

Surface Engineering for Corrosion and Wear Resistance Application
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Lecture - 06
Surface dependent physical and chemical property

So, welcome to the 6th lecture which is on 2 types of surface dependent properties ash namely the physical and chemical. In the 5th lecture we talked about overall classification of surface dependent properties. In fact, we started discussing from how actually what do we mean by engineering properties and how do we define them. And subsequently we went into those classifications and talked about various types of surface dependent mechanical properties.

We now need to discuss two other major classes which are of consequence which are which have influences on various engineering applications and these two are the physical and chemical properties related to the surface. So, the distinction arises purely from the fact that the activation is coming from either chemical or from physical forces or physical types of activation. So, if you now look into the slides the very first one since we are discussing physical properties.

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Topography

❖ A local deviation of a surface from a perfectly flat plane is termed as surface topography. Surface topography is the nature of a surface as defined by the three characteristics:

- **Lay:** The **direction** of the predominant **surface pattern** ordinarily determined by the production method used
- **Surface roughness:** Closely spaced **irregularities** (cutting tool marks, grit of grinding wheel).
- **Waviness:** More **widely spaced irregularities** (vibration and chatter). These usually occur due to warping, vibrations or deflection during machining.

Fig.1 Optical System in Ultrahigh Accurate 3D Profilometer

Surface topography

Cold Rolled Steel Galvanized Steel

So, the one of the foremost thing that we need to talk about is the topography, I probably did mention in the last lecture that no matter how careful you are when you synthesize

any solid by either a solid state or a liquid to solid or vapour to solid kind of transformation the surface will definitely have certain degrees of asperities.

In fact, the surface that we generally referred to as a very smooth and flat surface if you bring it under just a simple magnifying glass or maybe an microscope would definitely reveal certain levels of asperities. For example, you can see here that this is a cold rolled steel sheet and when you actually the sheet comes out of the roll it appears very shining and normally you would not expect that the surface can have such dents or certain surface deformation marks.

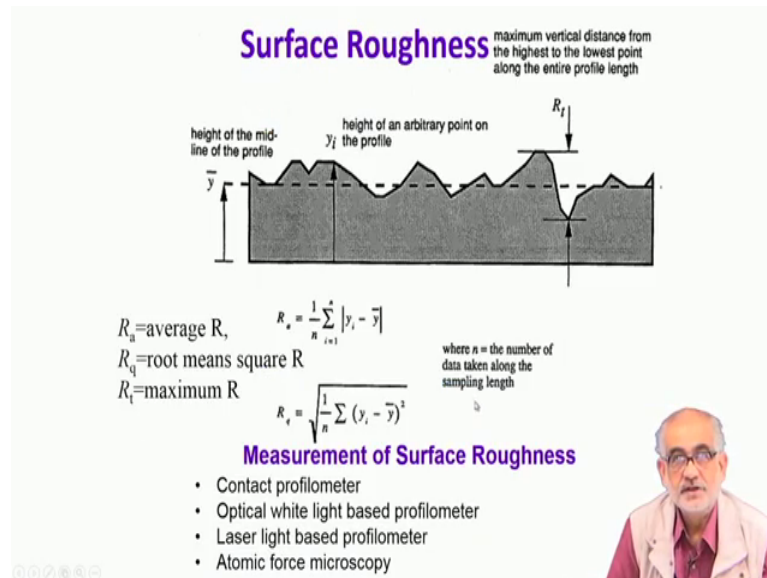
And these deformations actually are the this kind of dents actually could be just a hardly of micron even less than a micron depth. On the other hand the steel sheets which are coated with zinc and applied for car bodies and various other applications or even painted on top of that. Even they also will have certain roughnesses and typical amplitude of these roughnesses would be again a few micrometers if not more.

So, topography essentially is description of the surface quality in terms of the waviness or various kinds of asperities possible onto the surface and there are three characteristic features generally one talks about while describing their topography or topology of the material lay which essentially describes the surface pattern due to the direction of various deformation or synthesis processes which preceded the formation of that particular solid. One can the next important part is the surface roughness which actually arises primarily when the material is machined at some point of synthesis or fabrication.

And the grid size of the grinding wheel or the depth of the which the abrasives would have actually polished the surface or cutting tool would have cut the surface leaves behind certain marks of roughnesses. And then you also can develop waviness which essentially is arises because of the various surface contour variations of the counter phase or vibration and chatter happening during the fabrication process.

