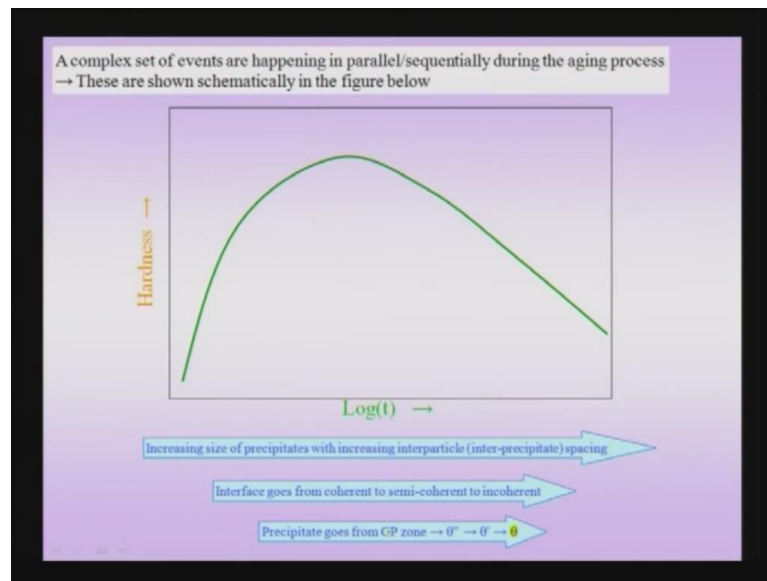


Structure of Materials
Prof. Anandh Subramaniam
Department of Material Science Engineering
Indian Institute of Technology, Kanpur
Lecture - 44
Phase Transformations

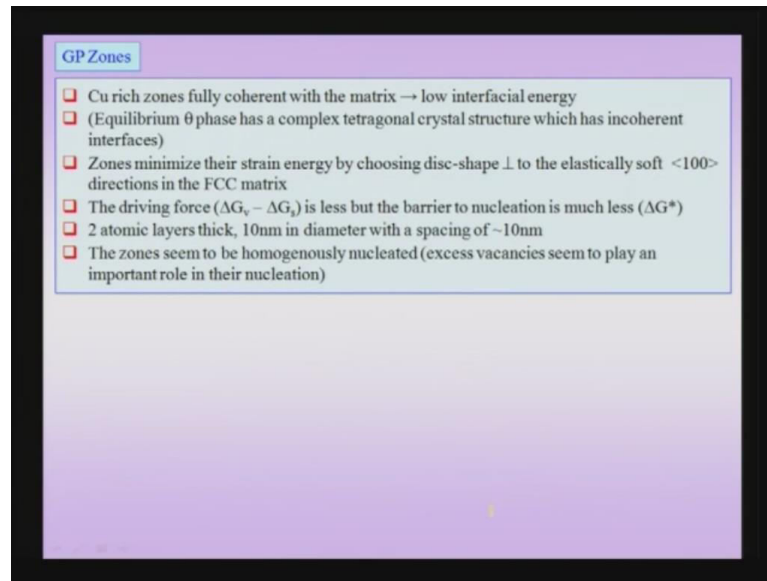
So, we need to understand that why that we do not directly get the equilibrium precipitate theta?

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But we go through a complex sequence of precipitation which involves intermediate meta-stable phases like theta double prime and theta prime.

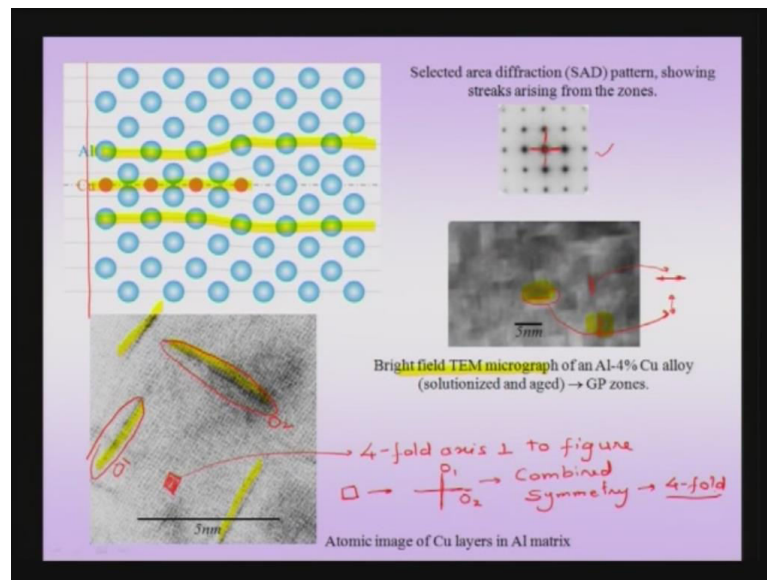
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And before that we have GP zones which are copper rich zones which technically do not come out of the class of the precipitates. But more like enrichment regions within the matrix of copper which have a low interfacial energy. We should note that the equilibrium theta phase as a complex tetragonal crystal structure which is incoherent interfaces. So we will come to that in a moment these zones minimize a strain energy by choosing a disc-shape with perpendicular to the disc being along the elastically softer 111 direction of the FCC matrix. That means the elastic energy is minimized by choosing such an orientation of the disc.

The most important point to note that the driving force of this is less than the, is less, but the barrier to nucleation is even much less. That means that we put up these meta-stable phases or meta-stable copper rich zone GP zone in this case we just not give as much delta g benefit. But the overall barriers activation barrier to the nucleation is less these GP zones are about 2 atomic layer thick and about 10 nanometer in diameter. And typically they are spaced at about 10 nanometer when they initially formed. And these zones seems to be homogeneously nucleated though excess vacancies if they are present in the matrix seems to play an important role. And we have noted before the quenching process actually gives as an excess vacancy concentration.

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So, you can see here suppose I consider this the half picture of the GP zone that means that the GP zone itself extends the other way about this is a mirror plain mid plain. And this is my disc of copper atoms right in the middle here. And this is what we call the GP zone and this is the copper red zone. And as I said it can be thought of a speakers to a precipitate and if you look at the area present in the matrix this thin copper layer which we pointed out can be about 2 atomic layers thick.

But in the schematic below it is only 1 atomic layer is shown you can see that they are present in 2 directions which are perpendicular So, this is perpendicular this direction and if you look at the bright field image of a such a region containing these GP zones. Then you would note that it is dominated by the strain contrast. So, you have of course, the region where you expect the GP zones to present like here this is now the disc copper atoms regions here and here.

But around this you find certain dark contrast then this dark and white contrast is coming from the strain fields. And therefore, you could keep thinking that we are actually imaging the strain fields in the bright field image. If you look at the selected area diffraction pattern apart from the diffraction spots is coming from the matrix. These are all coming from the aluminum with aluminum copper alloy. But additionally there are streaks which you can observe there are streaks which are joining these spots like here. And these streaks are coming from the fact that now, my dark condition are relaxed

perpendicular to the zones that means if the GP zones are thin in the direction. So, they are constant in real space.

So, they tend to expand in reciprocal space along these 2 directions means. 1 direction coming from these kind of orientations the other direction coming from these kind of orientations. And therefore, you can see that 2 kinds of streaks are produced, 1 coming from this vertical 1 and the streak in this direction. And the other streak is coming in the vertical direction. Therefore, there is a distinct signature of the GP zones in 2 forms 1 in the selected area diffraction pattern where you observed that there are streaks. And 1 in the bright field image where not only you see that there are you can get some contrast in the presence of these GP zones. But additionally the string fields surrounding the GP zones is also imaged. And this can also be seen in the schematic here that now, the lattice plains which are you know going straight here are curved around this precipitate. That means a straight lattice plains have been curved around these GP zones regions.

And therefore, there is considerable strain around the lattice where ever there is copper enrichment forming these GP zones. Now, originally before the GP zones formed you can notice that the aluminum matrix for instance had a 4-fold axis of symmetry here. So, this is my 4-fold down I am looking down on the 4-fold axis now and on the formation of the GP zones this symmetry is broken. But the symmetry is broken such that you get 2 orientations of the GP zones orientation 1 and orientation 2. And the And if we put these 2 orientations together the combine symmetry of these orientations is the 4-fold that means that there was originally 4-fold. And then when the GP zones came out there are 2 orientations orientation 1 and orientation 2 such that the combined symmetry of these 2 orientations gives us back the original 4-fold. Therefore, we see that in the sequence of precipitations we start with GP zones as we noted before later on we obtain the metastable theta prime precipitate then the theta prime precipitate. And finally, the equilibrium theta precipitate and of course, we would note that we do not want be aging so long that we produce the equilibrium theta precipitate.

