Structure of Materials

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Lecture - 43
Chapter - 08
Phase Transformations

We have seen that if you look at the T T T diagram for plain carbon steel, the nose of the curve is very close to the origin, that means is the order of seconds. And we would like to add alloying elements for various reasons and one of the reasons is to move the nose of the T T T diagram to the right.

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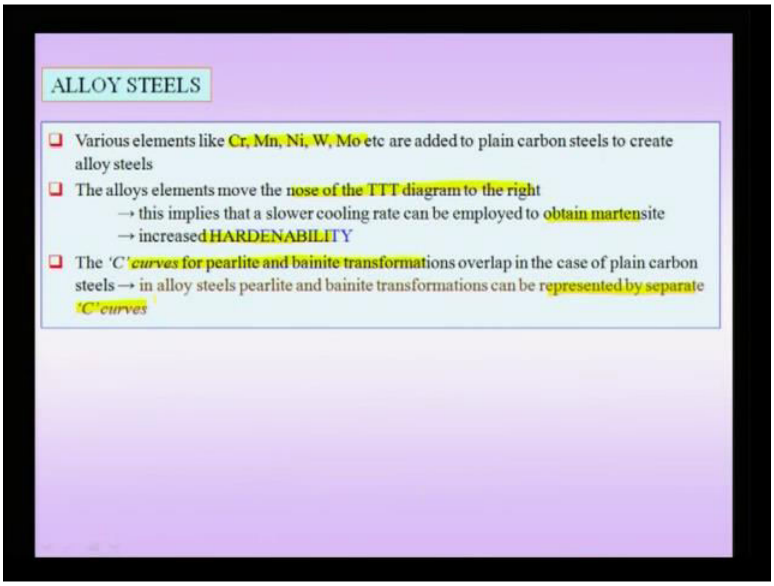

ALLOY STEELS

- Various elements like Cr, Mn, Ni, W, Mo etc are added to plain carbon steels to create alloy steels
- The alloys elements move the nose of the TTT diagram to the right
  - → this implies that a slower cooling rate can be employed to obtain martensite
  - → increased HARDENABILITY
- The '*C*' *curves* for pearlite and bainite transformations overlap in the case of plain carbon steels → in alloy steels pearlite and bainite transformations can be represented by separate *'C' curves*

So, that we can employ a less sever quench to obtain full marten site. This implies that we have increased the harden ability of the material, we also noted like for instance suppose, even though I may apply a very server quench on the surface of the material. The interior of the material is dependent on the thermal conductivity of the material and therefore, I feel a less sever quench. Therefore, it is all the more imperative to move the T T T diagram to the right, this also avoids residuals thermal stresses, which I generated during the sever quench.

Typically, many alloying elements are added each one of them giving certain benefits, and a combination of alloying elements are also added to give a better properties to the material. Some of these alloying common alloying elements are chromium, manganese, tungsten, molybdenum etcetera.

In this current set of lectures, we will not going to all the details of alloy steels, but we will keep our focus on this aspect, that how it effects the T T T diagram and broadly of course, outline what are the benefits of adding alloying elements. The C curves are pearlite and bainite transformations overlap in the case of plain carbon steels as we have seen. And in alloy steels, we will see that they can be represented by separate C curves that means, even a cooling constant, cooling rate experiment can give you bainite unlike in the case of plain carbon steels, where you need an isothermal hold to obtain bainite.

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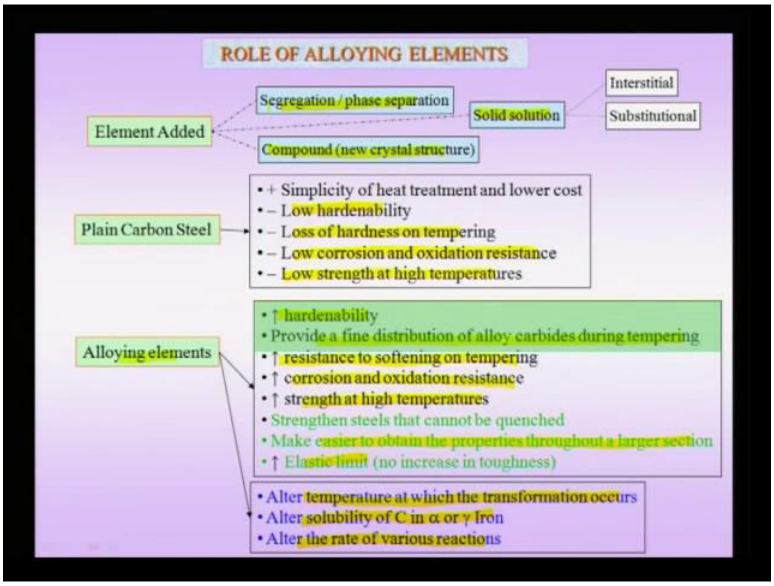

ROLE OF ALLOYING ELEMENTS

Element Added
- Segregation / phase separation
- Solid solution
  - Interstitial
  - Substitutional
- Compound (new crystal structure)

Plain Carbon Steel
- + Simplicity of heat treatment and lower cost
- – Low hardenability
- – Loss of hardness on tempering
- – Low corrosion and oxidation resistance
- – Low strength at high temperatures

Alloying elements
- ↑ hardenability
- Provide a fine distribution of alloy carbides during tempering
- ↑ resistance to softening on tempering
- ↑ corrosion and oxidation resistance
- ↑ strength at high temperatures
- Strengthen steels that cannot be quenched
- Make easier to obtain the properties throughout a larger section
- ↑ Elastic limit (no increase in toughness)

- Alter temperature at which the transformation occurs
- Alter solubility of C in α or γ Iron
- Alter the rate of various reactions

So, what are the broad role of alloying elements, they are added for instance to plain carbon Steel to increase the harden ability, they are added to provide fine distribution of alloy carbides during tempering. They are added to increase resistance to softening on tempering, they are added for corrosion oxidation resistance. They also give strength at elevated temperatures and they can often increase the elastic limit.

Now there are many, many more benefits which are not listed here, especially when added in a combination. They can give a unique combination of properties, which are not available in plain carbon steels. Now of course, all these alloying elements also combat some of the negative points, which are there in plain carbon steels like low harden ability, low lower hardness and loss of hardness on tempering. That means, that the severe loss of hardness on tempering, low corrosion and oxidation resistance and lower strength at high temperatures.

Now, this increased hardenability automatically implies that we can make it easier to obtain properties throughout, the larger section more easily. Now these alloying elements also alter the temperature at which the transformation occurs alter the solubility of carbon in alpha or gamma iron and alter the rate of various reactions. So, there are lot of complex things, which these alloying elements do, but in this set of lectures we will not be able to go into detail into all these aspects.

But, we will take up a few points especially, with regard to heat treatment and the aspect, we have mentioned that the effect on the T T T diagram. We should of course note that, when you add a second alloying element we have already seen previously that it may actually segregate of phase separate.

And this could be deleterious for instance suppose, you had phosphorus which is not a interstitial adding element for instance present as an impurity may segregate to the grain boundaries and cause problem sulfur can do the same thing. It may this alloying element may go into the solid solution as we have seen before or actually may form a compound.

And which of these ways to be warned to influence the properties is done via this microstructure engineering, which we are studying. So, in this lectures we will worry about hardenability and we will see that, how this alloy carbides also are produces a fine distribution, which gives us superior properties.

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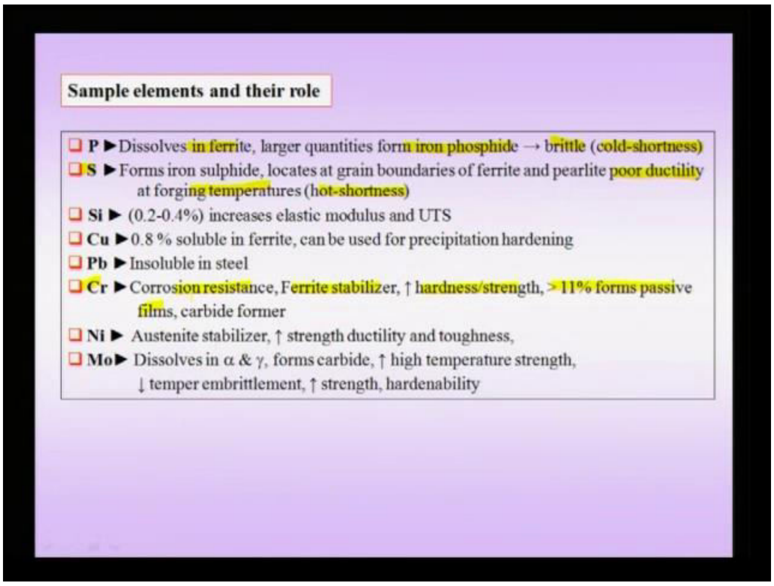

Sample elements and their role

- ☐ **P** ▶ Dissolves in ferrite, larger quantities form iron phosphide → brittle (cold-shortness)
- ☐ **S** ▶ Forms iron sulphide, locates at grain boundaries of ferrite and pearlite poor ductility at forging temperatures (hot-shortness)
- ☐ **Si** ▶ (0.2-0.4%) increases elastic modulus and UTS
- ☐ **Cu** ▶ 0.8 % soluble in ferrite, can be used for precipitation hardening
- ☐ **Pb** ▶ Insoluble in steel
- ☐ **Cr** ▶ Corrosion resistance, Ferrite stabilizer, ↑ hardness/strength, > 11% forms passive films, carbide former
- ☐ **Ni** ▶ Austenite stabilizer, ↑ strength ductility and toughness,
- ☐ **Mo** ▶ Dissolves in α & γ, forms carbide, ↑ high temperature strength, ↓ temper embrittlement, ↑ strength, hardenability

The role of very many elements in more than one context very diverse, but a small distinguish mentioned here, for instance phosphorus is dissolves in ferrite and larger quantities form iron phosphide, which causes cold shortness and makes your material brittle. So, that means we want to avoid phosphorus in the material. Sulfur can cause hot shortness again that means, during deformation at high temperatures at forging temperatures we have poor ductility and therefore, sulfur also should be avoided most materials.

But there are good elements for instance, chromium for instance is improves corrosion resistance, it is a ferrite stabilizer. It gives you a high hardness to strength ratio and hardness or strength. And typically, more than 12 percent chromium forms a passive barrier that means it gives you good corrosion resistance to iron. So, a person who is working on steel should also know the role of each one of these alloying elements, the synenergistic effects of these alloying elements and how they should be added. So, that they do not segregate etcetera. But as I mentioned that we will not go into details at this point of time.

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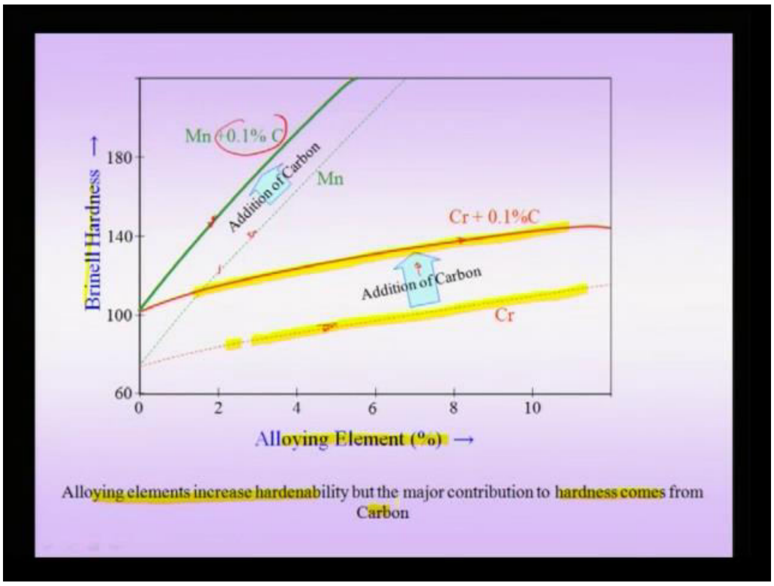

Alloying elements increase hardenability but the major contribution to hardness comes from Carbon

One point which might be noteworthy at stage is that, suppose I am plotting the hardness of material along with the percentage of alloying element. If you add chromium, you would knows that the hardness increases with the percentage of chromium, but additionally suppose, you are able to add carbon. So, this first curve is for chromium, suppose I add chromium and I add percentages of chromium, I note that my hardness increases with percentage of chromium in the material.

