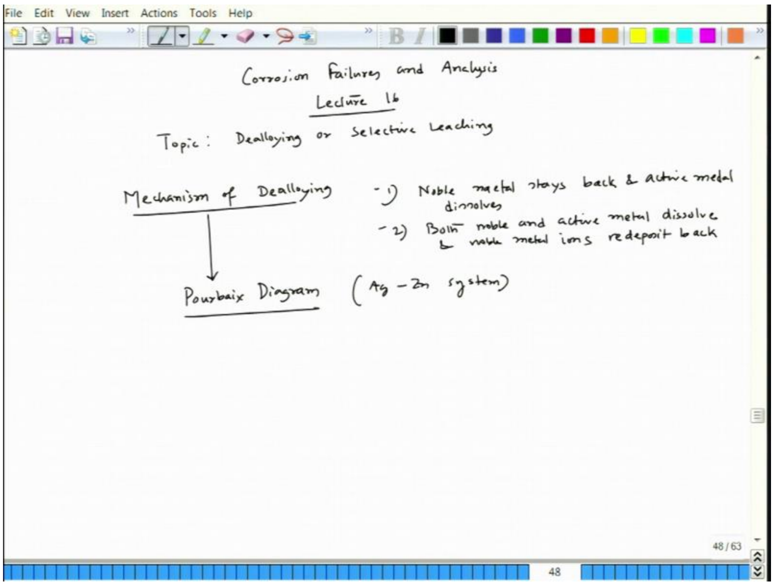
Corrosion Failures and Analysis
Prof. Kallol Mondal
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur

Lecture - 16
Dealloying or selective leaching: Mechanism

(Refer Slide Time: 00:24)



Corrosion Failures and Analysis

Lecture 16

Topic : Dealloying or Selective Leaching

Mechanism of Dealloying

- 1) Noble metal stays back & active metal dissolves
- 2) Both noble and active metal dissolve & noble metal ions redeposit back

Pourbaix Diagram (Ag – Zn system)

Welcome, we will have lecture 16 for the course Corrosion Failures and Analysis and topic what we discuss we continue our discussion on Dealloying and or selective leaching. Now in the last lecture at the end of last lecture we have shown some examples of dealloying and while analysing the mechanism, we said that there could be possibility of both mechanisms are working.

So, in one case first few layers zinc dissolves in case of dezincification, leaving copper and then finally, its basically the second mechanism which becomes predominating mechanism or dominating mechanism where both dissolves either in case of copper zinc, copper and zinc both dissolve in case of silver zinc silver and zinc both dissolve and later on zinc stays back, silver deposits back in case of silver zinc alloy or copper deposits back in case of copper zinc alloy.

So, that way we develop that nice porous structure on the surface and where ligaments are either copper in case of copper zinc and in case of silver zinc its a silver, but remember that it may not be possible to get to 100 percent copper or 100 percent zinc for that reason we have to also have some special requirements to be met in the solution, but definitely we would get close to around 90 to 95, 97 percent purity of the noble element in that particular couple.

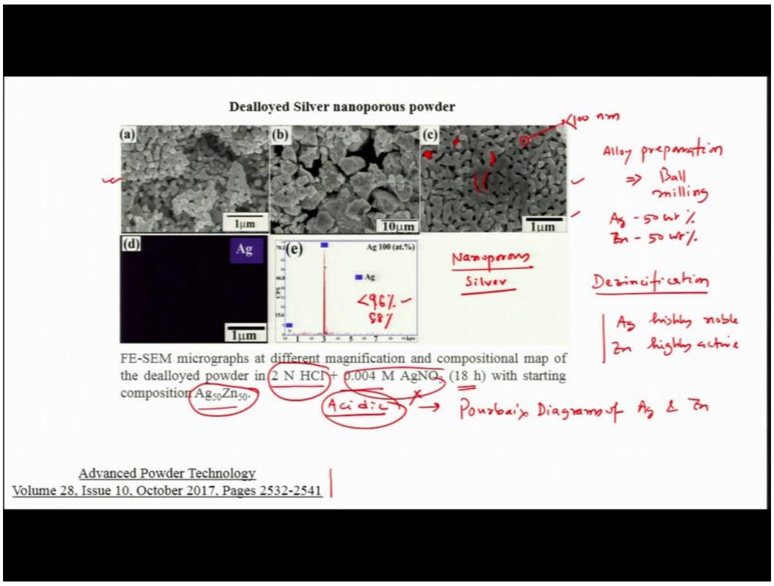
So, it might also happen in case of; in case of multi component systems. Remember in case of multi component system this is also possible ok for example, we have seen in our work that multi component zirconium based alloys we got to see that when there was palladium or platinum we did see that platinum and palladium are actually enriching on the surface leaving copper zinc behind ok.