So, whenever we have such topological or topographical variations and we need to actually measure them then we employ one of these profilometers which could be a contact like here or can be a non-contact profilometer. So, in a non-contact profilometer we generally expect we follow the reflection profile and the surface. If it has certain levels of waviness or roughness then we will definitely show our different kinds of contour.

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For imagine a surface or a solid component which is freshly machined and when you machine then the cutting tool actually moves over the surface and removes material by application of mechanical forces. Or for example, do you think of a solid surface which is freshly ground through grinding wheel or polished using certain abrasives.

So, the those grits onto the grinding wheel or the abrasive particles their size and geometry would leave such asperities onto the surface, but if this amplitude is submicron less than a micrometer then you do not actually distinguish them by your naked eye. So, you essentially tend to see a very flat and shining surface, but if you take it under the microscope then you see certain levels of roughnesses which could be average roughness, which could be described in terms of root mean square roughness or maximum roughness.


And this maximum roughness the total amplitude could be fairly large, but of course, these are randomly occurring not uniform. So, in order to measure these roughnesses we as I said we use contact profilometer we can use also non-contact profilometers like optical white light based profilometer. Or laser light based profilometer even atomic force microscopy where the if its not in or tapping mode the tip actually will not even touch the surface, but will, but still be able to measure the forces onto the surface when it is brought to very close proximity to the solid surface that we are investigating.

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Color

- ❖ Color derives from the spectrum of light interacting in the eye with the spectral sensitivities of the light receptors. Thus color is a visual property corresponding in humans to the categories called red, blue, yellow of spectrum.
- ❖ **Spectroscopy**, an important investigative tool in astronomy is the study of objects based on the spectrum of color they emit, absorb or reflect.
- ❖ The ability of the human eye to distinguish colors is based upon the varying sensitivity of different cells in the retina to light of different wavelengths (A typical human eye will respond to wavelengths from about 390 to 700 nm)


color	wavelength interval	frequency interval
red	~ 700-635 nm	~ 430-480 THz
orange	~ 635-590 nm	~ 480-510 THz
yellow	~ 590-560 nm	~ 510-540 THz
green	~ 560-490 nm	~ 540-610 THz
blue	~ 490-450 nm	~ 610-670 THz
violet	~ 450-400 nm	~ 670-750 THz




Primary Colors



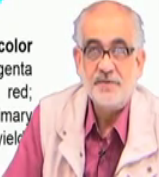
Secondary Colors



Tertiary Colors



Subtractive color mixing: adding magenta to yellow yields red; adding all three primary colors together yields black

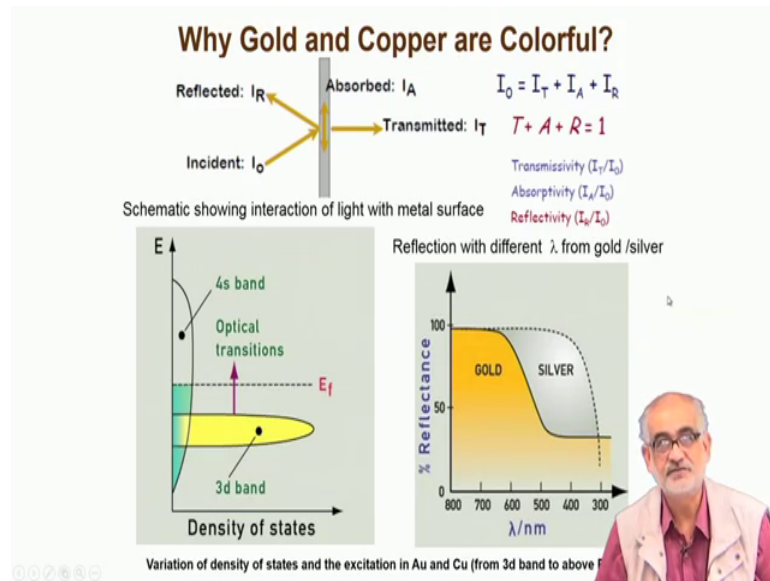


The color is a very important engineering property. In fact, aesthetics to a large extent depends on the color and the ability to reflect light, but we must realize that the color that we see essentially is an reaction or coming the activation is the incidence of light on it which could be white light a combination of various wavelengths typically in the range of about 350 to about 700 nanometer wavelength. And in that kind of a range depending on the surface nature and its chemistry or the composition, we tend to absorb certain wavelengths more than the rest and as a result we see not a white or a composite color of the surface, but a typical color.

And so, these colors are the manifestation of these colors will depend upon what kind of wavelength we are prone to absorb or scatter and more and essentially that would be that would determine. In fact, when we have 2 or 3 very dark colors or very monochromatic colors incident onto the surface, then this combination of these colors actually can create a sensation which is going to appear as dark or black.

