Aqueous Corrosion and Its Control
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Lecture - 24
Forms of corrosion: Intergranular corrosion (Part- IV)

We shall continue our discussion on the weld decay. I have shown in the previous lecture that when you weld a stainless steel, intergranular stress corrosion cracking does not occur adjacent to the weld fusion zone. Just immediate vicinity of the weld fusion zone there is no decay.

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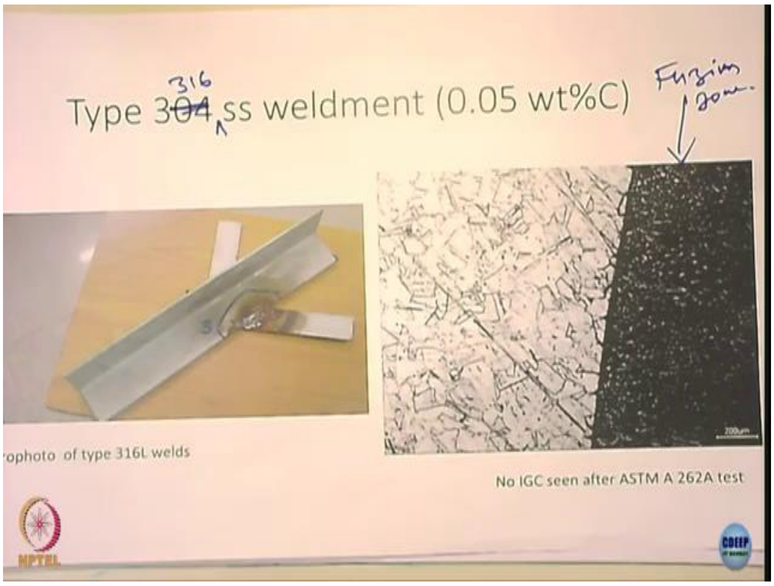

Type 3~~04~~ 316 ss weldment (0.05 wt%C)

Fusion zone.

ophoto of type 316L welds

No IGC seen after ASTM A 262A test

And it occurs at the heat affected zone which is away from the diffusion zone. This is a kind of welding done on a stainless steel. And this is 316 stainless steel weldment is carried out.

So, kind of welding that people do to make the structures actually. And you can see that this is the fusion zone, you see this fusion zone here. And immediately next to the fusion zone you do not see any kind of weld decay.

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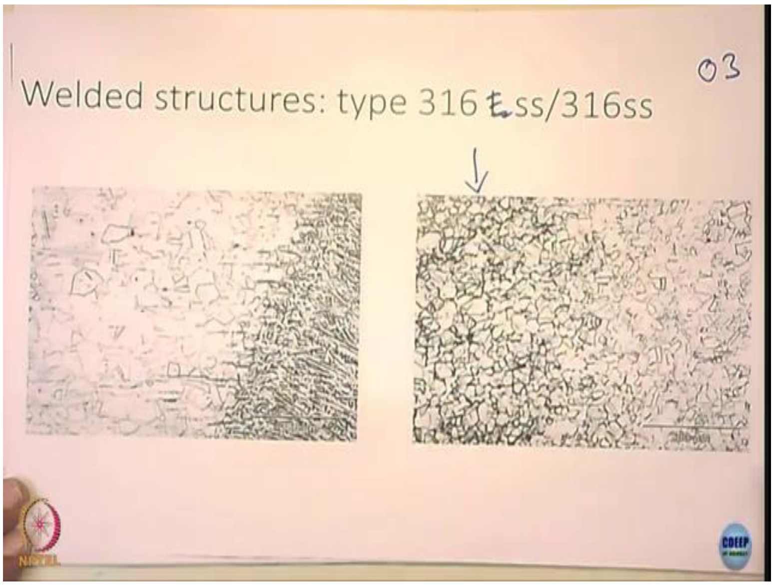

Welded structures: type 316 L ss/316ss

03

And, but if you just move away from the fusion zone you will get, in heat affected zone. You see kind of problems that you normally you get in this actually again. This not L actually, it is containing 316 stainless steel. Very close to that if you do not really see any kind of weld decay.

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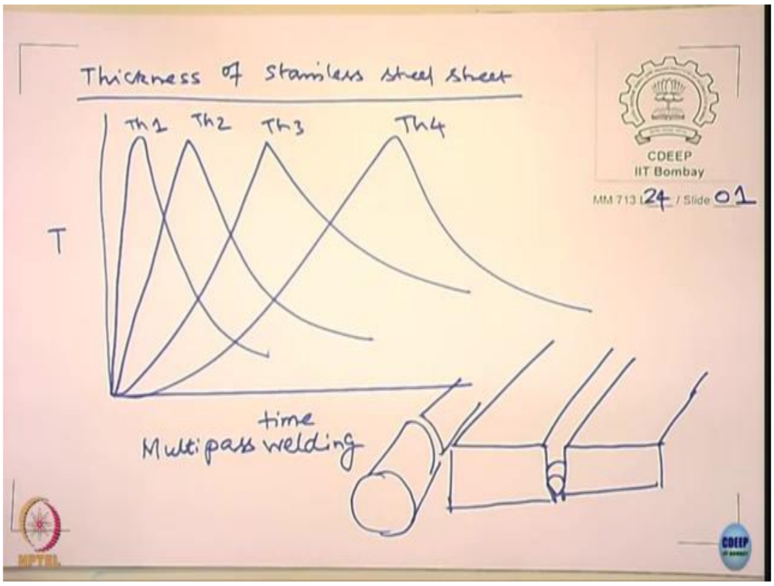

Thickness of Stainless steel sheet

CDEEP
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MM 713 L24 / Slide 01

This is kind of recapitulating what we saw in the morning. We looked at the various weld techniques morning and we said that the sensitization behavior of a given stainless steel could change based on the welding technique for a given composition of the stainless steel.

That is basically happening because of what, why does the different technique would lead to different sensitization welding technique? It is the heat input given by the welding techniques are different, and so the extent of sensitization differs in depending upon the welding technique. The other important factor that is required to be understood is the thickness of stainless steel. May call a sheet. Suppose you want to weld the thickness of the stainless steel plate, a sheet.

Now if I have go for a thicker sheet or thicker plate, if you want to weld at one go the amount of heat that is deposited per unit area is going to be quite large. Is not it?

You are going to build up layers, right? We build up layers and so, the more amount of heat is now deposited onto the unit area and so, it takes long time to cool and what will happen then? It is possible that the cooling rate is lower than the critical cooling rate required to avoid the sensitization.

So, that can be depicted by the simple schematic diagram of time versus the temperature for sheets of different thicknesses. They are welded at one go. I use thickness 1, thickness 2, thickness 3 and thickness 4. I have this is enlarged, its not going to be that wide actually. I just enlarge for convenience to make it. Now can you tell me in this case what order the thickness is increasing?

Student: Right.

From the right the thickness 1 what represent here is a least thickness. The thickness 4 is the most thick one, right? In practice we need to weld the thicker plates, the thicker tubes in a nuclear industry for example, the tubes of one inch at above thickness are welded. Now you are going to deposit heat more, but you need avoid sensitization. How to do that? How do you avoid sensitization in that case? You understood my question, you cannot avoid I mean you cannot say that all the time I have only thin sheets, I have to go for thick sheets.

So if you are going for thick sheets, and even it weld, how do I avoid sensitization? How to avoid? Can at least some guys have already taken a welding course right?

Student: Multipass welding.

Yes, so good answer. So, you do not deposit a one go. You deposit once, you continue the layer allow it to cool, then what you do? You deposit the second layer, allow it to cool. So, each time when you weld, you are allowing the weldment to lower its temperatures. In which process you are able to maintain adequate cooling rate so that sensitization is avoided. So, we do what is called as multipass welding.

In some cases if it is a tube for example, you are welded tube what do one can do? A circumferential weld, suppose there are two tube and you want to weld them. What you can do? First you can weld and you can have water inside, you start welding then what happens?

