Surface Engineering for Corrosion and Wear Resistance Application Prof. Indranil Manna Department of Metallurgical and Materials Engineering Indian Institute of Technology, Kharagpur

Lecture – 32 Diffusion Coating Principle

Welcome to the 32nd lecture of Surface Engineering. In the previous lecture we discussed the theory the basically, the reason, why Diffusion Coating is why does it take place at all? Why does diffusional layer form? And what is the mechanism by which diffusion occurs? And what are the elements which are generally applicable for diffusion coating? And so on and also alluded to some of the practices.

But, in this lecture we are going to talk specifics about; the diffusional coating processes; concerning the 3 main diffusions here, the aluminum, chromium and silicon because, as I mentioned in the previous lecture; these are the 3 most important elements which, actually provide high temperature oxidation resistance or protection in aggressive environment to metallic substrates.

(Refer Slide Time: 01:11)

So, aluminizing as a name suggest actually, involves material which actually is created or creates, a thin aluminum rich or aluminum alloy rich layer. So, this is coated or the entire purpose is twofold; one is, atmospheric corrosion resistance not necessarily at high temperature including at room temperature and also elevated oxidation and environmental resistance against high temperature oxidation and environmental degradation.

This process is very much competitive and comparable with the, so called zinc coating and steel, but remember zinc coating is never exposed to high temperature whereas, whenever you expect the steel or metallic substrates to be exposed to high temperature like, we took the example of the compressor blades made of titanium or the turbine blades made up of single crystal nickel alloys exposed to 150 or so.

At such, high temperature we require something different than zinc and aluminum is one of the biggest bet for that kind of a foundation, but there is a large similarity because, both zinc and aluminium provide a sacrificial layer. So, essentially still the base substrate will remain cathodic but, the top layer of either zinc or aluminum. Let us talk about aluminum particularly. We will actually, reactant and then, form an oxide layer which. So, it sacrifices itself to protect the underlying substrate, which is steel or some other alloy.

Now, aluminum coating actually is more expensive than zinc coating, but when you are talking about high temperature you do not have a choice, because zinc is not an effective oxidation protection element at high temperature, because it has a tendency not only for reaction, but also reaching the volatile state but, so for high temperature this is certainly cost effective. So, the aluminum coating on steel or other metallic alloys can be obtained by hot dip coating, hot dip mechanism rolled in coating, spray coating or pack cementation a solid state process.

The important thing is that the coating that we apply actually grows with time. So, when we coat aluminum on steel then, this is how it appears as the cross section. So, essentially you will have a coated layer and then, you have also an inter diffusion layer where, this is this will this first layer will be very rich in aluminum and then, aluminum concentration as a function of depth will decrease and then, this is the substrate, which is unaffected. So, this layer thickness will depend upon the process parameters typically, the chemical potential, temperature time and so on.

(Refer Slide Time: 04:22)

O When a steel substrate is dipped in a pure aluminum melt for a sufficient period of time which may vary from 1 min and above, the intermetallic phase formed in the steel consists almost of only n phase (Fe,AL).

 \Box The growth of the layer is alloy usually represented by the diffusional growth rate: Here. σ is the thickness of the allov layer, k is a constant known as the growth rate constant, and t is Progressive development of intermetallic layer & interface between 1040 steel and pure Al after dip the holding time. periods of : (a) 10 min; (b) 20 min; (c) 40 min; (d) 6

So, when aluminum diffuses; see for example, when carbon diffuses in carburizing it does not form any of the compounds; it does not form cementite for that matter. It defuses goes dip inside and we retain carbon, then we convert that solid solution into martensite by certain heat treatment.

So, the hardness and wear resistance comes from the phase transformation product. In case of nitriding, we do form nitrides and they are the principal reasons for wear resistance, but that is done, the nitrates that form at high temperature, but the application is at room temperature. Now, when you expose steel or nickel or titanium or these elements which opted high affinity for oxygen to high temperature; you need elements to form a diffuse coating onto the surface, which will sacrifice itself form an oxide and prevent further ingress of anions.

