Aqueous Corrosion and its Control
Prof. V. S. Raja
Department of Metallurgical Engineering and Materials Science
Indian Institute of Technology, Bombay

Lecture – 25
Forms of corrosion: Selective leaching or dealloying

Today we shall discuss an important topic which is called as Selective leaching or also called as dealloying, sometimes they called as partitioning; they are all mean the same. Now, why does the problem of selective leaching occur in the first hand? Why does really it happen? It happens because it is concerned with the alloys, they are not concerned with the pure metal, they are concerned with alloys.

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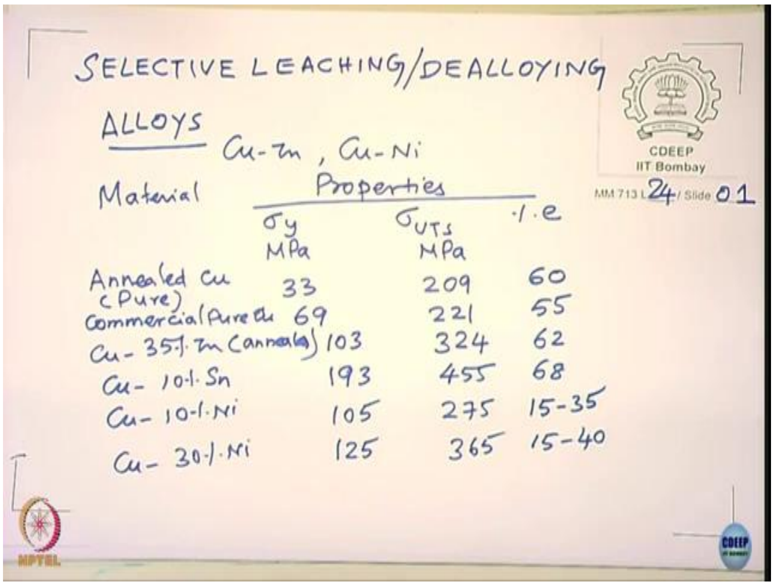

SELECTIVE LEACHING/DEALLOYING

ALLOYS Cu-Zn , Cu-Ni

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Material	Properties σ_y MPa	σ_{UTS} MPa	% e
Annealed Cu (Pure)	33	209	60
Commercial (Pure Cu	69	221	55
Cu- 35% Zn (annealed)	103	324	62
Cu- 10% Sn	193	455	68
Cu- 10% Ni	105	275	15-35
Cu- 30% Ni	125	365	15-40

Some examples if you want me to give, I can say that copper-zinc, copper-nickel they are well known examples. Now, the question is why do you really need an alloy? Why not we use a pure metal? Strength is a consideration. So, the strength is a consideration why you go for alloys. I you want to give an example in relation to copper-zinc and copper-nickel.

Now, if you take a let us say a material and then the properties and the properties, what are the properties mechanical properties maybe the yield strength, the ultimate tensile strength and you look at the elongation is the percentage elongation. The units of that can be mega Pascal (MPa) and you can see that you can appreciate how the alloying helps to improve the mechanical properties.

Suppose you take an annealed pure copper; copper is its very pure. If you look at the mechanical properties, the yield strength of that is hardly 33 MPa. The ultimate tensile strength is 209 MPa, the percentage elongation is about 60. If you take a commercial pure copper, take this the strength increases considerably. Of course, the strength and elongation are many times inversely related to each other.

But you take a brass which is a brass which is a copper - 35% zinc which is annealed. You will see the strength increases quite significantly. In this case even the elongation also is improving in this case. If you take let us say copper - 10% tin take this, you can see that the strength level is again increasing and like this. If you look at the copper nickel the alloy systems say copper - 10% nickel; I am talking about weight percent.

Strength level is the yield strength is 105 MPa and the UTS is 275 MPa the ductility varies depending upon cold work or not it can vary from 15 to 35 it depending upon how they are done and vary quite widely. If you increase the nickel content further let us say 30% nickel, see again there is an increase in the strength level, again it can vary in the range something like that.

So, in essence we go for alloys because we want to improve the mechanical properties especially strength of the metal. But, if you look at this, you have seen earlier when you talk about the galvanic corrosion. When you have copper, when you have zinc as two different entities a copper block and a zinc block; if you couple them galvanically in the environment what is expected to happen?

Student: Zinc will corrode.

The zinc will corrode preferentially, it becomes the anode and the copper will act as a cathode. So, the active metal dissolves and the noble metal gets protected. They are macroscopic, there is a clear entity of a copper block and a clear entity of zinc block; between these two the current flows.

Copper act as cathode and zinc act as an anode, the current is flowing between the between them. But, in an alloy let us take a copper - 35% zinc which could be homogeneous alloy we will talk about little later.

They mix it at atomic level, they are homogeneously dissolved and more so, in the copper nickel systems. The copper nickel system is known for having extended solid solubility. So, at atomic level they mix very nicely, but even then the electrochemical property of copper is different from the electrochemical property of zinc or the electrochemical in the case of brass. And, in the case of copper nickel alloy nickel is different from that of copper. So, you could able to see having a different electrochemical properties.

And so, you expect at atomic level exhibiting different corrosion behavior with respect to two different alloying elements. So, that is why we talk about selective leaching or we call about the dealloying.

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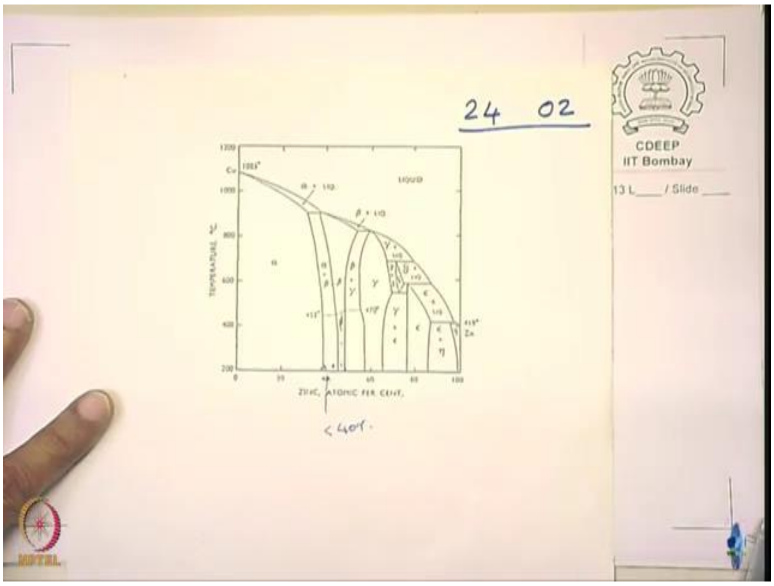

Now, to just give an example how the system can become complicated let us take this the phase diagram. This is a famous copper zinc phase diagram, I think most of you might have studied in a physical metallurgy course. And, you will see lot of peritectic transformations we call it. The copper zinc system they exhibit different phases. When the zinc content is less, you have an alpha phase. As you increase the zinc content what happens?

Now, you can get a beta phase somewhere here, the composition lies between them you get an alpha plus beta phase. Of course, you have a gamma phase, you have epsilon phase, you eta phase and so on so forth. From the point of view of real engineering applications, the alpha phase and alpha plus beta phases are important. We call them as alpha brasses, we call them as alpha plus beta brasses, we call them as the beta brasses the most metal.

So, these are all very familiar with you, what I want you to understand is the amount of zinc varies depending upon the type of brass that you take. Now why you take different brasses? Because they have different mechanical properties; the alpha plus beta brass will have a different mechanical properties. In fact, it could be much harder as compared to alpha brass. So, from the structural point of view we need to use a different type of alloys which means they have different electrochemical corrosion properties.

