Materials Science and Engineering

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Lecture – 23
Precipitation

Hello friends. We were discussing about heat treatment in steels and we saw different type of microstructure which you can get by this heat treatment. And this is one type of treatment where you can have bulk transformation. So, austenite is transforming into ferrite or transforming into pearlite or transforming into martensite. There is another type of transformation where you get new phase, but the phase which forms are volume of that phase is very small and that is usually in form of precipitates. So, this is another type of kind of heat treatment where you have precipitates in the material and that is why we call it as precipitation.

And this is very important in one class of material these are these are widely used material though this type of treatment will be important for large class of material. So, another class of material which is normally used in engineering application is aluminium alloys. So, aluminium alloys are strengthened by doing precipitation by introducing precipitate in the material.

So, we want to understand one this type of heat treatment now, and we will take example of aluminum alloy only and we will use aluminum copper alloys ok. Now, nowadays in fact, aluminum is become a very what you call very interesting material in the sense and very fancy material because nowadays in fact, even phone companies are advertising that there are phones for example, in iphone the body is made up of aluminium ok. So, it is something very and it is all these are all high strength aluminium alloys and so on ok. So, it is not only an very boring engineering application it can be advertising this kind of fancy products also ok. So, in aluminium alloy precipitation is one of the very important process to enhance the properties of the material.

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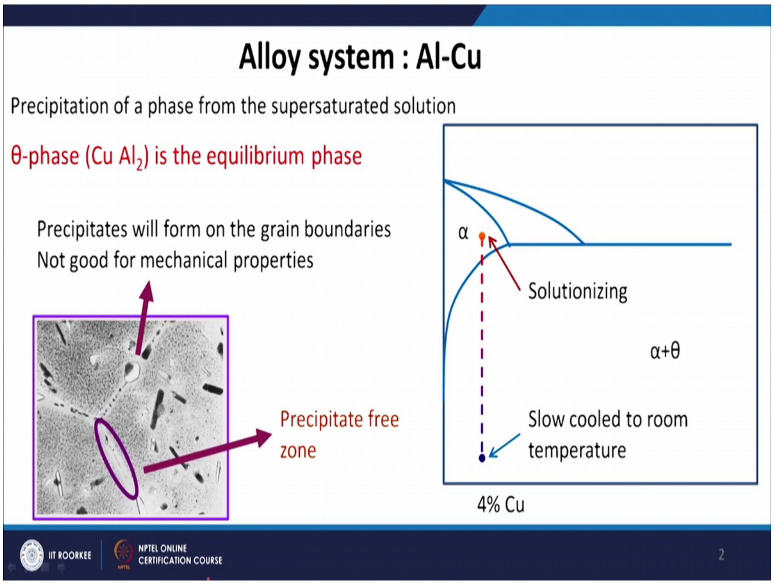

Alloy system : Al-Cu

Precipitation of a phase from the supersaturated solution

θ-phase (Cu Al$_2$) is the equilibrium phase

Precipitates will form on the grain boundaries
Not good for mechanical properties

Precipitate free zone

So basically if you look at alloy which is more of aluminum and less of copper this is aluminium copper system which we are using as an example here. So, we are only considering the part of the phase diagram where you have aluminium rich alloys. So, it is aluminium 4 percent copper which we are using as an example here ok. So, what is the process here is that I do a solutionizing.

So, let us take, let us say I have developed a aluminium 4 percent copper then I will take it to the solutionizing temperature; that means, all the this is the solvus line; that means, if I go above this temperature then all the copper will go into solution ok. So, this is my alpha phase in which all the copper will go,.

And if I quench it from that temperature or if suppose if I do slow cooling from that temperature and come to a temperature let say this is my room temperature ok, then I will get a precipitate which is copper aluminium 2 precipitate which is the equilibrium phase in this case and that precipitate we call that precipitate is theta phase. Theta phase copper aluminium 2 will precipitate out because copper cannot be more than given by this phase diagram. So, the extra copper as to come out and that will come out in form of another phase which is going to be your aluminium copper aluminium 2 or Al 2 Cu ok, and it has to come out from that in that form ok. And we have seen that in heterogeneous nucleation that grain boundaries are the preferred site for any transformation.