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- ❑ Due to large surface to volume ratio the fine precipitates have a tendency to coarsen
→ small precipitates dissolve and large precipitates grow
- ❑ Coarsening
 - ⇒ ↓ in number of precipitate
 - ⇒ ↑ in interparticle (inter-precipitate) spacing
 - ⇒ reduced hindrance to dislocation motion ($\tau_{\max} = Gb/L$)

And now, if you look at a few important points the first this is that due to large surface to volume ratio the fine precipitate tend to coarsen that means the small precipitate tend to dissolve and large precipitate tend to grow. And an coarsening produces a decrease in number of precipitates with an increase in inter-particle spacing which gives reduced hindrance to dislocations motion. So, these are aspects which we seen before that we want to age such that we do not have a core setup precipitates. We have fine set of precipitates that means we are close to the maximum in the hardness verses time curve or the hardness verses log time curve.

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The diagram illustrates the structural evolution of θ phase precipitates in Al-Cu alloys:

- Distorted FCC:** A precipitate with a thickness of 10 nm and a diameter of 100 nm. It has a UC composition of $Al_2Cu = Al_2Cu$. The lattice parameters are 2.60 \AA and 1.82 \AA . It is initially coherent with the matrix.
- Coherent/Semicoherent:** As the precipitate grows, it becomes semicoherent and eventually incoherent. The lattice parameters are 4.04 \AA and 5.80 \AA . The orientation is $(001)_{\theta} \parallel (001)_{\alpha}$ and $[100]_{\theta} \parallel [100]_{\alpha}$.
- Tetragonal:** The precipitate becomes tetragonal with a UC composition of $Al_2Cu = Al_2Cu$. The lattice parameters are 4.04 \AA and 5.80 \AA .
- BCT:** The precipitate becomes body-centered tetragonal (BCT) with a UC composition of $Al_2Cu = Al_2Cu$. The lattice parameters are 6.07 \AA and 4.87 \AA . The orientation is $(001)_{\theta} \parallel (001)_{\alpha}$ and $[100]_{\theta} \parallel [100]_{\alpha}$.

Legend: \circ Al, \bullet Cu. θ Incoherent.

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

Now, what is the crystallography and interface characteristics of these 3 precipitates? We take that of the first before we go to their understanding of why is that we get these meta stable phases? 1 of the reason we have seen that when even the GP zones comes out the orientation is so chosen that it is the disc diameter or the disc perpendicular is along the elastically softer direction of the gallium matrix. So, the theta prime precipitate has a unit cell which looks something like this which is like this here which is a distorted FCC. And typically the theta double prime is about 10 nano meter thick and about 100 nano meter in diameter. And sometimes it can be in the form of amorphous which is shown on the right side and unit cell composition is about Al_6Cu_2 that means there are these blue atoms are aluminium the brownish ones are copper.

So, for every copper there are 3 aluminium atoms. So, there are the copper atoms and for every copper atom. There are 3 aluminium atoms and these 3 aluminium atoms are present in this plane which are between the copper atomic planes. So, there are planes which have completely only copper atoms and the other planes where there only aluminium atoms. And this is a distorted FCC structure and the unit cell composition Al_6Cu_2 which boils down to Al_3Cu , Now, this theta prime precipitate has an orientation relationship with matrix like the 001 direction of the theta double prime is parallel to the 001 direction of the aluminium copper solid solution which is alpha the 100 of the theta double prime is parallel to the 100 direction of aluminium.

It is therefore, some important directions are parallel the most simplest ones. And if you look at the precipitate typically all phases of this precipitate are coherent means the 100 phase the 010 phase and the 001 phase. All are coherent with the matrix thus producing the chemical energy between the theta double prime phase and the aluminium matrix. This implies that the activation barrier for nucleation will be low But of course, we because of coherency; we pay in terms of the strain energy which needs to be supplied while the nucleation takes place. The next phase which comes out is the theta prime phase which is if you look at the morphology looks very similar to the morphology of the precipitate morphology looks very similar to the theta prime. But here we have to note that this phase the 100 and 010 phases are incoherent. And while the 001 phase may be coherent initially but as the precipitate grows even this coherent or semi coherent phase becomes incoherent as a precipitate grows this structure.

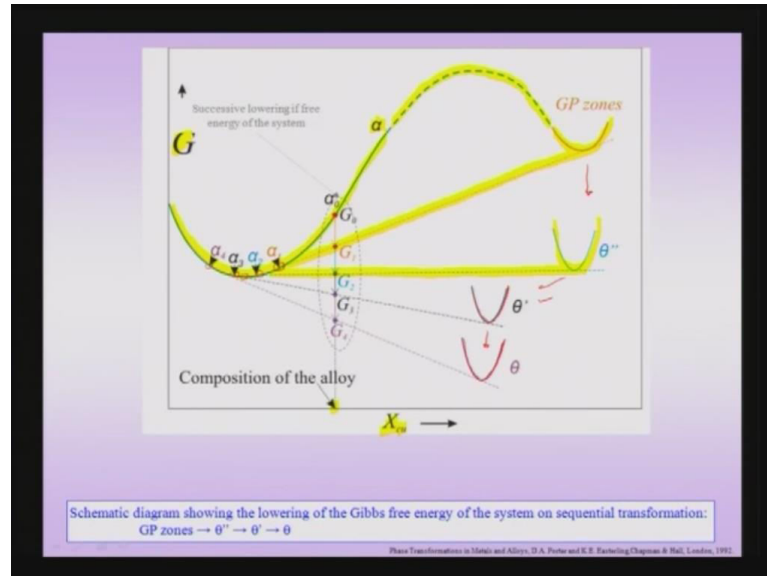
If you look again there are plains of like previously there are plains of aluminium and copper here also there are plains of aluminium and copper. So, there are aluminium plains and copper plains between 2. So, I can take this plain in between which contains purely only of copper at zee is equal to 1/4 the unit this is my copper plain. So, there are copper plains in between the aluminium plains and the unit cell composition is Al_4Cu_2 which means it is equivalent to Al_2Cu . That means that the precipitate theta prime is richer in copper as compared to the precipitate double theta prime. And even this theta double theta prime has orientation relationship which is very very similar to that of the theta double prime that means the 0 0 1 phase of the theta prime is parallel to the 0 0 1 phase of the alpha. The 1 0 0 direction of theta prime is parallel to the 1 0 0 direction in alpha.

So, the important difference between the 2 precipitate is that of course, the crystal structure is different the stoichiometry of the phases is also different. But additionally the phases typically the precipitate has mostly incoherent phases the, but only 1 phase the 0 0 1 starts out to be coherent. But as a precipitate grows becomes incoherent progressively the final equilibrium phase which is theta is such that all phases of this theta are incoherent with the matrix. So, therefore, this is the equilibrium theta phase wherein there is no coherency within the matrix this is the body center tetragonal structure. So, we started off with the we started FCC in the case of theta double prime the theta prime is an tetragonal structure, And now we have a body centered tetragonal structure again having plains which have pure copper like for instance like in this plains top or the bottom plains. And there are other plains which have pure aluminium and this along the 0 0 1 direction. Now, this tetragonal body centered structure has 12 atoms per unit cell and the unit cell composition is Al_8Cu_4 which means it is Al_2Cu which is very similar or which is identical to the composition.

We saw for the case of the theta prime that means as the precipitate goes from theta prime to theta there is no change in the composition. And additionally we note that both are tetragonal phases, that means there is the overall crystal system does not change however all the interfaces is a incoherent. And that means that the as we have noted before the incoherent interfaces are more this side that means they grow faster. And therefore, the theta prime precipitate tends to coarsen must faster as compared to theta double prime or the theta prime precipitate in that means that if you get a even fine

distribution of theta in the matrix. But additionally it will tend to coarsen much faster. And therefore, you will have a large size theta precipitate if you produce it in a matrix.