So, that is the crust of the matter. Now, these are all some examples; you can also have various other alloy systems. And, these processes are classified depending upon which element is selectively dissolving selectively leaching.

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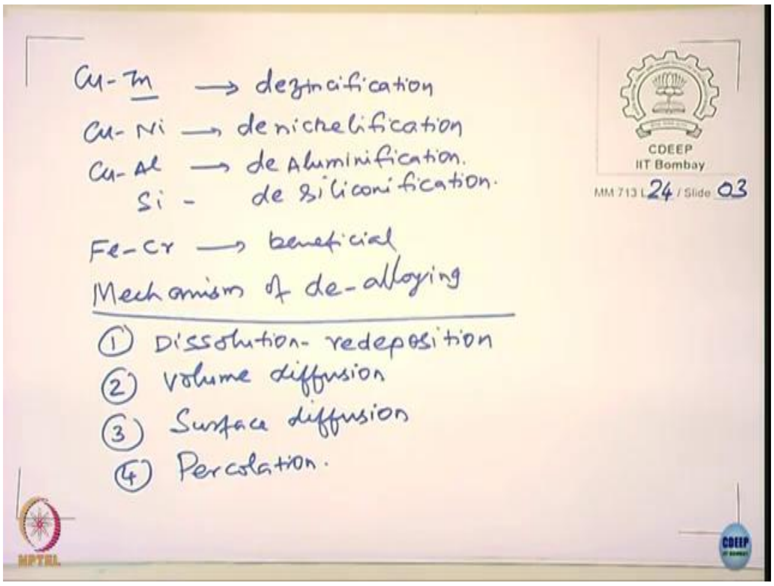

Cu-Zn → dezincification
Cu-Ni → denickelification
Cu-Al → de Aluminification.
Si - de siliconification.
Fe-Cr → beneficial
Mechanism of de-alloying

① Dissolution- redeposition
② volume diffusion
③ Surface diffusion
④ Percolation.

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In a copper zinc system you expect what which one will dissolve first selectively?

Student: Zinc.

Zinc will dissolve and you call them as dezincification, a very familiar term. In the case of copper nickel, we call them as denickelification. You may have some word similar to copper aluminum and aluminum can be with even other alloying elements you can have, you call them as dealuminification.

Suppose you have silicon we call desiliconification and so on and so forth. These elements are selectively dissolved because they are relatively anodic compared to the next element. Sometimes selective dissolution, perforated dissolution is beneficial. What are example? Iron chromium it is beneficial. Why? They form the passive films. So, you need to contrast you need to contrast and how this really happening.

Now, in order to use this alloys let us say copper zinc, copper nickel and whatever alloys if you talk about, we need to understand the concept of selective leaching or dealloying we call it; in terms of mechanisms, in terms of the factors that affect the dealloying actually. And, if you know both of them then you can able to device means to control dealloying actually. So, what we will do is we will discuss now in terms of how this mechanism of dealloying occurs.

There are about four different types of a theory important theories I would say: 1 dissolution re-deposition mechanism, the 2nd is volume diffusion, the 3rd we talk about surface diffusion, the 4th we talk about percolation model. I will be very brief in discussing these mechanisms and they are fairly simple, they are not really that complex.

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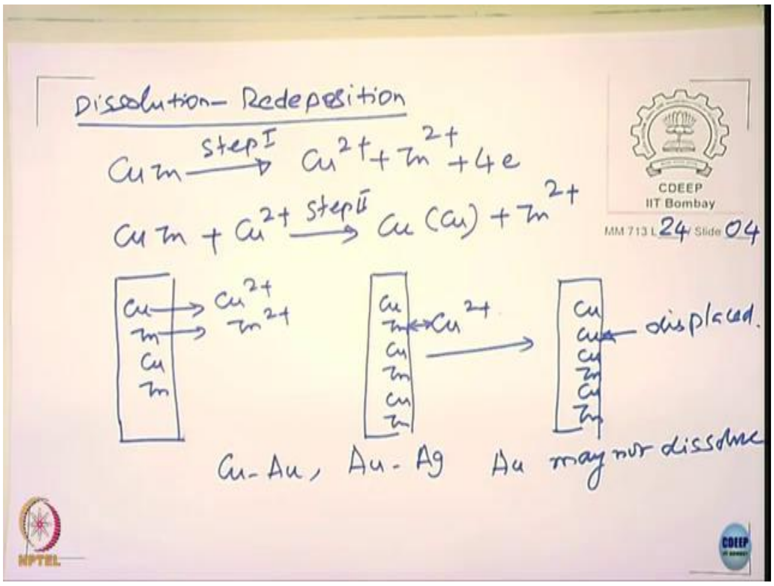

Dissolution – Redeposition

$$CuZn \xrightarrow{step\ I} Cu^{2+} + Zn^{2+} + 4e$$

$$CuZn + Cu^{2+} \xrightarrow{step\ II} Cu(Cu) + Zn^{2+}$$

Cu-Au, Au-Ag Au may not dissolve

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Let us look at the first mechanism, we have talked about dissolution and re-deposition. Let us take the case of brass, a copper-zinc in the system. In this alloy is exposed to the environment, we consider that both the alloying elements they undergo dissolution or corrosion process like this. This is your step number I.

The step number II, what is expected to happen here is; now look at this you can have in the solution your copper ions and zinc ions, the copper ions the Cu^{+2} equilibrium is nobler compared to Zn^{+2} equilibrium.

So, your copper ions here, this copper ions would displace zinc in the lattice. So, you have copper coming over as a copper here, over here. So, you see now the copper ions in the solution will undergo a cementation process we call it, we call a cementation process. Wherein the zinc transfers the electrons on to copper ions and the copper ion get deposited, zinc dissolves as Zn^{+2} ions. So, this is your step II process.

Student: So, this Cu^{+2} is in the lattice of the alloy.

Cu^{+2} is in the solution.

Student: This is occurring in a solution.

Yes, see I put a pictorial like this; initially both they dissolve, of course it does not go from the bulk, it goes from the surface; it goes to the surface. Then what happens now? You have copper ions, they get exchanged that leads to copper here, copper here you have again copper here zinc copper zinc so on. So, this is what is the displaced. So, it is from solution, the solution consist of copper ions.

The copper ions being noble, they replace zinc from the lattice of the alloy and the copper is getting redeposited. And, you will form a porous structure, see look at now it forms a porous structure. It is not going to be a complete a normal metallic structure. If this is the case this is one mechanism where we talk about, this one mechanism. And, this theory has some limitations for example, suppose you have copper-gold for example, or you have gold-silver for example, like this both are noble.

So, in you do not get and in this case look at this in this case the gold may not dissolve, only copper may dissolve, only silver may dissolve; because copper is quite noble. Suppose, I take I give you a copper-gold alloy system and put it in environment, not necessarily the gold dissolves like you have copper dissolution in the brass system, because gold is noble in this case.

So, without dissolution of the noble metal, is possible only the active metal can dissolve. So, it is so, in this case what happens now? It is saying in this case its talks about the dissolution of only the active metal; the noble metal need not dissolve from the surface. So, is really a selective dissolution and not a redeposition process. Do you understand the thing now? So, it is; so, this mechanism may not be valid in a system like that simply copper can dissolve and this can dissolve, it is done also.

You know how people, how does the goldsmith separate your gold, the gold has got copper and gold the ornaments for example. How does he separate? He takes this one and melts with the silver and then forms an alloy and then pours it into the aqua region solution. What happens now? Only silver comes out; copper of course, comes out, gold does not dissolve at all.

So, you can have a selective dissolution process wherein noble metal need not dissolve actually. So, this mechanism does not explain in those metals where those alloys where the noble metal will not dissolve at all. So, there is no question of redeposition process. So, you have the second mechanism which talks about the volume diffusion.

