Corrosion Failures and Analysis

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Lecture - 22
Intergranular Corrosion: Control of Sensitization-weld decay

Let us start lecture 22 for the course Corrosion Failures and Analysis. We have been talking about intergranular corrosion and we talked about weld decay ok, which is the problem that is experienced in case of 304 stainless steel welding. And that time we saw that weld decay or the sensitized zone forms little away from the weld zone in the base metal.

Where the temperature profile keeps the metal during cooling stage within that temperature within that magic temperature zone which is 500 to 5850 degree Celsius where precipitation of carbide can take place along the grain boundary leading to chromium depleted zone and subsequent sensitization.

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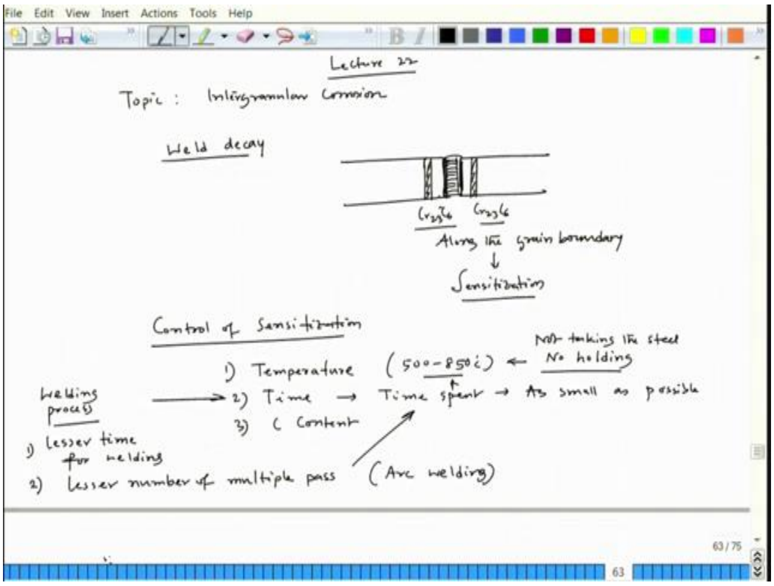

Now, so, this is course is corrosion failures analysis, lecture 22 and topic intergranular corrosion, fine. So, we talked about weld decay weld decay which happens if we see this part and this part ok. Now, you have this is the weld part which is going little inside the base metal and then little away from the weld part we have a zone narrow zone which has chromium carbide precipitation, fine. So, this kind of precipitation happens ok.

So, that is what it becomes and this precipitation happens along the grain boundary along the grain boundary and leading to sensitization. And in fact, if you have this kind of situation and if you dip it in fuming nitric acid or boiling nitric acid, so, you will see that zone will get corroded and heavily. And there could be a possibility that if it is a thin sheet there could be possibility that it can leak through that.

Now, question is we know that why it happens because its a chromium carbide precipitation. So, now, we have to see that how we can stop it. So, that brings into the part which is control of sensitization ok. Now, as we have explained in the last lecture that 3 factors are important. One is temperature, second is time, third is carbon content ok.

Now that means, this is 500 to 850 degree Celsius. By any means if you do not take the metal to this temperature range and hold it, so, no holding this is one part not taking the steel to this temperature and no holding. So, no problem. When that no problem starts?.

Because if you make the alloy take it to high temperature, let us say around 1200 and 1300 degree Celsius where chromium carbide dissolve because we know that around 1050 degree Celsius chromium carbide dissolves. So, once it dissolves and homogenized then you quench it to the room temperature.

It will not have any time for the precipitation to happen because the time of retention during cooling in this temperature range will be very very small which will be less than the time required for precipitation no problem, fine. But, interestingly sometimes you have that particular steel which is stainless sometimes you have to take it to high temperature.

Now, one possibility is welding ok. So, welding you have to do welding because when you have make a component you have to sometimes instead of using fastener you have to weld it. So, that time you have to take it there. So, when you take it there within that temperature zone you have to make sure the time of retention should be less.

Time spent there in this temperature range should be as small as possible as small as possible, fine. So, then of course, you are not having any problem ok even if you do welding. So, how you can do that? For example, you have to use some welding process.

