Surface Engineering for Corrosion and Wear Resistance Application
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Lecture –31
Diffusion Coating Principle

Welcome to the 31st lecture of Surface Engineering. We have discussed various processes; we are now actually considering various types of coating processes possible. We have done with mostly so far mostly with interstitial elements and now we are going to go into a different types of coating which are branded as Diffusion Coating.

But before we go into the coating processes and the mechanism and motivations, I first would like to pose or say a few words as to why a diffusion coating is so important for one of the most elegant engineering machine that we can think of.

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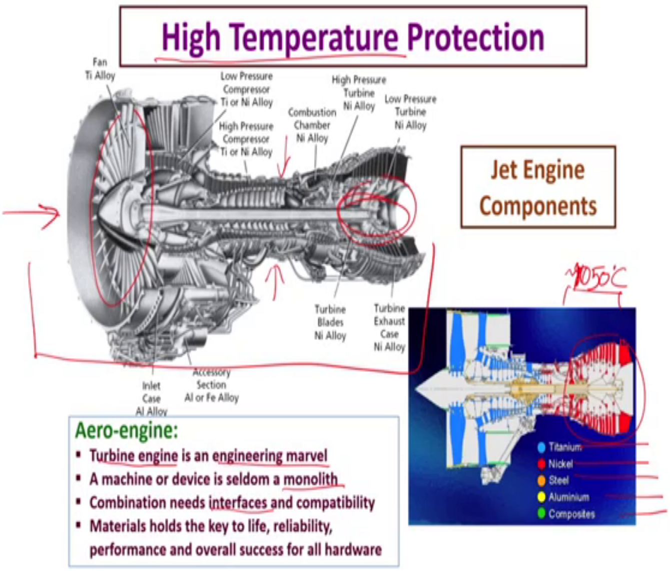

High Temperature Protection

Jet Engine Components

Aero-engine:

- Turbine engine is an engineering marvel
- A machine or device is seldom a monolith
- Combination needs interfaces and compatibility
- Materials holds the key to life, reliability, performance and overall success for all hardware

So, if you look at this view graph what you are seeing here is an engineering view of jet turbine engine. So, this is the compressor part through which you suck in air and perpendicularly you feed in fuel and then at the specific combustion chamber. The air and fuel they are mixed and led to combustion and that creates the thrust and this is happening at the high temperature zone.

The basically their combustion zone and these materials while in the compressor part is made up of these blades are made up of titanium alloys, because the temperature expect it is less than 500 degree centigrade somewhere around 354 degree centigrade. There is the combustion zone we expect easily that much higher temperature, say to the tune of 1050 degree centigrade.

Now, at such high temperature in order to maintain the integrity and life and reliability of the component this is a very major task; primarily, because of the high temperature and also very aggressive environment because of the presence of oxygen and other oxidizing elements. So, it is probably not an exaggeration to say that the turbine engine is really one of the biggest engineering marvels.

And in particular the materials that make up this compressor part and in particular the combustion zone that turbine blades they truly represent one of the biggest trials of materials engineering. For one single reason, the turbine blades are made up of usually by nickel based super alloys; so, this red colored region represents the nickel based super alloys, which contains easily about 8 to 10 elements of very different melting temperature, density, specific thermo physical properties like specific heat and so on vapour pre pressure.

And also including some of the interstitial elements to have all those 8 to 10 elements into a single solution and retain them through a process of solidification which leads to not only a usual poly crystalline aggregate, but actually single crystal is a enormously difficult. Yet, these blades which actually make up the turbine part of the blades for the turbine at the combustion zone, they are made from single crystal nickel based super alloys.

Now, protection of these alloys at that high temperature and high oxidizing condition is a major issue. So, in all these major engineering progresses we actually have to realize that none of these materials that we use are a monolith. So, they actually first of all they are multi-component systems and then there are interfaces; so, we actually need to combine say titanium with nickel or weave as we move from one region to another the kind of materials that we use change from place to place.

So, the outer shell can be the made of aluminium, some other load bearing components which are not exposed to high temperature can be made of composites. We do use steel quite a large extent, but as I said the compressor part is made up of titanium alloys and the combustion zone that the turbines are made from nickel based super alloys.

So, multiple types of alloys and materials. So, we need since we have multiple types of materials we have interfaces and they need to be compatible with each other. So, the materials that we use they must offer the right kind of properties and as a result of which we can ensure the life of the component, the reliability, the performance efficiency and the overall success.

So, for any hardware whether it is a turbine engine or a machine at room temperature or a tiny little component sensing some gases in all those hardwares. Ultimately we must realize that is the material which holds the key for the success because the kind of functionality that we want to derive will depend upon whether the material the inherent material is able to perform to the extent desired.

In this particular case while we are discussing high temperature protection of metallic components, we first should realize that as we exposed metals to high temperature they have a natural tendency of converting into oxides, because that is how they are stabler in terms of the Gibbs energy.