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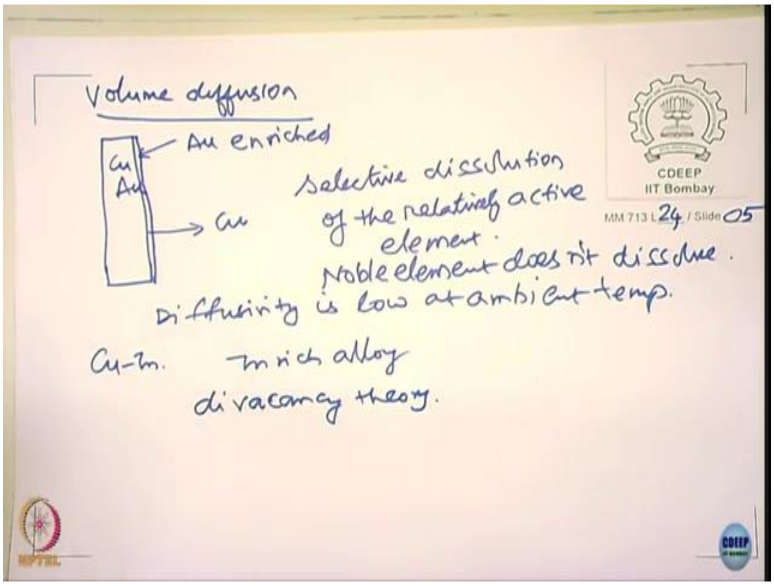

Volume diffusion

Selective dissolution of the relatively active element.

Noble element does not dissolve.

Diffusivity is low at ambient temp.

Cu-Zn. Zn rich alloy

divacancy theory.

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Please understand the remaining three mechanisms, we talked about the volume diffusion, surface diffusion, the percolation model may not invoke the dissolution of the noble element of the alloy. It could say that only the active element dissolves, the noble element does not dissolve in the system.

Now, if that is the case suppose I have a bulk alloy, let us say it consist of say copper and gold something like that. In the surface see you have a surface here, in the surface it is possible that only copper comes out and gold get enriched. So, it is a selective dissolution of the relatively active metal, active element and noble metal does not dissolve.

So, only copper comes out, gold remains on the surface and there is a problem here. Can you tell me what is the problem? The problem is that you know the diffusion of the elements at ambient temperature is so low. If this process has to continue unless the copper comes to the surface, it is not possible for the dealloying to continue. Am I right? For the dealloying to continue, the copper from the lattice.

Has to diffuse and then come to the surface and then only there can be dealloying, if it does not happen a few atomic layers of the alloy will dissolve where the relatively active metal goes to solution. And, then after there will be no dealloying taking place because the diffusivity is low at ambient temperatures.

You might have heard of high temperature oxidation right, there you talk about diffusion of aluminum, diffusion of chromium to surface, diffusion of silicon to surface get oxidized forms a nice protective firm and all possible.

But, at ambient temperature the diffusion of these elements are so low, you do not expect them to continue with the dissolution process. But however, what people have done, they have noticed that when there is a dealloying taking place; people who observed change in the phases. For example, if I take copper zinc system I take zinc rich alloy. And, when it dissolve, when it dissolve what happens? Just look at the phase diagram here.

If I take an epsilon alloy here then the surface will be alpha, then alpha plus beta, beta beta plus gamma and gamma. So, it will go this way because if you remove zinc from the surface you will get more rich copper rich phase.

So, copper will I mean that the brass will have copper rich on the surface because zinc is removed. So, as you move from the surface to the bulk the phases will be alpha, alpha plus beta, beta beta plus gamma and gamma and so on so forth; that is what it happens.

So, that is how people have detected in some cases to show that there is a selective dissolution of these elements, but however, the thickness of these layers are so small. So, this theory is little bit a problem, but of course, they have proposed what is called as divacancy theory, they say that if you have two vacancies together it is easy to migrate. So, that is a theory that have been proposed, but it is a not been well proven across a various alloy systems.

So, the volume diffusion is considered to be more difficult and it is not be very favorable for dealloying of various metals.

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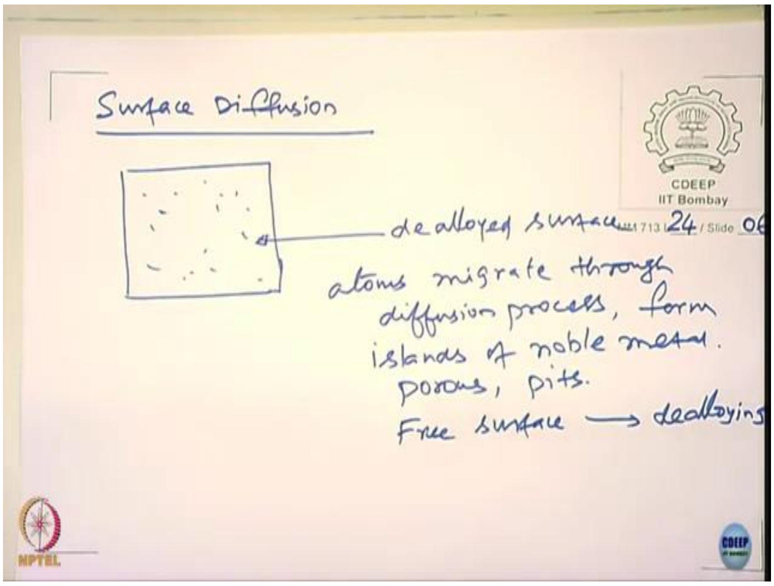

Surface Diffusion

dealloyed surface

atoms migrate through diffusion process, form islands of noble metal.

porous, pits.

Free surface → dealloying

There is something called as surface diffusion mechanism, this is very interesting. Now, I have a surface and I get de alloyed, it is a dealloyed surface. The dealloyed surface, when we dealloyed then what will happen to the surface? Surface will be rough and porous; there will be atoms loosely held.

Now, these atoms migrate through diffusion process because when the atoms are alone the energy of the atom because surface becomes quite large. So, when the energy of the surface is more then what happen they try to they try to agglomerate; they try to agglomerate actually. So, what happens they migrate diffusion process and then form islands of noble metal clusters noble metal, you will see porous structures porous you see pits.

So, the initial process is the active element dissolves, the noble element remains on the surface. But subsequently what happens? The noble elements, the atoms they diffuse on the surface and they form clusters. In the process what happens? You are going to generate a free surface again, am I right? You can create a free surface because the atoms are moved and formed as a clusters. So, it creates a free surface that again leads to dealloying.

So, this is I have been people have been modeling this and then trying to show that the dissolution is by clustering process. People have shown a nano structures, people have shown the porous structures. And, that is how and that the dealloying continues, it is not just the surface process, it can go sub surface process.

So, surface the diffusion process is a result of dealloying of the active element, the clustering of the atoms because of the surface energy leading to creation of the fresh surfaces. And, subsequently again there is a dealloying and the process continues and dealloying happens eventually to a larger thickness in the in the alloy. There is a small variation in this concept which is called as percolation.