So, it depends on actually the hour the receptors that we have in our eye which is sensitive to different types of wavelengths. So, what receptor is active for a particular view and what wavelength is actually able to excite those receptors for a particular incidence.

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So, in fact, we tend to be always these a common saying all of us are aware all that glitters is not gold, but actually its that glittering property or the reflective reflection or reflectivity property that determines or that actually is the reason why gold is so, popular and so, wishes for all the ornaments and various other decorative purpose.

But the fact remains that gold actually is able to reflect light over a wide range of wavelength incident wavelength. So, that is why its always flattering compared to that there are other metals which are not as efficient as gold and that is exactly the reason why gold is. So, precious as ornament.

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Reflection

- ❖ **Reflection** is the change in direction of a wave front at an interface between two different media so that the wave front returns into the medium from which it originated. The law of reflection says that for specular reflection the angle at which the wave is incident on the surface equals the angle at which it is reflected.
- ❖ Reflection of light is either specular (mirror-like) or diffuse (retaining the energy, but losing the image) depending on the nature of the interface
- ❖ Electromagnetic waves of light incident on a material induce small oscillations of polarization in the individual atoms (or oscillation of electrons, in metals), causing each particle to radiate a small secondary wave in all directions, like a dipole antenna

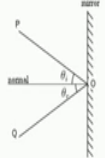
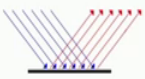
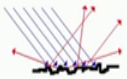


Diagram of specular reflection



Specular Reflection
(smooth surfaces)



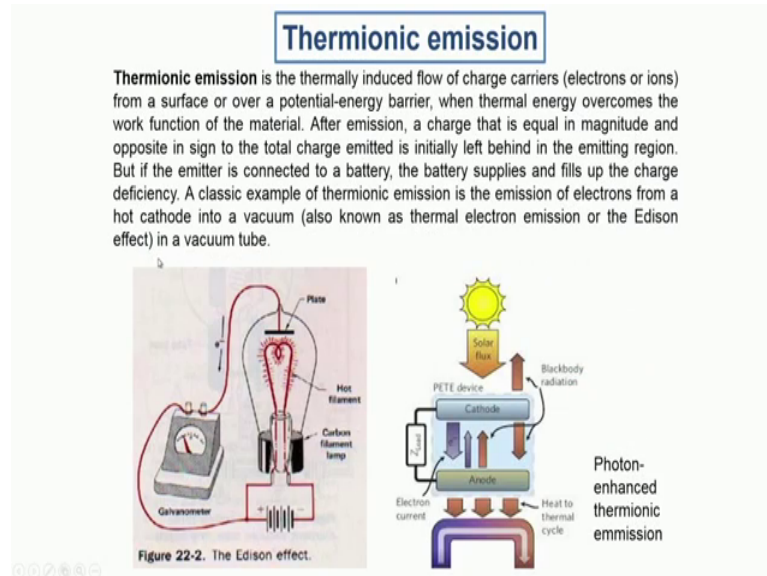
Diffuse Reflection
(rough surfaces)

Some surfaces exhibit **retro-reflection**. The structure of these surfaces is such that light is returned in the direction from which it came.

For various purpose for example, the surface of a mirror you would not like to have a situation which is like this. If you have a lot of roughness on to the surface then the incident beam will get scattered in all directions and then the reflected light will have certainly not be able to gather all the scattered rays and not only the image could be distorted, but more importantly the intensity of the image that you will create will be weaker or poor.

So, reflection is a property which is very much very much dependent on the surface topology and topography and hence that is something we need to know before we design a surface for particular reflection including creation of a mirror surface.

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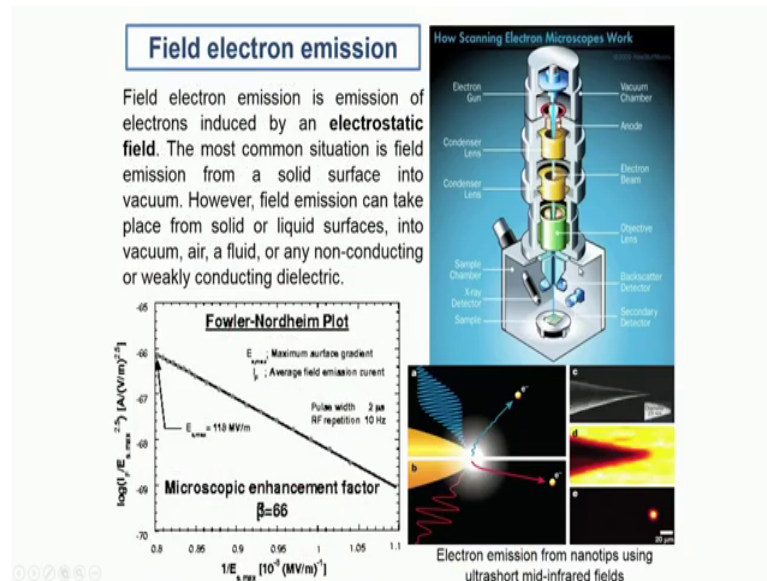