So, it leads to the welding process which allows lesser time for welding one is lesser time. Second is for example, if you somehow do a multiple welding, for example, one layer of welding then second layer of welding. So, that multiple welding pass if you do, so, then of course, it will spend more time. So, then also there is a possibility. So, lesser time less lesser number of multiple passing pass.

So, then of course, there is a possibility that the time spent in that temperature zone will be less. So, you can avoid that. So, which are the welding processes? If you do gas welding it is a problem because the gas welding takes long time for heating and their heat intensity of the gas welding process is less compared to the arc welding.

Arc welding heat tension intensity is very high. So, that it melts quickly and quickly it joins. So, that you do not have to hold that weld that particular torch longer in that weld pull gene region. So, you can take it out quickly. So, that heat dissipates quickly and does not have time for retention within that temperature zone even if there is a heating and then cooling process. The cooling would be faster if the heat intensity is very high less time spent for the welding cooling would be faster ok.

So, that time you do not have that problem. So, that is what we always use arc welding arc welding fine. But, now this arc welding could be quick and less number of pass if it is a thin section to be welded, but if it is a thicker section then you cannot avoid doing multiple passes ok. So, that time you have experience you would experience this precipitation of carbide again. So, thinner section this is fine.

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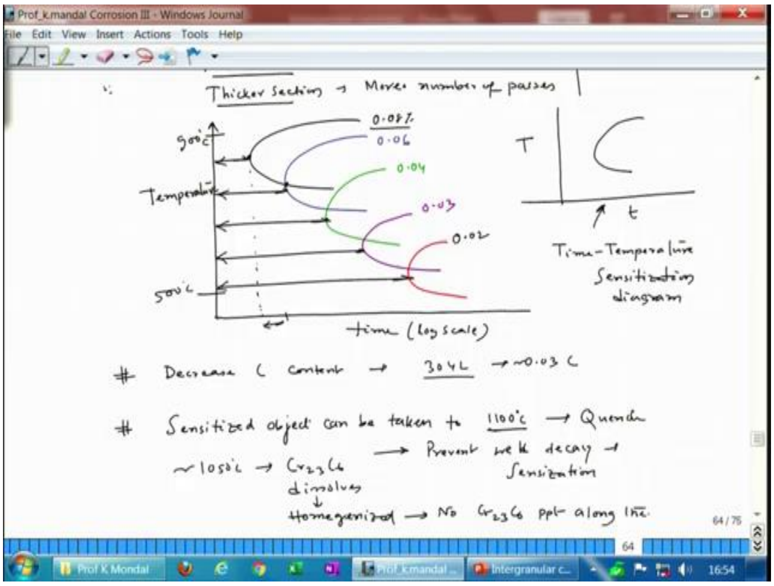

So, thinner section less number of passes, but thicker section, you have to use more number of passes that time the steel can be subjected to weld decay or sensitization around that zone of zone away from that weld pool. So, when we have such situation how to prevent that? So, now, we have to get to the third factor which is carbon content fine. Now, the carbon content.

If we see the diagram related to time temperature sensitization diagram schematically we can have a diagram like this. This is you can also people have actually studied it quite substantially and then they have seen that this is temperature and this is time fine and now just like a TTT diagram you know time temperature transformation diagram. So, that diagram looks like a C curve ok.

So, similarly you can also have time temperature sensitization diagram which actually has a direct relation to that temperature zone and chromium carbide precipitation. As we have said in the previous lecture the carbon is a factor chromium we have to keep fixed 18 to 20 percent. So, carbon if you increase or if you decrease there would be change in this kind of time temperature sensitization diagram which is similar to TTT diagram.

So, now, if the carbon content is high, so, the graph shifts upward and moves to the left. Let us say this is 0.08 percent carbon. If it is 0.06 it goes to the right and drops down ok. If you go to this is 0.06. If you go to 0.04 then it again shifts to the right and then moves down ok.

So, then again you can go to 0.03. It drops down and go to the right. So, like that way the diagram shifts to the this is 0.03. If you further down then it will also go to the left. So, the right and this peak point or the nose point we call it nose point of a TTT diagram that also that is the minimum time for the transformation into a sensitization mode.