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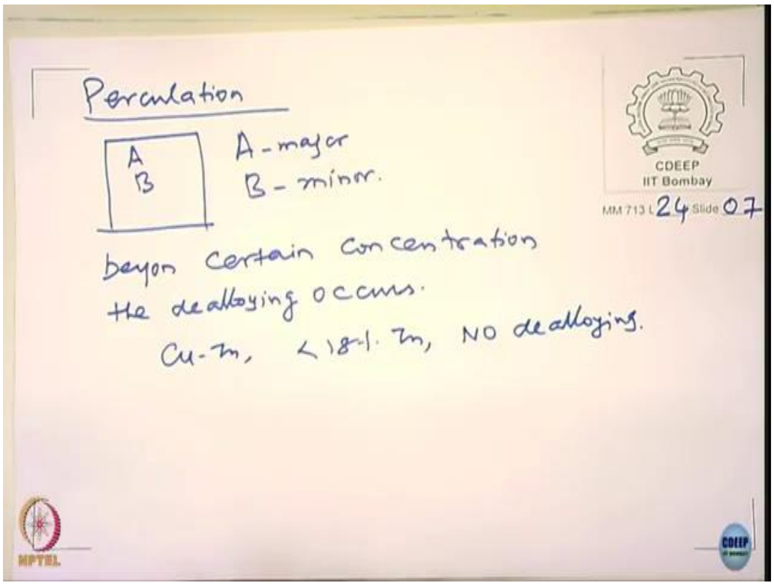

Percolation

A - major
B - minor.

beyon certain concentration
the dealloying occurs.
Cu-Zn, < 18% Zn, NO dealloying.

You know what is called percolation right, this model probably many many of you might have studied and various context of that. You take a solid containing A and B, now any entities that you have, you mix them thoroughly; you mix thoroughly. Suppose assume that A is the major element and B is a minor element, you mix them thoroughly. The B's can come in contact with each other when you exceed the concentration of B beyond a level.

Do you get it? So, when I have A and B, I mix it, if the content of B is very low, then the all B are isolated or all the B are surrounded by A nicely. But, if you keep on increasing B at one level, the B and B will come in contact with each other. So, that is so; that means, that makes a continuous path for the B to dissolve, am I right? When the B and B are come in contact with each other then it is not dissolving actually.

So, the percolation model tells that beyond certain concentration the dealloying occurs, this is a very interesting theory. For example, take copper and zinc less than 18% of zinc no dealloying.

If you increase a zinc content beyond that the dealloying occurs. So, the percolation theory talks about the active elements coming in contact with each other; so, that the dissolution path is quite continuous; it goes like that. But, please notice that the percolation model and the diffusion model can work together.

I can have some threshold level of active element that leads dissolution, but even then there can be diffusion of the noble element in the surface; so, that they can form clusters.

So, the percolation model does not totally exclude the surface diffusion model actually. So, it is quite possible. So, the percolation model explains why you need critical concentration of alloying element in order to get the dealloying without that it will not happen. So, that is an important thing when we talk about the dealloying of materials actually.

So, we will talk about the factors affecting dealloying shortly. But, these concepts are important in order to understand the factors that control the dealloying of the metals and alloys. Is it clear now actually? So, we so far saw four theories: one involving that both the noble element and the active element they dissolve in the first instance.

And, subsequently the noble element what happens? It deposits back onto the surface and it displaces, and then the active element goes to the solution. This is called displacement process.

Student: Sir, in each of these cases there are two processes, opposite process are occurring first is that electrochemical, the difference in the potential between the elements and second should be the thermodynamic kinetic property of diffusion. So, in this percolation thing still there is a potential difference between copper and zinc even after such a low concentration.

Very true, yes.

Student: So, why is not the dealloying occurring? How is this theory of prompting factor?

You are saying that why do you need a percolation model, this is what you are saying?

Student: Because the zinc here is active, it had to dissolve; not deposit like on the surface copper used to move around and then form pits.

See now look at the model for example, the dealloying model, I mean in the redeposition model that we talk about it is simply that at one go both elements dissolved and get redeposited into the system. In which case irrespective of the amount of alloying element added, what I mean you talk about concentration of element. The dealloying should continue to happen. It does not happen if you have copper zinc if it is 18% or famous red brass.

Red brass you do not get dealloying, we will see later; yellow brasses occur. The yellow brasses and red brasses are all alpha brasses, but then the amount of zinc in red brass is only 15%. So, 15% zinc does not lead to dealloying, any amount of time you expose to the environment nothing happens. So, how can you explain that? The only way that you can explain is that you need a critical concentration in order that the dealloying occurs.

Now, the critical concentration how much is required that also will depend upon what it may depend upon temperatures, it may depend upon the environment, it may depend upon the two alloying elements. For example, if the alloying elements have wider potential difference, then the critical concentration may come down also actually ok; the factors that you see little later.

So, yes they are all going to decide what is the critical concentration or threshold concentration above which the dealloying occurs. But, these factors are to be taken into account which that is what we are going to see in the subsequent discussions. So, the percolation model explains the need to have critical concentration of the active element in order to have dealloying process, that is what the discussion all about actually.

And, the surface diffusion model is also proven because when you take out and see there are ions, and there are you know we are not going into details. If we look at the R. C. Newman's work and all they are shown very clearly there are nano-grains there actually. How you get a nano grains? They get nano grains because these atoms will get clustered and form the nano grains actually.

So, the clustering they do happen and then since the nano grains are porous and then there is a continuous dissolution of metal really taking place at all. So, what is after all mechanism? The mechanism is what we propose in order to explain the observations that taking place, that is what its all about actually. And, then these mechanisms should also explain the fundamental processes that are taking place.

For example when you say volume diffusion, the issue there; the issue there is that how much, what should be the thickness over which this can happen. So, this can be happen; so, they also used a theory called as divacancy theory, but then still it is very limited. You cannot have an extended dealloying of metal, it cannot take place at all actually. So, that is where the volume diffusion was put forward by Harvard Pickering, in his own paper.

So, you see some papers appeared in corrosion science a long ago very nicely demonstrated that there are, if you see the surface as I told you, the volume diffusion is what?

When you dealloy it, the surface you will have least amount of active element as you move inside the active element concentration increases; that is why it is called volume diffusion of taking place. And so, that is proved he has shown it by using electron diffraction pattern that these phases are changing from surface to this.

But the thickness over which they are happening are very limited taking place at all. So, each of these theories is not that as though that there is no evidence, but there are limited amount of evidences and each theory have their own limitations to explain, the completely observed phenomena in the dealloying of the metals actually.

I hope I have made the made the point clear to you in terms of you know these models in explaining dealloying of metals. Any other questions you have? Fine ok. So, let us move on to the next one actually.

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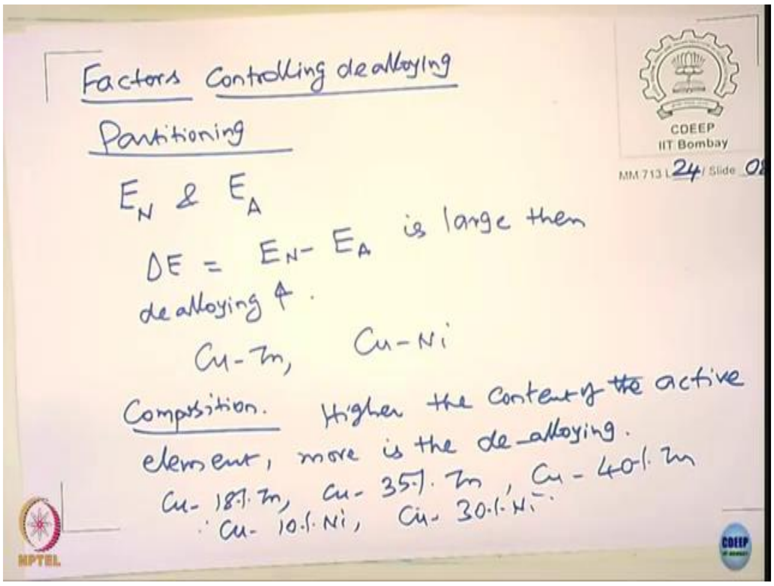

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Factors Controlling dealloying

Partitioning

E_N & E_A

$\Delta E = E_N - E_A$ is large then dealloying ↑.

Cu-Zn, Cu-Ni

Composition. Higher the content of the active element, more is the de-alloying.