In case of zirconium copper system copper enrichment might be possible leaving the zirconium behind ok. So, I will show you so, those data in a little while. But coming back to the mechanism part, mechanism of dealloying, it has a strong and there are two processes one is noble metal stays back and active metal dissolves and second part is both noble and active elements or metal dissolve and noble metal ion redeposits back redeposit back.

So, these are the two processes and those two process can processes can go on parallelly, now coming to a mechanism. So, it has a strong correlation that even if we try to see that noble metal stays back or noble metal dissolves it has a strong correlation with pourbaix diagram fine. Now if we try to look at the pourbaix diagram in case of silver copper system because we have test we have done that study in our lab.

So, we will talk about silver sorry silver zinc system and let us see whether we can have this situation that silver indeed would stay back or would deposits back, silver ion if it is forming on the surface and zinc would dissolves ok. So, in order to do that so let us go to the PPT again.

(Refer Slide Time: 05:31)



Dealloyed Silver nanoporous powder

FE-SEM micrographs at different magnification and compositional map of the dealloyed powder in 2 N HCl + 0.004 M $AgNO_3$ (18 h) with starting composition $Ag_{50}Zn_{50}$.

Acidic → Pourbaix Diagram of Ag & Zn

Alloy preparation
⇒ Ball milling
Ag - 50 wt %
Zn - 50 wt%

Dezincification

Ag highly noble
Zn highly active

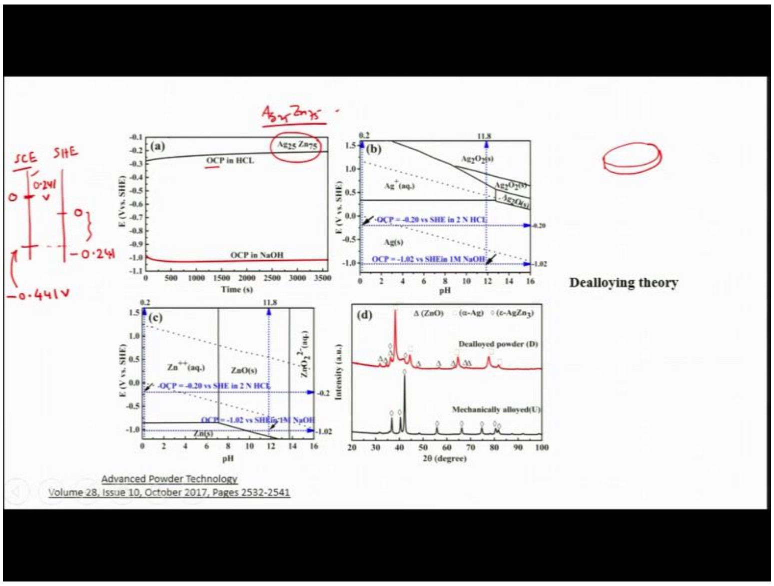
Advanced Powder Technology
Volume 28, Issue 10, October 2017, Pages 2532-2541

If I see this PPT. So, this particular PPT we have seen in the last lecture if we see that we could see that we started with silver 50, zinc 50 that was the alloy powder we took and then finally, we got 100 percent silver over the entire powder the entire zinc 50 percent zinc content has dissolved ok in the form of ions in the solution and that solution was two normal HCL and 0.05 molar $AgNO_3$.

So, its $AgNO_3$ was added you know in the beginning when we are we were doing this particular operation at two in two normal HCl, 100 percent silver was not obtained there still there were little bit of zinc left out. Some places we could see around 2 percent zinc, some cases we could see 1 percent, some cases we could see 3 percent zinc were left out even after we went up to 48 hours of dealloying in that same solution fine.

So, then we thought that we should add silver nitrate solution which will increase the silver activity silver ion activity in the solution which will allow zinc to further come out and everything would become pure silver ok, but still it is acidic. This is important information remember this is very very important information still it is acidic. And that is what would see that its correlation with pourbaix diagram of silver and zinc fine.