Then there is as a good coolant not only that it also builds up nice compressive stresses. So, its entire advantages for minimizing sensitization, it also minimizes stress corrosion cracking. Will see later at when you normally weld a material you get a tensile stress or we are not discussing this point here.

So there are various ways people weld in aerospace industries also, they normally cool it using a copper blocks. You can put a copper block and then start welding, the copper block extracts the heat. There are several ways of lowering the quantity of heat and then increase the cooling rate. So, that you can avoid sensitization of weldments.

So, these are the some factors which I think are important in welding of stainless steels. There is one more problem that is concerned with stabilized grade stainless steels.

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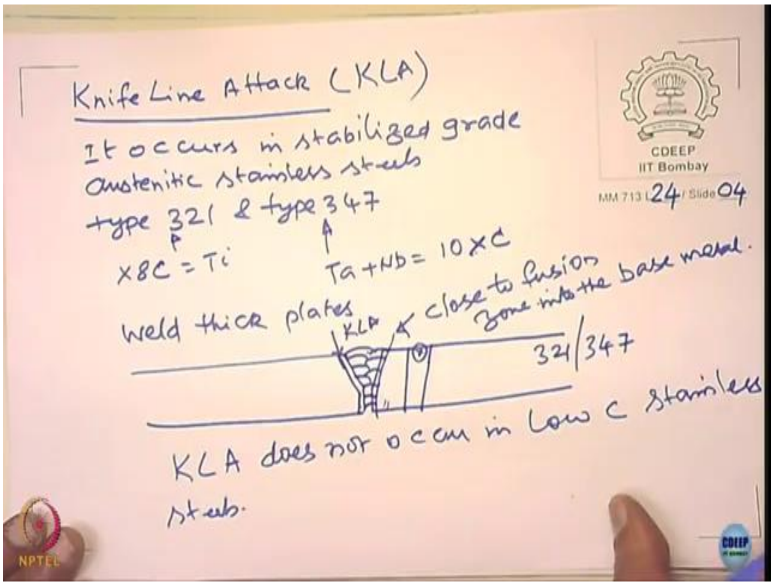

Knife Line Attack (KLA)

It occurs in stabilized grade austenitic stainless steels

type 321 & type 347

$\times 8C = Ti$

$Ta + Nb = 10 \times C$

weld thick plates

KLA

close to fusion zone into the base metal.

321/347

KLA does not occur in Low C stainless steels.

And that problem is called as knife line attack. It occurs in stabilized grade austenitic stainless steels. We talked about two grades of that, one is type 321 other one is type 347.

And in this what you do? In this case I mean type 321, it is titanium containing right how much titanium you normally add anybody remember?

So about 8 times the carbon content is equal to the titanium added in this case. In this case tantalum plus niobium at together is equal to 10 times the carbon content. So, you can have 0.08% carbon and accordingly you can add titanium. You all know that the titanium combines with carbon and no free carbon available, when you weld it there is no sensitization. But knife line attack is a special case that happens when you weld thick plates.

So, you weld it as I told you. Thick plates require multipass welding without which you are going to lead to sensitization, and in this case, this is anyone of that it could be a 321 or 347.

What they found was, the attack occurs very close to fusion zone and into the base metal. So, the base metal side you will have very close to this. It happens, very close. This is called KLA, very close it happens, very interestingly KLA does not occur in low carbon stainless steels.

We need to understand this and please notice they do not occur at the regular heat affected zone that happens in a normal 304 stainless steel. It occurs very close to the to the fusion zone in the in the base metal. Why does it happen?

In order to understand this you need to understand the thermal cycle. If you weld a single pass weld, if you do a single pass weld, what is the thermal cycle for that?

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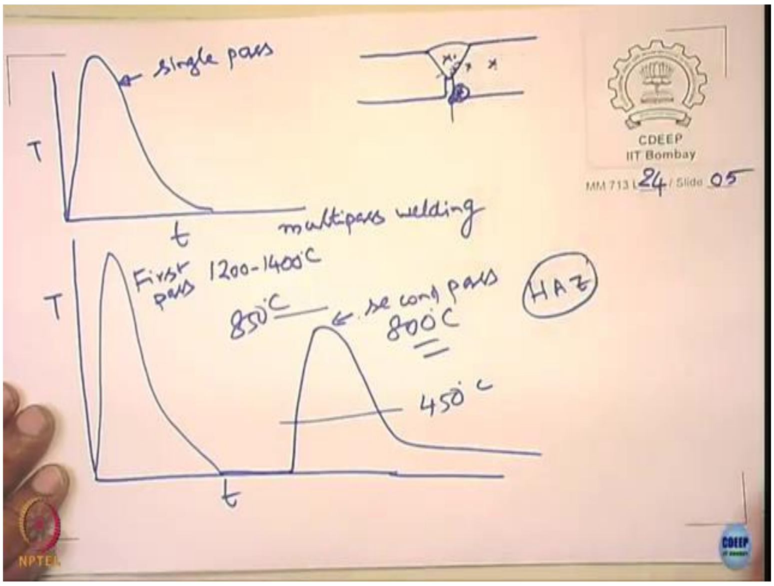

Student: (Refer Time: 15:40).

Temperature, height it goes up, it cools like that. Single pass right; that means,, but if I have to cover it at one go, and I measure this temperature here, you measure anywhere the temperatures any here or here, anywhere it of course, the highest temperature may change, but the cycle is going to be same.

If you are going to do a multipass welding. Suppose, let us assume that this is the place I want to notice here. I am going to put a thermocouple here and I do a single welding goes like this. If I am going to put one more layer over here, what happens? Again, look at this, this zone very close to the, close to the fusion zone.

This is the first pass, the second pass. In the first pass when I weld here, when I weld at this location temperature goes very high, maybe around 1200-1300°C may go it does not melt, please look at next to the fusion zone it does not melt, but the temperature goes much higher than the weld decay zone maybe the temperature may be around about 1200 to 1400 °C.

When I move up here, suppose I start welding here this location is going to follow something like in heat affected zone for this area. When I start moving up, this somewhere move up, what happens? This the distance is sufficient enough for me to consider this as heat affected zone.

So, this temperature is in the range of what? In the range of this probably, it goes around about 800 °C. And this temperature region may be 450 °C and 850 °C.

So, here it is acting like a heat affected zone for this, because it is sufficiently far away from the location. This is the heat affected zone for this; if I move away from this, this becomes heat affected zone for this. Is not it?.

The distance is almost same. Am I right or not? So, what happens now? So, this is the reason why the knife line attack occurs. Now let us look at what is happening to the metallurgy of this particular weldment. In this case and this case.

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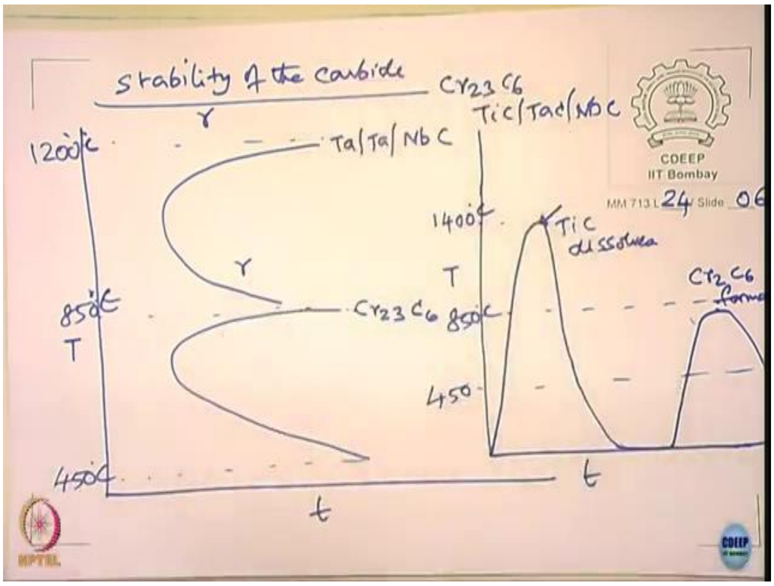

We need to understand, stability of the carbides. $Cr_{23}C_6$ is a carbide, performs; what is the temperature region? It is between say 450°C and 850 °C; and is a gamma phase. What other carbides you have here?