So, all these because we are doing a very slow cooling in this case all the precipitate will form on the grain boundary of aluminium matrix. So, if the precipitate forms on the grain boundary it is not good for mechanical properties as we saw in case of cementite also in steel if it is forming on the prior alpha austenite grain boundaries and forming a network it is not good thing for mechanical properties. And when this precipitate form on grain boundary they leave a precipitate free zone around that where there is not going to be any precipitate that is also not good for mechanical properties and other corrosion properties also. So this type of microstructure we do not want.

So, we want precipitates, but precipitate we want to have such that this precipitate should form within the grain not at the grain boundary and that is what the whole heat treatment is about that how to form this precipitate within the grain. So, if you look at the sequence of precipitation it is something like this.

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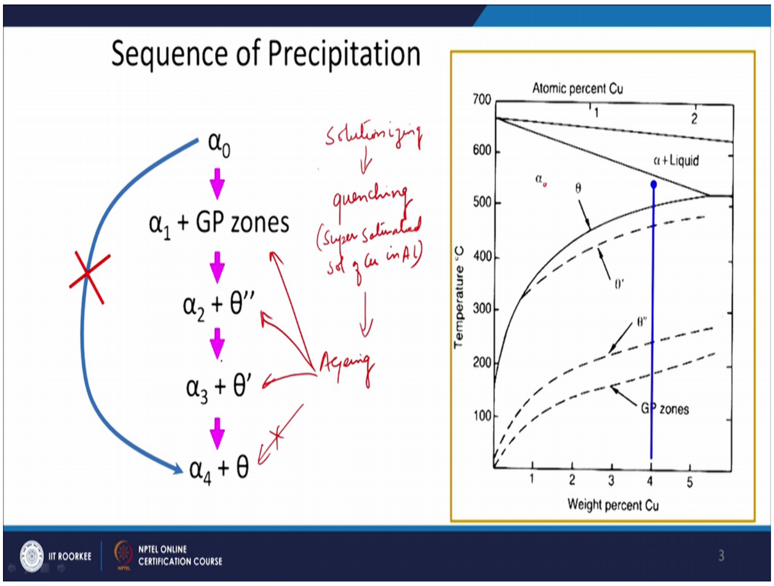

Sequence of Precipitation

α_0

α_1 + GP zones

$\alpha_2 + \theta''$

$\alpha_3 + \theta'$

$\alpha_4 + \theta$

Solutionizing

↓

quenching

(Super saturated sol of Cu in Al)

↓

Ageing

That alpha naught is basically your single phase alpha where the copper is going into the solid solution ok. There is another then the phase diagram is shown here aluminium rich part of the aluminium copper system ok, and you can see there are some solid lines are there and some dashed lines are there. And if you remember I told you that in phase diagram we only plot the equilibrium phase boundaries and any non equilibrium phases have to be shown by dashed line. So, you actually get lot of non equilibrium or meta stable phases also which are shown here as dashed line.

So, have one boundary for GP zones another boundary for theta double prime then theta prime and then the equilibrium phase theta. So, this GP zones are called Guinier Preston zone ok, which form in the alloy during precipitation we are not going into all those details how this form and so on because it will be a again big topic you just take it from me that while doing a precipitation reaction what we want is the sequence of precipitation should be such that the solid solution should dissociate into phase alpha 1 plus GP zones which are Guinier Preston zones ok.

Then it should be another combination of phases should be there next sequence it is alpha 2 plus theta double prime, then alpha 3 plus theta prime, and alpha 4 plus theta ok. And we do not want direct transformation of alpha solid solution alpha into alpha that is the alpha phase plus the equilibrium precipitate this we do not want. So, we want to have sequence like this ok.