Um So, until now the entire effect was due to the reaction to an excitation coming from optical rays and instead of emitting light we actually can even emit electrons and this emission can happen because of multiple possibilities of excitation. Over here when we talk of thermionic emission we are talking about a situation where we apply a very high amount of potential difference and current.

And as a result of which certain elements for example, tungsten or a compound called lanthanum hexaboride LaB_6 actually can emit very high density of electrons from the surface and these electrons have their own utility we make use of them as.

So, this is a gun and a cathode ray gun or there are multiple other applications, but what is even more important is that all the solar cells actually would also like to make use of such properties of either organic or inorganic substances which actually can create electron and hole pair. And on a particular photosensitive coating and those separated electrons can be either stored or carried away to form current and that gives us energy.

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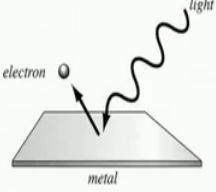
So, thermionic emission is a phenomenon or a property which is dependent upon the ability to emit electrons from the surface due to excitation purely which is of thermal in nature. We can also have field emission phenomenon where electrons are emitted because of the application of field electrical field and such kind of phenomenon is utilized in for example, this scanning electron or transmission electron microscope where we have this large column.

And the primary part stream of electrons is emitted from this electron gun which either could be such due to such thermionic emission what we just saw coming from tungsten wire or l a b 6 compound tip or it can also come from due to field emission happening because of large electron large potential difference created at the tip.


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Photoelectric effect

- ❖ The **photoelectric effect** refers to the emission, or ejection, of electrons from the surface of, generally a metal in response to incident light. Electrons emitted in this manner can be called **photoelectrons**.
- ❖ The photons of a light beam have a characteristic energy proportional to the frequency of the light. In the photoemission process, if an electron within some material absorbs the energy of one photon and acquires more energy than the work function (the electron binding energy) of the material, it is ejected.
- ❖ The measurement of the energy distribution of photoelectrons produced by a photon of a single energy (monochromatic) is called **photoelectron spectroscopy**.



The diagram illustrates the photoelectric effect. A wavy line labeled 'light' represents an incident photon striking a flat surface labeled 'metal'. An arrow labeled 'electron' points away from the metal surface, indicating the ejection of an electron.



A small portrait of a man with glasses and a white lab coat is positioned in the bottom right corner of the slide.

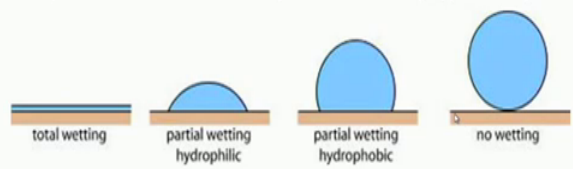
Electrons can be emitted also because of excitation coming from optical ray in some metals we if we have or particularly on some because of certain coatings we actually can see a situation, where incident wavelength can raise electrons from the valance to conduction band.

And these electrons now are ejected because of the excitation coming from the incident light and these electrons are captured and then carried away and which creates a current and that is what we call photoelectric photo electricity or photoelectric effect.


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Wetting

- ❖ Wetting is the ability of a liquid to maintain contact with a solid surface, resulting from intermolecular interactions when the two are brought together. Wettability is determined by a force balance between adhesive and cohesive forces.
- **Non-stick frying pans** are coated with teflon, a low energy surface and hence poorly wetted surface
- **Rain coats** are made of hydrophobic material so that rain drops don't stick to the surface and can be removed by just shaking the rain coat.
- **Wax paper cups** from a beverage counter are hydrophobic, so that your coke doesn't stick to the cup and hence, the cup appears shiny.



The diagram shows four scenarios of liquid wetting on a solid surface, represented by a horizontal line. 1. 'total wetting' shows a thin blue layer spreading across the surface. 2. 'partial wetting hydrophilic' shows a blue droplet with a small contact angle. 3. 'partial wetting hydrophobic' shows a blue droplet with a larger contact angle. 4. 'no wetting' shows a blue droplet that is nearly spherical and does not touch the surface.