You also have, you have $Cr_{23}C_6$ can be there, and you can have titanium carbide, tantalum carbide and niobium carbide. Look at this all carbides.

What the temperature? On about 1200°C. Understood or not? The titanium, tantalum, niobium carbides form in the temperature region of 850 °C and 1200 °C. The chromium carbides form between 450 °C and 850 °C; above 850 °C what happens to chromium carbide?

Dissolves. Then what is happening to titanium carbide and all? Starts forming. This carbide dissolves and these carbides form. And above this temperature only gamma is there and no tantalum carbide, niobium carbide, all this stuffs are not there.

Now let us look at the weld thermal cycle; In a multipass welding, what you do this is the temperature, time. I am going to draw about 1400 °C, I am going to put it about 1200 °C.

So what is happening here? A stabilizer grade stainless steel consists of what it consists of tantalum, niobium or one of these carbides. They are present in that right? When you raise this temperature, what is happening to these carbides?

They all dissolve. When you again raised this temperature what happens now? This is in the range of 450 °C and 850 °C. So, what happens now, suppose you reheat it again what happens now? What forms?

Student: Chromium carbide.

Chromium carbide forms. Please notice, In a weldment, I just come back to this place here. In a weldment this is the melting temperature here, it goes beyond melting temperature. This place very close weld fusion zone in the base metal, does not melt lower than melting point, but the temperature is sufficient for the titanium carbide to dissolve.

In the heat affected zone, what happens here? In the so called weld decay zone what happens here? Here, the temperature is between 850 °C and 450 °C, but nothing happens because the titanium carbide still remains as a titanium carbide. It does not dissolve and so, chromium carbide also will cannot form.

So, here you have no issue; here it is dissolves here. When it dissolves, please understand no sensitization chromium carbide form because you are reheating it. You are reheating it by welding process. If you see for example, if you take 321 you do a single pass welding. What will happen?

There will be no sensitization. Why? Titanium carbide dissolves, but does not mean the chromium carbide forms automatically; that means, still the carbon is in solid solution, chromium carbide does not form. So, if you happen to weld 321 single pass welding, a thin plate suppose you do that, then you have no issue. Because the thick plate, because you are welding at different, heights. The lower one becomes heat affected zone for the upper ones.

And so, the chromium carbide starts forming. So, these places the chromium carbide starts forming. When the chromium carbon starts forming then you get sensitization and that is why it is very close to this.

Please notice if you move away from it, if the temperature is lower than 1200 °C nothing happens. Titanium carbide is still stable. So that means, you do not want to get any sensitization here, nor here and you get only very close to this. So, that is the reason why it happens.

In the thermal cycle basically the first one leads to dissolution of titanium carbide. The second one, when it becomes heat affected zone for the subsequent welding, chromium carbides form. So, it leads to what is called as sensitization taking place. And that is the problem that happens. We stabilize grade stainless steels.

It does not happen in low carbon stainless steels because what, why? Because low carbon stainless steels, carbon is not there to form chromium carbide at all and any way you are going to cool it down. So, in the case of low carbon stainless steels you will not get knife line attack.

You get knife line attack only in the case of the stabilized grade that too when you weld the thick plates. Everyone weld a thick plate, you will not get this kind of problems. Have any questions; any of you have any doubts?

Student: Why does TiC, titanium carbide not dissolve at lower temperature and lower temperature range curve?

Yeah.

Titanium carbide is stable; titanium carbide is stable at ambient temperatures. Does not form. See, if you hold the stabilized grade stainless steel at this temperature, what is the likely phase formation?

Only titanium carbide forms. Chromium carbide does not form. For some reason I do not hold here, I first take it to this temperature; I hold it here, I dissolve all of them then I bring it to this temperature. What will happen, chromium carbide is a form, sensitization will occur.

Whereas, when I move from this temperature to this temperature, chromium carbide does not form instead you get titanium carbide or tantalum or niobium carbides all the carbon is gone. When you lower the temperatures the chromium does not get enough carbon to form chromium carbides.

So, this is why the stabilized grade stainless steels are resistance against sensitization and that is the reason why, it is see; why they called stabilized grade stainless steels? The stabilized grade stainless steels are made in this manner, please note down. You normally hold the stabilized grade stainless steels above 1200 1250 1235 °C depending upon the carbon content you hold it here, that means in which case all the carbides dissolve.

Then you bring it down, this temperature region somewhere around 850 900 °C you hold it here. Then what happens? All the carbon combines to form titanium carbide in 321, tantalum niobium carbide in 347. Then you cool it. That is the way use your stabilized grade stainless steel. The stabilized grade stainless steels have carbides.

What carbides are they? They are titanium carbide in one case, tantalum and niobium carbide another case. If they do not have it then you weld it you still are going to have problems. So stabilization treatment means the formation of these carbides in these stainless steels. That is why these stainless steels are always given a stabilization treatment.

What do you mean by stabilization? Just fix all the carbon so that no free carbon is available for subsequent sensitization process. So, is it clear actually to you? Any of you have any questions? Ok.

So, you should know now the difference between weld decay and knife line attack. Weld decay occurs in stainless steels having higher carbon content whereas, knife line attack occurs only in the stabilized grade stainless steels.

The second issue is that, it depends upon the thermal history. If you do not reheat it, then what happens? You will not get any sensitization. The third difference is the weld decay occurs quite away from the fusion zone, the knife line attack occurs very close to the fusion zone. There are three distinct differences occurring here.

So, these are the important factors. I am going to ask another question to you. Suppose I taken a stabilized grade stainless steel is not very thick, but it is thin, I welded only once, but I am going to apply to a process where the temperature is held in the range of 500 °C.

Liquid is kept at 500 °C. So, what will happen? I have two cases. I have taken 304 L stainless steel, I weld only once only the thin tube. 321 also is a thin tube. I only weld only once on a single pass, right?

You please tell, let me know. So, I am going to leave that question to you, you please think over. Let us discuss it in the next class.

I want you to get into the problem and by doing so; you will understand the basics of weld decay and knife line attack, ok? These two are important things. So, we have reasonably covered what is called as sensitization and weld decay.

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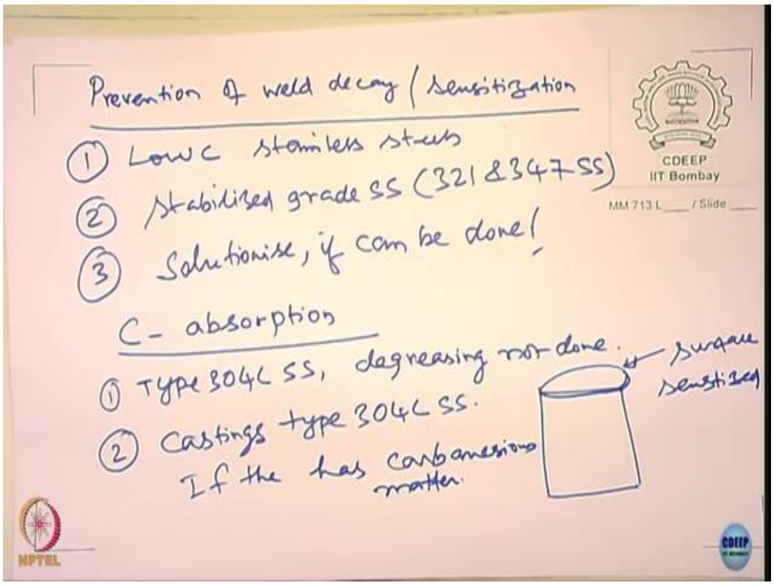

Prevention of weld decay / Sensitization

① Low C stainless steels

② Stabilized grade SS (321 & 347 SS)

③ Solutionise, if can be done!