But additionally, suppose I am adding carbon. So, this gives the further benefit to the fact that chromium is already there. So, if you have a chromium carbon steel then I have an increased hardness also similarly, in the case of manganese, pure manganese gives you a increased hardness.

But manganese along with carbon gives that means, for a fixed percentage of manganese here say 2 percent. I can get a higher hardness, if carbon is present in 0.1 percent. Though the that implies, that this in the solid solution form the alloying elements increase hardness, but the major contribution to hardness comes from carbon.

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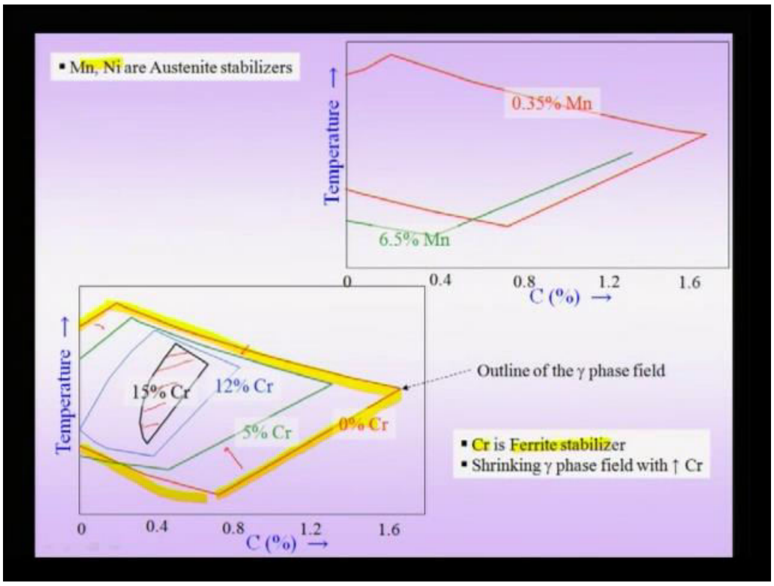

- Mn, Ni are Austenite stabilizers

- Cr is Ferrite stabilizer
- Shrinking γ phase field with ↑ Cr

But, the point is that these alloying elements, increase the hardenability, which has to be an important point which is to be noted, when you have these alloying elements for instance if you had chromium. Chromium it is a B C C structure and is a ferrite stabilizer that means that if I add chromium in increasing percentage then for instance this is 0 percent chromium. This is my boundary of the gamma phase field at high temperature.

So, this the boundary if I add more and more chromium, you can see that the gamma phase filed actually shrinks because gamma is F C C and chromium is a ferrite stabilizer. Therefore, this phase flied decreases and at a certain critical percentage of chromium, you can see that 15 percent. The phase field has been reduced to a such a small region.

That means that if I add a ferrite stabilizer, then the gamma phase will increases on the other hand. Suppose I add an austenite stabilizer like manganese or nickel, which are both F C C structures, then the austenite phase filed actually expands. So, these are some of the things, which we would like to note when we are actually adding an alloying element that, what is it is crystal structure. What role does it play in stabilizing or increasing or decreasing the various phase fields as compared to the original iron carbon diagram.

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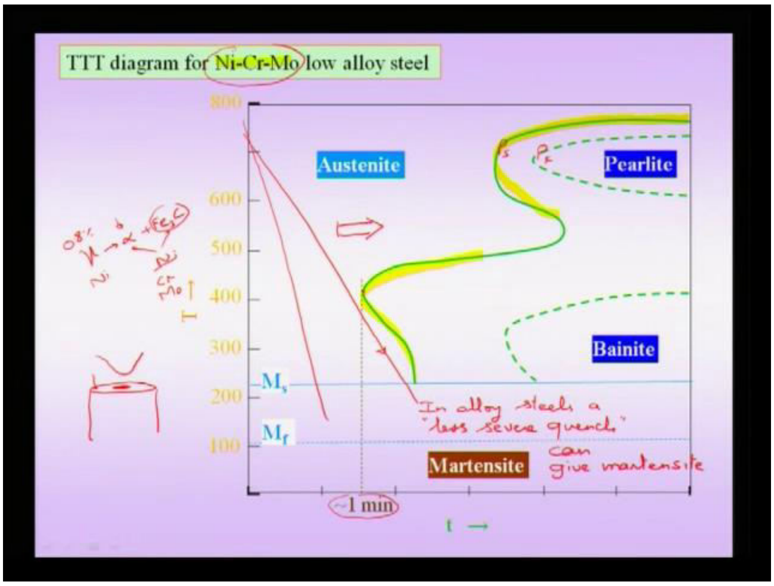
TTT diagram for Ni-Cr-Mo low alloy steel



So, this is the point we wanted to stress, that now this is a T T T diagram for nickel chrome mole steels. The first point we would note of course, is that now there are separate branches for the and this is a schematic, we will come to a more actual looking curve in the next diagram.

That you would note that the pearlitic transformation curve, C curve is now distinct from the bainitic transformations c curve. So, that is the most important, first point you would note, now this is a nickel chrome mole low alloy steel that means, you have added nickel chromium and molybdenum to plain carbon steel. And now this is an alloy steel now.

The second point you anybody would note from this diagram is that the nose for formation of martensite that means, the nose which has to be avoided. Now has to be has pushed has been pushed to the order of about a minute, that implies now instead of quenching at a rate, which was very severe for instance initially I was to had to quench from the gamma phase field at a very severe rate. And of course, I am drawing a straight line their known log scale, they have to look like curve lines. Now we can actually quench at a less severe rate to produce martensite. So, this implies I need to employ a less severe quench to produce martensite so…

Now, what does this imply that my residual thermal stresses are also less and my overall quenching process becomes less vigorous. That means, suppose I initially, suppose may

I quench a steel, I need to worry about the bubbles are forming, which can actually reduce their cooling rate, now I do not have to worry about that. And further I can now harden larger cross sections of the material throughout.

That means, I will get a uniform hardness across larger cross sections and we have noted before that, suppose I am talking about plain carbon steel then you would note that, even though at my surface I may produce a martensite. So, it consider the cylinder before and on the surface you may get martensite and higher hardness.

The hardness may actually fall towards the center, because in the core you may have only pearlite. Therefore, such problems can be elevated to a large extend by using an alloy steel in which case my T T T diagram has moved to the right hand side. So, this is my direction, which a T T T diagram has moved, now for instance what is the reason that this T T T diagram is moving to the right.

Initially of course, the carbons have to partition itself between alpha and F e 3 C. Suppose, you had an gamma, which was giving my alpha and F e 3 C in my pearlitic transformation. Now if you have an alloying element for instance, which is present in gamma say for instance now in this case it is nickel. This nickel has additionally to partition between the alpha and F e 3 C and nickel being a substitution alloying element is sluggish in its diffusion and therefore.

It takes a longer time for the pearlitic transformation to start and to complete. So, this is my pearlite start curve and this is my pearlite finish curve. So, this partitioning issue that, now my alloying element has to partition between 2 phases the alpha and F e 3 C. In addition of course, the carbon, which is say I am taking about 0.8 percent carbon gamma, then this carbon also has to partition.

Because, alpha has very low of carbon F e 3 C is 6.610 percent carbon. So, in addition to the carbon being partitioned between alpha and F e 3 C. Now the alloying elements and each has it is equilibrium solubility in alpha and F e 3 C. This is true for nickel this is also true for chromium in the current case and also to molybdenum that means, all these alloying elements have to partition between the alpha phase and F e 3 C phase, which implies that, now my overall eutectic eutectoid transformation is sluggish and my T T T diagram is to the right.

So, we can see that there are many properties, which can improve by forming an alloy steel like the nickel chrome mole low alloy steel.

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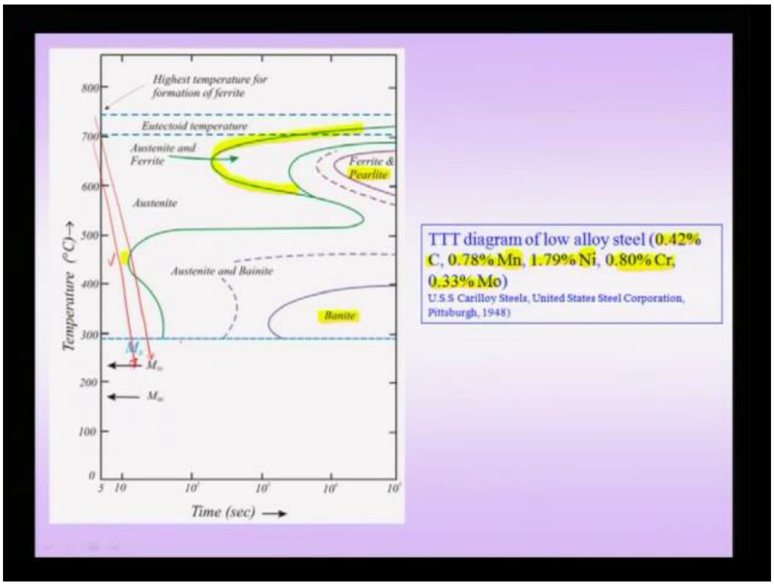

TTT diagram of low alloy steel (0.42% C, 0.78% Mn, 1.79% Ni, 0.80% Cr, 0.33% Mo)

U.S.S Carilloy Steels, United States Steel Corporation, Pittsburgh, 1948)

But, additionally you have these benefits in terms of the particle process of producing martensite, which is the quenching and also the ability to obtain a complete martensite across the cross section. Now this is a diagram for and other alloy steel, which is now my it contains 0.42 percent carbon, 0.78 percent manganese, 1.79 percent nickel, 0.8 percent chromium and 0.33 percent molybdenum. That means, that now this is as all the alloying elements in the small percentages, nickel is an austenite stabilizer manganese an austenite stabilizer, while chromium is an B C C element, which stabilizes the ferritic phase. Now all these alloying elements have now to partition between the alpha and F e 3 C phase.

And that means, that now my overall T T T diagram is going to be sluggish and here like before we are having the extra arm, which corresponds to the ferritic transformation. Because now this is an hypo eutectoid steel and we have the other phase transformations. But the important point to note is that, we have a separate c curve for the bainite and a separate c curve for the pearlitic phase. There are other complications to this curve, which we are not considering in detail, but this is similar to the semantic, we considered before that, we have 2 separate c curves.

And now if I can avoid the nose of this curve and quench at a certain high rate, then I can produce my martensite starting from this austenitic phase. So, I am sorry this is a little intersection here, suppose I can avoid the nose here. So, this is my correct curve. So, I can produce martensite therefore, and suppose I intersect the nose of the curve, then there will be a partial formation of bainite, which is not possible of course, in the case of the plain carbon steels.

So, there are certain benefits of working with alloy steels and one of them we have considered here in detail. The other benefits of course, the percentage interested may go through different text.

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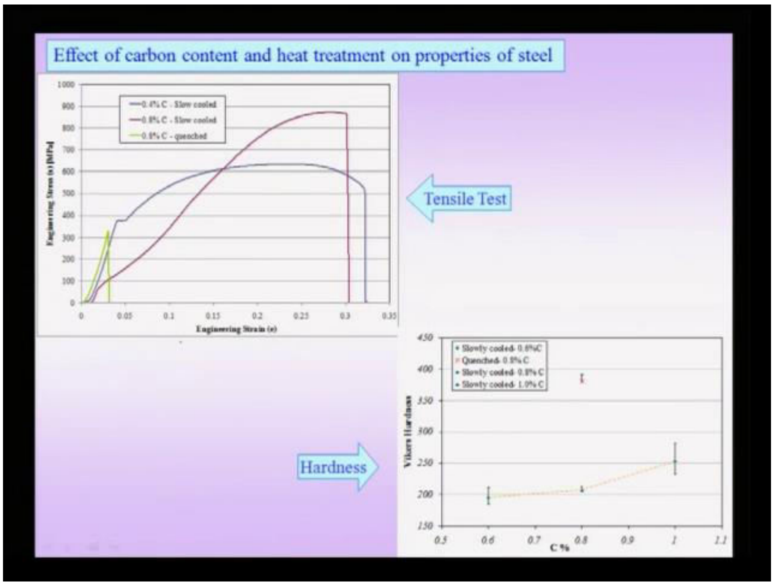

Effect of carbon content and heat treatment on properties of steel

Tensile Test

Hardness

Will give you lot of these things in detail. Previously we have already seen that how does the hardness vary, here with the microstructure.