(Refer Slide Time: 07:19)



Dealloying theory

Advanced Powder Technology
Volume 28, Issue 10, October 2017, Pages 2532-2541

So, let us see the next page ok. So, now, this page let us look at ok. So, now, before doing dealloying actually we did a free corrosion dealloying. Free corrosion dealloying is basically we have made that solution and in that solution we dip the powder ok.

And we have churned it little bit because if the powder is if powder accumulate accumulates at the bottom of the bottom of the beaker, there could be possible that the outer layer of that powder accumulated powder or the heap of powder would get dealloyed, but the centre part of the powder heap may not get dealloyed that is what we did we actually churned it how did we churn? We put it on a magnetic platform magnetic stirrer ok.

So, that magnetic stirrer would give us a kind of churning effect ok and we had put a small iron that I think just a minute let me just recall no it was basically fish bubble we had used. You know if you see aquarium we have a bubbler used there is a small pump which is used which actually gives bubble formation which allows bubble formation in the water and that is what it looks beautiful in the aquarium ok.

Fish aquarium small household fish aquarium there we have a bubbler we call it bubbler fish bubbler bubble where bubble forms by sending air into the solution. So, that leaves the bubble and that bubble formation will have a little bit of churning in the in the solution ok.

So, that is what we did and in the that is what we did and we saw result and in the beginning we saw that; in the beginning we saw that silver enrichment is taking place. In order to understand that we what we did? We measured the OCP open circuit potential if we go back to our earlier lectures ok.

So, where electrochemistry has been talked about the electrochemistry related to corrosion has been talked about you would see that OCP is open circuit potential when you take a metal you dip in a dip in an electrolyte, you measure the potential of that electrolyte with time at some point of time it will stabilize and that time you are actually not sending any current from outside ok. So, this is open circuit condition circuit is not closed in that particular potentiostat.

So, that potential we call it open circuit potential. So, that is what it is opc OCP ok. Now in HCL two normal HCL we took another composition this is the composition we took silver 25, zinc 75 still we got 100 percent silver. So, this is a silver by a zinc enriched alloy, but still we got 100 percent silver nano porous particles those each particle became nano porous. So, their entire zinc actually go out it goes out into the solution in the form of ions.

So, we measure the OCP of those powders how did we do it? We to we what we did we made? A pallet out of it that powder we pressed it mechanically pressed it and we made a pallet. So, that pallet look like this. So, this is this alloy powder pallet and then this disk was placed in potentiostat to measure the OCP ok.

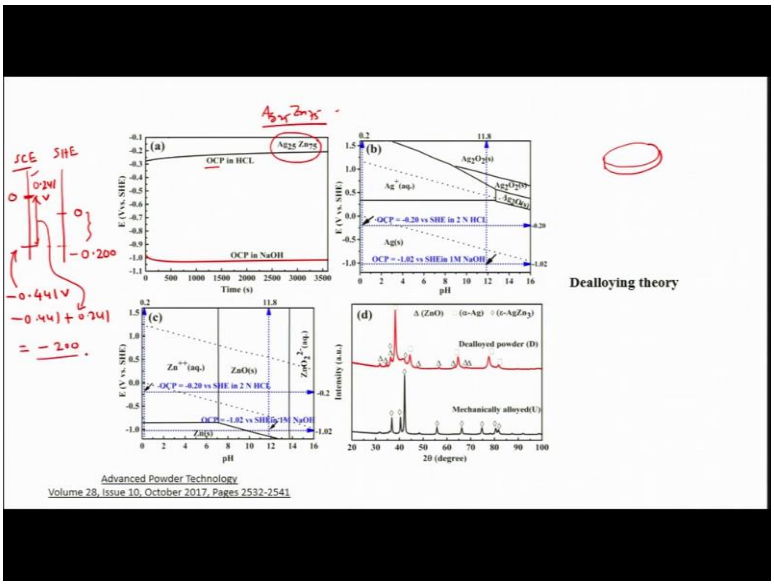
Even though there are porosity, but still we could have that OCP measurement and even after 35, 100 seconds ok more than close to around one hour ok. So, that even after that we could see its a very stable OCP ok so; that means, OCP is with respect to standard hydrogen electrode we initially measured in terms of with reference to standard calomel electrode and then converted that potential into standard hydrogen electrode ok I hope you will be able to know what is the conversion.

Let us say if it is a standard calomel electrode and if it is a standard hydrogen electrode, this is standard calomel electrode ok standard hydrogen electrode and standard hydrogen electrode 0 point is here and with reference to standard hydrogen electrode the standard calomel electrode that potential it is basically around 0.241 volt ok.