C - absorption

① Type 304L SS, degreasing not done.

② Castings type 304L SS.
If the has carbonaceous matter.

And you also know how do you avoid or prevention of weld decay or sensitization. Come on tell me how do you avoid it?

Student: Low carbon.

Low carbon stainless steels.

Two.

Student: Carbide former.

Stabilized grade for example, 321 and 347 stainless steels. Third.

If you can solutionise, if can be done. Is not possible in practice in a structure you are going to do heat exchanger and how are you going to do this. But small you know, small sections small components it still can be done.

One of the important thing that which we need to consider in weld decay is carbon absorption. So, I have taken, let say a type 304 L stainless steel. Suppose I have taken this, and guy has welded is found nicely sensitized.

What he did? He did not do degreasing. The surface adds some carbonaceous matter, right? Some grease or something, when you weld it picks up carbon quite a bit. So, carbon pick up in low carbon stainless steels or quite easy it happens. So, you need to be extremely careful in welding low carbon stainless steels. This is process related ones.

Two, it also happens in the castings. Suppose, I go for type 304 L stainless steel casting. I got a casting. The very interestingly the surface sensitized. Center looks fine and as you start moving inside the extent of sensitization decreases.

Please note it is casting. How many of you are familiar with the foundry technology here? Foundry, you prepare a mold, in the mold you pour the 304 L stainless steels, the carbon content is 0.03 or lower. The surface is getting like this what do you think happens? If the mold as carbonaceous matter. If it has got carbon, in the material; it can pick up.

So, the mold it depends on the mold so, but that is why its only on the periphery not in the center. You can shave off, it can happen or better way is that go for a like a ceramic mold or something which does not give away the carbon content. So, you see sometimes it is its happening and so, you must know how do you tackle the problem.

Among all the corrosion issues, two types of problems we have developed extensive testing. One is on sensitization, weld decay, the other one is on stress corrosion cracking. Several type of test you see that. Industrially they are very important.

I will be very brief here and you can always go to the standards and you can read; you see one can take about an hour or so. Even more also, because it is a very important topic, but we do not have time.

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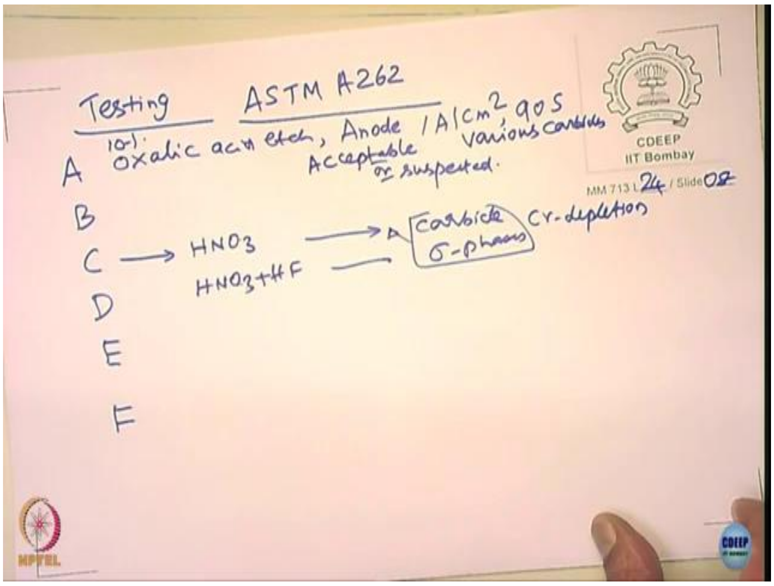

Testing ASTM A262

A 10% oxalic acid etch, Anode 1 A/cm^2, 90 s various carbides

Acceptable or suspected.

B

C → HNO_3 → A [carbide σ-phase] Cr-depletion

HNO_3+HF →

D

E

F

So, will not go into in details about this, ASTM A262 is a standard. And this standard has type A, B, C, D, E and F. So we have type A type B. ASTM A262A, ASTM A262B, they call it like that various types of tests people do that. The predominantly people use a type A, this is called as oxalic acid etch test. You might have done a test in the lab. What you have done there? You applied, you used 10% oxalic acid. You would applied, you made this sample into an anode.

And what did you do? You applied a current of 1 A cm^{-2} for about 90 seconds.

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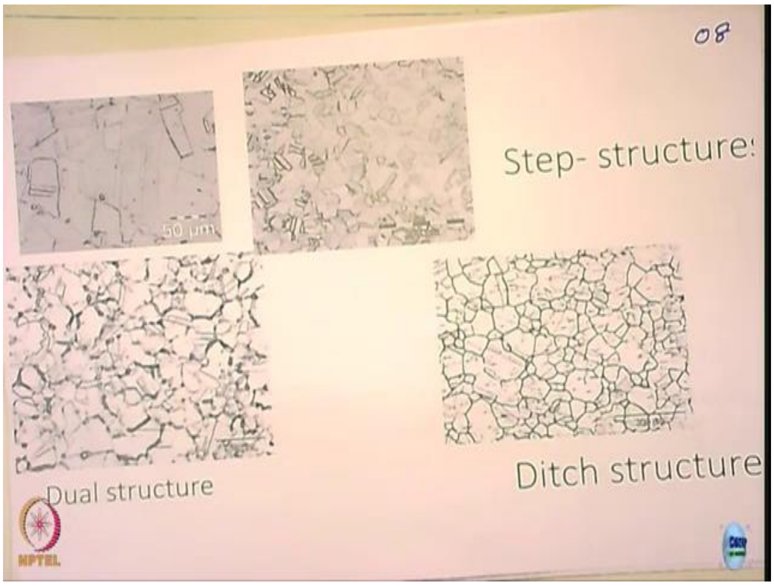

Step- structure

Dual structure

Ditch structure

And you look at the specimen in the microscope, you would have got somewhat similar to this structures. Please notice that there is a magnification. Supposed to be between 250 and 500, that is a reason behind that, very low magnification, you might not able to see grain boundaries properly. Very high magnification, you will not see many grain at all.

So, magnified actually. So, you will not see many number of grains. So, it is that range it is seen. Now you can see the step structure, we discussed already; and then this called dual structures, then you have a ditch structures.

What is the definition of a ditch structure anybody? If you observe the sample in the magnification 250 and 500, at least one grain is completely enveloped with these structures, at least one grain completely enveloped. So, not necessary that all of them are completely enveloped, only one that is one is sufficient to do that.

Please do understand, you guys have to be precise in your thing otherwise, you are going to do some advice someone I think it will be pathetic. You have to be precise in the things.

Now this is your dual structure because it is not completely enveloped. Please look at, I just want you to point out one you may able to see here. Can you see this? This grain, what do you see here, do you see here, what do you see here, what you see here?

Student: twins.

Twins right. The twins you see there is not sensitize. We talked about low angle grain boundary, high angle grain boundary; you see there the annealing twins are not at all sensitized. So, its a grain boundary. So, they are least sensitive to sensitization. So, that is another story altogether. With that you can see here also, you see because this is right. You see this, you can see that there, you see here also.

Now this test, what you need to understand primarily, I am not going to tell everything. What you need to understand is, what is the purpose of these tests A, B, C. This one is talks about only various carbides. Please notice when you apply 1 A cm^{-2}, it goes to a very high transpassive region, and so the carbides also dissolve at this particular potentials.

And this one talks about acceptable or suspected. Acceptable means there is no sensitization, if it is a dual or ditch structure; that means, you may do further test with B, C, D, E, F to confirm whether that material is good enough for application.