So, when we reduce and win metal from those oxides and yet exposed them to high temperature, all these metals will have a natural tendency of going back into the more stabler form which is primarily the oxides. And the job at hand is how we protect them at high temperature and that to one of the highest possible temperature where any kind of metalic system is exposed to for any type of engineering application.

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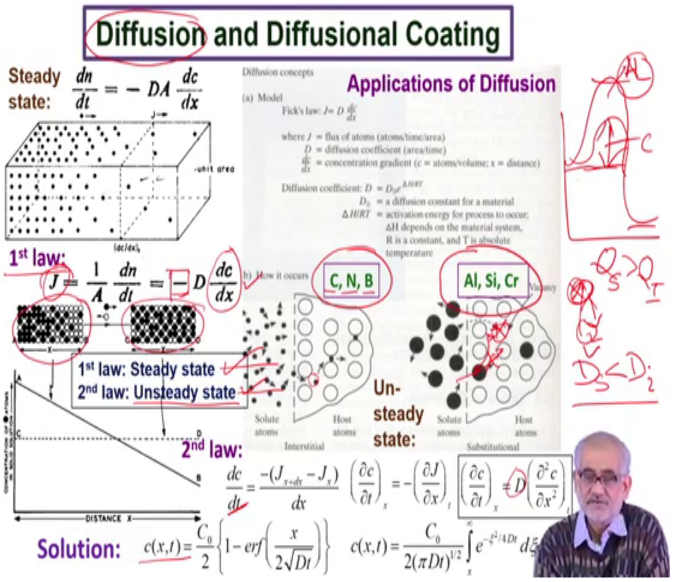

Diffusion and Diffusional Coating

Steady state: $\frac{dn}{dt} = -DA\frac{dc}{dx}$

1st law: $J = \frac{1}{A}\frac{dn}{dt} = -D\frac{dc}{dx}$

1st law: Steady state
2nd law: Unsteady state

Applications of Diffusion

Diffusion concepts

(a) Model

Fick's law: $J = D\frac{dc}{dx}$

where J = flux of atoms (atoms/time/area)
D = diffusion coefficient (area/time)
$\frac{dc}{dx}$ = concentration gradient (c = atoms/volume; x = distance)

Diffusion coefficient: $D = D_0e^{-\Delta H/RT}$
D_0 = a diffusion constant for a material
$\Delta H/RT$ = activation energy for process to occur; ΔH depends on the material system, R is a constant, and T is absolute temperature

(b) How it occurs

C, N, B

Al, Si, Cr

Un-steady state:

2nd law:

$$\frac{dc}{dt} = \frac{-(J_{x+dx} - J_x)}{dx} \quad \left(\frac{\partial c}{\partial t}\right)_x = -\left(\frac{\partial J}{\partial x}\right)_t \quad \boxed{\left(\frac{\partial c}{\partial t}\right)_x = D\left(\frac{\partial^2 c}{\partial x^2}\right)_t}$$

Solution: $c(x,t) = \frac{C_0}{2}\left\{1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)\right\}$ $\quad c(x,t) = \frac{C_0}{2(\pi Dt)^{1/2}}\int_x^\infty e^{-\xi^2/4Dt}\,d\xi$

So, the protection actually comes from diffusional coating or so called diffusion coating. So, at this point we have been talking about multiple processes surfacinging processes including carburizing nitriding and so on which are diffusion based. And I did mention the importance of diffusion in such cases, but let us take a look at the exact that mechanism and the kinetics of diffusional processes.

So, there are two types of diffusion one can think of when we actually have a steady state diffusion and also a situation where we can have an unsteady state diffusion. So; that means, where the composition between two specific points, changes or does not change. If it does not change then we say steady state diffusion and if it changes with time then we say non steady state or unsteady state diffusion.

So, in a steady state situation we all know that we refer to the Fick's 1st law, where the flux per unit area will be proportional to the compositional gradient. And of course, D is the diffusional diffusion coefficient, the negative sign as we all know is because of the fact that composition actually decreases right down the distance.

To be more precise actually the diffusion rate depends more upon the partial molar free energy or the chemical component. So, essentially diffusion occurs down the chemical potential gradient, but here in we since there is we are not bringing the enthalpy component for our discussion here. We simply can say that the flux of diffusion under steady state will be proportional to the composition gradient.

In the non-steady state where we have applied a finite quantity of diffusent then over a period of time, the diffusent or the diffusing atom we will the amount of fit available for diffusion will reduce. And as it reduces then obviously, the potential the chemical potential gradient or the composition gradient also changes. So, that is what is known as unsteady state.

So, typically if the steady state is maintained then we see that over a distance, the composition remains along the line C D, but as the composition changes with distance that is the typical non-steady state or with time that is the situation when we have the. So, initially if this is the kind of profile we have in the solid then after a period of time when everything the solute atoms have mixed well in the system and have come to a steady state then we will end up in a situation where the composition will be governed by this line C D.

But, in the beginning will when we have a definite gradient that is enough of a reason for diffusion to occur. So, as we say that Fick's 1st law governs the diffusion under steady state, the Fick's 2nd law governs the diffusion kinetics for the non-steady state situation. So, here we are bringing the time component; so, compositional change as a function of time actually through this mathematical.