Now, to get sequence like this what we will do is first we will do after solutionizing. So, first will be your solutionizing operation. So, we will be heating at any temperature above the solvus line and let say may be 20-30 degree Celsius above the solvus line. So, for aluminium 4 copper may be heating it up to around let say 525 degree Celsius. So, from after solutionizing we do we will do the quenching operation ok. Why we are doing quenching? We want to retain all the copper which is in the solution in that form only.

So, basically if you do the quenching you will get the super saturated solution ok, super saturated solution of copper in aluminium ok, that is what you will get. After quenching we will do some operations which are called etching process. And during etching you will get all this intermediate phases which will come out of the solution, but we are doing it in a very controlled way.

So, that you do not form this you will get these in sequence ok. And why you get these in sequence because transition phases though these are not equilibrium phases, but why we get this is this phases is because the activation barrier for formation of these intermediate phases is low and because I am doing the etching process at much lower temperature than the solutionizing temperature I need to have a very small activation barrier ok.

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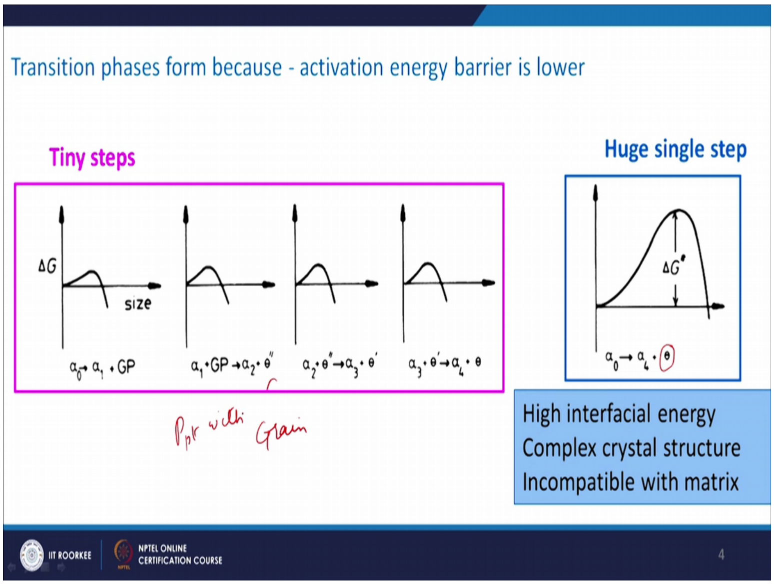

Transition phases form because - activation energy barrier is lower

Tiny steps

Huge single step

High interfacial energy
Complex crystal structure
Incompatible with matrix

Ppt within Grain

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So, if you have alpha naught forming into alpha 1 plus GP zone or alpha 1 plus GP is forming into alpha 2 plus theta double prime and so on for each of this process the activation barrier is very small. So, it is like that I am covering a the same path in very tiny steps which I can easily do.

For example, if you have to climb something if I make a step of very large height it will be very difficult for you to climb each of these step it will require lot of effort from your side. But if I divide the same height into small steps it is very convenient for us to climb that is what we are doing here that we are dividing the whole precipitation into tiny steps instead of one huge step which is basically alpha naught transforming into directly into the equilibrium phase theta ok.

Why we do not want that? Because it has a complex crystal structure and because of that you have high interfacial energy and it is incompatible with the matrix ok. So, it is not going to form within the grain when you do one single operation, it is always going to form on the grain boundary where it can accommodate or where it can minimize the formation the formation of a new phase by destroying the grain boundary. So, the destruction of the grain boundary actually provides the driving force for formation of this theta precipitate on the grain boundary.

So, if you take this huge step which as a very large activation barrier you need site which can provide that activation energy to that to you and that is where you use grain boundary for precipitation. So, we do not want this to happen ok. So, that is why we do quenching and then we take this tiny steps to form the precipitate within the grain. So, all this process we are doing is so that we can have precipitate within the grain you want precipitate within grain ok.