 For example, oxygen. Now this is done not necessarily through a solid solution layer. So, the surface is an alloyed layer, which will have higher concentration of aluminium or chromium or silicon onto the surface, but they actually are confined to a thin layer, but they do not necessarily form only a solid solution of aluminum in iron or nickel or titanium.

In state, they are known to form certain intermetallic phases and these intermediate phases are very easy to understand as to why to they form? When you come; when you refer to the corresponding say, iron aluminum or nickel aluminium or titanium aluminium kind of a binary phase diagram.

 You will see there are multiple intermetic phase as possible to be formed in these binary systems. So, in case of iron typically, one such eta phase that form is an iron eliminate. Now, this is beneficial and matter of concern both; beneficial because, they are extremely stable has very high melting temperature and prevents oxygen ingression or cation say, iron or titanium to move out. So, they form a barrier layer.

So, this is the kind of barrier layer that, we are talking about and in fact, this barrier layer that we form aluminum rich layer will grow with time, if we increase the residence time in the furnace in the diffusion coating chamber. So, the cross section actually, will show us that, it is not pure aluminum. It actually, is an aluminum rich matrix phase with lot of these intermetallics. The thickness of that layer essentially, will depend upon the time at a given external condition and this k the constant here, is actually proportional to the diffusion coefficient.

And hence, one can write this k also very similar to a diffusion coefficient equation and can determine the value of k at a given temperature. So, this once this k is known, then we can predict what would be the thickness? So, sigma here is the thickness of the diffusion layer at a given temperature T for at the time of exposure small t and this is important for us to design the experiment through, which we actually, use or develop such coating.

Factors Affecting Aluminizing Process

So, there are multiple factors process parameters, which actually affect the thickness and the integrity of this coating. So, as I said, this is an intermetallic layer that we form. So, we have to be careful as to what is the time that we exposed to? Because, otherwise the layer that you form will be extremely hard and protective all right, but also is fairly brittle and most importantly, we will have a very different crystal structure and coefficient of thermal expansion than the underlying metallic substrate.

So, the coating substrate interface will be prone to development of very high stress as the layer of the thickness increases; thickness of the layer increases and hence, there could be spallation or crack formation at this coating substrate interface. So, the thickness or the interfacial layer adhesion will depend upon the dipping time and temperature. Now, if its steel, then the carbon content is important because, if you have a fair amount of carbon then, they actually not only change the growth rate and morphology, but also the composition of the intermetallic layer, that you form.

So, for low carbon steel, you actually can have a higher substrate higher thickness of the coating of the and the intermediate layer. So that means, ingression of aluminum faces less difficulty to diffuse in if the carbon content of the steel is low, but if the steel contains lot of atoms in the interstitial positions like carbon, then diffusion already the surface is stressed and further diffusion of aluminium, actually will be more difficult.

 The molten metal viscosity the bath, we are talking about is very important and also the wetting conditions a wettability or the angle of the surface with the angle of wetting also is very very important. So, we may actually at times add certain additives to change the bath composition. So that, the wettability increases at the surface he surface roughness; we are talking about the component, which is being coated. So, roughness of that surface is important because, generally the adherence to some extent depends on the surface roughness. In fact, a little bit of roughness is actually beneficial, because it causes a pigging effect on mechanical interlocking effect.

But, if it is too rough, then the penetration will be non uniform and the tip will melt or tip will actually get thicker coating and as a result the tip may get dislodged, because of the brittleness developed. So, thickness and morphology will; as I said, they can be changed by certain additions like silicon into the melt. So, instead of pure aluminum, here aluminum silicon then of course, the wettability decrease changes and actually, wettability increases and bath temperature can be little lower, but more importantly, you actually create a different kind of morphology onto the surface.