In our exercise can be expressed in the following form where dc dt the change in composition with time will be proportional to the second derivative of composition with distance. So, d 2 c dx 2 and obviously, D is the diffusional coefficient.

So, under very specific boundary conditions we can find an error function solution for the composition profile as a function of distance x and time t small t and this is how we actually can find out what is the concentration at a given distance or at a given time, at a particular distance. So, these kind of solutions are actually very important for us to determine what will be the depth of diffusion, what is the profile of diffusion and so on and so forth.

So, while talking about diffusion, we must not forget that we are talking about essentially two types of possibilities; one is where the species is so small that it does not need to displace any existing lattice atom and create a vacancy. So, there are interstitial holes available and the species being so small they can find their way through and go into go and sit into those interstitial positions. But this cartoon actually shows much bigger than what in usual situation we see as the possible size of the void available for interstitial atom accommodation.

In other words all I am trying to say is that interstitial atom invariably will be bigger than the interstitial hole diameter that is available. So, as a result each atom that diffuses into then interstitial position will create as the strain stress filled around and as a result this solubility will be restricted. But, the important point here is that these elements carbon, nitrogen, boron or for that matter even hydrogen and oxygen they all are much smaller than the usual lattice atoms diameter of a lattice atom in a metric system. So, they can find themselves easy to get accommodated in the interstitial positions and that is what we call as interstitial diffusion.

On the other hand when we talk of other atoms like aluminum, silicon, chromium, manganese, zinc or all kinds of other rest of the elements they size wise will be comparable to the size of the atoms in the lattice sitting in the lattice. So, then you require the other kinds of mechanism which is called vacancy exchange mechanism.

So, if you have a vacant spot here, this position was lying vacant for whatever reasons the atom which is supposed to be here probably managed to go into the surface or probably moved out to another place and left behind a vacancy. So, in such a situation it is easier for an species which is coming from outside either from the vapor phase or the liquid phase or even solid space solid state, they it actually finds a position here.

And from here when it wants to go to the next position instead of directly going here it will always try to go and exchange with the vacant position. So, if this is a vacant position and this is an atom, we what we see usually is a tendency of exchange. So, in the atom hops to a vacant position, it occupies the vacant position and then substitutes a vacancy and in the process creates a vacancy here.

So, this is applicable to all the atoms which size wise; which our size was comparable to the existing lattice atoms. And for such elements when we talk of a diffusional process, we have to realize the corresponding activation barrier, which is typically in a typical reaction; coordinate will say that this is the so called activation barrier and this barrier is usually higher for say aluminum than say copper.

Why so, because for substitution or diffusion you first have to create a vacancy; so, you spend energy in creating a vacancy either by the same process or must have been done earlier. So, you budget that energy component also into it so, that the amount of energy required to create a vacancy is a part of vacancy base diffusional mechanisms or so called exchange mechanism.

So, the activation barrier in the process is higher so, the Q for substitutional diffusion will be higher than the Q were the activation energy for interstitial diffusion. And as a result we all are aware that substitutional diffusion coefficient will be smaller than the diffusion coefficient for interstitial atom diffusion at comparable conditions of temperature.

So, keeping this in mind we also should realize that when we are talking about interstitial diffusion then exact quantity or the concentration is important, but not so important. But when we talk of substitutional atoms then we divide them into categories like impurity diffusion, where the amount of diffusion is very small or chemical diffusion where the amount of division is larger. So, there are different other categories of diffusion. So, this background was necessary for us to relate well to the process of diffusion coating.

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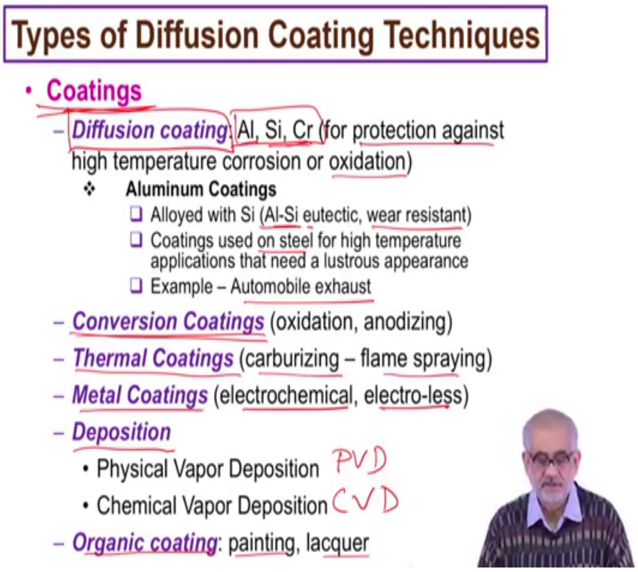