Cu-18% Zn, Cu-35% Zn, Cu-40% Zn

Cu-10% Ni, Cu-30% Ni

Now, what are the factors controlling? Now, this is called as partitioning, the partitioning would depend upon element a which is noble, I call it potential of the noble element. And, the potential of the relatively less noble element we call as active element ok; I do not call anode and cathode active element.

If the $\Delta E = E_N - E_A$ is large then dealloying increases. What does it mean? You take copper zinc and you take copper zinc and copper nickel. If you make if I make a tube for a heat exchanger that carries a seawater, one case it is copper zinc, other case it is copper nickel; both cases sea water we use. Which of the two tubes will fail earlier?

Student: Copper zinc will fail earlier.

Copper zinc fail earlier ok; so, that is what I meant here. So, because the potential difference between these two are quite large as compared to this and secondly, is the composition. Higher the content of the active element more is the dealloying. Say an example copper, let us say 18% zinc, copper let us say 35% zinc and copper 40% zinc.

This both are called alpha brasses and this is called as the beta brass, this called a Muntz metal, the famous Muntz metal is copper-40% zinc. So, the dealloying will increase from this to this and to this am I right because the ΔE is going to be the same in all cases. But, the content of the active element increases from this to this actually. Similarly, you can also have copper-10% nickel and copper-30% nickel.

The question then you will ask is why would people use alpha beta brasses in seawater? Because, the alpha beta brasses they have better erosion corrosion resistance, they have better mechanical properties. So, the damage mechanism need not be always dealloying, it can be simultaneous process when there is a flow line, there is a velocity you can have dealloying, you can also have erosion corrosion.

If the erosion corrosion is more dominating then what happens? Then you will see that copper-18% zinc will be failing faster than copper-32% zinc, because copper-32% zinc has got better mechanical properties. So, we need to look at overall perspective in terms of the metal selection, alloy selection for given applications. But, what we are seeing here is understanding the science of dealloying; so, that I think you should try to understand.

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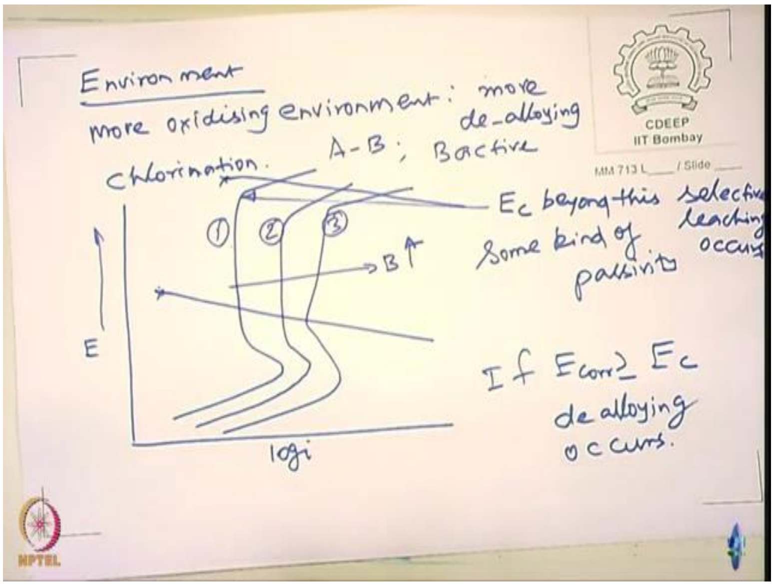

Environment

more oxidising environment: more de-alloying

chlorination. A-B; B active

E_c beyond this selective leaching occurs

Some kind of passivity

If $E_{corr} \geq E_c$ de alloying occurs.

Now, in addition to this it also depends upon the environment, more oxidising environment more oxidising more corrosive more dealloying. An example is chlorination, people do chlorination in cooling water systems and if you do chlorinate chlorine is an oxidizer and so the more dealloying occurs. Let me look at a more related to alloy chemistry towards the to the dealloying.

Let us take that I have element A and B, B is active. So, the B concentration increases as you go from this curve, curve 1, 2 and 3 the concentration of the active element increases. Now, they show some kind of passivity and you have a potential here and this is the potential we call it; we call the potentials. And, this is called as E_C beyond this selective leaching occurs; so, there is a driving force for corrosion to occur.

So, for these alloys a in order to find out whether they are undergo dealloying how effective they are you can carry out a polarization curve and get this. And, find out what is the E_C value, E_C here represents the potential above which the dealloying really occurs. And, the increase in passive current density here; so, called passive current density means that there is more dealloying is taking place.

Now, if the corrosion potential exist above E_C, if Ecorr is going to be greater than or equal to E_C then what happens? Dealloying occurs right or not because only above E_C you have dealloying, you get this polarization curves. So, how do you get how do you get Ecorr at that particular value? What is the basis? When will the Ecorr will go here? In actual situations when do you expect that will happen? What is the criteria for that?

Student: Only transpassive.

That is right you call it transpassive I do not want called as a transpassive here we called here this potential above which there is a dealloying taking place. When will the Ecorr I mean Ecorr will go above this?

Student: Oxidizing agent.

So, it depends upon the reducing reaction, you have one more react. This is your anodic reaction, you have cathodic reaction. If the cathodic reaction, if the kinetics support that, suppose I have this is by cathodic reaction it going to happen. But, if the cathodic reaction occurs somewhere here, what happen? The Ecorr is going to lie above the E_C. So, you are going to have dealloying here, no dealloying here.

So, what I mean is the environment also is important, the environment is less oxidizing then the dealloying will not takes place at all. And, this concept you have seen in so many number of times how the Ecorr really occurs.

The Ecorr is a mixed potential, mixed potential means it is both on the anodic as well as the cathodic kinetics. So, it depends upon on the alloy, it depends upon the environment as well that is the point that you need to be understanding at all.

Now the E_C of course, it depends upon what? It depends upon the alloy here right, if you E_C will keep reducing; if you are going to alloy more and more active element in system.

Student: E_C is same as Epit.

It is not pitting here; you do not see pit here in this case that is why in copper in a copper and zinc system and copper nickel system; you do not get a pit at all actually. If you observe the surface here you will see the surface is enriched more with what? With copper because zinc is just getting out of it.

Similarly, copper nickel also nickel comes out of the solution. In fact, if you take; if you take a copper nickel system, if you carry out a polarization here and see the solution, the solution color will turn into green. Why? There are more nickel is getting dissolved. So, you see a nice green coloration at this particular potentials, you will not see a you may see a nickel also here, but then the amount of coloration you see very small here.

So, that is where you can able to show that nickel is preferentially dissolving over this particular potential. Hope this point is clear to you. Now, we have seen this things that what does it really means in practical applications.

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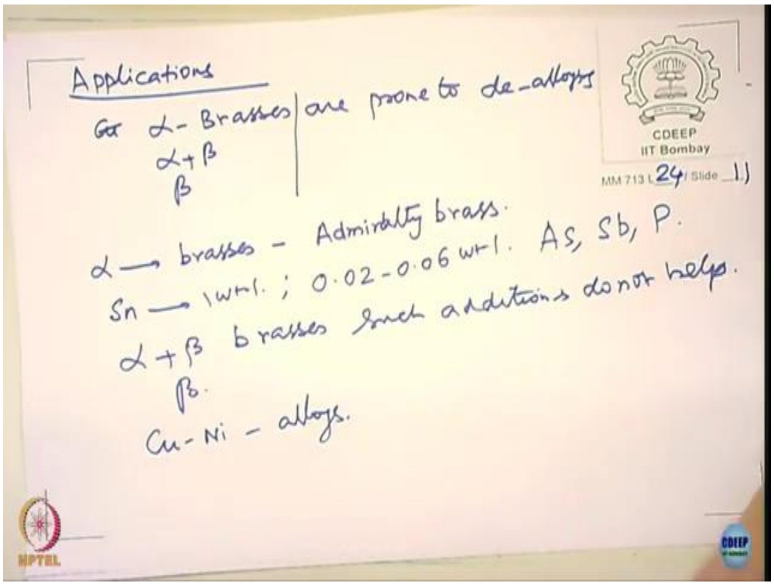

Applications

~~Gr~~ α- Brasses | are prone to de-alloys
$\alpha+\beta$
β

$\alpha \rightarrow$ brasses - Admiralty brass.
Sn $\rightarrow$ 1wt%; 0.02-0.06 wt%. As, Sb, P.
$\alpha+\beta$ brasses such additions do not help.
β.
Cu-Ni - alloys.