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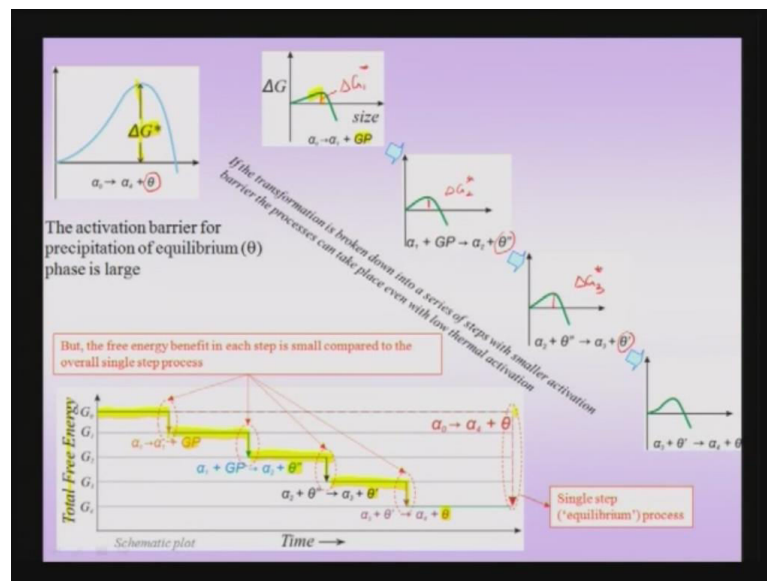
Now, using gift free energy composition diagram let us try to understand that what is the gift free energy benefit when you go from the meta-stable phase which is now initially we have now super saturated meta-stable which is only alpha. And we are plotting gift free energy verses composition that means copper percentage. And of course, we now that starting with the mean composition of copper about 4 percent in the aluminium matrix. So, initially of course, we saw that the GP zones come out that means initially, we start with pure alpha that means the single gift free energy alpha curves. And the composition of the alloy is say for instance here which is about 4 percent copper. And when GP zones comes out its composition is somewhere here.

And we you have to note that we even think of a some sort of a continuous line gift free energy goes from the alpha to the GP zones. And the concentration of the matrix which is I equilibrium with the GP zones is somewhere here that means in the alpha 1 progressively as we. Then later on we find theta double prime phase forms whose gift free energy curve is as shown in the blue curve. And now, by doing a common tangent construction like before, first we have done this common tangent construction. Now, we can make a common tangent construction. And we can note that now, that the composition of the alpha in equilibrium with theta double prime is now getting poorer in

copper in other words which are in aluminium. Then later on theta prime whose gift free energy consumption curve is even lower.

And finally, we have theta which has the lowest of the gift free energy consumption curves that means the overall direction is the gift free energy is moving downward. And the matrix which is in equilibrium with this is getting richer and richer with respect to GR intersections here by drawing a common tangent constructions. So, each stage you can note that first of course, we start up with the gift free energy on the alpha phase just for solid solutions. Then on forming the GP zones my gift free energy is lowered to this point which is g_1 then further on forming theta double prime precipitate my gift free energy is further lowered. And further it is lowered while forming theta prime. And finally, when I get to the equilibrium phase I get the lowest gift free energy. But the important point to note that is of course, at each stage I am seeing a stepwise reduction in the gift free energy the question which we partially answered is that.

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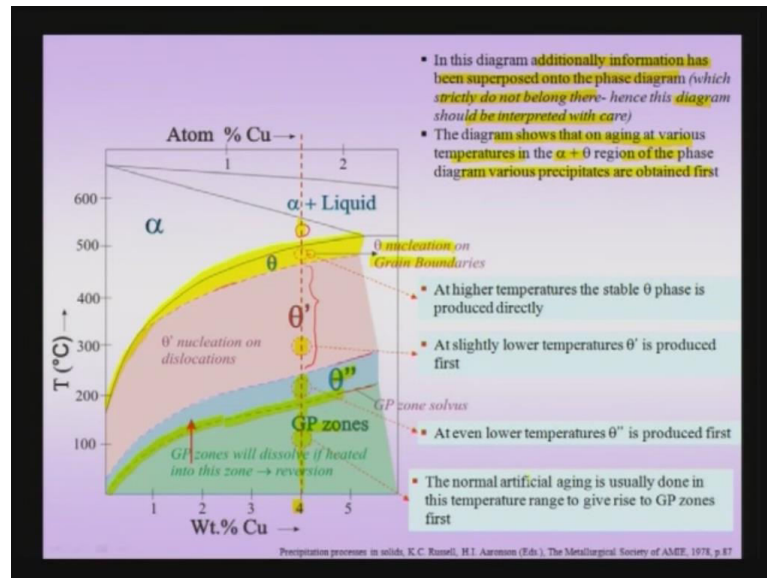


Why is that that we are getting these meta stable phases why do not why does not the theta form directly from the super saturated solid solution? And the reason suppose I try to form the theta phase from the alpha phase then the gift free energy barrier the nucleation barrier Δg not is pretty large. Now, this gift free energy barrier can be progressively broken down in to small steps that means now I can by forming GP zones I have to cross a lower nucleation barriers. So, we can think of this lower nucleation

barrier as we say for instance ΔG_1 star this is smaller barrier. Then when I form the from GP zones I form the θ'' I can think of barrier being crossed the ΔG_2 star. And from the GP θ'' when I form the θ' is another meta-stable phase. I have to cross it again a small barrier which is ΔG_3 star. So, at each stage the nucleation barrier is reduced that means the overall activation energy required for my process to take place is small. And we have noted that we do this aging not at high temperatures, but typically at low temperatures like 180 degree Celsius which means that there is not much thermal energy available to cross the activation barrier. Which implies that phase can only form for whom I can supply this activation energy so at each step.

So, that if you plot the total free energy initially you have a small lowering in the free energy when you call the GP zones. Then the next step is lowered even further when you form the θ'' it is lowered even further when you form the θ' . And finally, when form the θ we get down to the lowest equilibrium state and the overall reduction if you would have form from the α directly the θ . Then you got have the benefit like this So, this implies that the transformation is broken down to series of steps with small activation barriers. The process can take place even with low thermal activation and because this aging is carried at low temperatures. And we have noted that we want carried out aging at low temperatures, we want to get a p region where there is nucleation domination and the growth is lavished. Therefore, we get a lot of nuclei but each one of this nuclei do not grow very much that means that if am not going to supply any thermal activation energy. The system evolves to a state for which the barrier is small at least.

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Now, what we shall do next is that we will try to understand what happens during aging using 2 diagrams. One extended version of phase diagram which is shown here and other an extended version of the T type. Now, you have to note that in this phase diagram additional information has been super imposed on to the phase diagram and we should note that which strictly donot belong there. So, we have already seen that sometimes we use diagrams in regions where they are not strictly valid But then that enhances the utility of these diagrams. And we have to keep up in mind when we are extending the utility of these diagrams. And we have to interpret these diagrams a little bit of care this diagram shows that on aging at various temperatures. The alpha in the alpha plus theta region the phase diagram various precipitate are obtained first. That means that suppose I am aging in this grain region of the phase diagram that means.

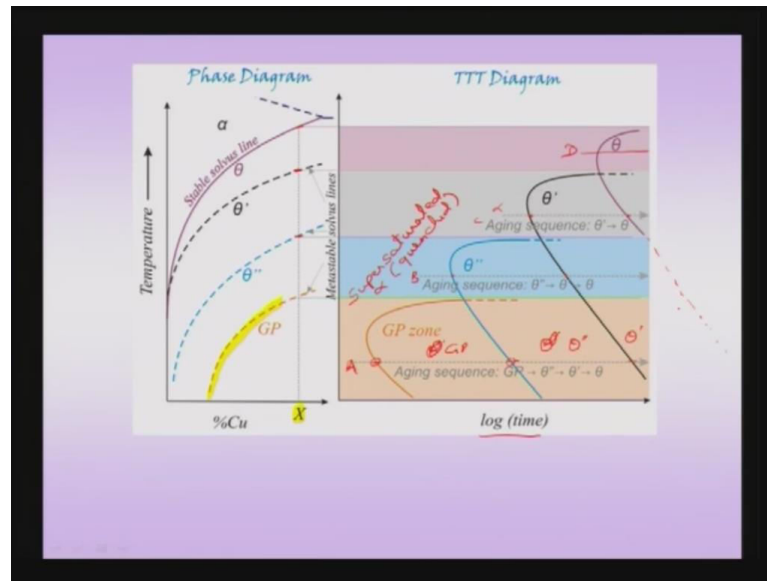
Now, I am taken my aluminium 4 percent copper I have solutionized it in the single phase read alpha. That means now, I have obtained full single alpha right here, And after that I have quench to room temperature that means I am now obtained the super saturated solid solution of copper and aluminum. And additionally as I pointed out we also land up with certain excess concentration of vacancies. Now, if we age this in this grain region right here like this in phase in the grain region. Then what will happen is that we obtain GP zones first and this GP zones as we shall note that will transform later on to the theta double prime theta prime into theta. If we wait long enough instead of aging at these

range of temperatures which are noted here suppose age at little higher temperatures mark in the blue region of the phase read.