Types of Diffusion Coating Techniques

- **Coatings**
  - *Diffusion coating*: Al, Si, Cr (for protection against high temperature corrosion or oxidation)
    - **Aluminum Coatings**
      - ☐ Alloyed with Si (Al-Si eutectic, wear resistant)
      - ☐ Coatings used on steel for high temperature applications that need a lustrous appearance
      - ☐ Example – Automobile exhaust
  - *Conversion Coatings* (oxidation, anodizing)
  - *Thermal Coatings* (carburizing – flame spraying)
  - *Metal Coatings* (electrochemical, electro-less)
  - *Deposition*
    - Physical Vapor Deposition PVD
    - Chemical Vapor Deposition CVD
  - *Organic coating*: painting, lacquer

Now coating is essentially creation of an extraneous layer on top of an existing solid so, this is an addition based surface engineering. So, in this defeat and when we talk of diffusion coating immediately you will think about the elements like aluminum silicon and chromium. Because, these three elements have very high affinity for oxygen and in the Ellingham diagram of standard Gibb’s energy as a function of partial molar energy of oxygen if you plot, you will see that these lines are usually always much lower than all other oxide lines for metals.

So, which means that they are the most stable oxides or if you have competition between a cation; some cation and aluminum for oxygen obviously, oxygen will win over because they have a higher affinity and also the oxide is stabler. So, taking Q from this discussion all the diffusion coatings which are used to protect; for example, the turbine blades at 1050 degree centigrade, they are usually based on some coating which will have one of these elements usually aluminum. Because aluminum has very high affinity for oxygen, it creates an oxide layer on top and this oxide layer will protect further ingress of oxygen from atmosphere into the metal and as a result further oxidation or loss of metal will be prevented.

So, this is the way we protect against high temperature and high temperature oxidation primarily which is a single electrode process or can be corrosion also possible at high temperature. So, aluminum coatings can be applied as an alloy for example, aluminum silicon eutectic alloy for various wear resistant applicant can be for various resistant applications as well. But usually, these aluminum silicon eutectic alloys are applied when wear resistance is an intention or objective.

But coatings on steel for high temperature also are based on aluminum for example, the automobile exhaust. Obviously, here we are talking about a few hundred degree centigrade certainly not very high temperature. Now we also so diffusion coating essentially is a process of applied development of a coating which is based on species diffusion from surface into the interior.

Conversion coating is a process which also is widely used for protection of metallic substrates in corrosive or oxidative or even tribological situations. But these are called conversion coatings because there is a chemical reaction that takes place at the surface, which converts the surface from metallic into and complex oxide or some other complex in to metallic form.

We also can think of thermal coatings which are essentially coatings applied at high temperature, the very process of coating is by exposing the entire substrate to high temperature. So, that elements like carbon or nitrogen can diffuse in and it can be through a pack process or can be through a process which actually does not need any diffusion at all. But with the existing amount of carbon you can apply certain phase transition and bring in a new phase onto the surface which can provide you high trouble resistance against wear; for example, flames spraying or induction hardening.

We can have also metallic coatings for example, we can use either by electro chemical process which typically we called electroplating or we can do it through electroless coating where we are to convert an oxide and allow certain elements to be diffused to the surface. So, processes are very similar sounding, but not exactly the same. We can also deposit directly a thin layer much less than of the order of a few micrometer or even less either by physical vapor deposition or by chemical vapor deposition.

In physical vapor deposition the composition of the target which is deposited onto the surface is the same as the as a coating that you develop. On the other hand in chemical vapor deposition you actually have a situation where the species actually could be multiple and there could be reaction occurring in the vapor state and then reaction layer is deposited or the species can diffuse to the surface and at the surface can lead to certain chemical reaction.

We can also have organic coatings particularly on polymers or even on metallic substrates in the form of paints and lacquer, which actually provides a protective layer against any kind of scratch or other damages at room temperature. So, in all these processes be diffusion coating, conversion coating or metal whatever, we are discussing they all actually are based on the principles of diffusions. So, diffusion plays a very major role in creating these coatings.

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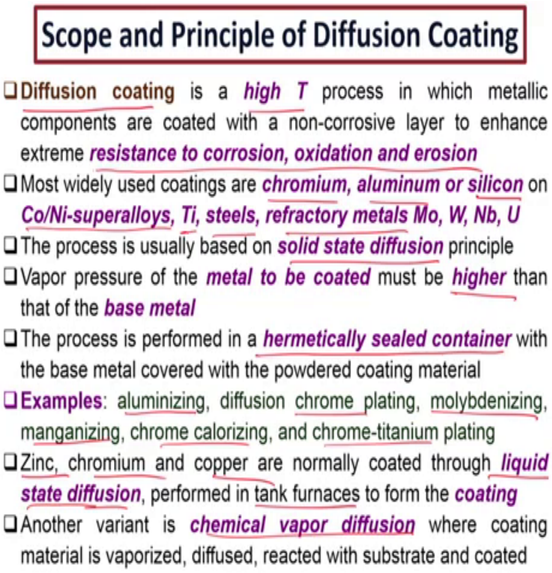