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Application where are these problems? I am not sure at what extent you can able to see this picture here.

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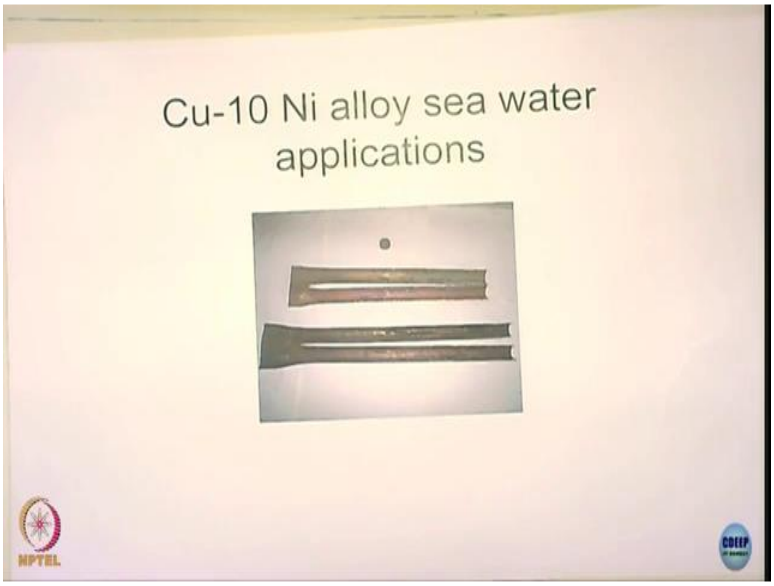

Cu-10 Ni alloy sea water applications

Let me try to, you see this black coloration here, they are greenish black color actually, I hope I do not know how far it is able to see. And, this is a copper nickel alloy in sea water application, in one of the refineries located in Mumbai; it is about of a couple of years; through this the sea water was passed through this heat exchanger.

Now, you see the coloration here, I hope you are able to see this coloration here. So, this is the coloration they will see, look at this color you can able to see this color here is a bright here right this is. And, this the black thing that you seen here is due to the denickelification, the nickel came out of surface and form this actually here. This is something which normally you see.

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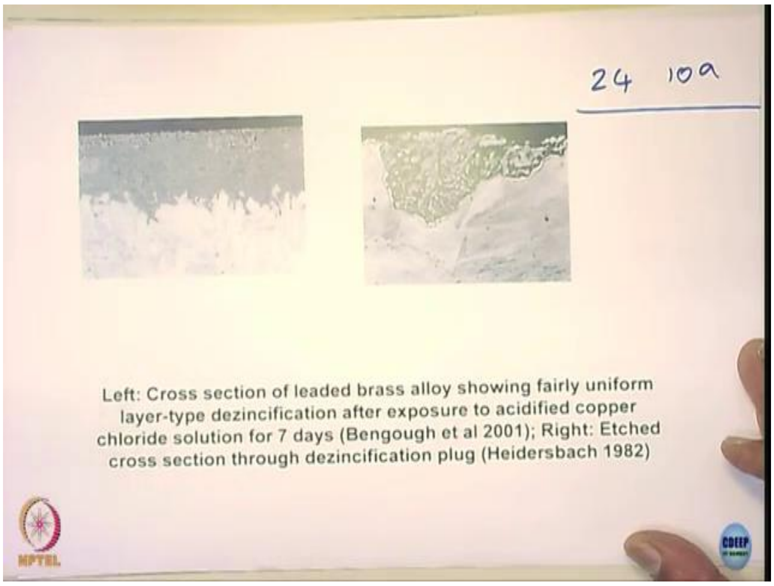

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Left: Cross section of leaded brass alloy showing fairly uniform layer-type dezincification after exposure to acidified copper chloride solution for 7 days (Bengough et al 2001); Right: Etched cross section through dezincification plug (Heidersbach 1982)

This is another example of how the dealloying can really affect. This is essentially its a dezincification process, the left side what you see here this layer is a dealloyed layer. If you can see its rich in copper, but look at this is a layered pipe; here is something like a pit type, you see here.

So, you can have two different types of dealloying taking place, it depends upon the alloy, it depends upon the environment, you can have a can have a plug type, it is called a plug type, it is called a layer type. So, if we have like this please notice now if I remove zinc from brass, what will happen what will happen to strength?

Student: Reduce.

Reduce because that is what it is giving strength. So, strength will reduce actually. And, in this case not only reduces strength it also begins stress concentration at this kind of pits here. So, this is the other kind of problem. So, these are the real problem happen, but fortunately dealloying is not as fast as your pitting corrosion all, but yes it does have effect over years.

And in this case of course, this is an accelerated one acidified copper solution. So, 7 days only, but in practice it may take a couple of years to get the dealloyed layers actually on the surface.

Student: Is sensitization same as leaching?

No, sensitization is not a leaching there, in sensitization what happens now; in a sensitization you talk about stainless steels right.

Student: Yes.

In stainless steels you are taking the chromium out of the.

Student: grain boundary.

Grain boundary area. So, you are going to have simply iron. So, iron simply dissolves that actually. And if you have in fact, this goes other way around; if you are going to have a stainless steel, iron and chromium; chromium dissolves preferentially and it forms a nice passive layer it stops actually. In fact, a sort of selective corrosion is happening in a stainless steels, but only thing that happens now the chromium forms a film. So, does not allow this subsequently dissolution of the alloy.

So, dealloying in some cases can be beneficial it can help, but in this cases where it is not passivating, it is not good because it is going to be reducing the strength of the alloy significantly and cause the problems. So, applications now you see that you have alpha brasses are prone to this to dealloying which is of course, beyond 18%. Alpha brasses, alpha beta brasses, and beta brasses all of them are prone to dealloying actually.

What people have done actually in order to avoid this the dezincification process, alpha brasses you might be knowing what is called as admiralty brass. I think people from the navy you knowing is it is this admiral who first you know formulated this particular alloy actually. So, that is why it is called as admiralty brass. The admiralty brass it consist of tin, its has got a tin, it is about 1 wt.% of tin is added to this to alpha brasses.

To support this they also add a small quantities weight percent of what? Of arsenic, antimony and phosphorus are added to this and they are effective in curbing the dealloying of alpha brasses. The mechanism is not completely known, there are some speculations, but not completely known. But, alpha beta brasses such additions such additions do not help.

So, they continue to undergo dealloying, same as the beta also and for more sea water application where you want to really have a safe thing, people go for copper nickel systems. People go for cupro-nickel alloys seawater, people use that predominantly.