So, what are the step involved as I told you taking all copper into solution above solvus line around 550 degree Celsius we will do the solutionizing ok.

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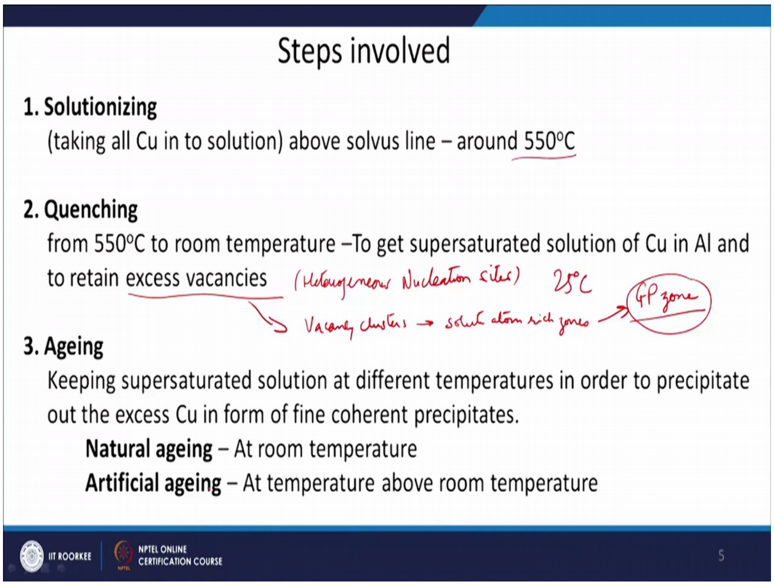

Steps involved

1. Solutionizing

(taking all Cu in to solution) above solvus line – around 550°C

2. Quenching

from 550°C to room temperature –To get supersaturated solution of Cu in Al and to retain excess vacancies (Heterogeneous Nucleation sites) 25°C

Vacancy clusters → solute atom rich zones → GP zone

3. Ageing

Keeping supersaturated solution at different temperatures in order to precipitate out the excess Cu in form of fine coherent precipitates.

Natural ageing – At room temperature

Artificial ageing – At temperature above room temperature

Then we will do quenching from 550 degree Celsius to room temperature to get super saturate solution of copper in aluminium and to retain excess vacancies ok. Please remember again this word when we were discussing heterogeneous nucleation we said that these are heterogeneous nucleation sites ok. Why we are having excess vacancies? If you remember again that we said vacancies are the thermodynamically equilibrium defects ok. So, at higher temperature you will have more vacancy in the system at lower temperature you will have less vacancies in the system, at 0 Kelvin you will have no vacancy in the system ok

So, as you increase temperature from 0 Kelvin as a function of temperature the vacancy concentration increases exponentially ok. So, there is a exponential dependence of vacancy concentration on temperature. So, temperature may increase linear linearly, but the vacancies will be increasing exponentially ok. So, at high temperature you will be having more vacancies at low temperature you have less vacancies. So, when you quench the material from higher temperature you are not giving enough time for this vacancies to go into equilibrium concentration ok.

For example, at room temperature 25 degree Celsius whatever is the vacancy concentration should be there from thermodynamics we are not giving enough time, for vacancies to be destroyed ok. So, that it can become it can come to a concentration which is given by the equilibrium concentration at 25 degree Celsius. So, basically you are retaining this excess vacancies.

Now, this excess vacancies kind of come together and form a vacancy cluster and in this. So, you can understand these vacancies will be because we are doing quenching we are at room temperature they cannot diffuse to longer distance they can only diffuse to some nano meter distances. So, they form very small clusters large number of clusters at very close distances. So, may be 5-10 vacancies will come from a cluster another 5-10 vacancies come from cluster and so on.