Scope and Principle of Diffusion Coating

- ❑ **Diffusion coating** is a ***high T*** process in which metallic components are coated with a non-corrosive layer to enhance extreme ***resistance to corrosion, oxidation and erosion***
- ❑ Most widely used coatings are ***chromium, aluminum or silicon*** on ***Co/Ni-superalloys, Ti, steels, refractory metals Mo, W, Nb, U***
- ❑ The process is usually based on ***solid state diffusion*** principle
- ❑ Vapor pressure of the ***metal to be coated*** must be ***higher*** than that of the ***base metal***
- ❑ The process is performed in a ***hermetically sealed container*** with the base metal covered with the powdered coating material
- ❑ **Examples**: aluminizing, diffusion chrome plating, molybdenizing, manganizing, chrome calorizing, and chrome-titanium plating
- ❑ Zinc, chromium and copper are normally coated through ***liquid state diffusion***, performed in tank furnaces to form the ***coating***
- ❑ Another variant is ***chemical vapor diffusion*** where coating material is vaporized, diffused, reacted with substrate and coated

So, what is a guiding principle for this; so, for diffusion coating we understand that we are talking about high temperature process and main intention is to induce sufficient resistance against corrosion, oxidation, erosion even in some cases wear and so on. So, the coatings usually that are used are based on chromium, aluminium, silicon. Typically for high temperature application hydrometer resistance applications on super alloys like cobalt and nickel base super alloys or on titanium on steel or refractory metals like molybdenum tungsten very high melting materials even the prone to oxidation.

So, you need certain coating to prevent oxidation of those metals. So, oxidation is essentially a degradation process which converts the precious metal into a non-usable form which is oxide; because it is fairly brittle and non-workable. The process is based on solid state diffusion as we have been saying all along and the metal to be coated actually should have higher vapor pressure. Because then only it can go into the vapor state very easily and saturate the atmosphere around with the vapor of the desired species and which can subsequently get deposited on to the surface in nescient form and then start diffusing.

So, we need a hermetically sealed container because we do not want oxygen to sneak into the chamber, because we all are aware that oxygen immediately will react with metal surface at high temperature and create an oxide layer. Moment it forms an oxide layer of the base metal itself, that oxide layer will actually create a barrier layer. And the desired species say for example, aluminum or chromium or silicon will not be able to penetrate a layer which is iron oxide on top of steel. So, the whole exercise will be futile.

So, we have to make sure that the chamber is not having oxygen or even if it has oxygen, we should use some getter to kill that oxygen residual oxygen and make it completely vacuum; either in vacuum or completely and non-oxidizing atmosphere or reducing atmosphere. So, we can; so, typically when we apply aluminum we call it aluminizing, when we apply chromium we call it chrome plating, but this can be in many ways. Whenever we use the word plating it usually involves a necklace electrolyte or even a vapour state. We can apply molybdenum and call it molybdenizing or manganese and call it manganizing chrome colorizing this is a solid state process or chrome titanium plating and so on.

So, plating as I said is a typically an aqueous or electro chemical process. Now, zinc chromium copper are also very popular materials for coating, but these are usually done through some liquid medium or a liquid electrolyte. And as they are a different subject altogether we will discuss separately, when we discuss electrochemical deposition or plating. And they are performed in tank furnaces maybe at room temperature, maybe at high temperature.

The other process that we alluded to is called chemical vapour deposition, where actually they are exposed to high temperature and then they can react in the vapor state and then deposit or at the surface can react with the base metal and create a different composition.

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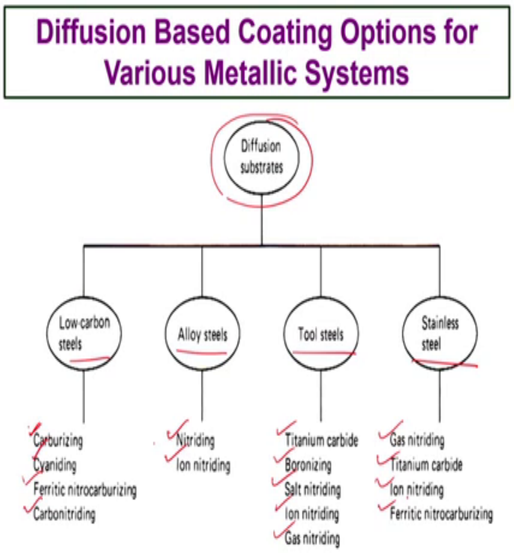

Diffusion Based Coating Options for Various Metallic Systems

Diffusion substrates

Low-carbon steels
- Carburizing
- Cyaniding
- Ferritic nitrocarburizing
- Carbonitriding

Alloy steels
- Nitriding
- Ion nitriding

Tool steels
- Titanium carbide
- Boronizing
- Salt nitriding
- Ion nitriding
- Gas nitriding

Stainless steel
- Gas nitriding
- Titanium carbide
- Ion nitriding
- Ferritic nitrocarburizing

Now, just for comparison I thought I would we should also refer to the competitive and comparable diffusional processes. So, if you have a substrate say for example, it can be a low carbon steel, alloy steel, tool steel or stainless steel various forms of steels with their own set of utility is very important with very important applications possible applications.