And again once more we should note that these phase diagrams normally drawn for equilibrium phases here. We have super super imposed meta-stable precipitates and meta-stable zones like the GP zones and theta double prime. And therefore, we have extended the utility of the standard diagram that means there are no now new meta-stable phase boundaries. And we have to understand this is there just to make us understand that what happens what is the phase regions obtained when we age the meta-stable solid solution in the blue region. We obtain, we do not obtain GP zones first we directly obtain theta double prime. Now, you should age even at higher temperatures like a region marked here in the brownish color.

So, we note that in the region of temperatures we would actually get theta prime directly that means you would not get GP zones. You would not get theta double prime that we get theta prime directly And for this further can transform in to theta if you wait long and at even higher temperatures directly we get the equilibrium phase theta. And this theta typically nucleate on the grain boundaries. So additionally apart from the original solvus line which is this, the normal solvus line. We have various solvus lines like the GP zones solvus line here this is the GP zone solvus line here. Similarly, we can think of theta double prime solvus line and the theta prime solvus line. So, normally of course, we have to age at low temperatures say typically less than about 200 degree Celsius. So, that we start with GP zones and a fine distribution GP zones. So, that we can get a good entrance to dislocations motion.

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Now, like you have done here a super imposed all meta-stable phases in the phase diagram. What we do here is that the left hand portion shows the phase diagram and here are of about the composition of 4 percent copper. And these are all the various meta-stable solvus lines which are we just saw in the phase diagram. And on the right hand side are T T curves which show what happened when we age. And please do not image case the starting point of course, we and if you low age at low temperatures. Suppose, you are tracking along a line a dotted line first initially we have the alpha transforms to get the GP zones on waiting long enough. We get of course, the log is the x log time is the x axis we get the theta prime so we cross the x theta prime line theta double line.

Then of course, we get theta prime and if you wait even longer we will cross the theta line if however you age at higher temperatures and you start off at a point b. Then directly you will obtain the theta double prime from the alpha solid solution And this theta double prime if you wait longer enough refer time: 23:00) will transform to theta prime and further to theta 1 aging at even higher temperatures So, in this region. Here you will of course, start with alpha alpha will directly transform theta prime And then to theta when you cross the line here So, there are 2 crossing point at which these alpha will transform first to theta prime And then to theta at even higher temperatures between the theta prime solvus and the actual solvus line of the phase diagram will age along the line for instance so this is c so and if you age along d.

Then directly we will obtain the equilibrium theta phase. So, the transformation sequence we can now understand in terms of an extended TTT diagram in which not only you have transformation to 1 phase. But progressive transformation to other phases previously we saw of course, in the case the steels we have drawn a line in which for instance the gamma phase would transform into alpha plus Fe₃C. Of course, we have drawn the start line and the finish line. But here we have seen a sequence of transformations and these are drawn with different kind of TTT curves. So, there is 1 curve for transformation of alpha for instance aging along a you have 1 curve for transformation of alpha 2 the orange curve from alpha 2 to theta double prime. And after transformation to theta double prime we have 1 more blue curve for transformation of theta double prime to theta and then from theta prime theta.

So, this is theta prime here from theta prime to theta extra sorry this is alpha to GP zones. We have GP zones here and GP zones to theta double prime here theta double prime to theta. And finally, whenever you intersect this curve this extrapolated curves here. Then you will note that you get equilibrium theta phase. Now, using our usual phase diagram which have been extended and the concept the simple concept of activation energy and extended versions of TTT diagrams. We can see that how instead of obtaining when you age low temperatures instead of obtaining equilibrium theta phase directly we are obtaining a series of meta stable phases. And depending on the temperatures which you age you may get the complete sequence starting from the super saturated alpha to theta.

Or you may start directly with one of the other phases like theta double prime or in the extreme example if you just age it at below the stable solvus line you may directly get the theta phase. So, the aging temperature matters because that will decide how much activation energy is available for the system to adopt a kind of a structure with though may be meta stable. But gives you a benefit in terms of the activation energy this frustration hardening process is industrially very relevant. And can be found in variety of systems which are frustration hardenable and you have noted the common characteristics among all that and we have a sloping solvus line.

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Precipitation Sequence in some precipitation hardening systems
(Morphology and compound stoichiometry are given in brackets)

Base	Alloy	Precipitation Sequence
Al	Al-Ag	GPZ (Spheres) → γ' (plates) → γ (Ag ₂ Al)
	Al-Cu	GPZ (Discs) → θ'' (Discs) → θ' (Plates) → θ (CuAl ₂)
	Al-Cu-Mg	GPZ (Rods) → S' (Laths) → S (Laths, CuMgAl ₂)
	Al-Zn-Mg	GPZ (Spheres) → η' (Plates) → η (Plates/Rods, Zn ₂ Mg)
Cu	Cu-Be	GPZ (Discs) → γ' → γ (CuBe)
	Cu-Co	GPZ (Spheres) → β (Plates, Co)
Fe	Fe-C	ϵ -carbide (Discs) → Fe ₃ C (Plates)
	Fe-N	α'' (Discs) → Fe ₄ N (Plates)
Ni	Ni-Cr-Ti-Al	γ' (Cubes/Spheres)

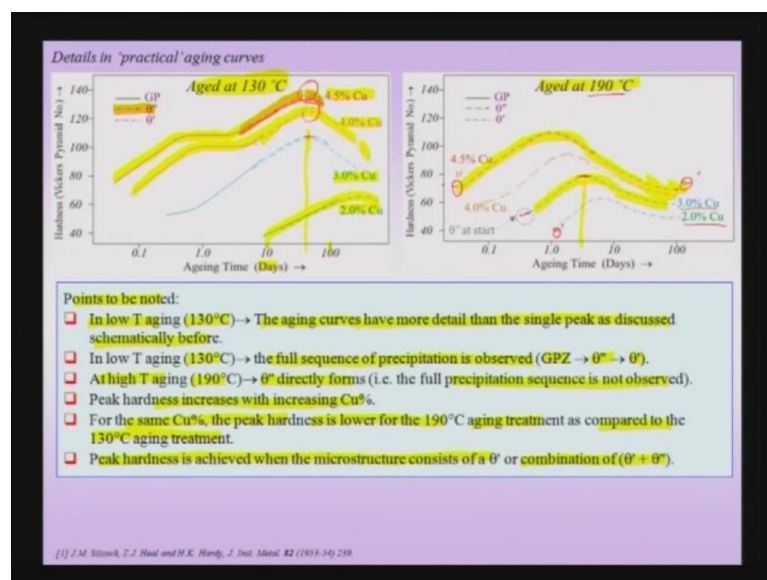
That means that we can quench from high temperatures to produce super saturated solid solution which can be aged to produce a series of zones and precipitates. And the common one which have found these are not the exhaustive examples. But a few examples there are aluminium based alloys there are copper based alloys and nickel based alloys which are age hardenable. Now, the aluminium silver system for instance we have precipitation sequence consisting of GP zones followed by gamma prime plates followed by gamma the prime zones, followed by gamma the prime. In all these cases denotes the fact that we are obtaining a meta stable phase like a this is a meta stable phase here. In this case we have already seen theta double prime denotes meta stable phase, the gamma prime in case of beryllium system. Again denotes the fact that we are obtaining meta stable phase in the precipitation sequence in some of these alloys is very very similar though in some cases we get GP zones to 1 meta stable phase to find the stable phase.