So, this voltage in standard calomel electrode is measured with reference to standard hydrogen electrode. So, when we measure some voltage with respect to standard calomel electrode this voltage becomes 0 the reference value would become this ok.

So, that is what if some value becomes let us say this potential is minus 0.441 volt so; that means, that potential if you measure with reference to standard hydrogen electrode. So, you just corresponding point. So, this would become minus 0.241 ok. Just a minute let me see this is four one no it would become 200 ok.

(Refer Slide Time: 13:02)

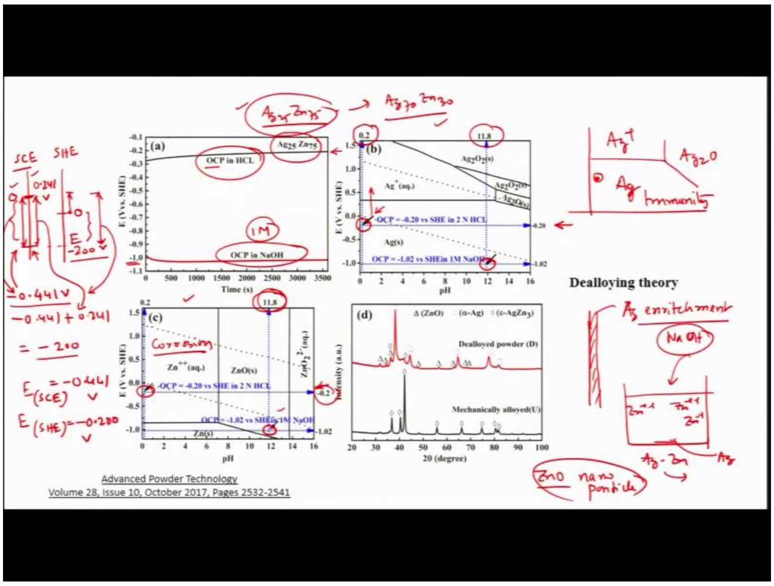


Dealloying theory

Advanced Powder Technology
Volume 28, Issue 10, October 2017, Pages 2532-2541

Because the entire gap is this gap would be 0.441 minus plus 0.241 it becomes minus 200.

(Refer Slide Time: 13:25)



Dealloying theory

Advanced Powder Technology
Volume 28, Issue 10, October 2017, Pages 2532-2541

Sorry this is not the potential minus 200 ok and then you have actually consume this much of potential. So, this is from here this gap is 400 minus 0.441 volt this gap. This gap is minus 0.441 because with respect to saturated calomel electrode this becomes my reference potential.

Now with reference to standard hydrogen electrode if you would like to measure, we know already to reach to that zero reference potential with respect to standard calomel electrode is actually plus 0.241-volt with reference to standard hydrogen electrode. So, the remaining potential would be 200 minus 200 volt. So, if you add this two part. So, then it would become again it would become minus 0.441.

So, in terms of with reference to if I try to measure this particular potential with reference to standard calomel electrode. So, that potential if it is E let us say this potential is E. So, this E would be in terms of standard calomel electrode it would be minus 0.441 volt, but if we try to measure with respect to standard hydrogen electrode, it would become minus 0.200 volt ok. So, that is the way we can convert from one scale to another ok.

So, now coming to here. So, we measured that particular potential of that pallet with reference to standard calomel electrode and then we converted everything in terms of standard hydrogen electrode, why we had to convert everything? Because the in the book the pourbaix diagram is measured with reference to standard hydrogen electrode ok.

So, now this is the potential of the alloy, this is the potential of the alloy in that particular solution with that pH ok. Now what we did? We had taken pourbaix diagram from the standard books and that pourbaix diagram in that silver pourbaix diagram and in zinc pourbaix diagram we actually plotted that potential ok. And we also know the pH of the solution what we are using which is two normal HCl and you could see that this potential which is around minus 2 to minus 4 volt around that volt. So, that is coming here ok.

Now, this is also coming in the pH in the zinc pourbaix diagram here. So, this is zinc pourbaix diagram, this is silver pourbaix diagram. Now if I see the potential here ok that OCP value that is the potential of that particular alloy that potential and the pH also we have measured. So, pH is around 0.2 is the pH of that solution ok and we that we have done from the by the by measuring it with a help of a pH meter.