So, for low carbon steels you can think of carburizing or cyaniding when we are talking about bringing in nitrogen or nitro carburizing with then both nitrogen and carbon are introduced or carbon nitriding. Depending on which is the preferred species; I mean nitro carburizing when nitrogen is preferred or carbonitriding with carbon is preferred.

So, in one case we form carbon nitrogen or compounds basically complex interstitial compounds and in some cases like here we can also have martensite along with those interstitial components. So, alloy steels actually can be coated with nitriding, or ion nitriding process, tool steels which carry elements like titanium or chromium or vanadium which have very high affinity for carbide formation. So, they can be subjected to processes which can form some titanium carbides or boron various kinds of borides. So, these processes like salt nitriding, iron nitriding, gas nitriding they can lead to formation of coated layer onto the surface.

On stainless steel we can think of gas nitriding, titanium carbide formation or ion nitriding and nitrocarburizing so on. So, what is the difference or what is the relevance here to this bring in all these subjects. They all are based on interstitial diffusion or process, they also diffusional processes. Hence they can be called diffusion coating, but then they have their own names like nitriding, carbon carburizing, carbon nitriding and so on, just to distinguish the generic process of diffusional coating.

So, whenever one talks about diffusion coating typically we are talking about chromium aluminium and silicon which have very high affinity for oxygen and the process will be through substitutional diffusion and the application usually is high temperature protection. Whereas, these things actually all these processes can be not necessary actually not for high temperature protection, but for room temperature or slightly elevated temperature resistance to wear and other tribe illogical purpose.

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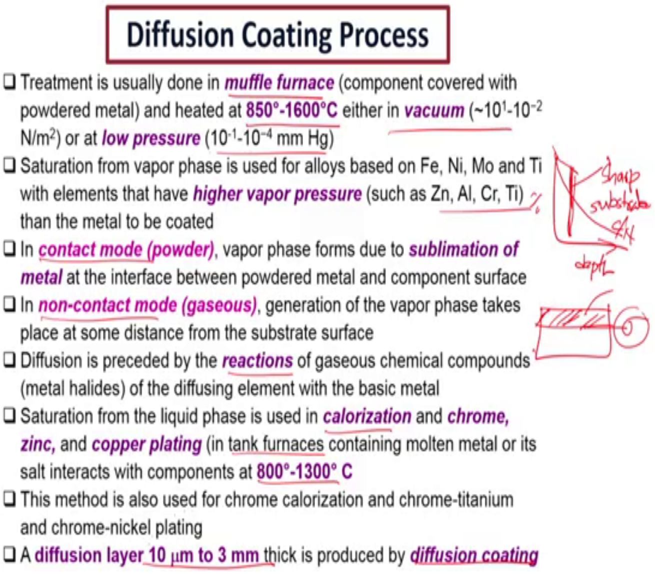

Diffusion Coating Process

- Treatment is usually done in ***muffle furnace*** (component covered with powdered metal) and heated at **850°-1600°C** either in ***vacuum*** (~10^1-10^{-2} N/m^2) or at ***low pressure*** (10^{-1}-10^{-4} mm Hg)
- Saturation from vapor phase is used for alloys based on Fe, Ni, Mo and Ti with elements that have ***higher vapor pressure*** (such as Zn, Al, Cr, Ti) than the metal to be coated
- In ***contact mode (powder)***, vapor phase forms due to ***sublimation of metal*** at the interface between powdered metal and component surface
- In ***non-contact mode (gaseous)***, generation of the vapor phase takes place at some distance from the substrate surface
- Diffusion is preceded by the ***reactions*** of gaseous chemical compounds (metal halides) of the diffusing element with the basic metal
- Saturation from the liquid phase is used in ***calorization*** and ***chrome, zinc,*** and ***copper plating*** (in tank furnaces containing molten metal or its salt interacts with components at **800°-1300° C**
- This method is also used for chrome calorization and chrome-titanium and chrome-nickel plating
- A **diffusion layer 10 μm to 3 mm** thick is produced by ***diffusion coating***

So, the processes would require exposure to high temperature, we use a muffle furnace a closed chamber which with certain which can and the material to be coated is usually covered with powdered metal. We do it either in vacuum; that means, the very low pressure; very low pressure ultra low pressure or reasonably low pressure condition.

So, the mechanism or the approach will require that we create the vapor species of these elements on iron, nickel or molybdenum or titanium based substrates. We cover them, we can do it either through contact mode; that means, back processes where we pack it with powder or non contact mode which is gaseous so, gas percolates all over. There will be reactions occurring which subsequently which allows the desired species to go to the vapor state and then there will be decomposition of that vapor and then deposition of the nescient form of atoms of the desired species.

So, typically this is the process used for very many systems, but there are also processes where we can have we may used to we may need to use tank furnaces. So, we exposed to high temperature and I have a liquid path in which the metal is to be dipped or immersed.