And we do not get 2 intermediate meta stable phases the morphology again change from system to system for instance in the case of aluminium copper system you have already seen discs followed by plates. And we of course, schematically shown the theta double prime as a plate here. But the morphology could be more like a disc, but which have incoherent ha which all have coherent phases in the aluminium copper magnesium systems we could have rods or laths. And finally, of course, a stable phase themselves are laths in yet another systems for instance you put use actually use the meta stable

phase as final state for harden system for instance nickel chromium titanium alloy aluminium alloy. You could use gamma prime phase which are in the form of cubes or spheres which have a low interfacial energy which can be used for pre-station hardening.

Therefore, we have a variety of systems which are frustration hardneable. And in all these cases the fundamental mechanism means the same that these fine distribution of precipitate or zones give a hindrance to dislocations motion. And they come in 2 forms, one of course that you precipitate has to be shared which gives a certain benefit. That means you have to drive the dislocations through the precipitate wherever they are coherent. And the pulse rate inside the precipitate should be higher and wherever the precipitate are incoherent. Then we have to operate double end source mechanism for a dislocations as to loop around the precipitates thus the precipitates act like pinning points where nearest to hardening. And we have already noted that these 2 hardening effects based on the radius could be have a different kind of functionality. The particle sharing mechanism increases with size while the particle bypass mechanism the stress required decreases with size. Because when you have the constant volume fraction precipitate and the precipitate size is increasing their, the inter-precipitate size is going to also increasing.

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Now, we are noted 1 more point when we pointed out that ha about the shape of the hardness verses aging time curve. And we have noted the, we have drawn the hardness

verses aging time curve which looks like the one on the right hand side the one which I highlighting. Now, which looks something like this but in reality hardening curves ha depend on the temperature of aging for instance here I consider 2 aging temperatures. One is 130 Celsius or 190 degree Celsius it also depends on the percent of the copper in the alloy for instance there are 2 percent copper alloy 3 percent copper alloy 4 percent copper alloy in the ha in the 4.5 percent copper alloy.

So, therefore, there are lot of details involved in the actual hardening curves that means the hardness obtained ha verses the time of aging the time of aging here of course, shown in phase. And these are actual sort of curves which would have obtained actually rather than the schematic which we are obtained before. So, this schematic which we drive before can be thought of as a some kind of master curve which is obtained. And this overall to understand that the hardness increases but if the age too then the long hardness decreases. So, depending on the copper percentage and depending on the aging temperature the nature of the hard hardening curve changes additionally these graphs also contain different curves to show what is the predominant phase precise this.

Of course, does not mean that the whole system is exactly that but what is the predominant phase present for instance if you look at a 4.5 percent copper alloy which is on the left hand side of the diagram. The 1 age at 30 degree Celsius initially the hardness changes it is due to the presence GP zones and GP zones persist till about a year. But later on when you change the, you wait even longer then the phase transforms to theta double prime. And which I am highlighting here in the orangish color and a theta double prime persist even beyond the peak hardness But even before my entire theta double prime has changed to there is also a paralley a process in which you are obtaining theta prime phase. Also, along a same line you notice that there is a dotted line here it shows there is a theta prime phase also coming out. So, as I pointed out before that overall aging sequence is rather complex wherein we are monitoring 3 parameters 1 is their size and their size of the precipitates. And their inter precipitate distance we are monitoring the crystallography of the precipitate is that cubic tetragonal or just a zone.

We are also monitoring that the morphology or the characteristics of interface that means is the interface is coherent semi coherent or incoherent. So, GP zones are coherent theta double prime we noted is coherent. But theta prime is only partly coherent which is also coming in incoherent while theta is fully incoherent. Therefore, putting together all these

pictures we see that the aging curves becomes rather complex. So, if you look at aging curves for instance aluminium 4 percent copper alloy and is aged at 130 degree Celsius. And you would note that again there is a hardness curve changes very strangely. That means that is 1 peak some sort of Plato followed by and all around the while initially GP zones are there. Then they transform after certain time in to there is a combination theta double prime and theta. And fine of course, we aged to long to land up with the theta prime and if you wait even longer. Then of course, you will get whole theta precipitate our goal would be to age only to peak hardness. That means we would try to reach some where here if you are talking about 4.5 percent copper alloy or you would aged to here to get a 4.5 percent copper alloy.

And if you take a low percentage copper alloy you would see that this kind of a sequence wherein you get the Plato is missing. And you land up with a single peak in the aging curve on either hand suppose if you age at higher temperatures like 190 degree you will get a our classic single peak curve single maxima. And this is 2 all the percentage of copper like 2 percent 3 percent etc. But the important point to note that suppose I start with the a 190 degrees. And I start with a the 4.5 percent copper alloy it directly obtain the theta prime precipitate which finely transforms in to sorry theta double prime transforms in to theta prime towards. So, what is present at the starting of this here? This is directly theta double prime which comes out and I land up here and I land up at this point of theta on either hand. Suppose I am aging a copper 2 percent aluminium 2 percent alloy. Then I directly start the theta theta prime even though I am aging at 190 degree Celsius which is a low enough temperature for me to give for instance. That means the T T T curves are changed such that you directly intersect the alpha line with the theta prime line. And therefore, you get directly theta prime.

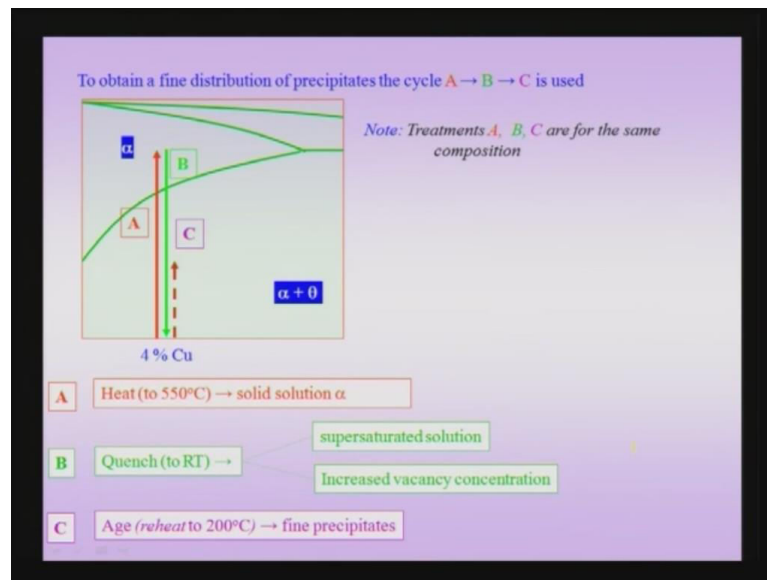
Now, if you are aging at 3 percent aluminium aluminium copper alloy copper 3 percent then there is a small range of times when you actually obtain theta double prime. But then later on throughout most of the curves you are actually obtaining the theta prime precipitate. So, let us note the silent variables the variables are percentage of copper and the temperature at which you are aging. If you are aging at low temperature at high percentage of copper the overall aging sequence consist of more features like 1 peak followed by a Plato followed by another peak rather than a simple single peak pictur. Aaging at lower higher temperatures like 190 degree Celsius gives us the sort of the

schematics single peak curve. But then the details are hidden in the percentage copper we are aging.

So, the point should be noted which are summarized below are in low temperature aging for instance 130 degree Celsius. The average aging curves have more detail than the single peak curve discussed schematically in aging at 130 degree Celsius. The full sequence of precipitation is observed that means GP zones giving theta double prime giving rise to theta prime now at high temperatures at 190 degree Celsius theta prime directly theta double prime directly forms. That means the full frustration sequence is not observed peak hardness increases with increase in copper percentage for the same copper percentage. The peak hardness is lower for 190 degree aging treatment as compared to the 130 degree aging treatment. That means that if you maintain a proper copper percentage it is better to age at lower temperature. But we have already noted that to wait for longer times to get the peak hardness once in. Now, if am working with the say 2 percent copper or let me take 3 percent copper. The 3 percent copper to get a peak age I have wait something between 10 days or about 100 days in a year.