If the oxalic acid is test shows dual structure or ditch structures. You need to do this test actually. Now each of these tests are again, I know there is no time to see here, they are all of different kind.

For example, this one we use nitric acid, this is nitric acid plus HF. It is a modified test of this, it is slightly milder. So, I wanted to people go through this. And these guys, they talk about carbides, they also talk about sigma phases. All this and all kind of things.

So you need to be looking at it. So, this is very aggressive test; sigma phases and carbides and again chromium depletion region, that is the primary thing in all cases. So, it is even you have a sigma phase you will start attacking. So, they are modified to this test.

Say D is better than that. So, each of them have some reason why people carry out different type of tests. I think you people should, when you have time go through in details and get to know why different types of ASTM tests are carried out.

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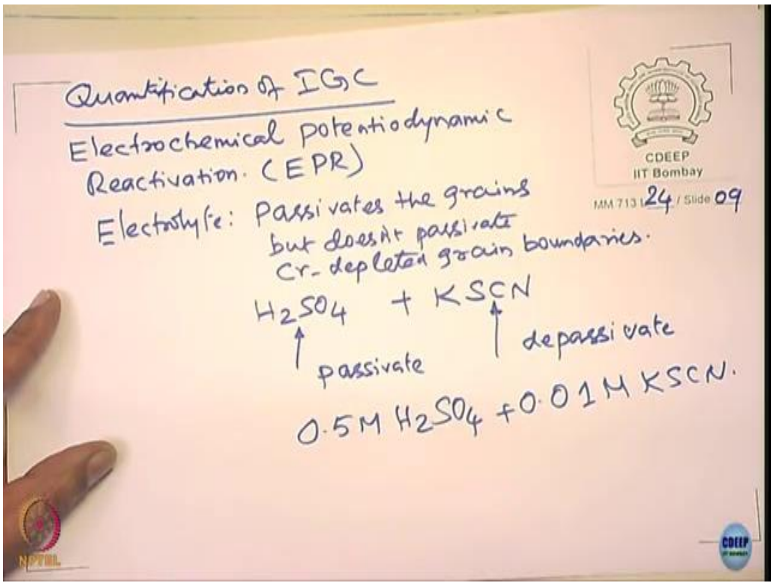

Quantification of IGC

Electrochemical potentiodynamic Reactivation. (EPR)

Electrolyte: Passivates the grains but doesn't passivate Cr-depleted grain boundaries.

$H_2SO_4 + KSCN$

H_2SO_4 ↑ passivate

KSCN ↑ depassivate

$0.5M\ H_2SO_4 + 0.01M\ KSCN$.

What I would like to focus on here is, the quantification of this test actually. Quantification of IGC. Please notice we are talking about IGC of stainless steels only. Quantification of this, and we use electrochemical potentiodynamic reactivation test. You might be also doing this, if you are not done. This is also part of your lab.

Now what is the basis of this test? What is the science behind here? The science behind here is, you choose an electrolyte that passivates the grains, but does not passivate chromium depleted grain boundaries.

Please notice this. Only chromium depleted grain boundaries, it does not passivate, but; that means, it is not sensitized, grain boundaries as well as the grains they remain passive. So, the selection of this electrolyte should be such that, this character is given to the electrolyte.

Now, the electrolyte has got two components, one is sulfuric acid, other is potassium thiocyanate; This one is to passivate, this is to depassivate. You know sulphur containing compounds are detrimental for passivation. We have seen it during our studies on pitting.

So, passivate and then de-passivate. Now this is a depassivator. If I am going to choose this concentration, very high concentration, it will depassivate everything; grains, grain boundaries and all of them. So, I need to optimize this concentration. I need sulfuric acid because the sulfuric acid is what passivates the stainless steel.

So, the concentration of sulfuric acid, this are optimally chosen and in this case of stainless steels 304, people use 0.5 M sulfuric acid plus 0.01 M potassium thiocyanate. Now, how they got this thing? By determination process, there is no real scientific extrapolation that we can do, all done shear extrapolation as shear iterations it happen. And so they arrive at this particular concentration for this stainless steel.

The same thing is not applicable for duplex stainless steel and nickel based alloys, no they are not applicable. This is applicable only for the 304 and probably 316 and so you need to change the composition in case the alloys are changed.

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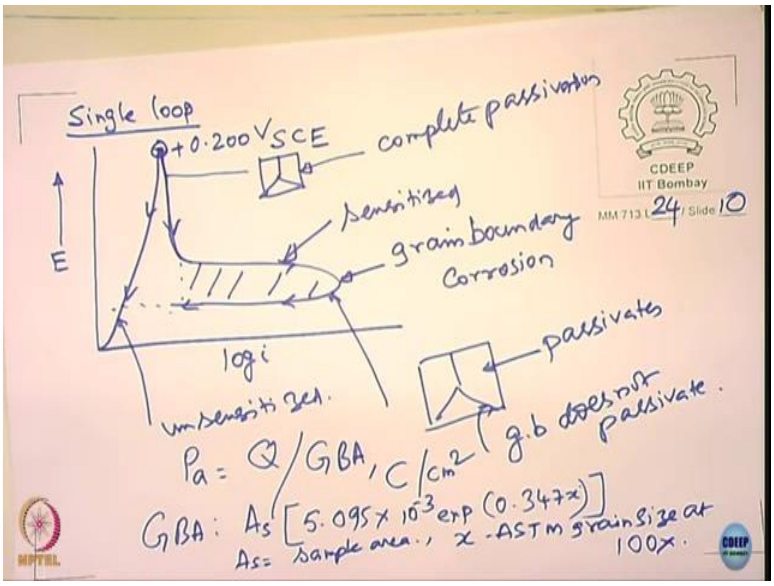

This is called as the EPR test, electrochemical potentiodynamic reactivation. There are two types of things that people do, here one is called as single loop test. What is done here is, I am not describing to you these scan rate and bubbling all kind of stuffs actually. I do not do that.

In a single loop EPR test, what you do is, you start in the beginning, you start from 200 mV with respect to saturated calomel electrode, from there you come down; so this is how it is done here. This is the sensitized case, if it is not sensitized, please correct the this.

If it is not sensitized, you get like this. When you hold it at +200 mV and completely passivating, please see that. Here in this case if you look at the alloy you may, everything passivates, complete passivation, both grain boundary and grain. But, here what happens? Here, passivates, grain boundary does not passivate. So, the current that is flowing here is essentially due to what? Due to the dissolution of the.

Grain, grain boundary. Now you can calculate the number of coulombs; what is the Coulombs? Current multiplied by the time gives you the Coulombs, the Coulombs of current by integrating this whole curve you get Coulombs.

Now the grain boundary area, then you can calculate the extent of sensitization. So, Pa = Q (Coulombs) / GBA (grain boundary area). This is nothing, but Coulombs per unit area; centimeter square; and grain boundary area, you guys who has done the metallography studies, you know how to calculate the grain boundary area, you calculate that from the ASTM grain size number.

So, GBA (grain boundary area) = A_s x [5.095 x 10^{-3} exp (0.347x)]. A_s = sample area for which you get the current, x is the ASTM grain size at 100x. This you might have studied in your metallographic courses. So, the grain boundary area and you can find out the Q value and you can find out the Pa and Pa is indication of the extent of sensitization.

