is aluminium and its very evident after looking at all the microstructures that all the sides of the theta double prime remains coherent with the matrix please go back to our lectures my lectures on interfaces. So, coherent remains is basically it remains almost completely coherent along the all slides sides that is what is shown all the plains of that 001, 100 and 010; they remains coherent that is why; they actually this separate.

Now, once you once this theta double prime transform to theta prime again is c axis changes a axis does not change; remember a and b; actually remains 4.04 Armstrong c becomes 5 point a may Armstrong because of that because of this transformations. So, some of these planes remains coherent is obvious because a and b remains same; the lattice parameters. So, therefore, 001 planes actually remain the coherent or in extreme case it will be semi coherent there will be some distortion of the planes, but these planes that is 100 that this plane 1000 is this sides and 00010, they become in not coherent they are become actually in coherent because of the copper atoms nicely sitting on these places.

Now, what is theta then theta is basically equilibrium precipitates it has a body center tetragonal structure as you see here is not a very simple structure to analyze initially it has a lattice parameter of 6.07 Armstrong a or b and c is about 4.87 Armstrong. So, what is happening where transform theta double prime to theta prime to theta is basically c axis is changing, but when it become theta both c and a axis values the a lattice parameter values are actually changing and it become completely incoherent with the matrix.

Now, if once you have analyze these crystal structures and atomic positions in these pictures is very evident why theta cannot precipitate directly from the alpha super saturated solid solution that is mainly because of the incoherent natures with the precipitate and the matrix the interfacial energy is very high. So, nucleation barrier becomes very high remember nucleation here in the solid state has 2 important aspects one is the interfacial energy other one is the strain energy because of the interfacial energy is very high for the theta because theta is incoherent precipitates. So, therefore, interfacial energy between the precipitate and the matrix alpha is very high.

Not only that it will also strain because of the difference in the elastic properties there will be lot of strain built up and these 2 aspects will lead to higher nucleation barrier that is why; it is very difficult to precipitate directly theta from the alpha super solid solution on the other hand if you look at GP zone is basically completely coherent structured GP zone is nothing, but segregation of the 2 to 3 layers of the copper atoms on the 001 planes of the alpha and because of that because of its basically few layers the interface remain coherent the strains do present, but they have very low very low because few layers of copper all the copper and aluminium atoms is a different it will not distort the lattice. So, much the strain energy will be high.

So, therefore, all the there will be strain, but strain energy will be less strain energy will be low and interfacial energy is; obviously, low because is a coherent with the matrix because of that is nucleation barrier is very low this will be followed by theta double prime again if you look at theta double prime only all the sides are coherent I have already discussed because of the nature of the coherency the nucleation various low only thing which will be increasing from GP zone to theta double prime is strain energy between illustrate energy between the precipitate on the matrix and. So, on theta prime will have some of the phases; phase sets are basically incoherent.

So, because of that something the surface energy the interfacial energy will increase and for the theta is basically is very high interfacial energy. So, these actually leads to sequence of precipitation and one can actually explain this sequence of precipitation using free energy morphine energy constructions that is what is shown here G versus x u plots this is directly taken from the book of portend and is telling as you see here this is my free energy curve of the alpha super saturated solid solution because GP zone is not a distinguish. So, therefore, we cannot show as a special free energy curve for that is nothing, but a extension of the free energy curve of the alpha remember GP zone is nothing, but a few layers of the copper atoms on the 10011 planes of the alpha.

So, therefore, if I draw a common a tangent between GP zone and these alpha, what I see I see that it cuts at the alpha one here and it cuts there. Now GP zones will have quite a lot of copper as you see concentration of copper is high here that is because a sheet of copper layers basically getting attached, but the alpha which is which is in equilibrium with the GP zones has a composition which is higher in copper also. So, and the energy difference between you know the this alpha and the GP zone mixture compare to alpha this is alpha and this is the this common tangent dealt you the get free energy or energy of the system consisting of alpha 1 and GP zone given by this point is basically G 0 which is very small.

So, therefore, it basically easy to transform from alpha super saturated solid solution to alpha 0 plus GP zone it should be alpha 0 I should have written it like that then it. Now if I again do it same thing for the theta double prime theta prime and theta; obviously, all of them will have separate free energy curve. So, because there separate phases the lattice parameters of different. So, if you see here theta double prime I can always joy common tangent between alpha and theta double prime and get the composition of these and these theta same thing theta that prime also super things and the free energy is gradually decreasing from del d 0 to G 4. So, system actually can reduces energy. So, alpha super solid solution can reduce energy by single sequence by forming GP zones theta double prime theta prime and theta this is possible.

And that is why this transformation happens one is the kinetic barrier that is a nucleation barrier other one is the energy decrease happens to the step manner that is much easier things to happen.