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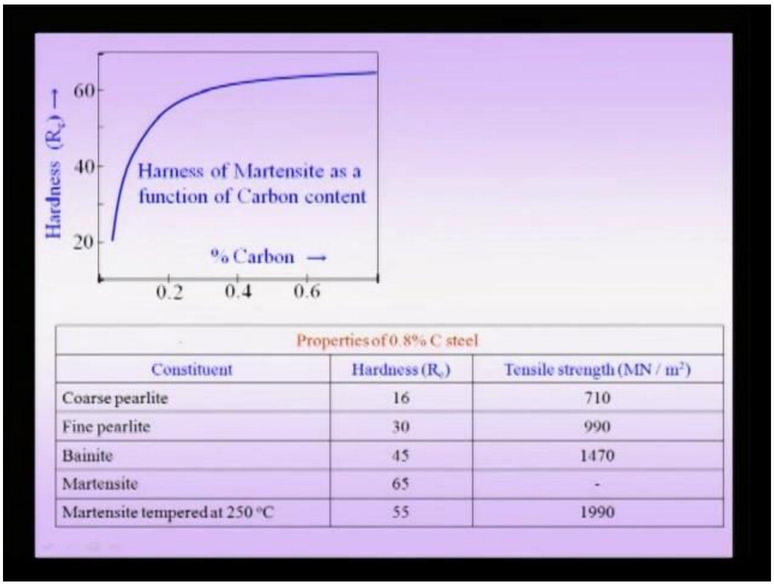

Properties of 0.8% C steel		
Constituent	Hardness (R_c)	Tensile strength (MN / m^2)
Coarse pearlite	16	710
Fine pearlite	30	990
Bainite	45	1470
Martensite	65	-
Martensite tempered at 250 °C	55	1990

And we pointed out that this is a very, very important chart, when we want to understand the properties. That for instance suppose, a student of material science as I pointed out is should be well works with what we call microstructure engineering. In other words not only does he engineer his properties by using suitable crystal structures, like he knows that F C C is more ductile than B C C.

But also additionally he manages his microstructure. So, as to get an optimum set of properties, we had noted that, that means that suppose I ask a question that what is the hardness or the tensile strength of 0.8 percent carbon steel, I pointed out this would be an ill posed question. And one need to understand what is the heat treatment given what is the microstructure. So, that the properties come out.

So, for the same 0.8 percent carbon steel, we can have a wide range of hardness as we saw before starting from 16 R c to 65 R c. And also along with the change in the hardness, we saw there is also a change in ductility in other properties. Now similarly, we will note some other properties, which are now important and we will see, what is the effect of carbon and also the effect of the quenching process. These are all done on samples and none of this stress should be taken ideally, they are just schematics tests. So, that we can understand the overall concepts involved and more accurate tests have to be done, to actually get the true nature of the stress strain diagram.

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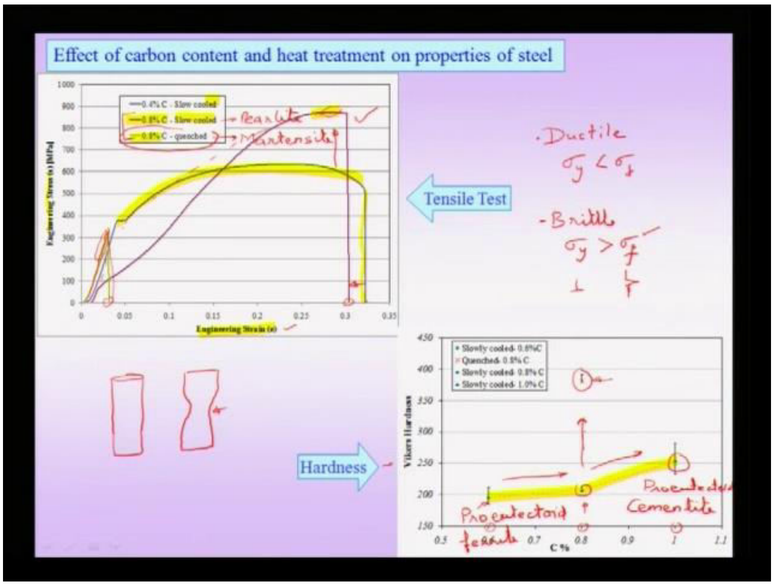

Effect of carbon content and heat treatment on properties of steel

Tensile Test

Hardness

So, in this case of course, I am plotting engineering stress with engineering strain and I am growing. So, for 3 materials 2 of them are 0.8 percent carbon steels, one has been slowly cooled and you know, when you slowly cool we produce pearlite. So, this in other words should have a pearlitic microstructure and when we quench, if we know that we produce martensite and there could be some retained austenite.

Now, if you take a 0.4 percent carbon steel, we know that the we have already seen that with the reduction in carbon percentage. the microstructure, now consist of pro-eutectoid ferrite followed by pearlite and also, that the T T T diagram for a 0.4 percent carbon steel is different from that of the 0.8 percent carbon steel. Now for the 0.4 percent carbon steel, you note that these curves perhaps are not ideal and you would like to the true curve may look something slightly different.

So, you may have a curve like this and you see that 0.8 percent carbon steel has certain ductility, but the point. So, this is my 0.4 percent carbon steel sorry, this is the 1, I am going to mark in yellow. So, this is my 0.4 percent carbon steel for which, my curve is like this. So, the 0.4 percent carbon steel has certain amount of ductility, but the strength is lower than the 0.8 percent carbon steel. That means, by adding more carbon I am increasing the strength of the material, but what is happening to the ductility you see that there is a fall in ductility with along with the increase in strength.

So, the 0.8 percent carbon steel has a lower ductility as compared to the of course, in this case I am not using the true measure of ductility here, I am using percentage elongation. But the true measure is not the strain or the percentage elongation, but has to be the percentage reduction in area. Because after making starts most of the deformation is localized to close to the neck, that means, when I am doing a test on a cylindrical specimen like this, what is expected to happen is that it will form a neck and during this necking process. Most of the deformation is localized here and therefore, percentage reduction in area is a better measure of ductility as compared to the strain or the percentage elongation.

But, here we are looking at the overall characteristics and we can take a few take off messages, but with the increasing carbon though, I have an increased strength, but I have lower ductility. On the other hand suppose I take the same 0.8 percent carbon steel and quench it to produce martensite. Now you notice that this material is very, very brittle and any preexisting cracks or quench cracks actually lead to the failure of the material.

That means it is not able to reach its true yield strength, because of the crack propagation we know that a ductile material is one, in which the yield strength is lower than the fracture strength. A brittle material is one, in which the yield strength is more than the fracture stress, in other words I in a brittle material approach fracture, before I cause plastic yielding. And you known fracture is related to the presence of cracks and in a material. And these cracks of course, could be preexisting cracks, they could be quench cracks, which are coming from processing, they could be surface cracks introduced by machining etcetera or and yield strength is related to typically, to the motion of dislocations.

They are of course, edges true dislocations or a mixed dislocation therefore, we see that when you quench this 0.8 percent carbon steel to produce martensite. Because of it is extreme brittle nature, it actually fails at very low stains that means, in the just it does not give you any much of plastic deformation.

So, here we can see that the properties of a material are drastically altered by heat treatment or what we can call as microstructure engineering and this theme of course, we have used plain carbon steel to illustrate. But this does not mean that this is limited to this case, you can use microstructure engineering, even to engineer properties like coursivity, magnetic coursivity, etcetera. Now, so looking at this plot now, we can the summary of that tensile test curves is that, if you should have same percentage carbon, but different microstructures, you can see that the ductility is severely limited.

So, this is 0.8 percent carbon steel, but it is slowly cooled giving pearlite, while the martensitic microstructure gives you a very low ductility and the material fails at very low strains. Now on the other 0.8 percent carbon steel, 0.4 percent carbon steel which is lower carbon gives you higher ductility. But it has got a lower strength, because this carbon itself can give you a solid solution strengthening.

Now, the same thing is also reflected in the hardness data and again, I would want you that, these are schematics or test done on some routine industrial samples. But more control test in do actually numerical data, which might be more accurate. Now if you look at the hardness data, you note that I am having 3 samples 0.6 percent carbon steel, 0.8 percent carbon steel and 1 percent carbon steel and all the while, you can see that with increasing carbon percentage my hardness is actually increasing. Now, if you take now my 0.8 percent carbon steel, which is means that I am now at the eutectoid composition and quench it, then you notice that you can obtain a martensitic microstructure, which is very very hard.

So, I can increase my hardness by increasing the carbon percentage along this curve or I can take a fixed percentage of carbon. Like my 0.8 percent carbon and do a quenching and which can give me a very high hardness and this is the rigorous hardness, which is being measured here. So, of course, we all known that for 0.6 percent carbon steel, we have a microstructure, which contains pro-eutectic ferrite. And in this case you have a pro-eutectic cementite.

So, I can increase my hardness by this carbon increment, which is my solid solution strengthening or I can quench to produce martensite, which is a very very hard phase and there can be a considerable increase in the hardness. That means, that I can clearly see that by doing microstructure engineering, I can alter the properties severely. And this gives me a handle on the properties, further to the handle I get from the compositions. That means, I can alter the composition to get a specific set of properties.

But, further I can use these compositions to engineer my microstructure to get various structure dependent properties, which are very different from that in the absence of the heat treatment. And as I pointed out we can also do a thermo mechanical treatment.

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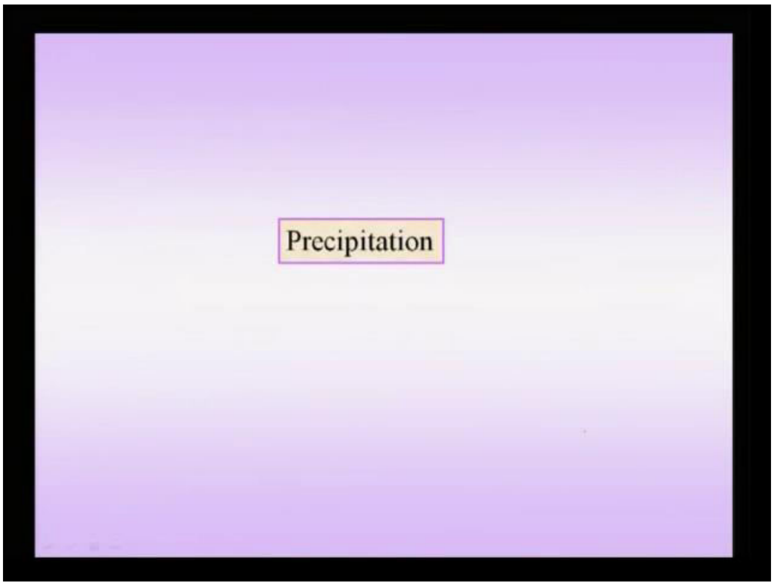

Precipitation

The second example, we will consider today is the example of precipitation hardening in an aluminum copper alloy. This here again, we do a detailed steps of heat treatment understanding the various parameters involved the process involved to engineer the microstructure. So, as to give on high strength in a material, which is otherwise not so hard.

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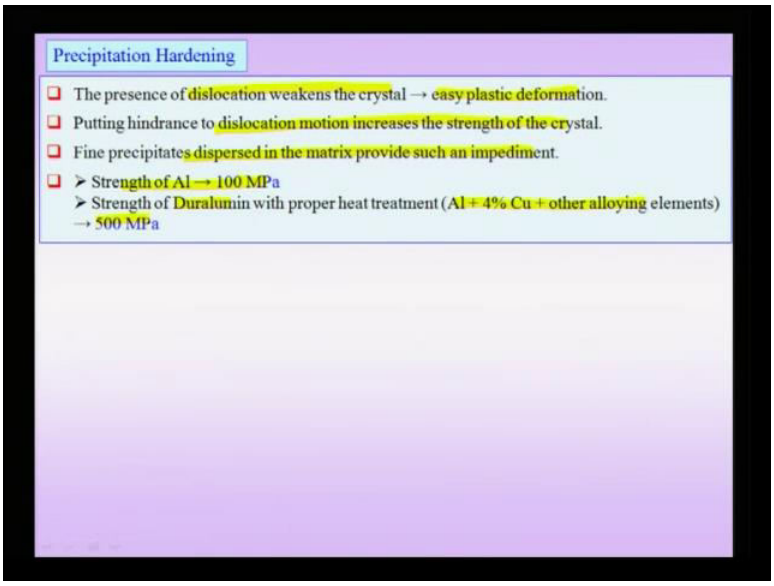

Precipitation Hardening

- ❑ The presence of dislocation weakens the crystal → easy plastic deformation.
- ❑ Putting hindrance to dislocation motion increases the strength of the crystal.
- ❑ Fine precipitates dispersed in the matrix provide such an impediment.
- ❑ ➢ Strength of Al → 100 MPa
  ➢ Strength of Duralumin with proper heat treatment (Al + 4% Cu + other alloying elements) → 500 MPa

So, in precipitation hardening, we have seen that the presence of dislocations weaken, the crystal and this weakening, we saw is a few orders of magnitude. That means, we can cause easy plastic deformation, because of the presence of dislocations. If you can put the 2 ways of course, hardening the material either hinder the motion of dislocations or removed dislocations all together. But we had already pointed out that removing dislocations all together is not a good stagey, because dislocations may nucleate in service causing the weakening of the crystal.