So, this particular temperature range also let us say this is around 900 degree Celsius nine 900 degree Celsius and let us say here it ends around close to 500 degree Celsius, fine. So, in that particular temperature range we have to see that when cooling ok, its not a problem during heating unless until you see the point C in the.

If you go to the previous lecture you will find that the point C where we put thermocouple that one during heating as well as during cooling. During heating it does not reach beyond 600 degree Celsius and during cooling it also comes back and that means, the time of retention within that 550 500 to 850 degree Celsius is quite lengthy ok.

So, in that case of C is the is that problem, but during heating if the temperature goes beyond 850 degree Celsius rather beyond 1050 degree Celsius chromium carbide even if it precipitates it will dissolve ok. So, the during heating is not an issue ok, but during cooling it is an issue because during cooling depend on the cooling rate. If the cooling rate is slow then of course, the time of retention would increase during in that particular temperature round.

Now, question is if you see 0.08 percent carbon the time where the nose point is actually very close to the has having a very less time. So, this is in log scale log scale. So, this could be a very small time maybe couple of seconds. Now, as we go right time towards right since its in log scale even if there is a small change in the small change in that particular length in the log scale there will be huge change in the time.

Because the time would increase that nose temperature that is the minimum time required for that sensitization. Now, here as you see 0.06 still it has a chance of getting sensitized because the time minimum time is sufficiently small. Now, here as we go to 0.04 the time is actually going further towards the right side. So that means, the time required you have to spend this much time this much time for the precipitation to happen.

In case of 0.06 this much time you have to spend considering the minimum point zone and here also this much time, but here if you see this is the time and this is the time ok. So, that much as you decrease the carbon let us say this is 0.02. As you decrease the carbon content the entire sensitization TTT curve is actually shifting towards right though it is also going down.

If it goes down that means the diffusivity as we decrease the temperature diffusivity also decreases or the diffusion coefficient is also actually increases in diffusion coefficient actually also decreases ok. So, that decrease does not allow that chromium carbide to precipitate out ok.

As you increase the temperature diffusivity increases as well as diffusion coefficient also would increase. So, that allow easy diffusion and easy formation of chromium carbide that is what this nose point is shifting towards left, ok. But at the same time if you increase carbon; that means carbon activity you are increasing and that carbon activity increase in carbon activity allows chromium carbide to precipitate out, fine.

So, that is what it is also as the carbon content is increasing it is going up because the diffusivity increases and it also goes down goes to the left; that means, the time required for chromium carbide precipitation is less. So, that allows easy precipitation.

But as you decrease them decrease carbon content precipitation of chromium carbide becomes difficult because diffusivity is less because it has dropped down in the temperature axis at the same time it has go to the right side in the time axis the time required for the chromium carbide precipitation would be very very large. So that means, if it is very large and during cooling if that time you are not permitting then it will never have any precipitation to take place.

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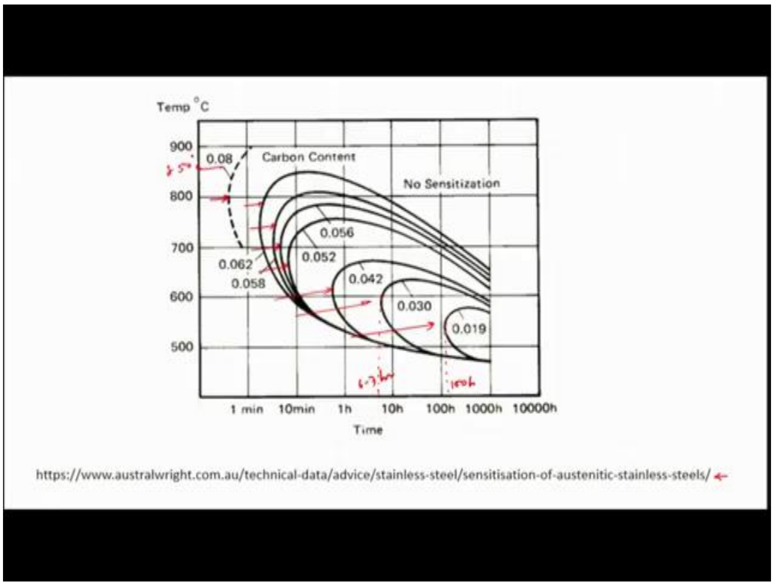

Now, in that regard I have taken something from the literature. So, if you see this PPT, so, the way I told you that as the temperature as the carbon content increases in the steel the sensitization TTT diagram shifts to the left and moves up and as the carbon content decreases it goes to the right and moves down the similarities.