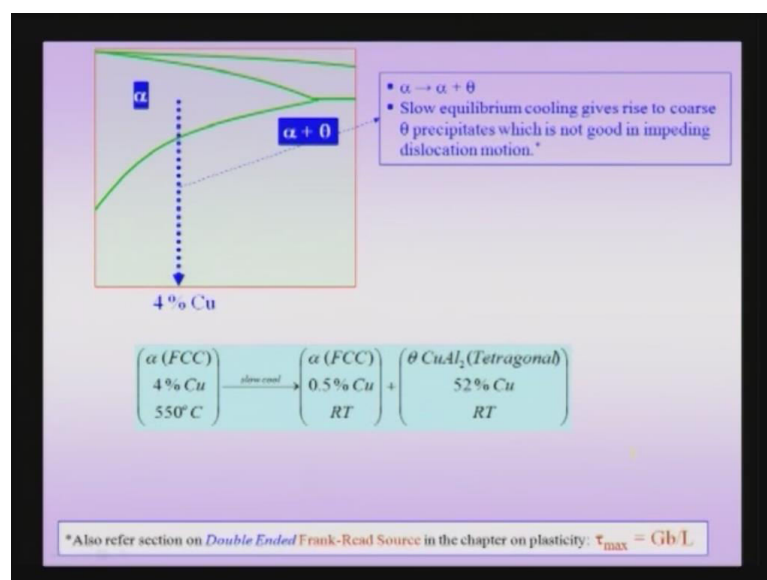
But if am working at higher temperatures I can get with 3 percent copper alloy the same peak hardness not the same. But the peak hardness between less than 10 days but overall the peak hardness value is of course, lower when I this value is lower than this value. Then this value is about say for instance 70 because pyramid number and this value is about hundred meter parameter. So, aging is at lower temperature is better because we get a peak better peak hardness. But then we have to wait for a longer time. So, the peak hardness achieved when the micro structure consist of theta prime or a combination of theta prime plus theta double prime. So, this is typically where the peak lies in some of these curves. So, this is a typical observation from studying this hardness verses aging diagrams.

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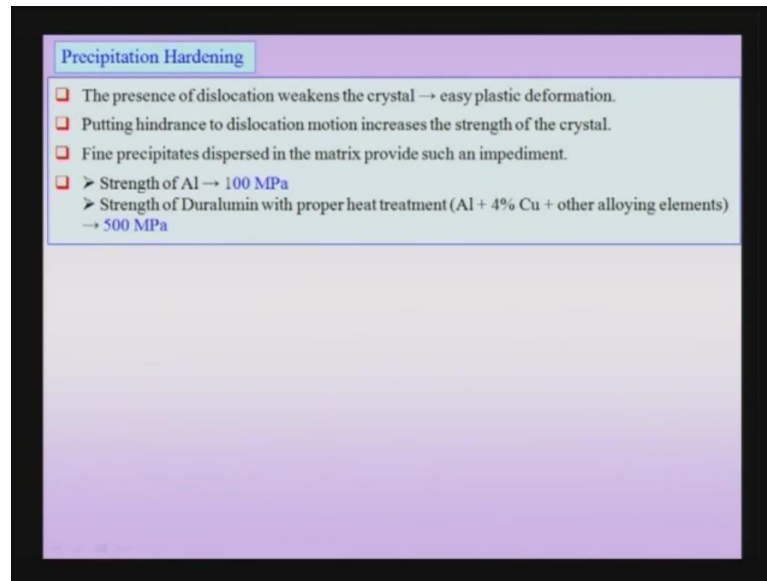
So, we are in a position to summarize whatever you are lead about studied about frustration hardening by using a sequence of heat treatments which involves solutionising quenching and aging. And knowing about the fact that where the peak in the nucleation rate lies, what is the barrier to nucleation? And we can engineer this treatments to get a fine distribution of precipitate in a say for instance aluminium matrix.

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The overall goal of course, as we noted.

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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

Before is to increase the strength of aluminium to a high values because aluminium is fantastic structural material due to other properties. Or instance it forms a tuff adurant oxide which give quick corrosion resistance it has a pleasing color metallic finish. And by doing this heat treatment I can actually improve the strength of aluminum which give a good structural applications in engineering these heat treatments. We are also engineering the micro structure that means we are getting for instance GP zones which have for instance as I said distribution in the matrix which have strain fields.

And these GP zones are the for instance even the metastable theta double phase etc give a hindrance to dislocation motion. And by getting a fine distribution of these precipitates or meta stable phases we can actually engineer the microstructure. Therefore, so for we have seen that we can actually engineer the microstructure to control the properties. One point we have noted is that if the precipitates coarsen that means that if the overall precipitate size increases while the number of precipitate decrease with time. Then hardness of the alloy decreases.

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Particle/precipitate Coarsening

- There will be a range of particle sizes due to time of nucleation and rate of growth
- As the curvature increases the solute concentration (X_n) in the matrix adjacent to the particle increases
- Concentration gradients are setup in the matrix \rightarrow solute diffuses from near the small particles towards the large particles
 \Rightarrow small particles shrink and large particles grow
- \Rightarrow with increasing time
 - Total number of particles decrease
 - Mean radius (r_{avg}) increases with time

Gibbs-Thomson effect

That means we want to retain the fine distribution of a precipitate and we want to avoid the coarsen, what is the methods to avoid coarsening is that.

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Rate of coarsening depends on $D \gamma X_e$ (diffusion controlled)

- Precipitation hardening systems employed for high-temperature applications must avoid coarsening by having low: γ , X_e or D

Low γ

Nimonic alloys (Ni-Cr+Al+Ti)

- Strength obtained by fine dispersion of γ' [ordered FCC Ni₃(TiAl)] precipitate in FCC Ni rich matrix
- Matrix (Ni SS)/ γ' matrix is fully coherent [low interfacial energy $\gamma = 30 \text{ mJ/m}^2$]
- Misfit = f(composition) \rightarrow varies between 0% and 0.2%
- Creep rupture life increases when the misfit is 0% rather than 0.2%

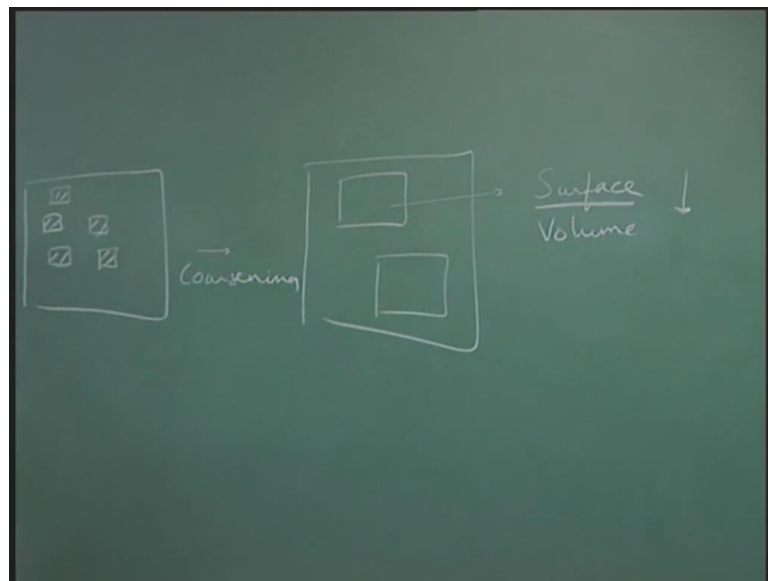
Nimonic 90: Ni 54%, Cr 18-21%, Co 15-21%, Ti 2-3%, Al 1-2%

We can either use a precipitate which has a low gamma. That means that the 3 strategies which we can use avoid the coarsening of the precipitate which is especially true if your alloy is used at in high temperature applications where the coarsening chances are very large. Then we can use either a low interfacial energy between the precipitate and the matrix to reduce the coarsening rate. We can use a an alloy for which the diffusivity is

very small or we can use an equilibrium concentration which is an of the solute which is in equilibrium with the precipitate to be very very small.

So, we will just discuss the first of this 3 strategies so that we understand that how a low energy will help in reducing the coarsening in pneumonic alloy for instance nickel chromium plus aluminium titanium alloys. The strength is obtained by a fine disportion of gamma prime precipitates which is an ordered FCC. And which is having a chemical formula initial in an nickel which is an FCC bridge matrix. Now, the nickel gamma prime matrix or nickel solid solution which is having a matrix of gamma prime has a very low interfacial energy of the order of 30 mille joules per meter square. And because of this you find that this alloy can be applied in high temperature applications. And can withstand long service hours at high temperatures without the precipitate coarsening Therefore, let me first draw the picture of what is meant by this starting and end points.