Therefore, putting hindrance to the dislocation motion is a good idea and we have seen before, that this can be done via various methods like solid solution making, the solid solution cold working etcetera or giving a fine grain sized material. One of the methods is to actually, produce fine precipitates, which can impede the motion of dislocations. And such an impediment has to be to get a fine precipitate, we have to engineer my heat treatment, so as to get that. Suppose, I am talking about strength of aluminum, which is about 100 M P a, which is means that aluminum is actually, a superb structural material it has got a good surface finish, it is light weight, it can easily be cut etcetera.

And it is because of the aesthetic appeal and it is easy ability to form and cut it would form a good structural material. But the big problem with aluminum is that it is being an F C C structure, it is actually very ductile. So, another methods to increase it is strength of course, is to cold work it, but the other is to form an alloy like duralumin and the proper heat treatment. And for instance, now duralumin consists of aluminum and copper and other alloying elements.

We can increase the strength to about 5 times, which is 500 M P a, which is a very good news. That now, I am alloying and following the alloying, I am doing a heat treatment and doing this heat treatment, I have knowledge of the phase diagram and the T T T diagram. So, as to engineer my heat treatment to get the desired properties, now let us look at the aluminum copper phase diagram.

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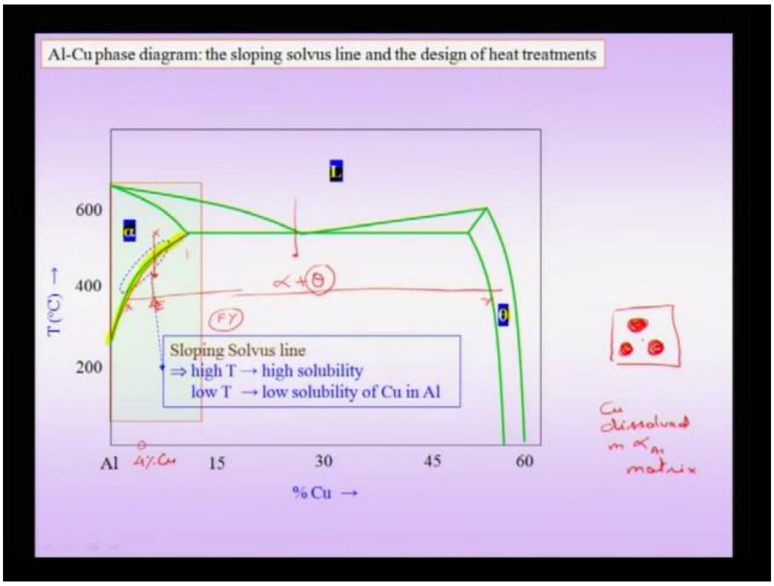

Al-Cu phase diagram: the sloping solvus line and the design of heat treatments

Sloping Solvus line
⇒ high T → high solubility
low T → low solubility of Cu in Al

And I am interested in the copper rich aluminum rich end, because this is where the sloping solves lane of the phase diagram lies. So, in this aluminum copper phase diagram the copper aluminum richened, you have the liquid phase and you have the alpha and theta phases, which form a slow cooling. That means, now suppose, I take an alloy, which is say for instance any where here, then my final microstructure would consist of alpha and theta. Theta being the equilibrium phase about, whose crystal structure we will be talking sometime soon. Now we are interested not in this part of the diagram, but in the lower copper percentage and we are talking about of this region, where is there is about four percent copper.

And this is model system aluminum, 4 percent copper not only to see the engineering applications of precipitation hardening, but also to understand the various fundamental processes, which occur during such a heat treatment. Now this line is a sloping solvus line that means that the solubility falls with temperature. That means, suppose at high temperatures I have a certain, solubility for of copper in alpha that means, now my copper is dissolved in the alpha matrix.

But, then when I am cooling, I will cross the solvus line and that means, that part of the suppose this is my tie line here. I will construct a tie line here and find out say for instance this temperature, what are my phase fractions of alpha and this arm of the, so this is my fulcrum f and say x y.

So, the fulcrum y line is proportional to the amount of alpha in the material that means, that if I slowly cool, I will produce the theta precipitate. And normally when slowly cooled the morphology is such that the theta precipitate is very large that means, that I would have theta in my matrix and the overall size of this theta precipitates.

Because, will be large because I would have a few nuclei, which grow very large and therefore, I would have a course precipitation course, precipitate morphology of theta phase in the matrix. Now, this such a material is not very good for hindrance of dislocation motion that means that, suppose I had A i will be go to the broad and explain, you and we have seen this before.

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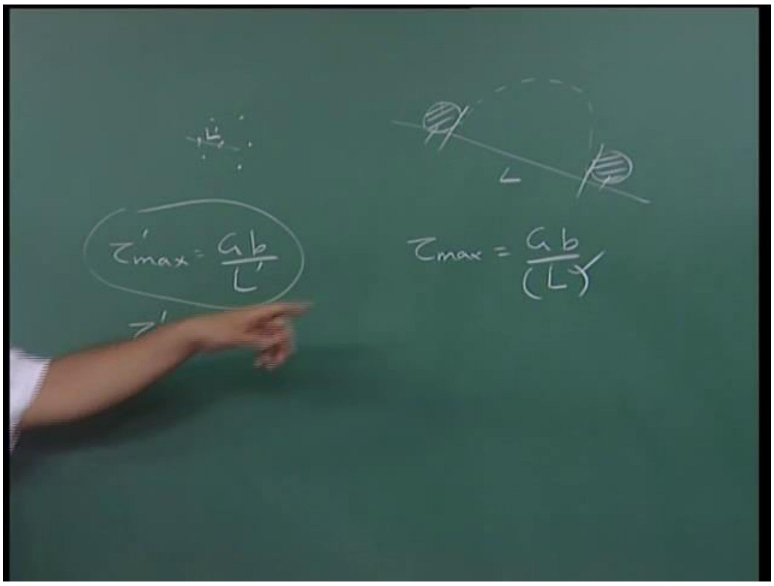

That suppose, I have a very fine distribution of precipitates in the material, we saw we course precipitates in the material. So, because now these precipitates are very course the distance between those precipitates are large. And now if a dislocation is being print this distance is now say L and actually the inner distance is L. Now the tau max is just as benefit is G B by L that means, larger the L lower the strength. On the other hand suppose I have a fine distribution of precipitates and now we have pinning centers from here to here and this is my distance L prime.

That implies now tau max prime is equal to G B by L prime and therefore, tau max is greater than tau. That means, at this say this is tau max to this shear strength, I get by fine stress precipitate distribution. Because now what we are assuming that, we are actually operating a double ended franked source in other words, this dislocation to move will have to actually bended here. Assuming these are incoherent precipitates and for that we need to apply the tau max.

That means, a higher shear stress as compared to just motion of dislocations in an unimpeded matrix. Therefore, if I have precipitates, which are far apart and there are course, they give a lesser hardening as compared to the fine distribution precipitates. Now how do I obtain a fine distribution of precipitates is the in, we are considering this phase diagram.

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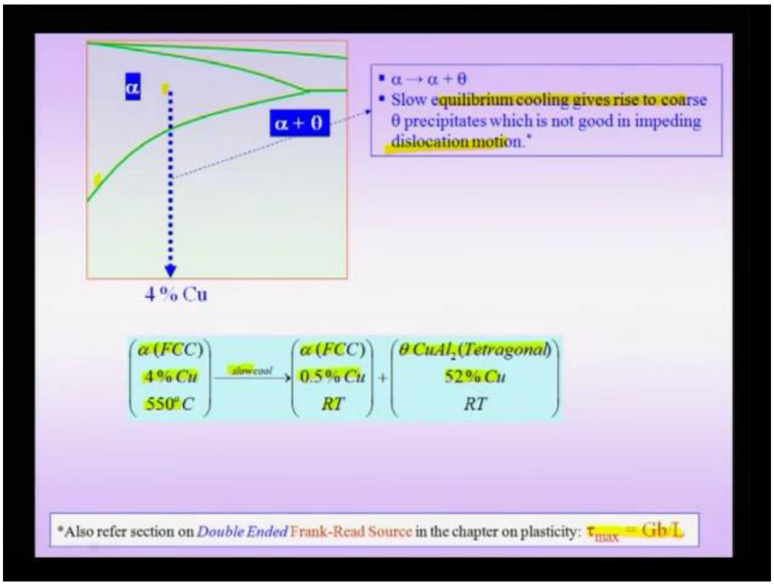

- $\alpha \rightarrow \alpha + \theta$
- Slow equilibrium cooling gives rise to coarse θ precipitates which is not good in impeding dislocation motion.*

$$\begin{pmatrix} \alpha\,(FCC) \\ 4\%\,Cu \\ 550^\circ C \end{pmatrix} \xrightarrow{slow\,cool} \begin{pmatrix} \alpha\,(FCC) \\ 0.5\%\,Cu \\ RT \end{pmatrix} + \begin{pmatrix} \theta\,CuAl_2\,(Tetragonal) \\ 52\%\,Cu \\ RT \end{pmatrix}$$

*Also refer section on *Double Ended* Frank-Read Source in the chapter on plasticity: $\tau_{max} = Gb/L$

So, let me summarize that you have this transformation, which is alpha F C C with 4 percent cooper at 550 degrees Celsius here. When slowly cool gives you alpha F C C with 0.5 percent copper at room temperature and the equilibrium precipitate, which is a composition of C u A l 2, which is a tetragonal phase. That means, that it has got lower symmetry than the alpha phase, which is a cubic phase and this contains about 52 percent of copper. So, most of the copper goes into the theta phase and unless the copper is present in the alpha, which anyway has a low solubility for copper at lower temperatures.

Now, this as I poi noted out slow cooling gives rise to a coarse theta precipitate, which is not good for impeding dislocation motion. And the benefit I was talking about term acts is G B by L. Now to avoid this formation of this coarse precipitate and again we are now altering, the composition we are keeping the composition of aluminum 4 percent copper.

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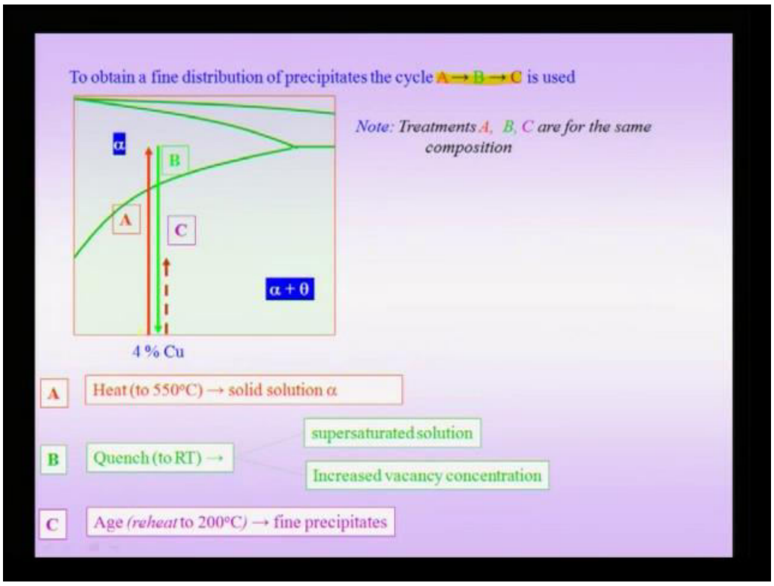

To obtain a fine distribution of precipitates the cycle A → B → C is used

Note: Treatments A, B, C are for the same composition

A Heat (to 550°C) → solid solution α

B Quench (to RT) → supersaturated solution; Increased vacancy concentration

C Age (*reheat* to 200°C) → fine precipitates

We follow theories of heat treatments and these heat treatments have been labeled A B and C. So, what are we doing in this heat treatments of course is first of course, the assuming that, I have somebody gives me a slowly cooled aluminum alloy with 4 percent copper.