So, that time I showed it by schematically, but here it is some data set and it is taking from this ok and remember, this particular link is used just for teaching purpose. It is not for any publication or anything. So, this is for teaching just to let people know that what happens.

Now, if you see that this point this nose point is actually shifting towards right shifting towards right and for example, when you go to 0.03 if you see the minimum time minimum time you will be of the order of let us say 6 to 7 hours ok. Now, if you go down to 0.019 almost about 0.02 the time minimum time will be around 900 hours 900 hours.

So, this is in the 500 range and this is around 850 range 850 degree Celsius. Now, point is in that when the carbon content is so, low and if you cool it you even if you cool it very very slow you cannot wait for the 100 hours to have take place or the spend in that temperature zone. Because when you weld you maximum time you can take maybe 10 minutes or 20 minutes my maximum because let it cool down cool. So, completely maximum 10 minutes.

So; that means, within that 10 minutes time it will never reach that particular point. So, it will not have any sort of precipitation of carbides. So, that makes that particular steel resistant to sensitization. So, that is what even if you consider 0.03 the time required would be around 6 to 7 hours. So, still it is very long time for precipitation.

So, no problem of sensitization, so that means, coming back to what we are talking. So, this is the schematic what I have drawn. Now, that senses that that gives a sense that if you can reduce carbon content sensitization can be controlled. So, that is what the one possibility is decrease carbon content ok. So, that is what some of the grades like 304L comes up. So, there the carbon content is 0.03 around that level.

So, the time for precipitation to happen would be so long and the time during cooling would be so slow so low within that temperature range 500 to 585 degree Celsius there will be no problem of sensitization ok. So, that is what the low carbon is one possibility.

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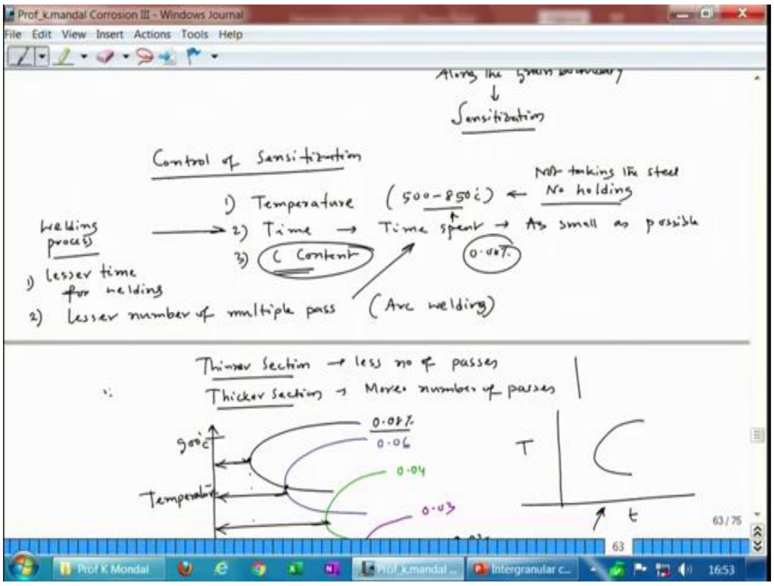

Now, coming back to this let us say you have carbon content 0.08 percent, ok so that means, there is a possibility of sensitization because the nose is coming very close few couple of seconds. So, you cannot prevent sensitization during cooling if it is sufficiently slow cooling ok.

So, now, let us say its sensitized then how would you prevent it? Let us say well decay has happened how do you prevent it? So, the one possibility is the entire world portion or the entire object can be taken to or we can say sensitized object can be taken to around 1100 or 1100 degree Celsius temperature and then quench. It will prevent it will prevent weld decay or sensitization. Why?

Because beyond 1050 degree Celsius around chromium C 6 dissolves and if you spend some time over there it homogenized and then no precipitate along the grain boundary. So, sensitization is avoided. So, now, whatever control I have with reference to carbon content temperature time.