So, typically the if you increase higher and higher amount of silicon, then the depth of the allured layer decreases with the distance. So, the depth of the layer decreases as we increase silicon concentration in the aluminizing bath.

(Refer Slide Time: 11:48)

Hot Dip Aluminizing

Process diagram of continuous hot dip aluminizing of steel strip and wire

So, an industry scale the process actually is done continuously, not as a batch process unlike what is done in carburizing or nitriding cases? Not always nitriding, but carburizing pack carburizing for example, for sure. Or even back cementation processes; even for aluminum it can be a batch process, but industry scale, when you use a molten bath it can be completely are continuous process.

 So, you feeding sheets of small thicknesses may be millimeter less than a millimeter much maybe much less than a minute whatever is the sheet thickness; you do not necessarily bring them in the form of a coil. So, you feed in use a welder to create continuous aluminum sheet trails of train of aluminium sheet and instead of coiling, you actually make them such loop in the and you do it through our tower.

So, you go back and forth and then, you accommodate a large length of aluminum sheet in this form. The sheet is fade through these rollers and goes into the furnace. So, in between you can have certain annealing process to remove surface stresses or also any other kind of heterogeneity in the microstructure then, they are subjected to this aluminizing bath and it goes back and forth into the bath and this is the residence time here and the temperature are the two most important process parameters.

And as soon as the coating is over, you immediately cool rapidly. Because, you do not want to extend the time of exposure to high temperature or bath temperature or near to the bath temperature because, once the process is over then, you do not want any further diffusion to take place. And to prevent diffusion exist way is to reduce the temperature, because the coefficient will be so low that diffusion effect will be negligible.

So, you do rapid cooling and then, you draw it; there is a online mechanism through which you can measure the gauge thickness of the coating and then, it goes through. So, the excess by the excess aluminium sticking to the surface is removed through an air jet. So, the air jet removes a surface excess aluminum and also pinches the surface temperature.

So, it goes through this kind of a trail and then. So, we also have a loop tower where, certain chemical treatments are done maybe, another protective another treatment to make the coating more adherent certain types of surface conditioning the physical conditioning of the surfaces, then there will be a inspection non destructive evaluation through radiography or through certain visual inspections and so on.

And then the whole coil comes out and then, coiled into large you know, very several kilometer length of coils. So, this is the overall process. So typically, this is the temperature we are talking about; temperature can be even higher, but this is good enough depending on the particular application. So, we need certain pretreatment, which involves surface cleaning both acid and alkali bath cleaning. So, the surface is fresh metal and not carrying oxide thin oxide layer due to atmospheric oxidation.

 Then we do fluxing again to increase the wettability of the surface. So that, its fresh and it actually comes in contact with the directly with aluminium and aluminium can immediately wet the surface and form aluminium and not any mixed oxide or varied composition coating. So, then the coating happens in the hot dip bath like here and.

So, which is a molten bath? So, this is a molten bath and then, we have to do the up after treatment, which is wiping, air blasting or removal of excess aluminium and even rolling to make the uniform coating depth and physical form and they are withdrawn from the coating bath and then, coiled after the mandatory value evaluation of the surface condition.

(Refer Slide Time: 16:12)

So, calorizing is a process, where unlike the previous hot dipping where, we apply aluminum through the from the gaseous or the vapour state. Here also, we form intermetallic compounds of various types and typically applicable say, in case of stainless steel. So, when you expose stainless steel to aluminium.

So, austenitic stainless steel, then you actually can form various aluminates or intermetallic phases. So, this is comparable to the hot dip aluminizing, but obviously, that differs in the fact that, here the diffusion of aluminium is occurring in the solid state or substrate is completely there is no molten layer at all on the in contact with the surface.