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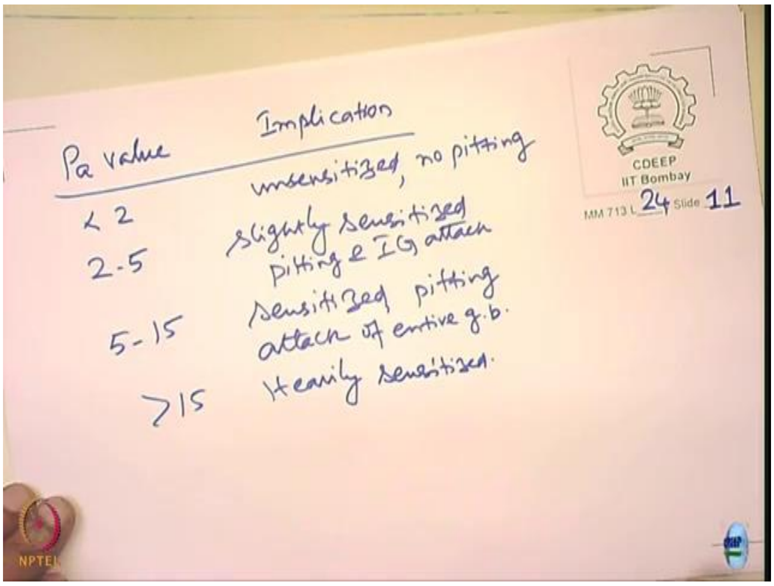

Pa value	Implication
< 2	unsensitized, no pitting
2-5	slightly sensitized pitting & IG attack
5-15	sensitized pitting attack of entire g.b.
>15	Heavily sensitized.

Now people use this technique for qualifying materials in the nuclear industries. And I give you some indication of this Pa versus Pa value; and what you call, what are the implications or interpretations that a Pa is going to be less than 2, unsensitized.

Please notice these are all empirical one; there is no fundamental principles in that no pitting. 2 to 5 slightly sensitized, pitting and IGC attack, intergranular attack takes place. 5 to 15 sensitized, pitting attack of entire grain boundaries. Greater than 15 heavily sensitized.

So, these are, in fact, routinely used in the nuclear industries to qualify the material for applications. In the boiling water reactors and all this stuff, this test is a little more complicated.

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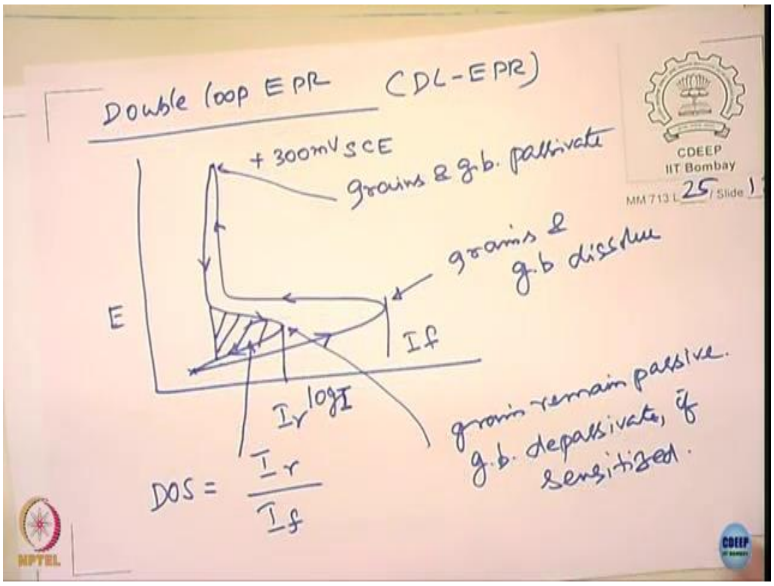

There is one more test which is more simple is, double loop EPR test. This what you might be doing in the laboratory, this also called as DLEPR. In this case, unlike single loop EPR where you rise a potential to the passive region and then you bring it to Ecorr. The double loop EPR test, what is done here is, you start from Ecorr, you go up to +300 mV with respect to saturated calomel electrode.

And what happens? You reverse this scan, when it goes like that, do like this. Only this forward reverse yes. And this is called as, I_f, forward, this is called as I_r, reverse. Actually you do not have to know the area of the sample and you can simply use any area and you can plot only current, not necessarily current density.

Now please notice, when scan from Ecorr up to this here, up to this point, grains and grain boundary they are all dissolved. Here what happens? Grains and grain boundary passivate. And what happens here? Grains remain passive, grain boundaries depassivate if sensitized.

Now; that means, this current if you can integrate, corresponds to what? Corresponds to the dissolution of the grain boundary and you integrate this one will correspond to the overall material. So, you do not have to integrate also, what you can do is you can simply take these values like the degree of sensitization (DoS) = I_r / I_f , is the fraction of this one.

This gives you the fraction of the grain boundaries that suffer intergranular corrosion. So, this also used as one of the quantitative tests to quantify to what extent the sensitization has occurred.

If there are no questions. I think with this now we come to end of intergranular corrosion and weld decay of stainless steels. I just want to move on to another type of intergranular corrosion, unless you have any questions or clarification to be sought. Let me go to the next important material, which is aluminum alloys.

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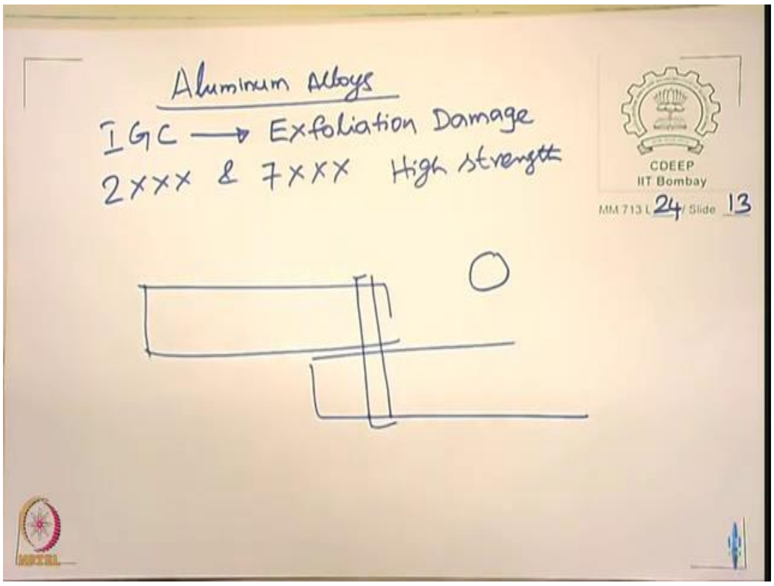

Aluminum Alloys

IGC → Exfoliation Damage

2xxx & 7xxx High strength

CDEEP
IIT Bombay
MM 713 L 24 / Slide 13

In principle I think the intergranular corrosion can occur in all materials. Aluminum is one of the material which is very susceptible to intergranular corrosion. Next is your, maybe your zinc alloys, you have zinc die castings. We will use right and magnesium alloys also can undergo intergranular corrosion, but those things I am not going to discuss now. We will end our discussions with aluminum alloys, because it has got wider implications in industries.

Now in aluminum alloys the intergranular corrosion turns with a different connotation which is called as exfoliation damage or exfoliation corrosion. What is mean by exfoliation; exfoliation what does it mean generally?

We call it layer by layer remover, it’s a kind of plane by plane removal kind of things. In aluminum alloy this intergranular corrosion takes into and especially 2000 series aluminum alloys and 7000 series aluminum alloys, these two alloys are they are all high strength alloys, right; they are high strength alloys.

They are used as a rolled sheets extruded, you know components. When you roll and then extrude what happens? You get a special kind of microstructures.