And in this vacancy clusters you are solute atom the copper atom which is in super saturated condition it does not want to be in the alpha phase it want to come out. So, it sees those vacancy clusters there and this copper atom go and will sit in those vacancy clusters ok. So, now, you can see that you have large number of location where this copper solute atom is going and sitting and these small clusters of copper are called GP zone Guinier Preston zone, given proposed by this two scientists and on their name these are known ok. So, this small ah, how it start? It starts with vacancy clusters. So, this excess vacancies will form this vacancy clusters in this vacancy cluster your solute atom will go and sit ok. So, this why these will be small solute rich zones and this solute atom rich zones are called GP zones ok.

So, excess vacancies are very important in this. So, one is super saturated solution. So, that you have more copper inside the solution which should not be there and then you have vacancy cluster. So, this copper atom will come and sit in this vacancy clusters ok. So, this is what is the formation of GP zone.

Now, we want to go to the next stage and for that we do etching process. What is etching? Keeping super saturated solution at different temperatures in order to precipitate out the excess copper in form of fine coherent precipitates ok. So, basically this GP zones are for formed now, ok. Now, this we will take to a high temperature ok. So, at high temperature etching will involve the formation of GP zone also. So, first step will be formation of GP zone, and from this GP zone you will form other coherent precipitate coherent we have not discussed still. Now, let me explain it to you just like that that when you have two phases you are going to have interface between them ok, if this interface is such that that the atom across the interface are having a very nice matching then we will call it as a coherent interface ok.

So, we will be forming this fine coherent precipitates by doing etching. Now, the etching also can be of two types, one is natural etching which can be done at room temperature. So, after quenching you just keep it at room temperature for sufficient amount of time then you will have all these precipitate forming. So, you will have natural etching. If you are not doing it at temperature of room temperature, but doing at any temperature above room temperature then it is called artic because it is done artificially. So, it is artificial etching and temperature about above room temperature ok.

These are the steps involved and because of this steps this is how the hardness of the material will be changing ok, hardness variation as a function of etching time.

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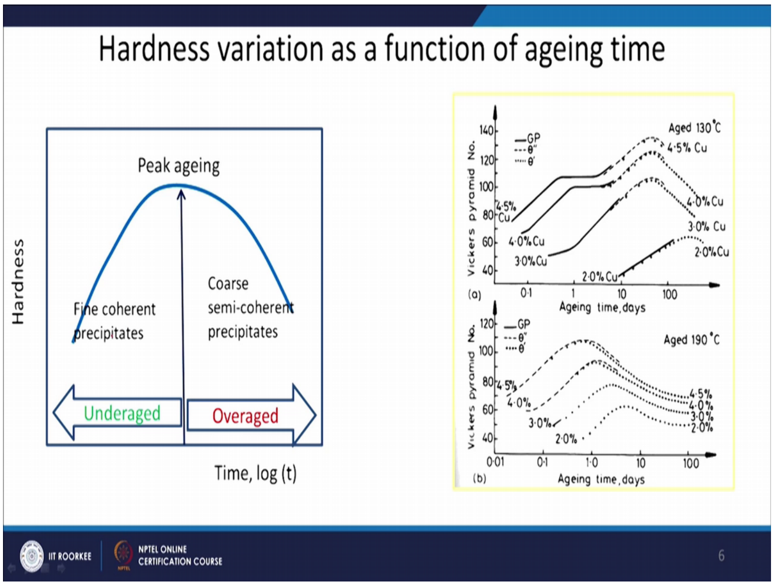

Hardness variation as a function of ageing time

So, at initially it will be GP zone fine coherent precipitate which will be forming and because of that the hardness or the strength of the material will be increasing. After some time the coarse semi coherent or coherent in coherent precipitate will be forming and then you will again the hardness will come down. So, this is called the peak etch condition where you get the maximum hardness.