And the entire amount of aluminium is coming from the vapour state. So, the objectives would be just like the previous case; high temperature oxidation resistance erosion or abrasion resistance, any protection against carbon ingress I mean in various cases for example, stainless steel or for that, matter any other steel or certain materials, when they are exposed to carbon containing atmosphere, there is a possibility carbon can come in and it may not be beneficial, because it may form certain interstitial compounds or changed crystal structure.

So, carbon ingress must be prevented and this kind of aluminite layer actually prevents carbon ingression; also this is helpful for stress corrosion cracking if you to have such aluminite layer and resistance to corrosion erosion by any other kind of molten metal. So, if you have a bath, which actually has these molten zinc or other metals there could be a large corrosive attack and that can be prevented by having such eliminate coating or aluminium coating.

Also protection against nonmetals like, these corrosive gases, liquids and ashes and so on. So, typically an calorized surface will have very high amount of aluminum. So, this is the depth and this is the concentration. So, aluminum will be very high; nickel is generally low, but if you have nickel already in the substrate, that will be fairly high only below a certain layer. So, this is the diffusion layer altogether, but within the diffusion layer, we see that, the surface is rich enriched with aluminum and having very low content of other elements like, nickel, chromium and so on.

We are talking about a alloy, which contains all these elements. So, this is the base level of chromium and aluminium, base level of aluminium. So, there is no aluminum in the substrate or very little aluminum in the substrate, but very high aluminium in the surface. So, this diffusion layer is because, of the principles of diffusion coating, but still, I must point out that, this dip is fairly sharp. So, the interface coating substrate interface is much sharper than, let us say carburizing carburized layer.

(Refer Slide Time: 19:20)

SILICONIZING

□SILICONIZING is the diffusion of silicon onto steel surface **OThere** are **pack** and retort processes in which parts are subjected to gas atmospheres that react with the heated part surface to produce nascent silicon that diffuses into the substrate to be coated

- □One process involves tumbling parts in a retort filled with silicon carbide: when the work load reaches a temperature of about 1010°C, silicon tetrachloride gas is introduced which reacts with the part and the SiC particles to produce a concentration gradient of silicon on the part surface. The silicon diffuses into the part and forms a case. \Box Case depths can be as thick as 1 mm.
- **This process is normally done on low-carbon steels which**
- develop a case that has a silicon content of about 13 %.

OSiliconized steels have very good corrosion resistance to a number of oxidizing aids, and they can develop case hardness of about 50 HRC.

We can also apply silicon, as an element to protect substrate from high temperature oxidation through a basically, a pack process pack; you pack the silicon containing elements or substances in a retort and intention is to get silicon in the nascent form. So that means, you will use a certain precursor say, silicon carbide and also use silicon tetrachloride in the gaseous form you bubble through the substrate as to the mixture containing this silicon carbide and this will liberate silicon nascent silicon and that, silicon can now diffuse into the surface.

So, we are talking about in case of aluminium coating we understood that, we are talking typically, a few tens to a few hundred micrometers of silicon aluminum rich layer, but in the limit it can go to several millimeters. But usually, silicon rich layers are less than a millimeter; purely because the silicides that form instead of aluminates are actually slightly more complex in crystal structure and also forms slightly more brittle layer. So, the silicon layer can be formed on low carbon steels and I would say, anything between 8 to 10 percent at the most 12, 13 percent would be the silicon content on the surface.

You can get fairly high hardness, but resistance against both corrosion and oxidation at high temperature is the benefit that we derive.

(Refer Slide Time: 20:54)

CHROMIZING

O Chromium can be applied from a pack as in siliconizing.

- **Q** Parts are packed in **chromium** powder and an inert filler such as aluminum oxide, and a salt is introduced that will go to a vapor phase at the processing temperature and serve as the carrier gas to bring chromium to the surface of the part.
- One such gas is ammonium iodide, which transforms to chromous iodide at the processing temperature of about 1800° to 2000°F (980° to 1090°C).
- □ A process (Chemical Vapour Deposition) without the pack is also used to coat the parts in a retort and introduce the chromium rich gas with a carrier gas such as hydrogen.
- \square The species to be coated is introduced as a gas mixture into the treatment/coating chamber where the desired species is deposited after decomposition and condensation. As sufficiently high temperature, diffusion of the condensing species will occur and a diffusion coating is obtained.