So, the thickness of the diffusion layer that we talk about can be several millimeters; can be fairly thick, but usually it is in the order of few tens at the most few hundred micrometers less than a millimeter, because these diffusional coatings usually create not a very diffuse interface. For example, when you compare them with carburizing or nitriding, in case of carbon or nitrogen so, if this is the depth and this is the concentration then we in case of carbon and nitrogen we expect a diffusion profile like this. In case of silicon aluminum; so, this is typically you expect in case of carbon and nitrogen.

In case of silicon aluminium or these kind of substitutional species this profile is diffusive, but then there is a certain drop. So, we do see a sharp interface between the coating and the substrate so, this is the substrate. And this kind of a sharp interface actually creates a certain stresses at the surface so, if you actually make a very thick coating on a substrate, then this stress that we generate; residual stress that we generate that the coating substrate interface is fairly large.

And this stress can be much larger than the yield stress or the tensile stress of the material and as a result the coating may follow; so, which we do not want. So, we generally do not go for very thick coating, typically less than a millimeter at the most a few millimeters, but if needed you can make several millimeters.

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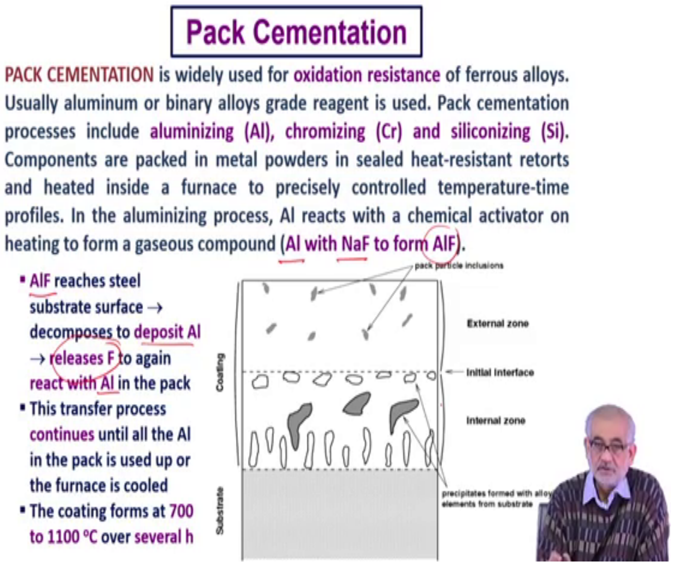

Pack Cementation

PACK CEMENTATION is widely used for oxidation resistance of ferrous alloys. Usually aluminum or binary alloys grade reagent is used. Pack cementation processes include aluminizing (Al), chromizing (Cr) and siliconizing (Si). Components are packed in metal powders in sealed heat-resistant retorts and heated inside a furnace to precisely controlled temperature-time profiles. In the aluminizing process, Al reacts with a chemical activator on heating to form a gaseous compound (Al with NaF to form AlF).

- AlF reaches steel substrate surface → decomposes to deposit Al → releases F to again react with Al in the pack
- This transfer process continues until all the Al in the pack is used up or the furnace is cooled
- The coating forms at 700 to 1100 °C over several h

So, pack cementation is a typical way in which; so, what you do is you want for example, aluminum to go to the surface. So, you pack aluminum with sodium fluoride and at the reaction temperature they form aluminium fluoride because aluminum has higher affinity to fluorine than sodium.

So, this aluminum fluoride is in the vapor state, but when it reaches a substrate surface it tends to decompose and deposit aluminium. But this aluminum is in the nascent state, and when it releases fluorine from aluminum fluoride this fluorine goes back into the atmosphere then again acts with unreacted aluminium and forms again aluminum fluoride. So, this is how the fluorine is used up in cyclic way, but since this is maintained at some evacuation some evacuated condition or there is always a possibility of this gas going into different parts of the chamber or being sucked out by diffusion of pump.

The fluorine actually is an extremely corrosive material, extremely corrosive agent. So, wherever it goes all the pump bearings or the pipings and so on they tend to get corroded. So, this process has to be done with certain amount of precaution. But the main process is to deposit aluminium in the nascent form and thence aluminum diffuses; so, typically temperatures we are talking about could be 700 to 1100 degree centigrade. And this would be the kind of zone that which actually produces such kind of coatings.

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Pack Cementation:

- ❑ Metals are aluminized by pack cementation by packing the parts in a metal container filled with a material that will provide a concentration gradient for diffusion of aluminum.
- ❑ The coating obtained can be from 1 to 40 mils

Spray Coating:

- ❑ In this method an aluminum coating of a precise thickness is sprayed on pre-cleaned surface.
- ❑ The process includes melting and spraying the metal with a jet of compressed air (at 25-60 psi pressure) with special metallizers.
- ❑ The bond thus obtained is of low strength, although the adherence can be improved by roughing the surface of the substrate.

So, these are examples of small engineering components which actually can be subjected to such pack cementation process, but if you are thinking of a very large pipe for carrying gas or any reactive material or petroleum or something, then the coating has to be done through a spray process like what you are seeing here.