If you do any etching below this then it is called underaged condition, if you do any etching above this it is called over etched condition ok. These are the actual experimental curves plotted for different copper percentage. So, you can see as the copper percentage is increasing my response to etching process is improving. So, initially this is the formation of GP zone ok, as I told you during the etching process the etching is done at this temperature 130 degree Celsius. Then this dashed curves are for theta double prime precipitates then the dotted one for the theta prime precipitates. So, after formation of theta prime precipitate the actually the hardness started coming down ok.

And you can also look at the etching time it is around 10 days here 100 days here. So, you reach the peak etch condition may be at around let say 60, after 60 days for which is for industrial application is not a feasible solution. So, if you are doing at 130 degree Celsius. But if I do the same etching at 190 degree Celsius for example,. So, after solutionizing quenching after quenching you take it to 190 degree Celsius.

Now, you can see that I am able to achieve the peak aged condition in let say less than one day may be in like 22 hours, 23 hours or so, But the problem is the my peak hardness is somewhere around 100 where is in this case the peak etch value was around more than 130. So, I have reduced the time for peak etching condition my, but my hardness or the peak hardness which I am going to achieve is now, lower ok.

And other thing you can notice here that there is no formation of GP zone. Now, directly I am forming the theta double prime precipitate. I am not telling you what do we mean by theta double prime, theta prime precipitate and so on just take it from me that these are some precipitate which there are steps involved and these precipitate form within the grain and these are coherent precipitate. Coherent precipitate means they have coherent interface. So, this precipitate as you can see that the precipitate is Al 2 Cu, and the matrix is alpha aluminium, ok.

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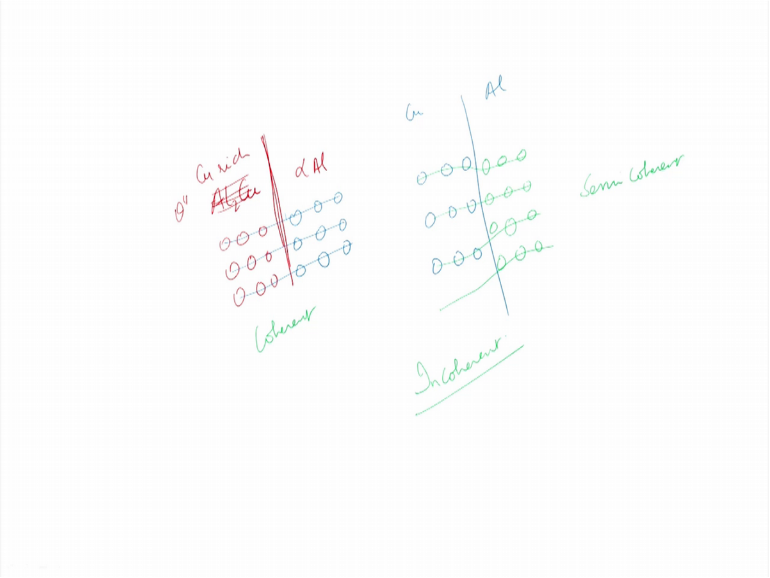

So, now, when you have a precipitate like this it is going to have some interface between the two ok. So, when the coherent interface is there ok. So, suppose this the atomic arrangement here for Al 2 Cu. The same atomic arrangement I will not call it as Al 2 Cu let say there is some copper rich region because Al 2 Cu is your equilibrium precipitate in that case you will not get this coherent interface ok. So, let say some copper rich region is there. So, this is the atomic arrangement in the copper rich region, it can be copper rich region, it can be theta double prime precipitate and so on and these are the arrangement of aluminium atoms.

Let me show it with some other color. This is the atomic arrangement in the aluminium rich region. So, if it is a coherent precipitate then the interface between the two will be coherent you can see that the atomic arrangement is continues across the interface ok; that means, whatever unit cells will be there or what is the lattice arrangement here is continuous ok. If it is not a coherent interface it can be very complicated interfaces also just for explanation I can show you another arrangement. Now, this is the arrangement for may be let say copper rich region ok, and for aluminium rich region let say the arrangement is something like this, but in aluminium side let say the arrangement is something like this.