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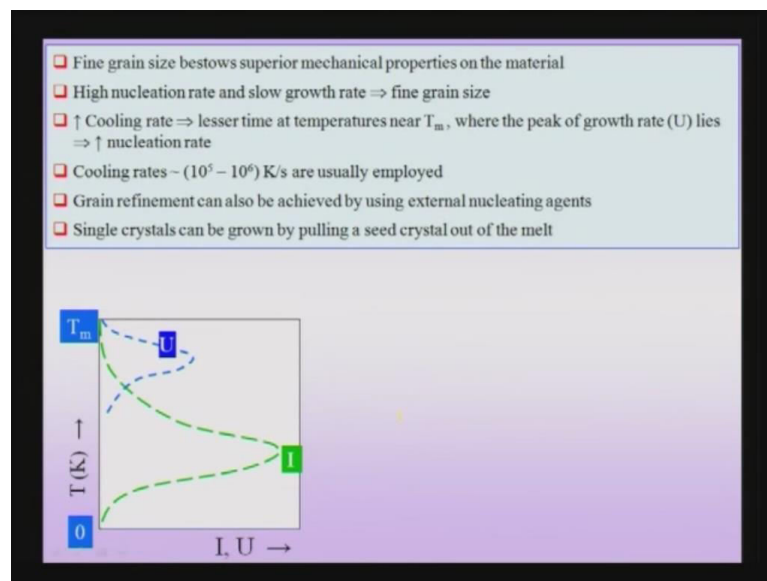


Suppose, you had this precipitates and now suppose you have a combinations of these coherent precipitates. And if you land up with the finial state which is a few large precipitates. Then this is not a good news for alloy of course, on either hand suppose you are able to avoid this coarsening wherein and during coarsening. We have to note that overall volume fraction of the precipitate does not increase. But it is only the number of precipitates. That means now, in this whole process the volume to surface area this ratio decreases and this is the driving force for this coarsening process. Therefore, we do not

want this coarsening and avoid this coarsening one of the strategy is to use a low interfacial energy between the precipitate and the matrix. And this is especially true if your application involves high temperatures for the alloy.

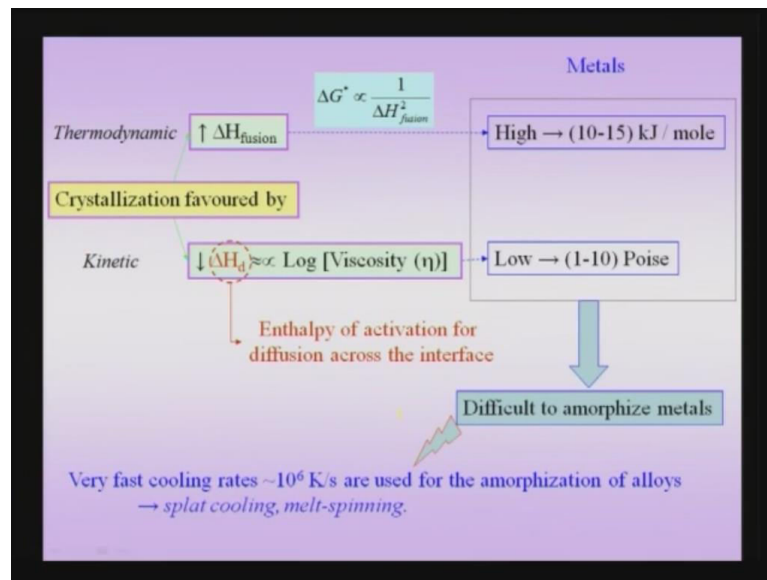
So, you have noted that we can obtain the fine distribution of these precipitates. And further by choosing an appropriate precipitate which has a low interfacial energy We can avoid coarsening And the alloy can be kept in a fine scale of precipitates for a long time yet. We take another example wherein we do the microstructure engineering. But in the case of course, we are doing microscope engineering not on a crystalline material. But on a glass and what is glass of course, we have already noted we said it is a disorder state of matter based on atomic structure. Therefore, there is no unit cell and there is we cannot use this standard tools of crystallography and glasses. Now, how do we form glass?

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It is easy to form glasses in inorganic materials like silicate glasses for instance. Suppose, I take my window pane glass which is silicate glass then actually slowly cool the glass.

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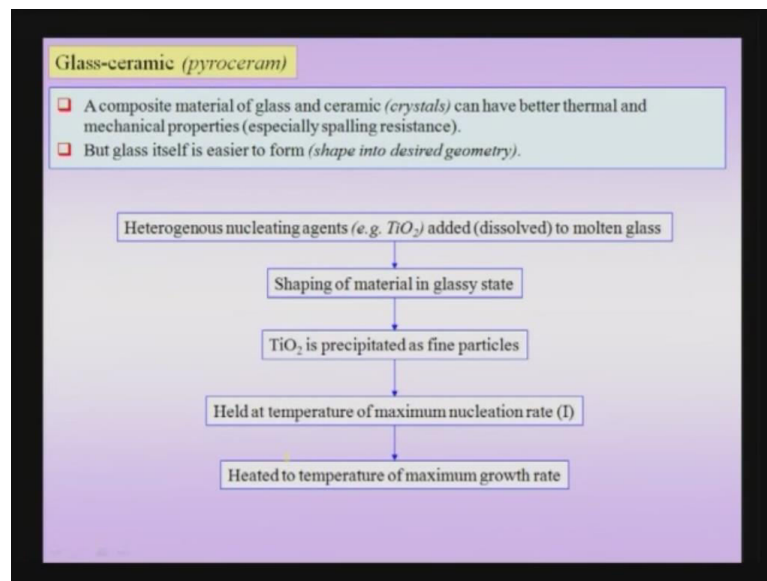


And form a amorphous structure or glassy structure or a disorder structure and the reason being that in silicate the enthalpy of fusion is low and the overall viscosity is also high. So, you have a high viscosity melt which slowly cool can give you a glass on either hand it is actually difficult. And that means that silicate are easily amorphize on either hand you would note that if you have metals which have an high enthalpy of fusion. And which have a low viscosity such cases it is actually difficult to amorphize standard metals like aluminium. And simple alloys like aluminium copper alloys on either other hand there are special metallic compositions which are based on zirconium. And another they usually contain many alloying elements such typically a turned is quaternaries higher number of alloying elements. And such alloys are can have a low critical cooling rate that means they can also cool considerably slower than the for instance cooling rate required to amorphize for instance aluminium or some simple alloys.

So, there are special compositions of metals which can also be amorphize by this assembly slow cooling rates. However if you want to amorphize metals you may have to sometimes employ very high cooling which are achieved as we saw by the process like melt swinning and splat quenching. Now, the important point to note that is of course, suppose I have an atomic ceramic. Can I use my T T T diagrams and knowledge these in to engineer my microstructure to obtain a set of properties which are normally not found in the glass or in the pure ceramic.

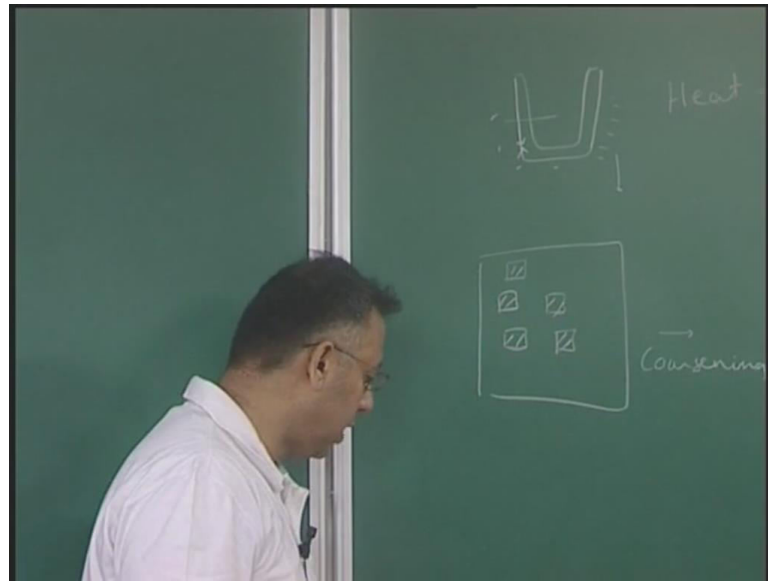
So, glass is being the disorder state ceramic being referred to the crystalline state. Now, before we even go to that we have noted that typically a fine grain size bes to superior mechanical properties to the material high nucleation rate and a slow growth rate being a fine grain size and normally. And of course, we are talking about normal solidification process for instance we have already noted that the peak of the growth rate curves lies at higher temperatures as compared to the peak of the nucleation rates. And we want to use this knowledge to actually produce a fine crystallite.