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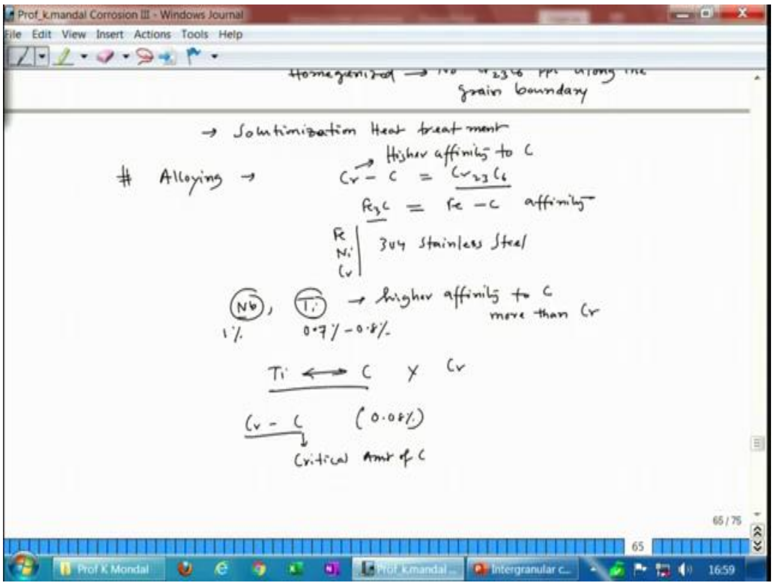

Now, there is one more way ok and of course, there is one. See this is temperature time temperature control is you do not take it to that temperature and even if you take it to the temperature you do not allow sufficient time to hold. These are the two conditions time you do not spend time.

So, you use some welding mechanisms welding methods which will have which will be very quick to weld and the heat spend that the heat dissipation would be very fast. So, no problem in that because the time retention in the temperature change which is sensitization temperature zone would be very small to have any precipitation of carbides.

And then another process which is carbon content and the process what we have said that this process what we have said that taking to higher temperature and then homogenized and bringing back. So, this is called solutionization heat treatment. So, solutionization heat treatment is similar like in case of age hardening alloy. What you do?.

We take it to a single phase zone which is alpha zone in case of aluminium copper system. Take it to alpha, solutionize it; that means, homogenize and take all the precipitates into the melt. So, it becomes single phase and then quench it. When you quench no precipitate forms in the edge hardening alloy and after that if you hold it at a little higher temperature then precipitate comes back again ok because that time it becomes super saturated.

But here its not about super saturation, here it is about allowing those chromium carbides to get homogenized. So, that entire steel becomes free of sensitization, fine. So, this particular process is that. So, there is one more process to control sensitization is basically called alloying fine.

So, this alloying let us say we have chromium carbide precipitation reacts and then form C 6. Why chromium carbide forms? There are iron also. The iron carbide can also form because iron carbide we know that Fe_3C forms which is a cementite. So that means, it forms why because iron and carbon they have affinity which allows iron Fe_3C to form.

Now, we have iron, we have nickel, we have chromium all those elements are present in the 304 stainless steel stainless steel. So, there could be possibility of chromium as well as iron carbide, but question is who has the higher affinity to carbon. The chromium has got higher affinity to carbon. So, that is what chromium carbide comes out.

Now, let us say I have another element which is either niobium or titanium if we add them in a small amount. So, this is maximum 1 percent and all this is also around 0.7 percent 7 to 0.8 percent if we add then these two elements have got a huge affinity to carbon and if we compare affinity to carbon between niobium and chromium or titanium and chromium, titanium has higher affinity to carbon more than chromium.

So, now if we have carbon and if we have titanium if we have chromium this will try to join together this will not because this has higher affinity. So, the titanium carbide would come out. Now, question is for the chromium carbide to form you need a critical amount of critical amount of carbon.

As we have seen that the as the carbon content decreases chromium carbide formation becomes more and more difficult because the time knows time in that time temperature sensitization diagram goes to the extreme right. So, the time taken would be very very large.