Now, you can see that there is no continuous arrangement if I see the arrangement here ok. There is some kind of mismatch is there ok. So, now, it is not a coherent interface it will try to be a incoherent interface, in fact, it is going to take care of this mis-feet by may be introducing one dislocation here ok. So, if it is introducing a dislocation here then it is called a semi coherent interface. So, this is coherent the semi coherent and in coherent infect due cannot have any relationship between the two ok. So, just for understanding sake I am telling you about this that you can have different type of interfaces with different and different type of precipitates. So, that is what you can see the effect of that on the mechanical properties here ok.

So, a smart guy what he will try to do is that you can see that at one ninety you are getting peak hardness at much lower time, but the maximum hardness is low here ok. So, what you can try to do is you can combine the two etching processes what you will do is you start with 130 ok. So, that you have large number of GP zones and you try to have maximum number of GP zone forming and then you go to 190 degree Celsius to speed up the process ok. So, this is can be called as two step etching treatment. So, initially you want to have more GP zone formation. So, 130 degree Celsius and then you go to 190. So, this type of smart thinking is what makes this treatment processes is very popular and important ok.

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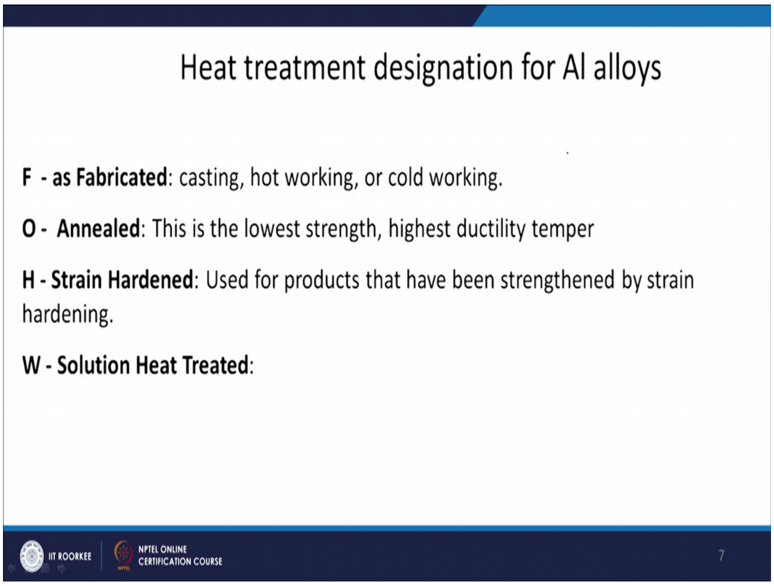

Heat treatment designation for Al alloys

F - as Fabricated: casting, hot working, or cold working.

O - Annealed: This is the lowest strength, highest ductility temper

H - Strain Hardened: Used for products that have been strengthened by strain hardening.

W - Solution Heat Treated:

Now, for the heat treatment designation for aluminium alloys if you want to discuss these are the different designations. So in industry or if you want to go in market in want to buy some aluminium alloys that guy will simply ask you that what do you want which alloy and, so you have to tell which alloy you are interested in; aluminium this, aluminium that, aluminium magnesium alloy or aluminium copper zinc alloy or aluminium magnesium zinc alloy or aluminium silicon alloy that also have designations that we will discuss later on ok. Right now, we are interested in heat treatment.

Similarly, there will be designation for heat treatment that in what form you want. So, if it is written as F then it is as f F either it can be casted or hard hot worked or cold worked. So, in whatever condition it is a fabricated that is what you want. O is for annealed; that means, after doing fabrication this is the lowest strength alloy which you can get for a particular composition, but highest ductility temper is available. So, after fabrication you can ask him to I want it in fully annealed condition. So, you that designation will be O.

Another designation H can be there which is called strain hardened again where we will discuss mechanical property you will understand what do we mean by this term. Use for products that have been strengthen by strain hardening or by deformation basically. Or W which is solution heat treated ok. So, if you I say W then you know that it has to be solution heat treated that is it if I say O you understand that it has to be fully annealed and that is it ok.