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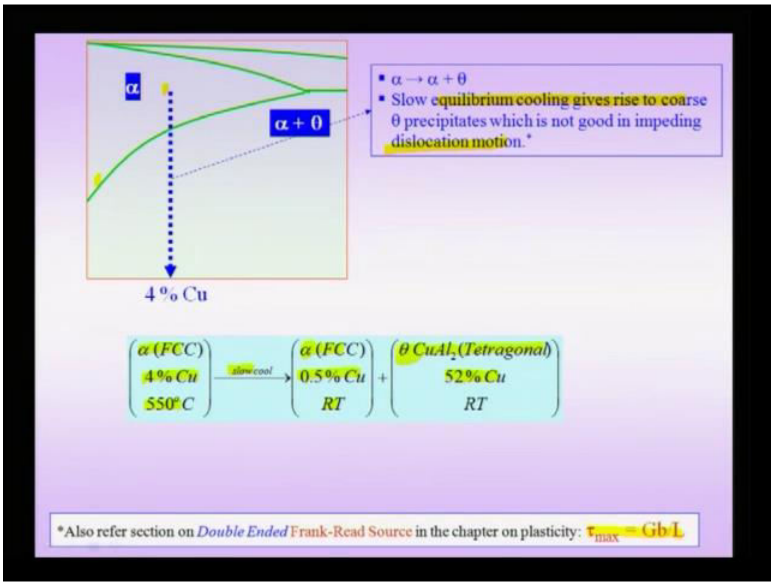

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*Also refer section on *Double Ended* Frank-Read Source in the chapter on plasticity: $\tau_{max} = Gb/L$

That means, I would already have a combination of alpha phase and the theta phase, which is the lower symmetry tetragonal phase. And as you know that, if the system is as a lower symmetry and it is a inter metallic and typically, the pearl stress of such a inter metallic could be larger. So, we expect that theta phase, the dislocation motion will more difficult with in the theta phase.

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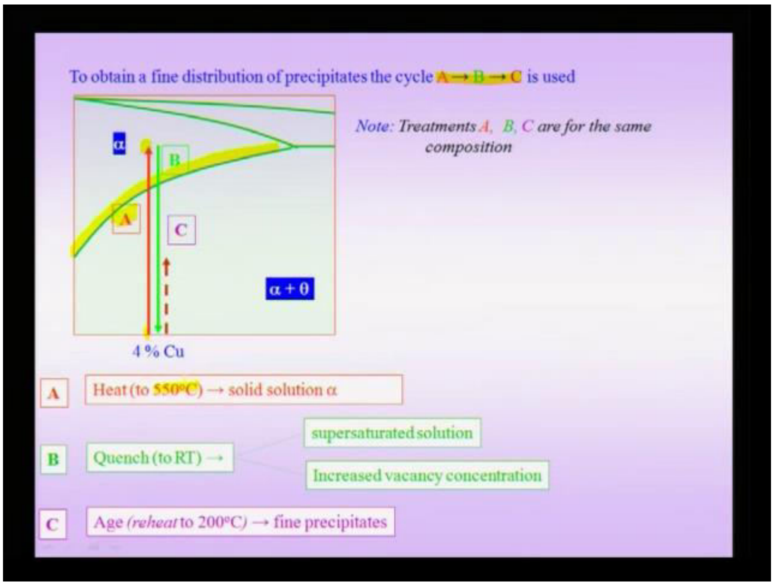
To obtain a fine distribution of precipitates the cycle A → B → C is used

Note: Treatments A, B, C are for the same composition

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C Age (*reheat* to 200°C) → fine precipitates

Now the heat treatment cycles, I would follow to get a fine distribution of precipitate is what has been labeled A B and C. So, I start with my material as we see, which is now contains alpha and theta phases. Theta being the equilibrium precipitate and assume that it is in the coarse state, I heat it above the solvus line. First using the during the A step to produce a solid solution, uniform solid solution alpha. So, by heating it and holding it all my theta precipitate will dissolve and I will get a uniformed solid solution alpha. So, I will at a hold long enough for that. So, typically temperatures I can heat to is about 550 degree Celsius, which is above the solvus line of these phase diagram.

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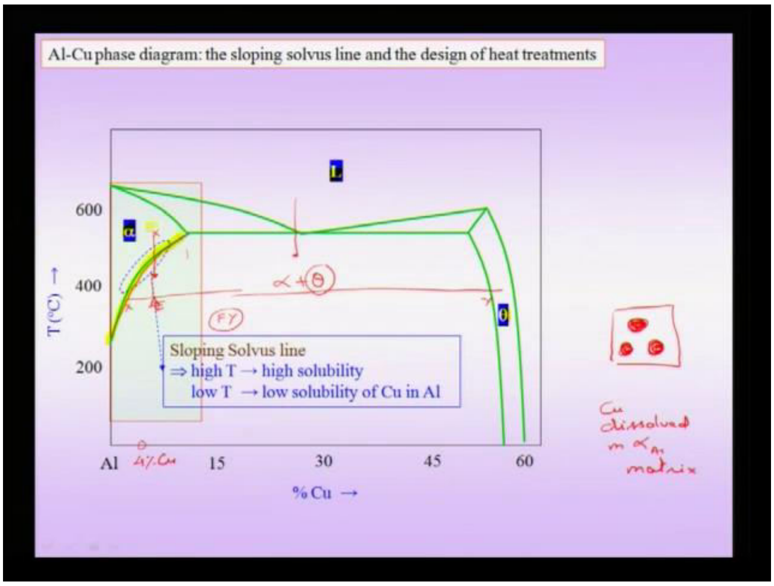

Al-Cu phase diagram: the sloping solvus line and the design of heat treatments

Sloping Solvus line
⇒ high T → high solubility
low T → low solubility of Cu in Al

So, we are heating some where here, so heating in this temperature regime, so as to get a uniform solid solution alpha.

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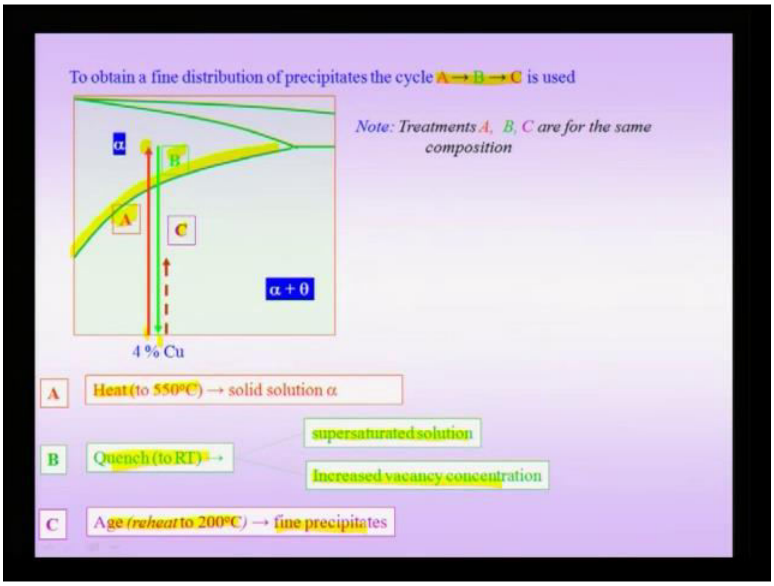

To obtain a fine distribution of precipitates the cycle A → B → C is used

Note: Treatments A, B, C are for the same composition

A Heat (to 550°C) → solid solution α

B Quench (to RT) → supersaturated solution; Increased vacancy concentration

C Age *(reheat* to 200°C*)* → fine precipitates

In the second stage, what I do is that I quench this material in step B, I quench it to room temperature and during this quench process 2 things are important to note. One is that I get a super saturated solid solution. This is now similar to for instance, when I opened a coca cola bottle, when I under pressurize the system. And therefore the carbon di oxide has been supersaturated in the aerated drink with respect to the high pressure that means, now I have a similar to that here, we have a it is like also like suppose I dissolve sugar.

In water at high temperature, that means at room temperature I can only dissolve a certain amount of sugar in water or certain amount of salt by heating the solution, I can dissolve more of sugar. But then suppose I immediately allow the I cool the system very fast, then I would note that all the sugar cannot immediately come out of the solution, which we are known is called the nucleation barrier opposes this. And therefore, you will have a super saturated liquid solution of sugar in water. Similarly here we have a supersaturated solution of copper in alpha iron.

Additionally, during the quenching process, we have an increased vacancy concentration, because the as we know the vacancy concentration depends erroneously on the temperature. That means, at higher temperature we had a higher vacancy concentration, but when we quenched it, there is no time for all the vacancies to escape. So therefore, we land up with a of course, all the some of the vacancies may be lost, but some vacancies are still trapped with in the lattice. And therefore, you have an increased vacancy concentration in step B.

In step C, what we do is that we reheat the material to certain low temperature and we will see what is the why this temperature 200 degrees Celsius come, when you consider the in the coming slides. But this temperature is definitely much lower than the original solutionizing treatment. So, we have the solutionizing treatment first, and then we have the quenching treatment. And finally, we have a process known as aging and the reason this word aging is used in this context is that originally. One of the investigators, who discovered this process left, is aluminum at solid solution at room temperature.

And then later on return to find that the hardness of the material had increased, when you looked under the microscope the optical microscope, he could not locate any micro structural features, which had change, but somehow the material has had aged. So, as to give an increased hardness you will see now, because of powerful electron microscope in other techniques that we now know the basis of why that hardening took place. And what is the as we have pointed out the micro mechanisms involved and.

So, the third step, we follow to get this fine precipitate is aging treatment in which case, we heat to a low temperature, this temperature could be around 180 or 200 degree Celsius and this gives us a fine precipitates inside the alpha matrix. So, let me summarize this slide these 3 steps.

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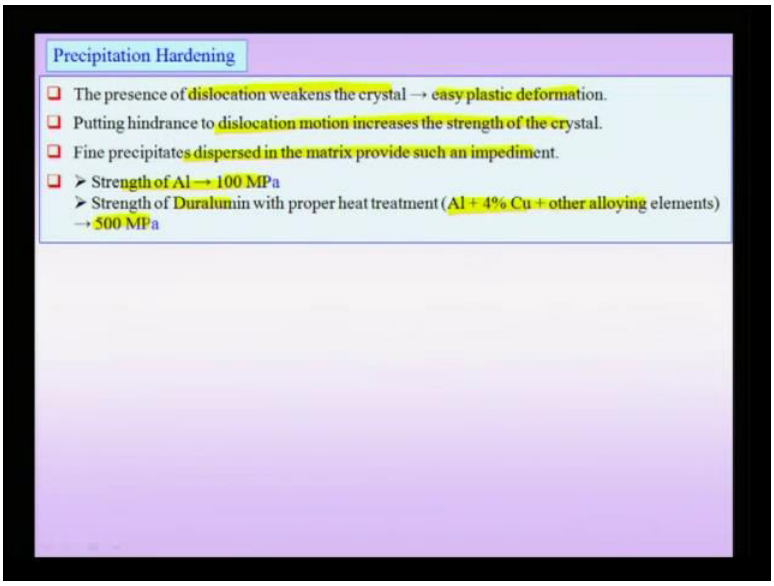

Precipitation Hardening

- ☐ The presence of dislocation weakens the crystal → easy plastic deformation.
- ☐ Putting hindrance to dislocation motion increases the strength of the crystal.
- ☐ Fine precipitates dispersed in the matrix provide such an impediment.
- ☐ ➤ Strength of Al → 100 MPa
  ➤ Strength of Duralumin with proper heat treatment (Al + 4% Cu + other alloying elements) → 500 MPa

Number 1 aluminum is reasonably soft and has low yield strength. I can increase the strength by various methods like cold working solid solution strengthening or grain size refinement. But an additional technique here is that by precipitation hardening in which case, I use a aluminum 4 percent copper alloy, which can give me an considerable and plus other alloying elements can give me a considerable benefit up to a factor of 5.