Instead of aluminum or silicon, we can use chromium for the similar purpose. Here the precursor will be pure chromium powder with aluminum oxide powder mixed with that and then we heat this salt in to create this vapor phase, the reactant here will be ammonium iodide. So that chromium reacts with ammonium iodide and forms chromous iodide which is a fairly unstable compound.

Comes in contact with the solid metal reacts typically about this temperature and then liberates chromium from chromium iodide. So, iodine comes back into the solute into the atmosphere again reacts with chromium forms chromous iodide and so on. So, this is how the process continues and its a batch process. So, beyond a certain period of time you need to recharge ammonium iodide, so that the remaining part of chromium can be utilized.

A similar process based on CVD; Chemical Vapor Deposition can be also used for diffusion coating of chromium on steel or any other metallic systems based on diffusion principles very similar diffusion principles.

(Refer Slide Time: 22:09)

So, another interesting process, which is not necessarily a diffusion based process, but is used for very similar purposes. So, I thought; I would just include then, here for comparison and these are called roll bonding process. In fact, they can be roll bonding; they can be diffusion bonding and so on.

So typically, when you talk of roll bonding you are talking about two or more metals as parallel layers fed into a roll and then roll together. So, when you roll together if the interfaces between different layers is free from grease or dirt or water or oil; that means, completely metal to metal surface is completely guaranteed and without any discontinuity then, during rolling the deformation occurs and during deformation they will also be possibility of mechanically driven inter diffusion. So that means, the metal from sheet a diffuses into sheet b and sheet b atoms can also diffuse into sheet a.

So, there will be an divisional layer inter diffusion layer. So, for the mating surfaces should be very well cleaned, ground, decreased to increase the friction coefficient and any amount of oxide layer or compound layer has to be completely removed by either chemical or physical means.

So now, you actually do a roll bonding or a cumulative roll bonding, when you push them into the roll. In fact, and there is no necessarily all of them should have same thickness. Actually, their layer to be coated has a much smaller thickness typically, a foil of aluminium for example, can be rolled together on sheets of metal; even nonmetal.

So, because there is no direct diffusional process, thermally activated diffusional process involved. So, we actually rely upon high reduction ratio and that is when, the inter diffusion takes place due to mechanically driven plastic flow. So, when somebody sections the division bonded layer, then one sees that, there could be certain amount of diffusional layer.

 Now, question is very why do we need such a process? What is the limitation of aluminizing, chromizing or siliconizing process? Think of a heat exchange here or large body heat transfer medium. So, you are talking about several meters by easily a meter width to subject such wide a long sheet for diffusional coating; you require a furnace of that nature or a path of that nature; if its a batch process; if its a continuous process.

Then you actually should have so much of consumption so much of demand to make it batch process, but for smaller substrates for smaller areas or a limited number of applications limited consumption, yet wider surface area, where we you need such protective coating roll bonding is a typical method. It can be a not only necessary batch process; it can be also a continuous process. So, this is an aluminium metal and this is a copper metal and this is how, you actually form a clad of aluminum copper through this role bonding processes.

But, remember here the pressure, whatever we apply is applied only when, you are passing through the rolls. So, temporary transient you can also do a diffusion bonding process, where you have alternate layers of let us say, gray and a red metal two different types of metals and they are pressed together in they have uniform thickness in they and also arranged in some alternate sequence and now, when you apply pressure and then expose to high temperature. So now, diffusion takes place all along the surface throughout the surface at this high temperature for a period of time.