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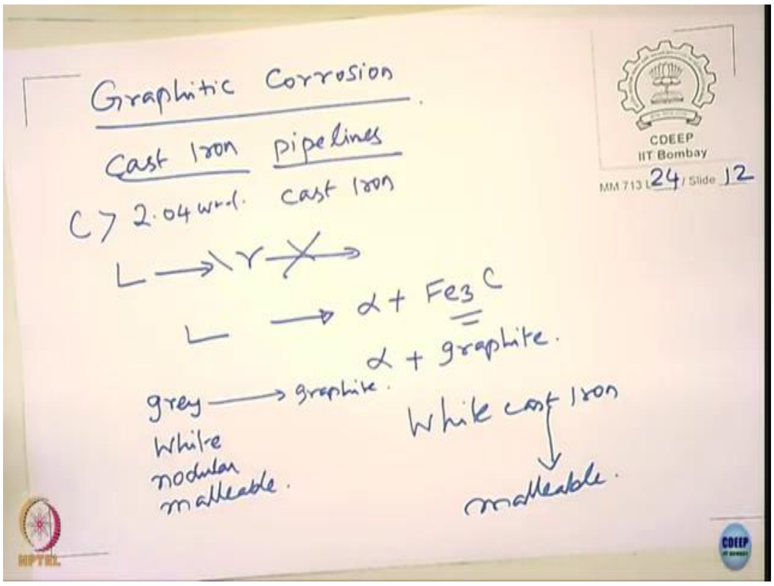

Graphitic Corrosion

Cast Iron pipelines

$C > 2.04$ wt% cast Iron

$L \rightarrow \gamma \cancel{\rightarrow}$

$L \rightarrow \alpha + \underline{\underline{Fe_3C}}$

α + graphite.

grey → graphite.
White
nodular
malleable.

White cast Iron
↓
malleable.

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I will just cover another topic which is relatively small and related to dealloying and this is called as graphitic corrosion. I mean see in the solid state diffusion of all these elements at ambient temperature is a very less very small, it is extremely slow actually taking place. And, I do not think zinc also the diffusivity is any significantly higher compared to that.

So, the diffusivity of zinc in copper is still is very low, if the diffusion is going to control the dealloying then the rate of dealloying will be very low. Now, then how do you explain the rate of dealloying which is higher. So, that is the question that comes now. Now the so, the bulk diffusion or the volume diffusion model that if you want to account for the rate of dealloying it cannot be accounted based on the diffusion, diffusivity of zinc at ambient temperatures.

A bit of the use of the divacancy; that means, you say that there are 2 zinc atoms which are dissolving and creating two vacancies and two vacancies are move little at a faster rate. And so, that assist the migration of zinc from bulk to this, the speculation taking place. Otherwise simply based on the diffusivity of zinc in the lattice at ambient temperature you cannot account for the rate of dealloying occurring in process at all these things.

So, that is where the volume diffusion theory lacks in explaining the experimental observations. So, we are going to go into the surface diffusion because in surface diffusion what happens is you are simply clustering.

The reaction, the dealloying is always happening in the surface only, it is not happening at the bulk. When you have let us say that zinc is coming out and your copper you may have you know a copper atom which are free atom there actually. They just move and they form islands of copper, which means they are clustering; that means, the free surface is done.

Now, this islands also start growing like you know in two-dimensional things now so; that means, you always have created a free surface and through the free surface the dealloying is taking place. So, there is no bulk diffusion that is accounted for in the surface diffusion process. So, that is why you are able to talk about it and people have done that actually again human model, yes looked at Monte Carlo simulation and then trying to see how these are happening and all this have done it.

So, that explains one part of it, the other part it does not explain is that why you need a the threshold level of the active element in the alloy in order to cause the dealloying that does not really tell, that is where the percolation model comes into pictures. Because, you see here what it means is that there can be the surface diffusion, but surface diffusion is not enough to account for the dissolution rate of it.

So, in addition to this surface diffusion the percolation model which connects the active element in the matrix, it dissolves and then it goes to connect like this only.

So, these are all in fact, we would talk about even composites and all you know people talk about composites, various properties the electrical properties of the composites for example. They are isolated then the electrical property does not happen. Suppose you have element A and element B, the element A is insulator and you add element B into the system actually and beyond certain level of B which is conducting element you see a nice conductivity increases, because the B is connecting the each other to the pathways actually.

So, this essentially that you are connecting them and then through the path they come as a channel and dissolve out of it. So, this is another way of looking at the selected dissolution of the atoms actually. So, they are not isolated. So, percolation model talks about critical concentration required for that. But, all are again related to potential difference related to the environment because the driving force for the corrosion again depends upon the other factors.

What the potential variation, the environment that you are going to be here, the Ecorr value that shift; they are all going to be a part of which talks about the rate of dissolution of dealloying. So, these two things should be seen separately the factors and the mechanism are to be seen should be properly understood I would say, I think that is the thing. Is that the answer now your questions? Ok.

Any other questions you people have? Ok. Now, let us go into the graphitic corrosion, I just want to finish off this here. People have been using cast irons, cast iron pipelines. Those who are not familiar with cast iron, we just spend a minute to get an idea about what it is. What is the difference between a steel and a cast iron?

Student: Castable grade.

So, what is the composition of carbon?

Student: From 2 to 4 % of carbon or greater than 2 wt.%.

So, more than 2 point something like 4 or whatever kind of weight percent, if the carbon content is going to be there, if the carbon is more than that you get it cast irons. Can you give a better definition of that? He is right?.

Student: Because the grade of iron carbon, that can be casted.

I can cast anything I want, I can cast.

Student: the presence of eutectic phase in this.

You are right. So, in the solidification process it does not go through from the liquid. It does not go through a gamma transition right, is not it? If you look at the iron carbon diagram, in all the cases the liquid directly can give rise to what? Give rise to alpha plus.

Fe_3C it can give, can give rise ok; it can give alpha and then it can give you give raise to alpha plus Fe_3C. So, it does not go through a gamma in the phase diagram first of all, first thing. The second thing is it can form a cementite along with alpha or it can also form alpha plus graphite. Am I right? Now of course, there are different types of cast irons, you know which is a very famous; grey cast iron.

Student: Nodular cast iron.

White cast iron, nodular cast iron or one more.

Student: Malleable.

Malleable cast irons. What is the difference between a malleable cast iron and a nodular cast iron?

Student: Morphology of the carbide component.

Anything more?

White cast iron is converted to malleable cast iron by heat treatment process whereas, the nodular cast iron goes directly from the liquid you get the graphite actually there. And what is the grey casting? Here also you get a directly, you get a graphite, but the graphite is in what form? It is in the flake form actually.

Now, you please read those people who have want to know more about for example, why should it form Fe_3C? Why, how is possible for you to move without forming Fe_3C, how you can have graphite? What are additions that added? All this you can read some books and there are nice books available, simple books you people read it.

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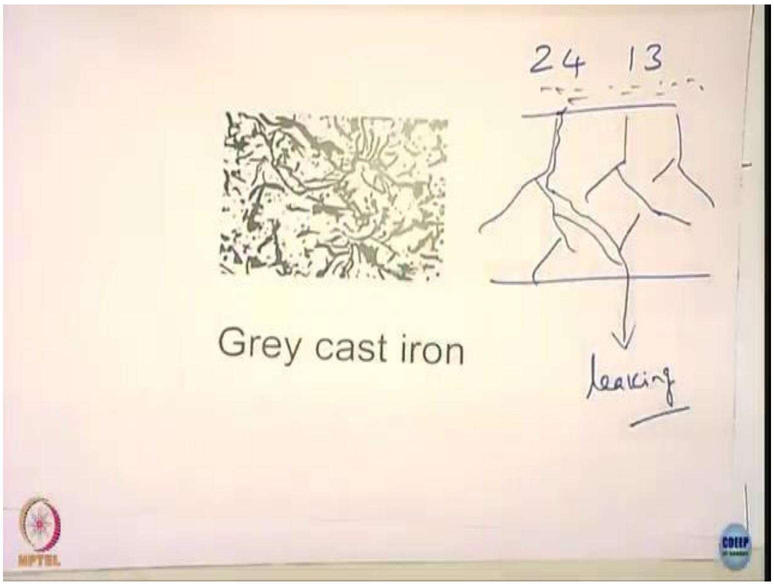

Grey cast iron

Now, it is important for you to understand the microstructure of cast iron in order to in order to understand what is called a graphitic corrosion. This is a grey cast iron. What you see these flakes, these flakes are all what? These flakes are all graphite, the matrix is a ferrite, it is alpha matrix. This is a gray cast iron.