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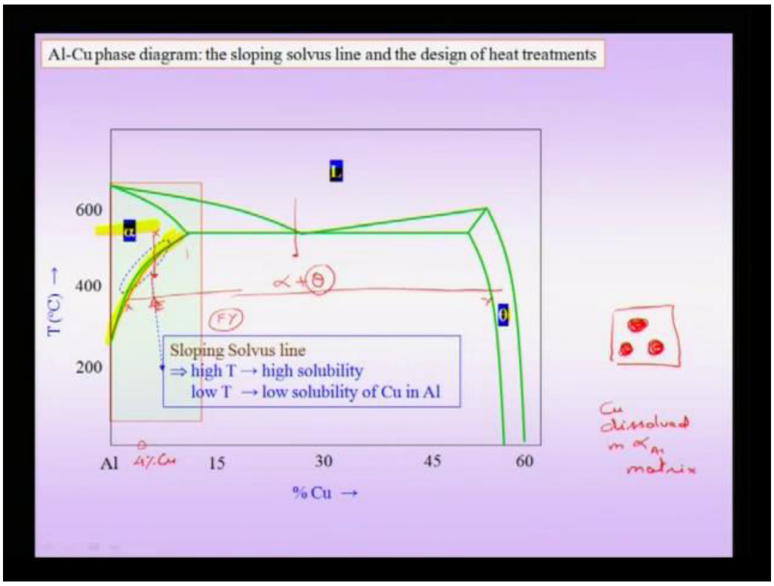

Al-Cu phase diagram: the sloping solvus line and the design of heat treatments

Sloping Solvus line
⇒ high T → high solubility
low T → low solubility of Cu in Al

Now, the heart of this whole thing is the aluminum copper system has a sloping solvus line. And I can decrease, I mean the solubility decreases with the decreasing temperature, but if I slowly cool it, I get my equilibrium theta precipitate, which is very course, which is not good for the hindrance of dislocation. And therefore, I would like to produce a fine distribution of precipitates in the aluminum matrix.

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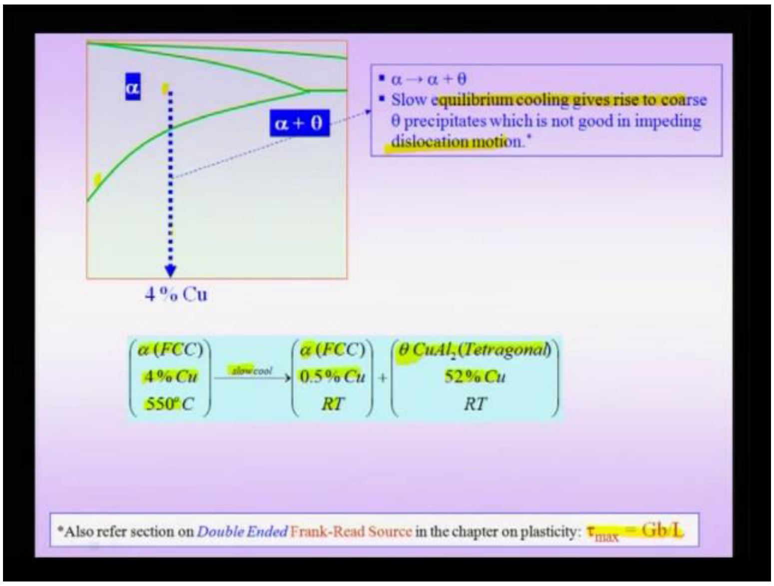

- $\alpha \rightarrow \alpha + \theta$
- Slow equilibrium cooling gives rise to coarse θ precipitates which is not good in impeding dislocation motion.*

$$\begin{pmatrix} \alpha\,(FCC) \\ 4\%\,Cu \\ 550^{\circ}C \end{pmatrix} \xrightarrow{slow\ cool} \begin{pmatrix} \alpha\,(FCC) \\ 0.5\%\,Cu \\ RT \end{pmatrix} + \begin{pmatrix} \theta\ CuAl_2(Tetragonal) \\ 52\%\,Cu \\ RT \end{pmatrix}$$

*Also refer section on *Double Ended* Frank-Read Source in the chapter on plasticity: $\tau_{max} = Gb/L$

What is the nature of these precipitates could be different from theta as we shall see soon it may not be the equilibrium theta precipitate, but we will get a fine distribution of precipitates.

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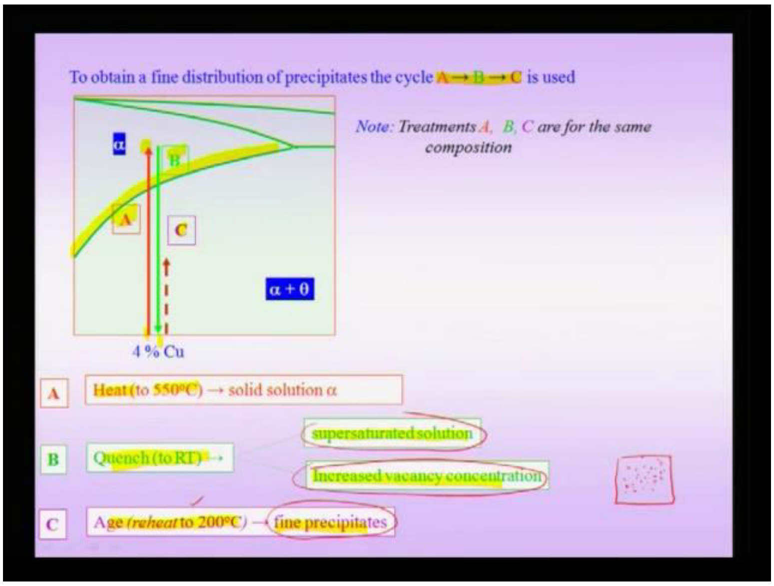
To obtain a fine distribution of precipitates the cycle A → B → C is used

Note: Treatments A, B, C are for the same composition

A Heat (to 550°C) → solid solution α

B Quench (to RT) → supersaturated solution
Increased vacancy concentration

C Age (*reheat* to 200°C) → fine precipitates

Now to get this hardness, what we do is that, we follow a 3 stage root, we first solutionazise an austherised material above the solvus line say about, 550 degrees Celsius. Then we quench the material to get a supersaturated solid solution, along with an increased vacancy concentration. This increased vacancy concentration is important to note. Because this gives us higher diffusivity of the substitution alloying elements during the aging step, which is following next.

And during the aging step, we heat the material to about 180 or 200 degrees Celsius to obtain a fine distribution of precipitates in the alpha matrix. So, my final goal is to produce a schematically, if I want to draw a fine distribution of precipitates. Inside the alpha matrix, which can effectively impede my dislocation motion and give an increased strength to the material.

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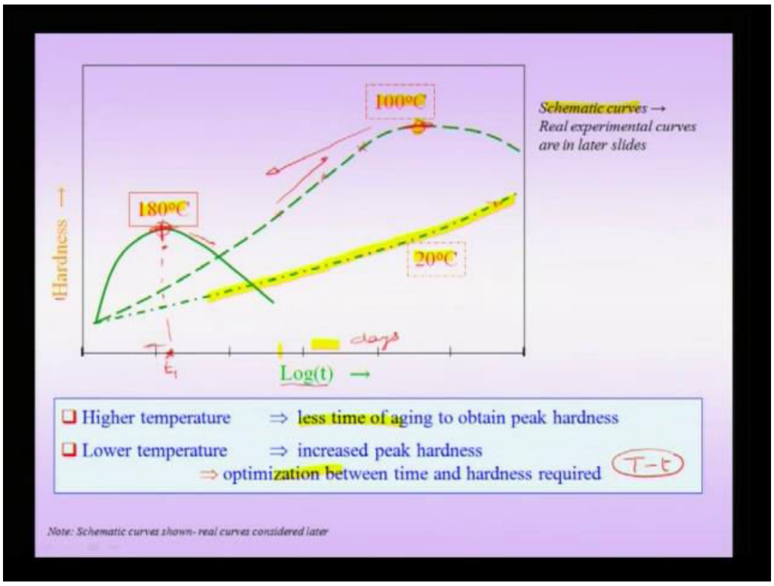

Schematic curves →
Real experimental curves are in later slides

☐ Higher temperature ⇒ less time of aging to obtain peak hardness
☐ Lower temperature ⇒ increased peak hardness
⇒ optimization between time and hardness required

Note: Schematic curves shown- real curves considered later

Now, there are some details to be considered, when I try to plot my hardness versus the temperature of time of aging. So, this is the next plot we consider. So, log time implies that, we are talking of the order of say for instance a few hours right here. In this regime to a few days of heat treatment and originally, in the experiment of let to the discovery of this age hardening treatment. Actually, there are aging was done under room temperature, which is close to this kind of a curve, in which case you can see that the curve is always increasing.

These curves, we can think of as schematic curve, schematic master curves and we will note later that more the actual curves are little more complicated. But the important lessons from this aging treatment can be understood by from these schematic diagrams. You note that in this case, there are 3 kind of aging curves drawn 1 at 20 degree Celsius, 1 at 100 degree Celsius, 100 at 180 degree Celsius with increasing temperature, you can see that the peak hardness is obtained at a less time.

That means, now if I increase my temperature of aging, then I get and of course, higher means of course, I am still much less than 550 degrees Celsius or where I intersect the solvus line, I am much lower than the solvus line temperature.

And in such a case, I get my peak aging. So, for since this is where the peak aging lies for the 100 degrees Celsius curve. This is where the peak age or the peak hardness curve lies in the 180 degrees and with 20 degrees, we have not yet reached the peak age even after a quite a few days of heat treatment. So, this is the of the order of days and more.

So, this implies that, if I want to obtain peak hardness in a short period of time then I have to go for a higher temperature. So, this is my hardness plotted with respect to log of time as before. And this log of time implies that more the time, I am spending in heat treatment more is my capital investment therefore, I need to worry about my production rate therefore, I have to worry about the time and hardness and properties optimization.

Now second thing to be noted from this graph apart from the fact, that the more higher the temperature the shorter the time for peak hardness to be obtained as we noted from here to here. But also that the peak hardness itself is less that means, if I age at a lower temperature, then I get a higher peak hardness. So, these hundred degrees Celsius the peak hardness is higher than at 180 degrees Celsius where my peak hardness is lower.

Now that means that I need to design the time temperature cycle. Such that I can get optimized hardness, which I require for my application with in a reasonable amount of time. So, this is something which is very important that means, I have to design my heat treatment cycle. So, that I can get the requisite amount of hardness, but without having to wait too long for the heat treatment to be completed. So, this is of course, in this curve we are assuming that, we are starting with a material which has been solutionalized and quenched.

And now we are just doing the aging treatment and we are plotting the hardness of the sample with various amounts of times of aging. That means, that suppose I age for say this is, now for instance a day for instance here, then I can note that at after one day aging at 100 degree Celsius, I get certain hardness with longer time of aging say 2 days, 3 days etcetera, I can see that the hardness is increasing.

But finally, the hardness after certain peak start should decrease as, you can see clearly from this curve. That means, that it is futile for me to suppose I am aging at 180 degrees Celsius, it is futile for me to age beyond the time, where the peak hardness comes. So, I have to note this time T 1, which is my optimum time and I would not like to age my specimen beyond T 1.

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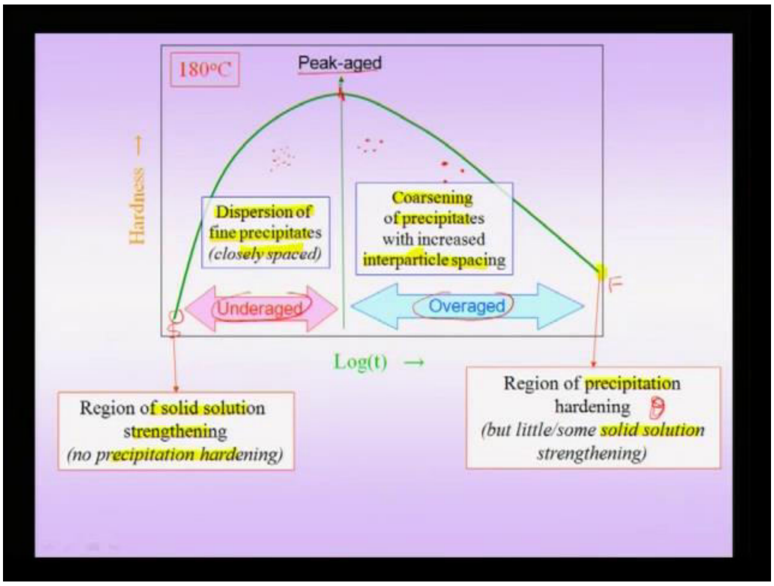

Dispersion of fine precipitates *(closely spaced)*

Coarsening of precipitates with increased interparticle spacing

Region of solid solution strengthening *(no precipitation hardening)*

Region of precipitation hardening *(but little/some solid solution strengthening)*

So, why is this curve has this particular shape, why is it that the curve is initially increasing and then decreasing. The hardness that is initially of course, I have a specimen in which most of the strengthening is coming from solid solution strengthening. That means, all the copper is in the form of the solid solution and aluminum and this is the regime of solid solution strengthening, where there is no precipitation hardening. Finally, I can assume that very long times of aging that, now I have reached close to my equilibrium that means, all the excess solute has now come in the form of precipitates.