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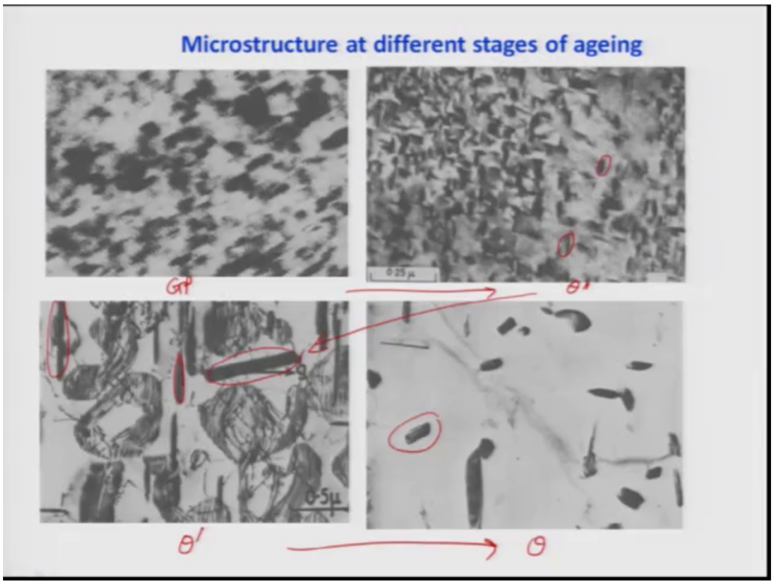

Microstructure at different stages of ageing

Now, let me just discuss show you some microstructure before end this part of the lecture. So, you see this is the microstructure of GP zone the first one GP zone why because there actually very thin layers of the copper attach to the alpha. So, that is why this only strain contrast in the transmits electro-microscope, they do not show a precipitate like morphology this was strain contract because its coherent to the matrix only thing is difference between the phase GP zone and the matrix is the strain develop similarly if I go to theta double prime here this is theta double prime yeah, let is write here.

Theta double prime theta double prime basically its current in all the 3001 planes and then look little bigger and you see this is one theta double prime this is another one there are this separate, but the moment you it has become transform the theta prime they become long you see here this is the one that is another one and that is another one you see and you see there are lot of strain contrast when other things represent and this is theta; theta is has a very specific separate precipitates is a long big separate precipitates.

So, that is why actually the step happen GP zone to theta prime theta double prime to theta and theta double prime theta prime. So, this is theta prime to theta that is always happens in the micro structures.

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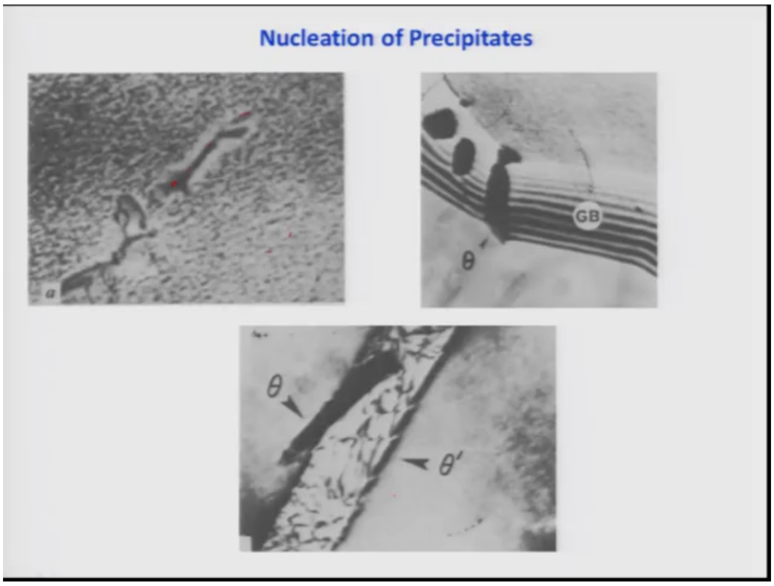
Nucleation of Precipitates

Now, if you look at nucleation; nucleation of these phases happens normally at the now the defects in the microstructures mostly the defects in the alpha grains; this is the nucleation of the theta double prime on in dislocation you see here these are the theta double prime they are forming on the dislocation.

And there are lot of precipitates present in the matrix also on the grain boundary normally precipitates happened more frequently this is a grain boundary of the alpha theta has precipitated on the grain boundaries is this another boundary between 2 alpha grains both you can see theta and theta prime I will precipitated. So, nucleation also happens on heterogeneously on this grain boundaries interfaces or dislocation structures this is also I have discussed in the last like few lectures earlier and this is basically the naturally observed in the aluminium copper alloy this is precipitates and remember this precipitates actually block the motion and the dislocations are causes barrier to the motion of dislocations because they present in the matrix.

So, whenever we try to deform this alloys they precipitates actually did allow us to retain; allow us to basically make the alloys form vey high strong in the sense that they basically cause they act as a barrier to dislocation motions we will discuss more about that in the next lecture. So, that is in a nutshell is the precipitation in the aluminium copper alloy.