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Size so, we do for the case of a glass ceramic the problem with or the beautiful thing about the glasses is that these glasses are easier to shape for instance when you might have seen in glass blowing. We can actually take a glass heat it up and actually blow it to various shape it is easier to shape glasses to any desired geometry unlike the ceramic. On the other hand these glasses have a poor thermal spalling resistance. This term of spalling resistance comes from the fact, that suppose I have a material.

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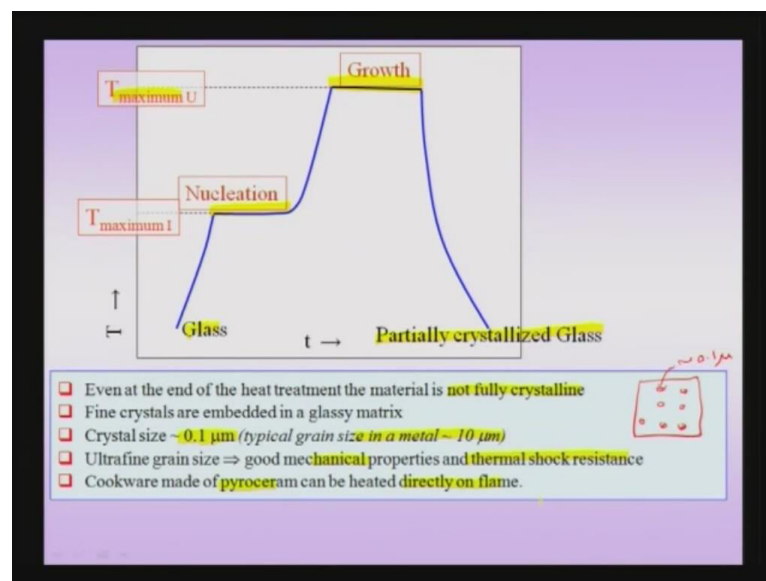


For instance which I suppose, there is a material or a crucible made up of glass, and we take it to high temperature and cool it in water heat that means first heat it followed by quenching. Now, what happens is that the outer surface will feel the cooling the for instance the inner surface may not feel. And therefore, across the cross section there is a temperature gradient. And therefore, the outer region will contract first while the inner region will not. And therefore, differential thermal expansion or in this case different thermal contraction you would note that there are normal stresses generated. And this material having poor factor toughness can leads to fracture of or spalling of this material. That means if a material has a ability to withstand different thermal stress or stresses arising from differential thermal expansion such a material is said to have good spalling resistance.

So, typically these glasses do not have a good spalling resistance. And we want to improve that for instance suppose I would like to have a cookware which I can put on a flame directly and cook. And if it is nice transparent material it may also help in the process we directly see the material being cooked. But we have noted that we now need to engineer the microstructure. So that we can endow certain amount of spalling resistance to the glass. So the way it is done is that we add heterogeneous nucleating agents like TiO_2 to to the molten glass or the fused glass.

So, glass is amorphous material that means it does not show a distinct melting point. Then we shape the material in the glassy state which is good. Because now, the glass are easily shaped in to the desired geometry then we pre-state the to a fine particles. That means we work at low temperatures where you get high nucleation rate but small growth rate. Then we that means you hold it at high nucleation after precipitating the fine particles we hold it at a temperatures where the nucleation rate is high. Then slowly we heat it to a temperature where the growth rate is maximum.

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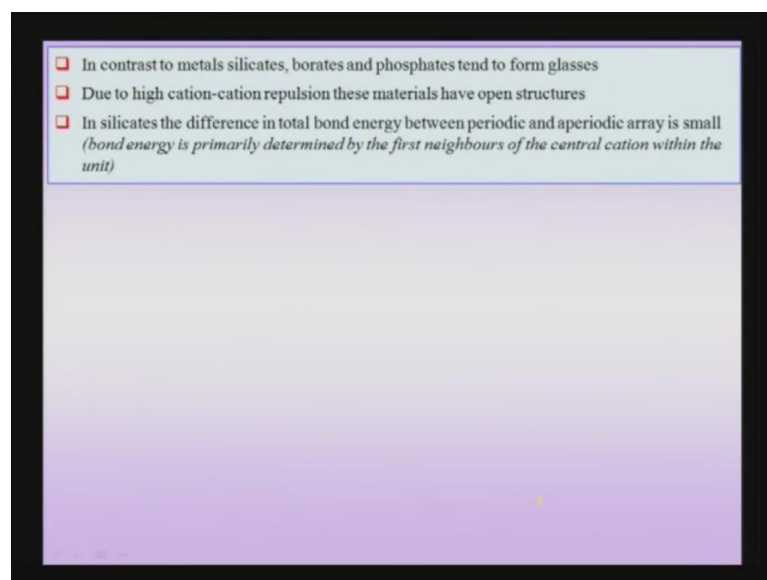
So, the overall heat treatment process consist of we have a glass then we cause nucleation then we cause further growth. And then finally, we have a partially crystalline glass the microstructure consist of crystals embedded in glass. That means the final product is not fully crystalline see critically crystallite size of the order of point 1 micrometer. And this is much smaller than the typical grain size in a metals that means we are not allowed the crystals to grow too much during growth phase. So, we are holding it higher temperatures where the maximum growth rate likes. But still we are not allowing this nuclear which are formed at lower temperatures to grow to a large size. That means typically we land up with the small crystallite size about 0.1 micrometer and the final microstructure consist of these crystals embedded in a glassy matrix.

So, you have a glassy matrix in which you have distribution crystallites. And this final product which we have obtained which is actually a fine composite of crystals and glass

as a good thermal shock resistance and has got otherwise also a good mechanical properties. There is a commercially available product which is called pyroceram which can be directly heated on the flame. And this is the advantage of having such a glass ceramic. So, to summarize the part which we have done so far, that we have 2 distinct levels of control over the properties. One is by what we call is at a crystal structure level and 1 is at the microstructure level. And we define the microstructure to be a combination of phases defects state and their distributions. And therefore, I can do microstructure engineering to get a direct handle on the properties.

We have seen how the hardness tensile strength etc changes when you talk about steels we have seen how the strength of aluminium alloys can change by microstructure engineering. And here in this example we have seen that even a glass can be a starting glass can be engineered by producing a fine distribution of crystallites to give a combination of not only for instance is the probability but also good resistance to spalling. So, let me summaries the final things we have done in the case of glass ceramic that the of course, we have noted that the silicate glass can be easily form glass by even slow pulling. Because of their high enthalpy of fusion and a very high viscosity that means sorry low enthalpy of fusion and high viscosity.

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They are easily amorphized that means that in contrast with metals silicates borates phosphates tend to form glasses easily and they typically hunt in to open structures. And

once I have this glass it can be shaped easily to the desired geometry. Then by using series of steps in which I for instance had some titanium which can then be used as nucleating agent to produce the fine distribute of the crystallites. And these fine crystallites can further of course, the volume fraction of these crystallites can be increased by using a growth step at higher temperatures. That the maximum of growth rates lies we can obtain a finial microstructure is a composite of a glass and ceramic. So, this final microstructure this good at spalling resistance the cookware made out of such a glass.

Indirectly we kept on the flame heated so that this is a advantage as we know typically you noticed that metals have this property that they can be easily directly heated on flame. But in this case we have noting that even a ceramic which is typically does not have a good spalling resistance can be heated on flame. And they do cooking directly in a ceramic vessel which is being kept on a some kind of thermal heating resistance or even a gas system. So, we are noted that we can actually do what we might call use our knowledge of phase transformations phase equilibrium and T T T diagrams to engineer microstructure get a series of properties which are not available if you do not have a knowledge on this tools.