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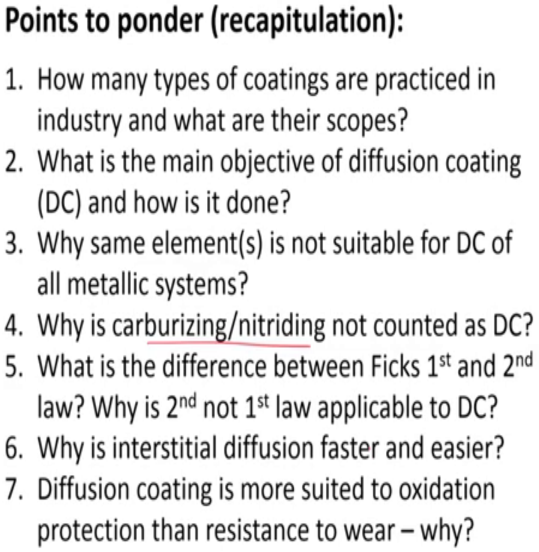

Points to ponder (recapitulation):

1. How many types of coatings are practiced in industry and what are their scopes?
2. What is the main objective of diffusion coating (DC) and how is it done?
3. Why same element(s) is not suitable for DC of all metallic systems?
4. Why is carburizing/nitriding not counted as DC?
5. What is the difference between Ficks 1st and 2nd law? Why is 2nd not 1st law applicable to DC?
6. Why is interstitial diffusion faster and easier?
7. Diffusion coating is more suited to oxidation protection than resistance to wear – why?

So, it is time to recapitulate; so, what all we have discussed. The whole process here is based on diffusion so, we discussed the reason for diffusion, the driving force for diffusion and the kinetics of diffusion. And we understood that in most of the industrial practices we generally resort to non steady state diffusion where the Fick’s 2nd law is applicable and the typical solution under certain boundary conditions, allows us to predict the diffusion profile or composition profile both as a function of distance and time at a given depth. And that is what helps us to predict what would be the diffusion coating thickness for a particular condition.

So, we actually can have various types of coatings possible and at the moment we are talking about diffusional coating. The main objective of diffusion coating is to create these aluminum rich or chromium rich layers which actually when exposed to oxygen will form the oxide layer and that would protect further oxidation.

The elements that are say for example, aluminum is appropriate for iron bearing substrates, but aluminum may not be appropriate for any other metal unless it has sufficient solubility in that metal. So, we have to select which exactly is the most appropriate one. So, among the three aluminum, chromium and silicon you choose elements depends upon the solubility and the kinds of phases they form either a solid solution or intermetallic phases and we all are aware that intermetallic phases can cause a lot of stress at the surface. So, we may not quite want such elements to diffuse which have the tendency of formation of various types of intermediate phases.

So, carburizing and nitriding carburizing and nitriding they are diffusional process. So, in principle one may argue that why not call them diffusion coating, but because their purpose and their the whole process has a slightly different approach we generally give them a different name. We have discussed that various laws applicable for diffusional kinetics, we have understood the differences between interstitial diffusion and substitutional diffusion and we understood why the activation barrier is lower and hence the rate faster for interstitial diffusion than substitutional diffusion.

And diffusional coating is more suitable for oxidation, resistance than where resistance is simply because for these the other processes competing processes like carburizing or nitriding and so on, they are based on a particular mechanism which is not very stable at high temperature. Whereas, diffusion coating creates certain oxides particularly based on this chromium, aluminum and silicon where these oxides are very stable at high temperature and can protect the substrate from further oxidation. So, they are more suitable for high temperature oxidation resistance.

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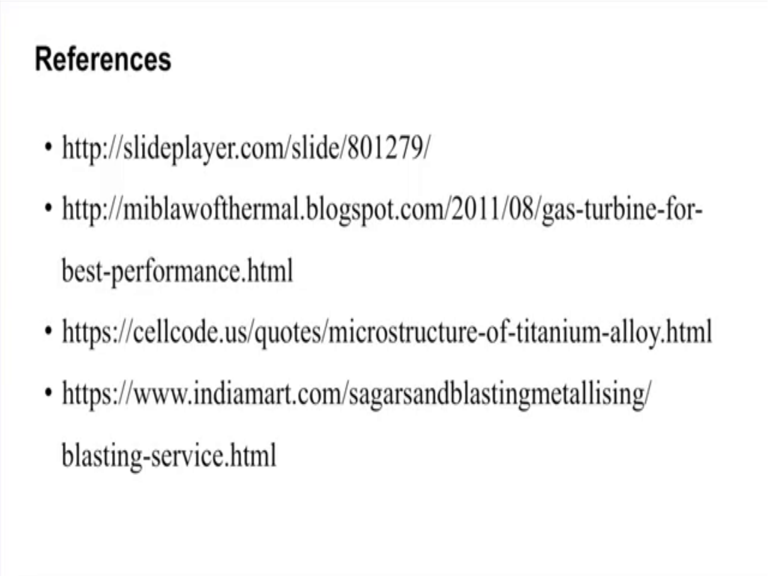

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So, we come to the end of this lecture now and now after this will discuss specifics of aluminum coating or chromium coating or silicon coating for high temperature oxidation resistance.

Thank you very much.