So, now this is crossing here. This arrow if you see this arrow it is crossing here and now where it crosses? It is crossing here that crossing point lies in the silver zone in case of pourbaix diagram. So, in case of zinc pourbaix diagram silver pourbaix diagram. So, if I try to draw the left part of it, it is here. So, then it is. So, this is Ag, this is Ag plus plus this is Ag_2O fine. Now we are having it here at this portion which is the silver zone which is immunity zone immunity zone.

So, now if we have that particular for example, if we take a silver block if you dip it in acid with this condition if the potential you have silver potential you have taken forcefully to this particular potential minus zero point zero point minus 0.2 volt with reference to standard hydrogen electrode it will lie here.

So, silver will not dissolve it will remain immune. Now the alloy experience the same potential and that potential with reference to the zinc pourbaix diagram let us see where it lies. So, here it lie. So, this is the OCP of that potential or the free potential of that particular alloy silver 25, zinc 75 and it is in weight percent remember and the pH we know which is 0.2 and that point is lying here ok.

So, that is let us see where it is lying. It is lying in the zinc plus plus ion region and this zone is called corrosion zone fine. So, now, this particular point if we take this alloy two normal HCl and if we see their position relative position with reference to the pH and potential of that particular alloy, it is lying in the corrosion zone of zinc and it is lying in the immune zone of silver. So; that means, silver should not dissolve and zinc should dissolve ok.

So, that is what zinc dissolves silver stays back, but finally, of course, the actual mechanism starts happening where both dissolves and immediately silver deposits back is a basically a kind of monolayer ion formation or few layers of mono that ions having silver ion as well as zinc ion, but immediately silver deposits back and zinc stays back in the solution, but that staying back also has a relation that it is actually that potential is always lying in the corrosion zone of zinc pourbaix diagram, but silver one is lying in the immune zone of pourbaix diagram.

So, that is the beautiful relation ok. Now another important thing is for example, the first monolayer is having let us say this is the first layer and the another layer is forming. So, this is the first layer that is having silver enrichment silver enrichment. Now once the silver enrichment happens one might have a query that this alloy initially it was silver is 25 percent.

Now once the first set of dealloying happens the first monolayer dealloying happens, it is becoming enriching with silver so; that means, this concentration might go to Ag on the first monolayer Ag let us say it becomes 70 zinc 30. So, that might happen. Now, if silver enriches the alloy itself become nobler ok. So, how to understand that which one is noble which one is active? The noble means its potential reduction potential goes up so; that means, this OCP will go up ok.

So, now, OCP go up means, it will try to reach to this level as it is going towards closer to that particular situation that silver is enriching. Now interesting point is even if OCP goes out of that section, then the second mechanism would still be there because silver has a higher reduction ability in compare to zinc quantity we have both.

So; that means, silver deposits back continuously and zinc continuously comes out in the form of ions so; that means, you can see that there is a strong relation for the dealloying with the pourbaix diagram of both the elements that is noble and active elements.

And that is very clear that you have to just do that experiment if you take any alloy system where one is noble, one is active ok you take pourbaix diagram of both the elements ok and now you measure the OCP of that particular alloy, that OCP and also the pH of that solution where you are dipping.

And that time if you see that cross section point the pH and potential cross section point if it is lying in you will see that the element which goes out in the solution that particular cross section point the pH and potential would lie in that active zone or the corrosion zone of active element and it will lie in the immune zone of the noble element, this particular phenomena will be true ok.

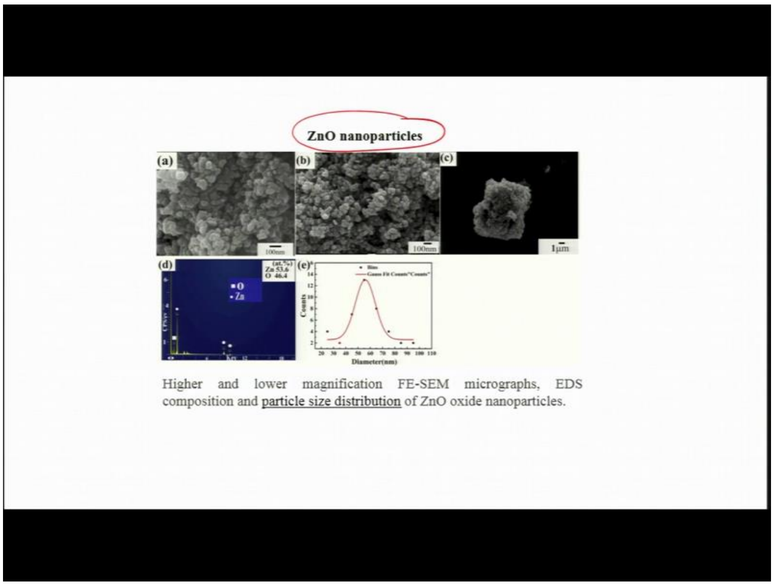
Now, coming to the point that if somehow we change the pH what would happen ok? The potential if we change the pH let us say we have made pH to a very large level and that OCP we have measured ok. This particular alloy same we have made a pellet and then we have dipped it in NaOH solution ok and which was one molar NaOH if you see this is the one molar NaOH we have dipped you can say this is one molar NaOH and we saw that the your that OCP value of that particular alloy is around this particular potential ok minus around minus 1 volt with reference to standard hydrogen electrode and we have also measured the pH of one molar NaOH with the help of a pH meter and that pH came out to be 11.8. So, 11.8.