And that means that the amount of since the solubility of copper in aluminum is small at room temperature. That there is some solid solution strengthening, but most strengthening most of the to more precise, most of the solute has now come in has been precipitated out and is in the form of the theta precipitate, which we noted is the equilibrium precipitate.

So, we are operating between 2 regimes, where the regime start and the regime finish in start, we have most of the solute copper in the form of solid solution. But in the end we have most of it in the form of theta precipitate and very little is in the solid solution. Now the regime below the peak hardness is called the under-aged state and regime above, the peak hardness is called the over-aged states and as I said, we would like to peak age a material, we would neither like to keep it in the under-aged regime or the over-aged regime.

In this under-aged regime, there is a fine dispersion of precipitates, which are being closely spaced and with this increasing aging time, we would note that there is a coarsening of precipitates. And therefore, the inter precipitate distance. So, this particle here has to be read as precipitate, we have an increasing precipitate distance. Therefore, initially we have a fine distribution of precipitates here in this regime.

But, here we have these precipitates starting to coarsen and further, if you wait long enough these precipitates distance would increase, but they would get little coarsen. So, this is what is happening this is leading to a decrease in hardness, after the peak hardness.

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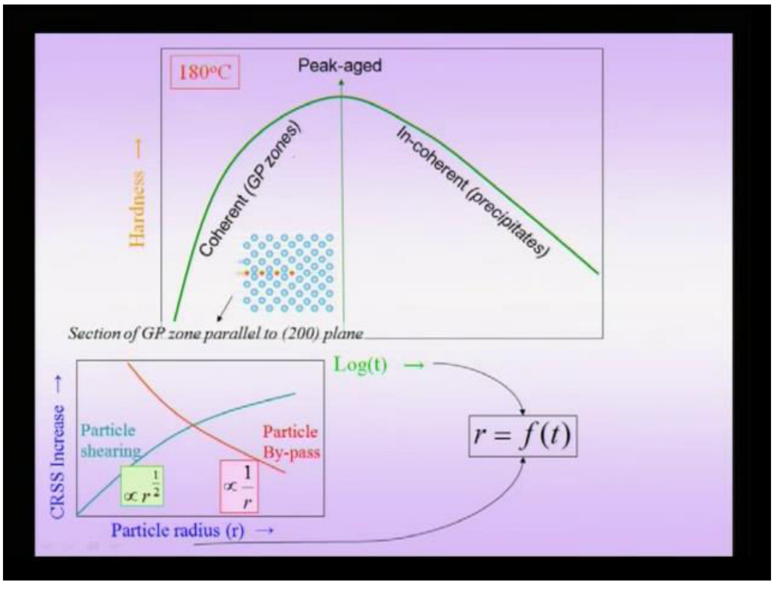

So, what are the mechanisms involved and what are the kind of precipitates involved is something, which we have to known, now 3 things, we have to track while we are talking about the aging treatment. Now one of course, number 1, I have to worry about solution from the precipitate.

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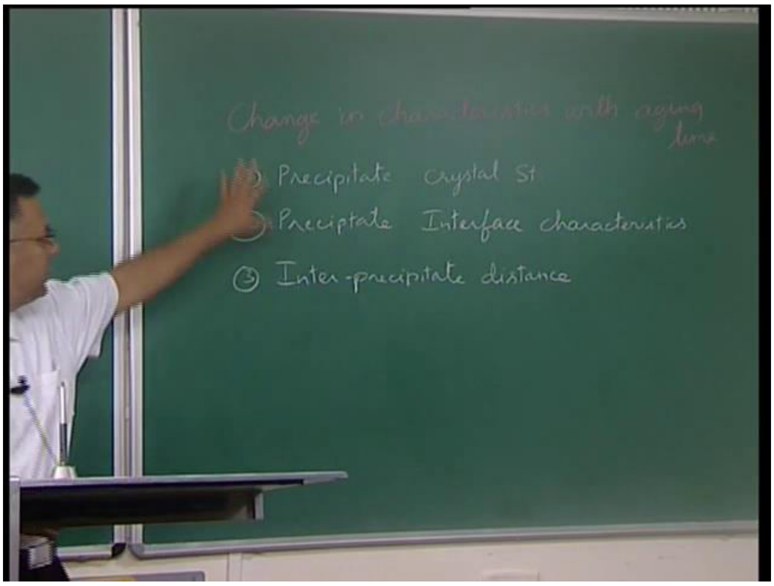

The precipitation process and in the precipitation process, first you have to worry about the precipitate crystal structure. Then I have to worry about the precipitate morphology and especially, I would worry about the precipitate interface characteristics. And the third thing, I have to worry about is inter precipitate distance.

Now, this aluminum copper system is the model system to study many complex process occurring and it is a good learning curve to understand lot of aspects of physical metallurgy. And this is because as you are doing the aging process, first of all the kind of its precipitate, which comes out and it is crystal structure is could be different for different times of aging.

So, 3 things are happening simultaneously, the crystal structures could be changing. The each precipitate, which forms it is interface characteristic could change for instance initially, you could have precipitate, which is coherent later on you could precipitate, which whose one of it is phases could be semi coherent. And finally, you could have incoherent precipitates. So, the precipitate interfaces characteristics also changing with aging time. So, what we are tracking is.

So, with aging time lot of complex say series of sequences are happening and this can broadly be brought into the category of crystal structure changes. Changes to interface characteristics and finally, there is another thing, we have to worry about is the inter precipitate distance variation. Because that is what is finally, going to determine that how much hardness, I am going to get.

Of course, what kind of precipitates what is this crystal structure all together, all have to be read together, because the mechanism operative leading to weakening of the crystal is dependent and all these 3 characteristics, which we have written here. So, let us see what is happening.

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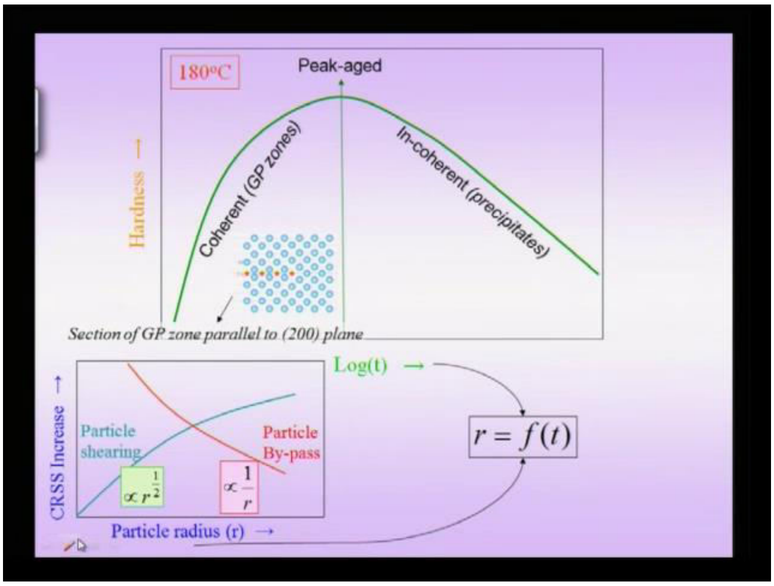

Initially, if my precipitate is coherent that means, dislocations can actually shear through, the precipitate and by a mechanism known as particle or precipitate shearing in other words, if I have a precipitate and I have a dislocation coming in, which we have seen before. So, I have my precipitate here.

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And dislocation coming in which is normal to the plane of the board and if this dislocation is location is moving in this direction, finally the precipitate would be sheared.

We have seen this before and therefore, such a precipitate, yes will give you some impediment to the motion of dislocations, but will not completely impede the motion of dislocations.

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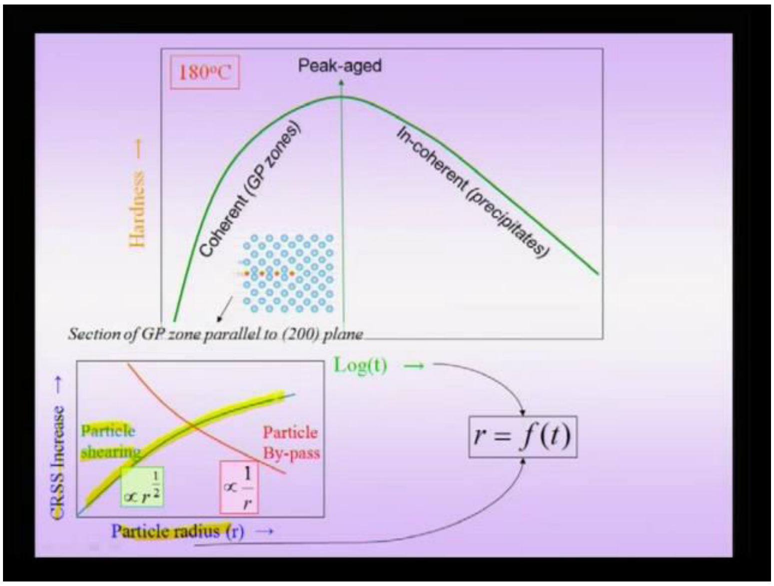

So, if you are plotting the precipitate radius or the particle radius and the increase in strength, the C R S S increased, which is known as the critical resolve shear stress in increase. That means, how much stress do I need to apply on the slip plane to actually, because or if you are doing a tensile experiment.

It is on the slip planes, what is the critical resolve shear stress, which is causing slip of dislocations and this is simply increased, because now this precipitates are providing an implement to the motion of dislocations. And if the particle is coherent, then it can be sheared and the dependence of with particle radius of the C R S S looks like this. That means, with increasing particle radius, and then you require an higher stress to shear the dislocations. Because some of these precipitates, themselves or could be for instance these particles could be inter metallic, that means the pearl stress within the precipitate is higher.

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That means the portion of the dislocation for instance, suppose I am talking about a dislocation line, which is shearing through. So, this is my precipitate and when the dislocation is passing through from here to here, and I am seeing that part of this dislocation line is with in the precipitate, then this part has faces the higher pearl stress as compared to the part, which is outside the dislocation line. That implies that now to drive the dislocation through the particle, I have to apply a higher stress or a higher resolved shear stress.

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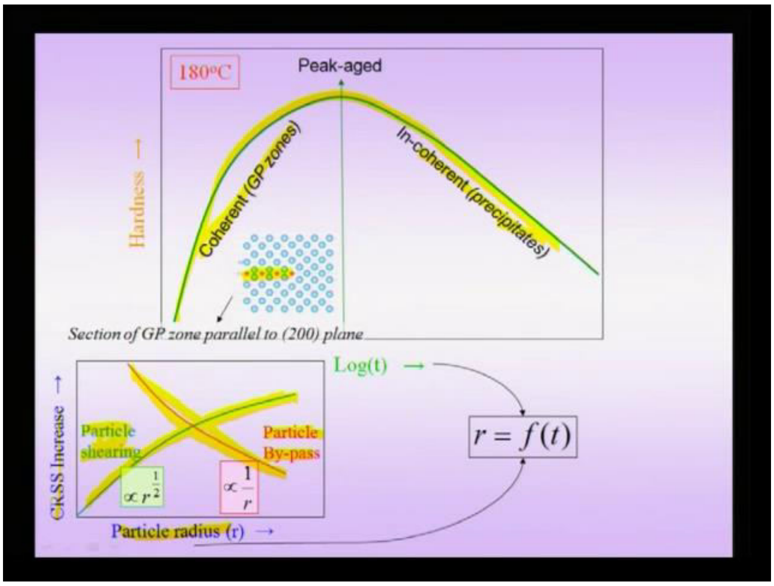

Now on the other hand suppose these precipitates are large and incoherent, then these precipitates cannot be sheared. That means, the dislocations have to bypass them by Frankie mechanism and for this, I would note that the stress actually decreases with increased particle size. And this is for the particle bypass mechanism that means, I have one kind of a dependence for a critical resolve shear stress for particles, which are coherent and the another kind of dependence for particles, which are incoherent and we have noted that with increasing time.