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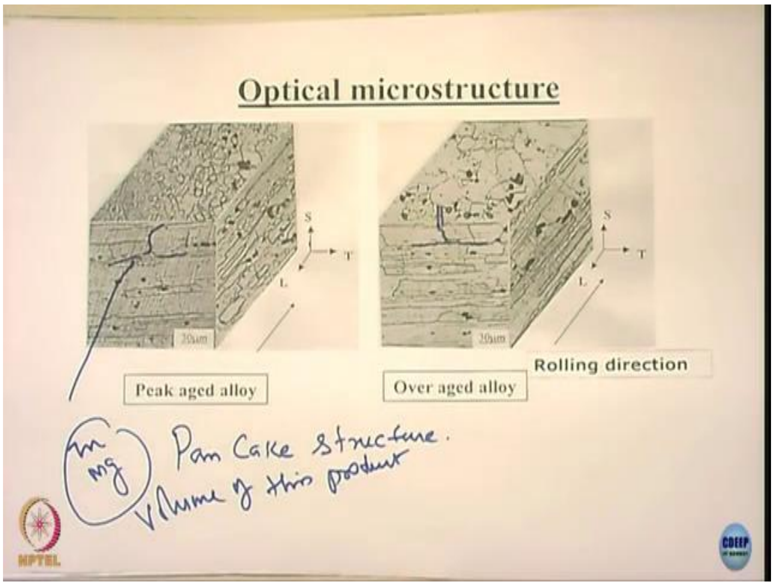

Optical microstructure

Peak aged alloy

Over aged alloy

Rolling direction

Zn Mg

Pan Cake structure.

Volume of this product

This is an optical montage of one of my students PhD students who worked on this alloy actually. And, you see how the grains look at different directions actually. This is the rolling plane, this rolling plane and this is the thickness, short transverse and this is the long transverse.

Now look at the grains now, look at these grains. They are all well elongated right I hope you are able to see this, elongated grains, can you see that, can you see this elongated grains? And these grains are called as pancake. You stack the pancake and you slice it, see at the sides you see nice, this one actually is intact the pancake only; you take a material and you roll it, you compress several layers are going to be there; they are called pancake structures.

In exfoliation what happens is that these grain just delaminate, just one after another they get removed from the surface, from subsurface. So, that is one of the specific problem that happens in the high strength aluminum alloys. Why do they really happen? How many of you studied aluminum alloys, physical metallurgy aluminum alloys? How do you get the strength of aluminum alloys?

Student: Aging.

By aging right; it is called precipitation hardening treatment. You age aluminum alloys. You age aluminum alloys what happens? The excess solutes which are super saturated, they dissolve and form precipitates and age ordering is of course, a big subject altogether.

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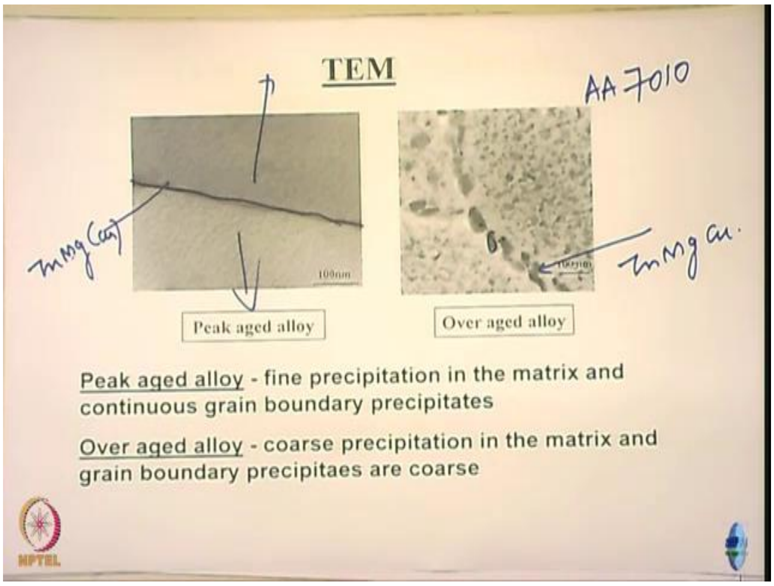

TEM

Peak aged alloy - fine precipitation in the matrix and continuous grain boundary precipitates

Over aged alloy - coarse precipitation in the matrix and grain boundary precipitaes are coarse

But to make it simple, the two types of aging are important for us. One is called as a Peak aging, other is called as an overaging treatment. What is peak aging treatment? The peak aging treatment is the treatment at which the hardness of the alloy becomes the maximum, the tensile strength becomes maximum. And you overage you continue the aging treatment or you rise the temperature you do whatever. The strength falls down, hardness falls down maybe 10 to 15% or whatever.

You normally do that in order to increase the resistance against test corrosion cracking. We are not talking about right now. I just want to give an idea why you do overaging, why you are losing your strength?

You are losing your strength because at Peak aging alloy are prone to stress corrosion cracking and so they do overaging. In overaging look at this the precipitates become coarse you see this it is a very coarse precipitates and the grain boundary precipitates also become coarse. These are the grain boundary precipitates you see here is very fine and these are grain interior precipitates are very fine, and so it has high strength.

In this case because of coarsening effect, strength becomes low. Not only that, the composition of these precipitates also change in this case this alloys is actually is a 7010 aluminum alloys is called AA 7010 alloy and this is essentially, what are this precipitate?

They are all zinc and magnesium precipitates and certain amount of copper is present here. And they are all almost equilibrium precipitates are there. Over here, it is it has again zinc, magnesium and have quite large amount of copper. So, the precipitates become relatively noble here as compared to this. Why? You take aluminum and compare that to magnesium. Magnesium is active, but even zinc is also active because zinc does not form a passivation.

When you add copper to it the precipitate becomes noble. So, they become noble precipitates with respect to the matrix. In this case the precipitate become active compared to matrix; that means, they can undergo selective dissolution here, there is no selective dissolution here taking place. So, the intergranular corrosion occurs more in the case of peak aged alloys as compared to the overaged alloys. I hope you understand the point; it happens here.

Now the problem that happens here is that when they are pancake structures, when corrosion occurs on the surface; maybe do repeating whatever the corrosion proceeds inside. The proceeds inside like that it, proceeds like that along these things now.

It can proceed like this also, like this you can proceed, like this. When the corrosion proceeds here it form let us say zinc dissolves, magnesium dissolves; what happens now? Now the volume of this products higher than the volume of the metal dissolved. Is not it? Because it has got a hydroxide all this is higher when this volume is more; what will happen, now in this case what will happen?

Student: Strain.

It is going to strain, is going to lift the thing now, it is going to lift up now; that means, the grain starts opening. These is going to be now internal stresses in addition to corrosion happening because of preferential dissolution of the grain boundary precipitates it is also going to exert certain stresses. And so, there is going to be delimitation along the grain boundaries.

The grains start lifting from the material, below the subsurface. So, it is exfoliates, they delaminate actually. So, that is what really happens in the case of in the case of this materials.

If you want to see how it happens; I can show you a diagram how these guys can happen see here.

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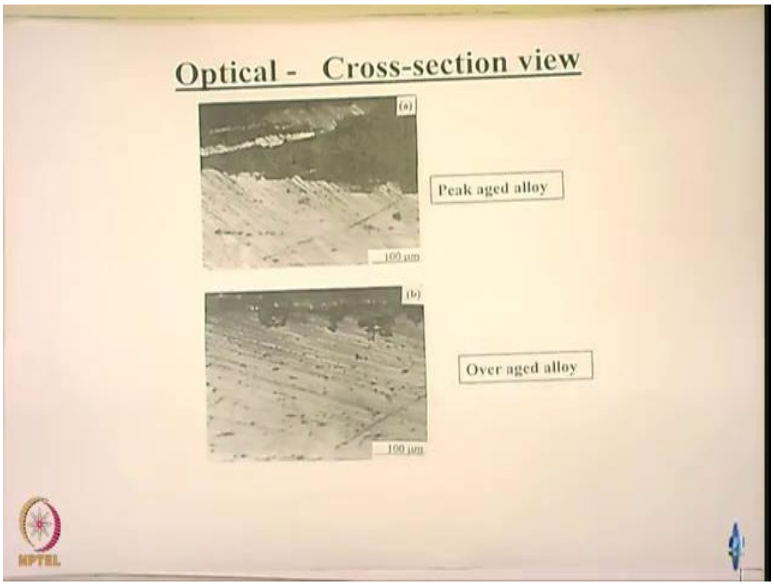

Optical - Cross-section view

Peak aged alloy

Over aged alloy

Now this is a peak aged you can see the corrosion has started from the surface it gone inside, it created so many corrosion products, it got lifted. Please see this, not corroded. It corroded, this volume of the product it got lifted actually.