But, what you need to know is this flakes they may look little isolated. Are they isolated? They are interconnected, these are all something like. So, if you have a thickness suppose you have a thickness of the cast iron, a flake may start from this end, it may end in this end actually. So, these are all not isolated, they are interconnected in the gray cast iron. This is a very important thing and for those who have not have an idea about gray cast iron, you should know this.

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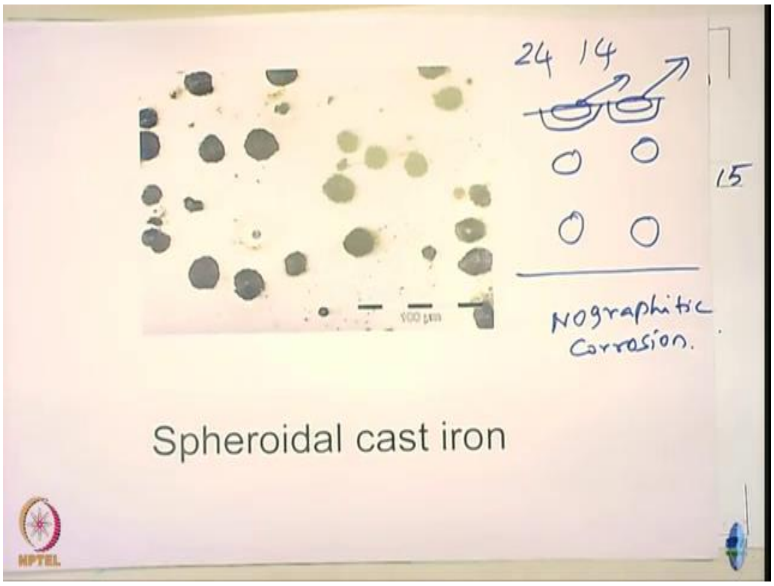

Spheroidal cast iron

If you take a spheroidal cast iron, it is a microstructure. Now, please notice these are graphites, it is a graphite and these graphites are not only spheroids spherical. And what difference does it make between the gray cast iron and this?

Student: They are not interconnected.

They are not interconnected, they are well separated. They are well separated; that means, each of this are surrounded by the matrix, it has got that good mechanical properties as compared to grey cast irons times, but anyway we are not going to discuss that that aspect. But, these microstructures have relevance for corrosion that I think you should be understanding it all. Please understand you have a graphite in the system, you have alpha in the system which alpha means its iron; a little bit of carbon dissolved there.

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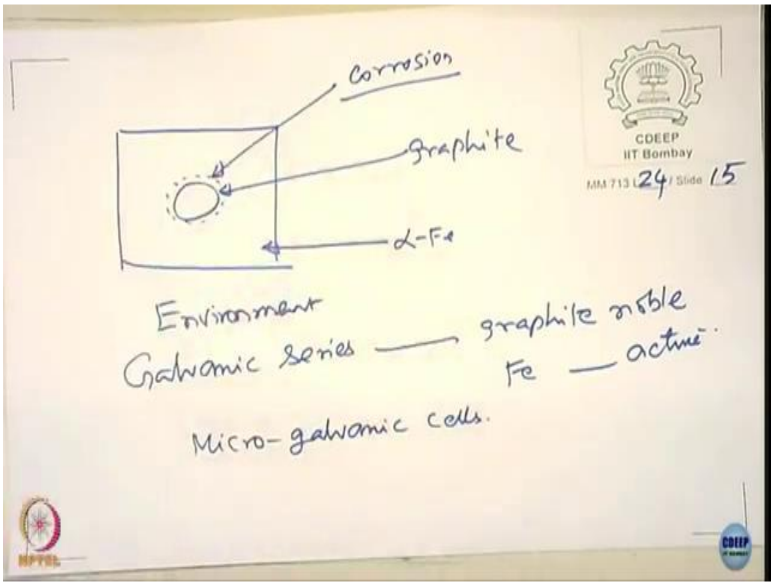

Environment

Galvanic series — graphite noble

Fe — active.

Micro-galvanic cells.

And so, that is what you normally see the system. So, what are the consequence of that? This alpha iron, it is a graphite here, I exposed to the environment, its an environment here what happens? What do you think will happen? I taken this alloy and exposed to the environment may be like sodium chloride solution or water moisture something like that. So, what do you think will happen?

Student: Iron will try to dissolve.

The iron will dissolve preferentially, why does it happen?

Student: Graphite is noble.

Yeah.

Student: Graphite is noble.

So, graphite is noble. So, if you look at the galvanic series, I hope you will able to recollect the galvanic series we have shown before; graphite is noble, iron is active. So, what is going to happen? You are going to have microgalvanic cells. It is not that typical dealloying like what you see in the in your brass or maybe in a cupronickel alloy system.

Here there is a distinct graphite phase and there is a distinct matrix of alpha iron and so, they have a have a different noble and active characteristics. And, the one which is noble will act as a cathode, the one with active will be suffering corrosion actually serious corrosion here.

So, what will happen? You will see the corrosion occurring in the interface the corrosion becomes severe. In the galvanic corrosion where is the attack more?

Student: At the interface.

At the interface ok, the interface corrodes. Now, it corrodes like that if you visualize this; so, what you have will happen here? In this case the corrosion suppose there the environment here environment, the corrosion starts it will proceed like that, proceed like this, proceed and start leaking here; because of continuous thing it leaks. On the other hand, if I take a nodular cast iron or a malleable cast iron, if you take a cross section like this; I may have some graphites here, I may have some graphites here and I have here, here like this.

Now, the corrosion will start here, here, start here. Now what happens? They fall off. Now, subsequently what happens to galvanic corrosion? Stops. So, galvanic corrosion does not proceed further, micro galvanic corrosion does not proceed further. So, that what happens now? That means, no graphitic corrosion. Now, the graphitic corrosion that occurs in the gray cast iron; obviously, depends on the environment.

So, see so, it is a pipeline, it is the soil, the soil chemistry becomes important, you have for example, you have an acidic soil and you have lot of chlorides; the attack it becomes more. Nowadays, they are not much of a problem because nowadays people do not use grey cast iron ion that much, because people have come to know there is a problem.

Earlier days when there were pipelines and the pipelines in fact, the problem started when they were paving the roads; I mean they start digging the roads, the excavator, the shock waves that went and hit this pipeline cause simply the cracking. See what happens imagine that I have a dissolution process here. What happens now? All the irons slowly dissolves, there is a residue of graphite just sitting on the surface.

So, it loses its mechanical integrity at all and so, even small impact given onto the pipeline if this fractures. So, this were the problems just after Second World War, there are lot of a problems, but nowadays of course, people are very clever; they do not use grey cast iron. But, it is important for us to understand the science behind this and why we do not use the grey cast iron for many of the pipelines, but cast irons are good.

If you compared a cast iron versus the steel, generally the cast irons corrode at a lower rate. I am talking about uniform corrosion, because the cast iron may have some silicon all the stuffs which they are more generally more resistance to uniform corrosion.

But, if a grey cast iron the problem comes that of the localized attack that happens between the graphite and the iron matrix leading to leaking of the pipelines. People in those days were storing even sulfuric acid, using the cast iron tanks. And, sulphuric acid will leak from inside to outside, old structure looks very intact.

But, it ooze out because this the corrosion occurs between the graphite flake and the matrix and so, start oozing out from the surfaces. So, only way to avoid here is that not to use grey cast iron people use, what is called as a malleable cast iron or the nodular cast irons. So, that should bring us to the end of the discussion related to the dealloying and the selective leaching and I want you to go through this and.