Now, we what we did? We tried to again plot that OCP which is minus 1 volt in NaOH of that alloy and the pH of that NaOH solution and we could see. So, in case of silver pourbaix diagram it is lying in the silver zone, but in case of zinc pourbaix diagram it is lying in the zinc oxide zone ok.

So; that means, you would we should expect that silver would stay back and zinc oxide should form fine. Now when you have a solution this is a solution in that solution initially let us say this is silver zinc alloy ok from that zinc is dissolving. So, this is full of zinc plus plus zinc plus plus ions and it is becoming interconnected silver ok.

Now this zinc ion we thought that let us recover that zinc ion ok whether it is possible in the form of some useful product. Now we took the powder out or rather filter it out and that we took solution and that solution now you do not have any silver the silver particle which is porous nano porous silver particle its only zinc plus plus and then what we did? We put NaOH solution ok till it reaches to the level of pH of 11.8 and interestingly we got zinc oxide nanoparticle ok zinc oxide nanoparticle.

(Refer Slide Time: 26:08)



ZnO nanoparticles

Higher and lower magnification FE-SEM micrographs, EDS composition and particle size distribution of ZnO oxide nanoparticles.

Let us see whether zinc oxide nanoparticle has been obtained you see this ok. Now there we after we have done the dealloying part we took the nano porous silver particles out, we took the solution remaining solution we started mixing NaOH solution in that.

So, first NaOH will neutralize HCl and then after that we keep on adding NaOH so, that the pH level goes to 11.8 and then we could see that zinc oxide started forming. So, these are all zinc oxide nanoparticles the particle size is of the order of around 60 to 54 to 60 nano meter.

So, those are pure zinc oxide nano particles. So, what I mean to say that, through that relation with the pourbaix diagram. So, now, you must have wondered that why we are trying to learn pourbaix diagram in electrochemistry, the pourbaix diagram can explain many of the phenomena the way it has explained the preferential dissolution of zinc and making of silver nano silver nano porous particles and then finally, we could recover that zinc in the form of zinc oxide and zinc oxide has got many uses ok. So, that part is different, but at least we could recover those zinc ions otherwise you just throw it out ok.

So, that is what I am telling this pourbaix diagram learning pourbaix diagram is very very important while learning any of the corrosion phenomena that can relate the practical situations ok. We will talk about this pourbaix diagram influence of pourbaix diagram as the time passes on and as we see many other examples like this ok.

So, let us stop here and next lecture we will touch upon this particular aspect we will take some of more practical examples and try to see what are the protection routes of dealloying. Now coming to another aspects if you could; recall if you could recall that while talking about galvanic corrosion, we said that galvanic corrosion sometimes it becomes good aspects.

Its not always bad we could see two examples one is sacrificial protection ok where the zinc magnesium dissolve and it becomes it become it protects the steel ok and another example we showed dry cell battery. In case of dry cell battery zinc casing dissolves and electric cathode reactions happens on the centre graphite or carbon electrode and zinc dissolution happens around that zinc casing and we get some potential output which is 1.1 volt and those are the dry cells.

So, those are actually examples of advantage of galvanic effect which is the advantage of corrosion. Now here also you would see in the next class also you would see that dealloying is a kind of tool to prepare many exotic porous materials we could make porous catalyst by using this dealloying process ok.

So, the corrosion phenomena is not all the time bad that can be useful for making some useful product ok. So, that is what I mean that corrosion is not bad all the time this is a kind of eye opener that it can be useful in many instances. We will also look at those issues as the time passes on as we go into learn go and learn this subject more and more ok. So, let us stop here.

Thank you.