In the over age condition it does not happen. Why does not happen? Because the precipitates here are noble compared to this, when they are noble the precipitates do not dissolve so much. And so, the grain boundary becomes stable. So, as compared to this; that means, exfoliation corrosion occurs only in the case of peak aged conditions.

Student: Peak aged.

They do not happen in the case of overaged conditions. Because of this particular things. Not only that, in the overaged conditions one more thing happens actually, you see in this case; if you look at closely the grain boundary precipitates. They become very coarse, they are separated. Look at this is this one precipitate separated. So that means, they are separated now.

So, there it is, even when it corrodes less, but even when it corrodes they are not good connect. So, they are not connecting, the grain boundary is not getting connected completely here. Whereas, in this case, because the precipitates are very fine get connected what happens. So, the crack or whatever corrosion products accumulates it starts lifting in this case actually; it has happened.

So, because of nobility of the precipitates, because these precipitates are well isolated, the grain boundaries do not continuously corrode and lift actually. So, the overaged alloys are more stable as compared to the peak aged alloys.

So, that is a reason why the overage alloys are better off compared to the peak aged alloys. So, in any case we do not use peak aged alloys for actual application, because peak aged alloys are more prone to stress corrosion cracking. Those days, you were using at all.

So, it is very essential for us to understand the chemistry of the precipitates and how do they dissolve. So, people have done extensive studies on that and those you people want to do a M. Tech. project or maybe a PhD work you can read more and understand them.

For the time being it is enough for us to understand that the grain boundary precipitates are very important, is chemistry is very important and even more important is the alignment of the grains they are pancake structures,. And so, they lift it and leading to exfoliation corrosion. Now there are different types of tests that people do and one test is called as EXCO test.

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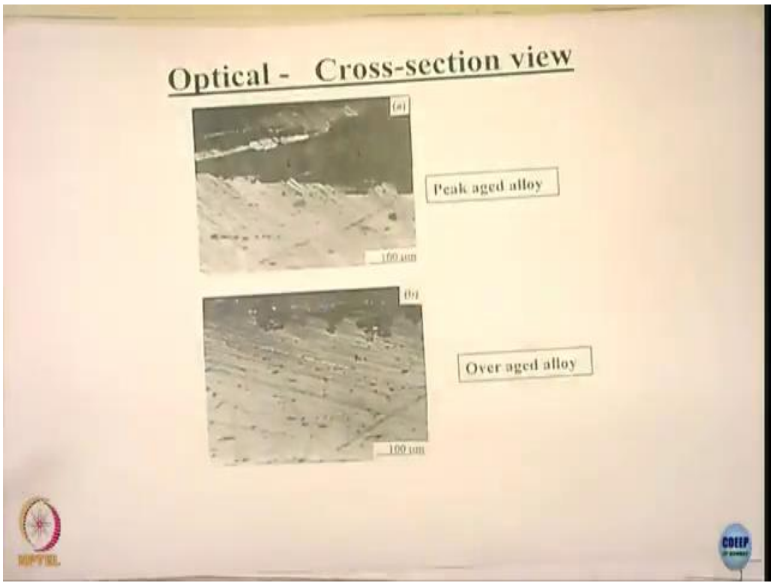
Optical - Cross-section view

And there is also ASTM standard, there is also ASTM standard which is used as EXCO test.

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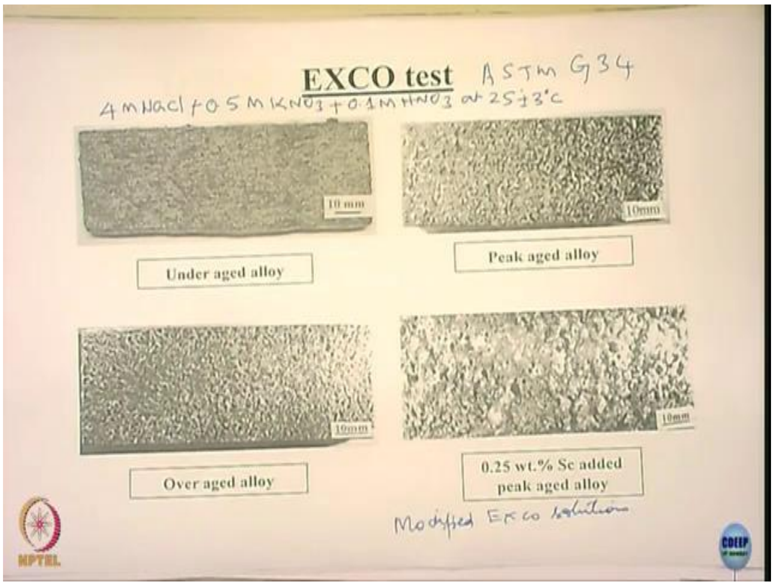

EXCO test ASTM G34

4 M NaCl + 0.5 M KNO_3 + 0.1 M HNO_3 at 25 ± 3°C

Under aged alloy

Peak aged alloy

Over aged alloy

0.25 wt.% Sc added peak aged alloy

Modified Exco solution

Where use highly concentrated sodium chloride + potassium nitrate + nitric acid and you see if it is peak aged thing and you see the surface is quite rough form and over aged less and this is a different kind of alloy system that you have.

So, when you do the EXCO tests and you can take a cross section and you can see them in the in the microscope, you see lifting of the grains as I shown in the previous slide actually. And this test is considered to be very aggressive, there is also modified EXCO test. ASTM things are available for you can use modify EXCO test to do that.

So, that is about the exfoliation and intergranular corrosion of aluminum alloys, there are there are several factors the way you temper, surface hardness, rolling conditions there also affect the exfoliation corrosion there are certain good research papers some of you are interested you can read them and my advise for this course I think it is sufficient for you to know that this is one of the serious problems. See what happens in aluminum alloys, in aircraft industries. How do they join?

Aluminum alloys are joined by riveting process. So, they drill a hole and then they riveted using other aluminum, metal; and this hole, look at this is a hole here; the hole is exposed, now the grains are all now exposed.

You see is a like pancake structure I hope you will able to understand it; you take a sheet and drill a hole and all this surfaces are now exposed to getting attacked in the horizontally. So, they get lifted. And there are very beautiful pictures available I cannot show you here because of copyright problems, but you guys can read and see its a very nice illustration of how a grain boundary attack can lift the grains up and causing the weakness, it weakens the structures actually. Well with this any questions anybody?

Student: How IGC of stainless steel is different from that of aluminum alloys.

So, very good question actually right, the intergranular corrosion in stainless steel the mechanism is different from the intergranular corrosion in aluminum alloys. I did not in fact dwell on it. In the aluminum alloy what is the element that passivates, the matrix itself the major element aluminum itself is passivating. So, when there is a precipitation taking place what is the precipitation taking place, what is the precipitation here, the precipitation in this one is what is zinc and magnesium.

So, the passivating element remains in the grain boundary area there, I mean basically the matrix passivation does not get affected for what is happening instead. The precipitates which form on the grain boundary are selectively attacked here because they are relatively active compared to the aluminum here. So, the mechanism in stainless steel is the chromium which is passivating is getting depleted and so, grain boundaries are getting attacked, here the passivating element is aluminum that is not getting affected. Rather what is happening?

The active elements is segregate and form precipitates in the grain boundary and so, they get corroded at all. So, it is not the depletion of passivating element causes problem here it is the formation of the active phases and the grain boundaries causing the problem. So the mechanism in both the cases are different actually. Any questions? If there are no questions further on this?

And I still given you one problem please think over it and come out with the answer when you meet next time.

So thank you very much.