Now, there large number of designation for etching treatment ok. So, after solution heat treatment if I am also want to do an etching treatment ok. So, I go to market I ask him no I just do not want solution heat treated it should be aged also and this is denoted by T.

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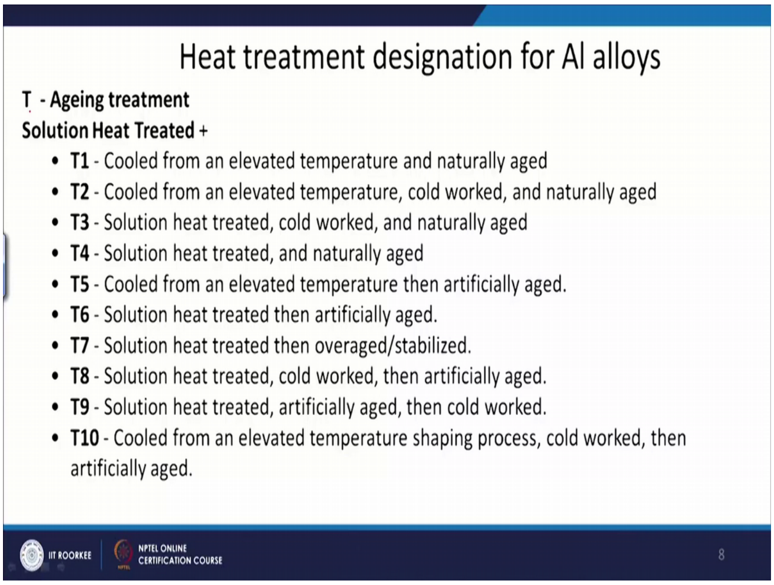

Heat treatment designation for Al alloys

T - Ageing treatment

Solution Heat Treated +

- **T1** - Cooled from an elevated temperature and naturally aged
- **T2** - Cooled from an elevated temperature, cold worked, and naturally aged
- **T3** - Solution heat treated, cold worked, and naturally aged
- **T4** - Solution heat treated, and naturally aged
- **T5** - Cooled from an elevated temperature then artificially aged.
- **T6** - Solution heat treated then artificially aged.
- **T7** - Solution heat treated then overaged/stabilized.
- **T8** - Solution heat treated, cold worked, then artificially aged.
- **T9** - Solution heat treated, artificially aged, then cold worked.
- **T10** - Cooled from an elevated temperature shaping process, cold worked, then artificially aged.

So, after solution heat treatment etching any etching treatment is done then it is will be referred by T and T has lot of sub sections here. So, T 1 is cooled from an elevated temperature and naturally aged. So, if you have naturally aged condition thus keeping at room temperature then you have to say I want T 1 alloy. If you have you want a cold worked and naturally aged you have to say T 2 ok, if you want cold worked and naturally solution heat treated cold worked and naturally aged then T 3, solution heat treated and naturally aged T 4.

See in this elevated temperature only we are seeing in this case we are seeing it as to be solution heat treated; that means, all copper should go into solution and then you are doing natural etching. T 5 is cooled from an elevated temperature then artificially aged, T 6 is solution heat treated then artificially aged, T 7 solution heat treated then over aged, T 7 condition is the over etched condition, T 8 is the cold worked then artificially aged, T 9 artificially aged then cold worked, T 10 cool cooled from an elevated temperature shaping process cold worked then artificially aged. So, there are different temper designation are there ok. So, when you go to market he will ask you which type of alloy you want ok. So, you have to specify I want this kind of alloy whatever (Refer Time: 28:50) you are going to use it for ok.

So, with that thank you. This is different type of system aluminium copper system where the heat treatment is of different type which is called precipitation heat treatment ok. Little bit different than what we discussed during when we were discussing about steels

Thank you.