And they form a complete diffusion bonding. So, this is diffusion bonding and not necessarily diffusion coating, this also is roll bonding and not necessarily coating. So, you actually retain exact composition of the coating material and like in the previous cases, where the composition varies various aluminize, various silicides or chromides form. Also, this is in case of roll bonding its a dynamic process in case of diffusion bonding, its a static process.

So, you actually place it inside the furnace and then, its a batch process, where you expose for a certain period of time. So, they also have their set of utilities particularly, as I mentioned for large heat exchangers or any other thermal heat exchange processes.

(Refer Slide Time: 26:57)

Points to ponder (recapitulation):

- 1. What is the difference between aluminizing and pack cementation?
- 2. Which process is faster and more adherent hot dip or pack cementation of any element?
- 3. What role does vapor pressure play in pack cementation or diffusion coating process?
- 4. How is Al-coating better than galvanaizing? $(\sqrt{1})$
- 5. What are the common process parameters for DC processes involving Al, Cr, Si, etc.? $\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{6}$
- 6. What are the merits and demerits of roll bonding compared to DC?
- 7. DC , diffusion and roll bonding are they same?

So, what did we discuss? We discussed about the typical differences between aluminizing and pack cementation. So, aluminizing is a hot dip process whereas, pack cementation is a solid state process primarily.

So, molten bath allows the aluminium nascent aluminum to come to the surface and then diffuse in whereas, in pack cementation you take it to you use a take the help of sodium fluoride to take to the aluminum fluoride vapors condition and then allow AlF to decompose and liberate aluminium to the surface. So; obviously, in the hot dip process this you are exposing to not only high temperature, but you are guaranteeing a very high wide coverage, very good coverage to the entire surface area.

The process can be actually faster because, its can be a continuous process. So, you can pull from one end to other and can make kilometer meter long of long strips coated with the aluminium and coil them into large coils at a faster rate. We actually must realize that, the vapor pressure plays a very important role in this all packs imitation processes or all diffusional coating processes, because the element should have actually very high vapor pressure. So that, it has a natural tendency at when exposed to high temperature to go into the vapor phase and saturate the atmosphere with that particular vapor.

So, it should have actually a vapor pressure higher than the substrate metal. Aluminum coating is better than galvanizing not always, but certainly is better than galvanizing at when the temperature is high at high temperature. The process parameters, when we talk of all these diffusional coatings are typically temperature, time then the concentration of the species or the chemical potential of the species surface condition viscosity of the bath; if it is a dip process and surface roughness is physical conditions and so on.

And we have to be very careful about maintaining such conditions or these parameters. So, roll bonding is a process where, we actually can cover wide area and we do not necessarily have to expose to high temperature. So, room temperature process can cover wider surface area and can actually coat with something, whose composition remains the same does not change.

Or the utility or the merit points the demerit is that; it is a roll rolling process. So, you cannot do for complex shapes, you cannot press under the roll something which has an non uniform surface contour. So, diffusion coating, diffusional processes, diffusional bonding and roll bonding, they are very similar, but not exactly the same. In diffusion coating with you are talking without no application of pressure both in diffusion bonding and roll bonding, you are talking about application of pressure, but these are essentially high temperature processes and allows diffusion is the primary reason for such coating and mechanical activation also in diffusion coating.

And mechanical activation is the main reason for roll bonding processes. So, these are the processes which we wanted to discuss. So that this is how we actually can create fairly high protection of metallic substrates against high temperature oxidation or other environmental degradation processes.

(Refer Slide Time: 30:51)

References

- Kenneth G. Budinski, Surface Engineering for wear Resistance, 1988, Prentice Hall
- https://www.revolvy.com/page/Cold-welding\
- http://35.185.168.255/clad-steel/plate-clad-steel-plate/ steel-plate-type-roll-bonded-clad-plate/
- http://www.shinto-lance.co.jp/others/others_e.htm

So, thank you very much for your attention.

 $47 - 4$