We will or we have not yet noted, we will note that very soon that with the increasing time, actually the precipitates tend to go from coherent to semi-coherent to incoherent. So, putting together these 2 pictures, the fact that in the low times regions, typically you have coherent G P zones are precipitates. We have introduces a new term called G P zones, which we will see, what it is very soon and if you go to larger aging times, you actually have incoherent precipitates. Therefore, in the initial regimes you expect the bypass or the particle shearing mechanism to be operative and for larger aging times, the dislocation will have to bypass the precipitate. Therefore, if you are looking at the 2 dependence that means, one of the curves increases the other curve decreases and sum of these 2 curves should be 1, which looks like this in, which case it is going up and coming down. That means, that now that because of the underling mechanisms involved.

Because of the nature of the interface of the precipitates, you expect that there are going to be different mechanisms operative, which gives you a peak age at a certain optimum amount of time. That means, I would not like to age beyond this time. So, as to retain my maximum benefit in terms of the time of aging, now what is this G P zones is actually, it is a disc of copper atoms, which is now embedded in the aluminum matrix a crude schematic is shown here. So, this is something between what you might call a local segregation into a disc and actually, a 2 precipitate. So, this is the, we can call of as a precursor for a precipitate.

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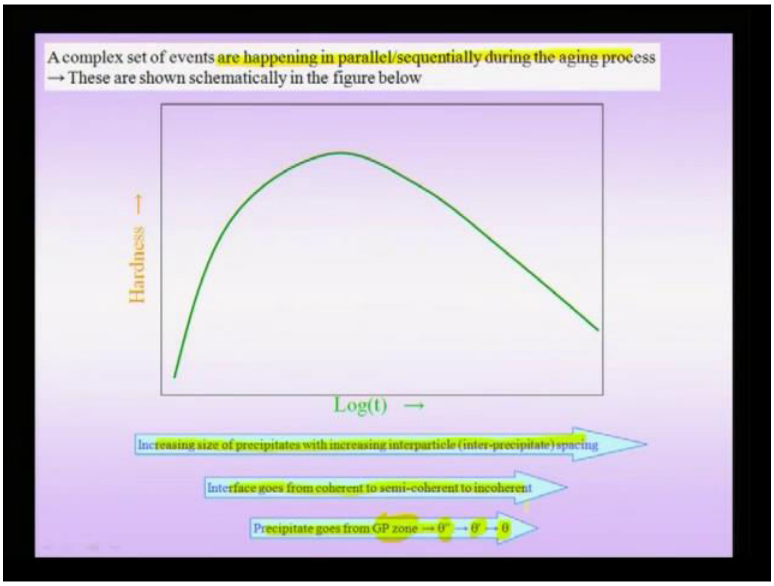

A complex set of events are happening in parallel/sequentially during the aging process
→ These are shown schematically in the figure below

Increasing size of precipitates with increasing interparticle (inter-precipitate) spacing

Interface goes from coherent to semi-coherent to incoherent

Precipitate goes from GP zone → θ'' → θ' → θ

So, once again summarize the complex set of events, that are happening parallelly or sequentially during aging process are increasing size of precipitates with the increasing inter precipitate spacing. That means, when I am aging the material, the size of the precipitates is increasing and the this also implies, that the inter precipitate spacing is also increasing.

The interface progressively goes from coherent to semi-coherent to incoherent and of course, when I am saying this I am worried about a single kind of precipitate and even as I told you the kind of precipitate, which also changes with increasing time. Initially of course, we get the G P zone, which is like a segregation of copper atoms on the one planes of aluminum, then later on you get a meta-stable phase, which is known as theta double prime precipitate. Then you get an another meta-stable phase, which is known as the theta prime precipitate and if you wait longer enough for age long enough, then you will get the theta phase precipitate.

In other words here, the process is very, very complex the underlying sequence of events is also very complex and but I can broadly understand that I go from the supersaturated solid solution to a G P zone to theta, double prime to theta prime and theta. And this implies all this sequence happens, usually at when I age at low temperatures like 180 degrees Celsius. I also have to as I pointed out track the interface characteristic, which tend to go from coherent to semi-coherent to incoherent and I also have to track the inter precipitate spacing.

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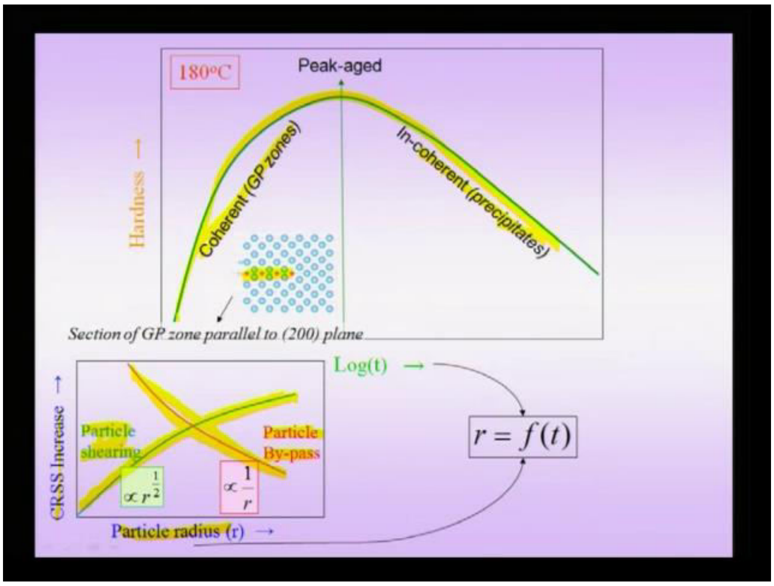

The overall two mechanisms, which I said we have to worry about are the particle shearing mechanisms and particle bypass mechanisms. Therefore, if I have a coherent precipitate, you can have particle shearing which gives you actually a low strength. But this strength increases with increasing precipitate size. And therefore, putting together all these data, we can see that the actually, the aging curve goes up and then comes down now If you are…

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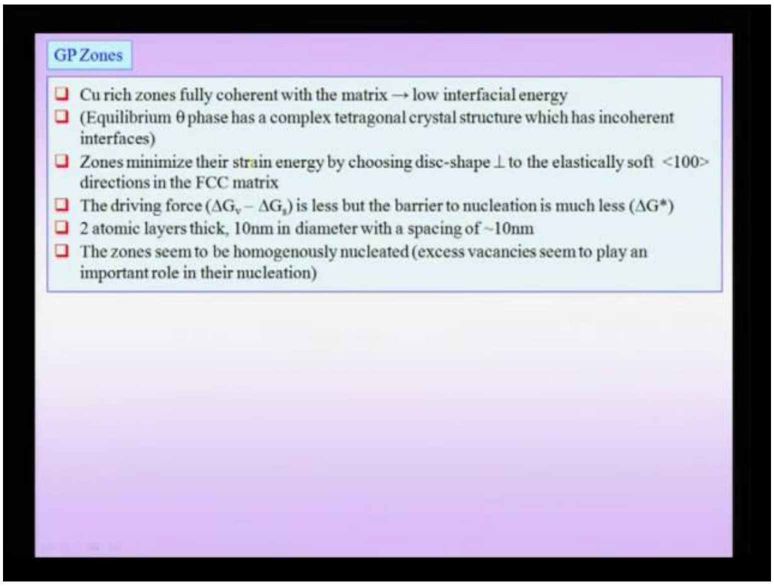

GP Zones

- Cu rich zones fully coherent with the matrix → low interfacial energy
- (Equilibrium θ phase has a complex tetragonal crystal structure which has incoherent interfaces)
- Zones minimize their strain energy by choosing disc-shape ⊥ to the elastically soft <100> directions in the FCC matrix
- The driving force ($\Delta G_v - \Delta G_s$) is less but the barrier to nucleation is much less (ΔG^*)
- 2 atomic layers thick, 10nm in diameter with a spacing of ~10nm
- The zones seem to be homogenously nucleated (excess vacancies seem to play an important role in their nucleation)

So, let us start by understanding, what is this G P zone and how this G P zone is different from some of the precipitates like the theta phase.

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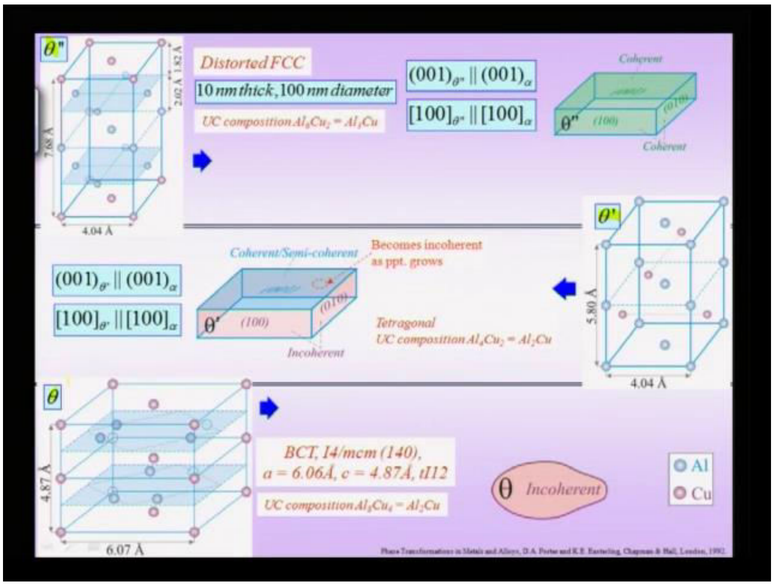

Distorted FCC

10 nm thick, 100 nm diameter

UC composition $Al_6Cu_2 = Al_3Cu$

$(001)_{\theta''} \parallel (001)_\alpha$

$[100]_{\theta''} \parallel [100]_\alpha$

$(001)_{\theta'} \parallel (001)_\alpha$

$[100]_{\theta'} \parallel [100]_\alpha$

Tetragonal

UC composition $Al_4Cu_2 = Al_2Cu$

BCT, I4/mcm (140),

a = 6.06Å, c = 4.87Å, tI12

UC composition $Al_8Cu_4 = Al_2Cu$

Phase Transformations in Metals and Alloys, D.A. Porter and K.E. Easterling, Chapman & Hall, London, 1992.

And the for instance the theta phase, the theta double prime phase and the phases, which are coming later on in the aging sequence.

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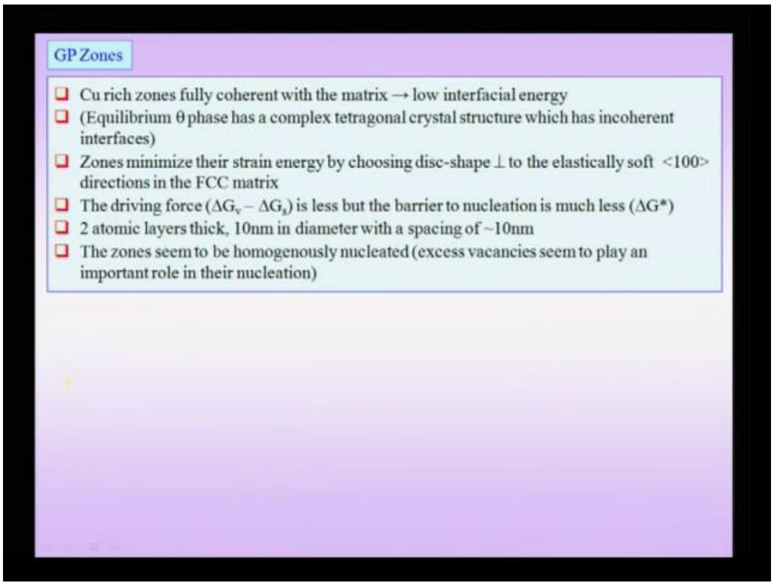

GP Zones

- ☐ Cu rich zones fully coherent with the matrix → low interfacial energy
- ☐ (Equilibrium θ phase has a complex tetragonal crystal structure which has incoherent interfaces)
- ☐ Zones minimize their strain energy by choosing disc-shape ⊥ to the elastically soft <100> directions in the FCC matrix
- ☐ The driving force ($\Delta G_v - \Delta G_s$) is less but the barrier to nucleation is much less (ΔG^*)
- ☐ 2 atomic layers thick, 10nm in diameter with a spacing of ~10nm
- ☐ The zones seem to be homogenously nucleated (excess vacancies seem to play an important role in their nucleation)

So, this G P zones is a unique thing and which is not found, if you age at high temperatures, but you only find it, when you age at low temperatures and we will say a few things about the G P zones next.