So, now it is not the problem in case of low carbon steel. Its about the problem in the high carbon steel where the carbon content is 0.08 percent. Let us say around 0.08 to 0.07 percent. So, that time it crosses that critical carbon content. So, that is what chromium carbide forms.

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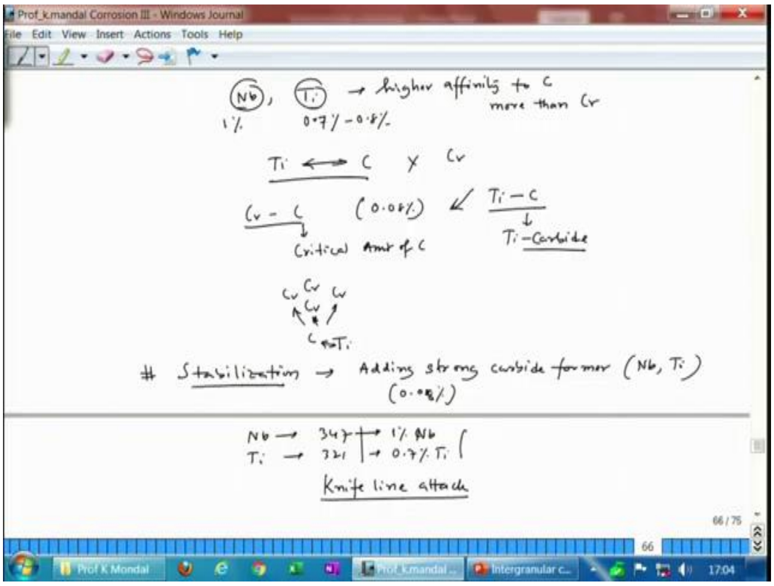

Now, if we add titanium ok, if you add titanium into it, so, it will curve collect carbon and it will precipitate out as a titanium carbide titanium carbide in this form it will precipitate out. So, what would it what it would do? So, chromium atom let us say you have a collection of chromium atom, fine. So, you need carbon to react with the chromium. Now, by the time you have taken titanium around that carbon. So, it reacts and joins that carbon.

So, it does not allow that carbon to go to chromium ok. And by the way the chromium by that way the chromium the carbon critical carbon content around chromium atom will reduce drastically and that reduction would allow that particular carbon requirement very low and that will also allow the TTT diagram or basically the time temperature sensitization diagram to shift to the right ok.

So; that means, what it happens? It actually makes the steel so resistant to sensitization because of the addition of titanium or niobium. So, the effect of niobium would be same as titanium what I have explained ok in the steel where carbon content is very high ok in that standard steel. So that means, this particular process of making the steel resistance to sensitization we call it stabilization ok.

So, the stabilization is basically adding strong carbide former like niobium or titanium which will take care of the carbon and does not allow any carbon availability for the formation of chromium carbide. Now, question is the chromium gives you the stainless property.

So, if you do not allow chromium carbide to precipitate out there will be no question of chromium chromium depletion zone. And so, the entire matrix we have homogenized chromium contain more than 12 percent and rather it will be homogenized like 18 percent in the base metal.

So, it will passivate uniformly all over and then it will give you the stainless property all over the surface ok. So, this process is called stabilization and this process is applied even in case of high carbon steel ok 0.08 or 0.07 percent. So, this is another route by which we can control sensitization in case of stainless steel.

And that is what whenever we add those elements, so, we have some grades. So, those grades are actually like niobium containing grades are 347 stainless steel, titanium containing grades are 321 ok. So, these this one contain around maximum 1 percent niobium and this one contains around 0.07 percent titanium ok. So, that makes the steel devoid of any sensitization, fine.

So, let me stop here. In the next class we will end our discussion on intergranular corrosion by taking one example which is called knife line attack which happens in case of stabilized steel ok. So that means, the steel which has been stabilized by adding that costly niobium and titanium which will tackle carbon which will take care of carbon and does not allow that chromium carbide to form, it happens in that particular steel during welding itself ok.

And the crack happens a very sharp crack happens and that sharp nature of the crack that because of the appearance it is called knife line attack. So, we will analyze that particular problem and then we will stop our discussion on intergranular corrosion and then take two will start discussing gravies as well as beating corrosion. So, till then let us stop here. We will take it up in our next lecture.

Thank you.