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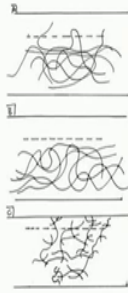
Wettability is a very important phenomenon we did discuss this in one of the earlier lectures look at the possible scopes of application I mean we have all we are all aware or would have possibly used a nonstick frying pans and similarly we use raincoats or umbrella or wax paper cups and so on all these are basically hydrophobic surfaces under different conditions. This is under high temperature condition, but this is in room temperature and in all these cases we do not allow the water to stick to the surface.

So, we exactly we do not want anything like this, what we want is somewhat like this; that means, the water droplet should not spread easily onto the surface. And this is made possible can be made possible either by changing the surface contour the topology of topography of the surface by creating certain patterns or changing the chemistry. So, that the surface tension is modified as a result of which the contact angle is very high.

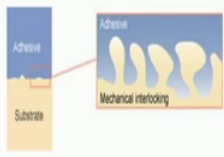
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Adhesion

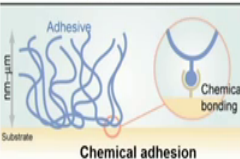
- ❖ Adhesion is the tendency of **dissimilar particles or surfaces** to adhere to one another
- ❖ Low surface energy materials like polyethylene and polypropylene are difficult to bond without special surface preparation




Diffusive adhesion: The interface is indicated by the dotted line. A) Non-cross-linked polymers are somewhat free to diffuse across the interface. One loop and two distal tails are seen diffusing. B) Cross-linked polymers not free enough to diffuse. C) "Scissed" polymers are quite free, with many tails extending across the interface



Mechanical adhesion



Chemical adhesion



dispersive adhesion

When we need to actually glue two different surfaces, two different dissimilar surfaces the adherence of these two different surfaces visually which will largely depend upon the adhesive forces that we can create either by either by themselves. The two surfaces can have a natural tendencies of aeration or we can apply material in between for example or a glue or a gum which actually can lead to chemical adhesion.

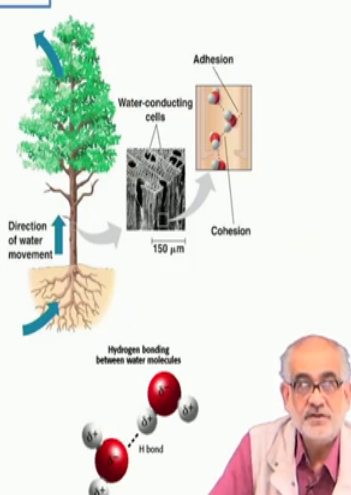
So, adhesion can be mechanical in nature or chemical in nature, but nevertheless is very important for us to be able to join two different solids which are of dissimilar nature and there are examples in nature. For example, this flower actually is a bright example of


how dispersive a nation can happen because of the presence of certain chemicals at the tip of this bud and that is how the pollen actually can get attached to the insects and then subsequent biological phenomenon can take place.

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Cohesion

- ❖ **Cohesion** refers to the tendency of similar or identical molecules/surfaces to adhere to one another
- ❖ It is an intrinsic property of a substance that is caused by the shape and structure of its molecules, which makes the distribution of orbiting electrons irregular when molecules get close to one another, creating electrical attraction that can maintain a microscopic structure such as a **water drop**
- ❖ **Water** is strongly cohesive as each molecule may make four hydrogen bonds to other water molecules in a tetrahedral configuration
- ❖ Cohesion along with adhesion helps explain phenomena such as meniscus, surface tension and capillary action





When you are talking about dissimilar then we talk of adhesion and when we talk of similar molecules or species then the bonding between them is described as cohesion. So, the quasi forces also is very important because they eventually will govern the meniscus of a fluid or a bulk of liquid or the surface tension that is manifested and even the capillary action.

So, for example, if you have two water droplets placed side-by-side and if they either due to mechanical vibration or for some reason if they are able to actually come in close contact then they will immediately merge and make a bigger droplet. And this kind of capillary action happens because of the forces of cohesion.

All these adhesion cohesion the topography photoemission, photoelectric emission, thermionic emission all these are surface dependent properties of solids due to various kinds of activation coming from different types of physical forces. And now we are going to examine what is going to be possible for similar properties which are dependent on activation coming from chemical forces.

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Reactivity

- ❖ **Reactivity** is the tendency of a substance to undergo chemical reaction, either by itself or with other materials, and to release energy
- ❖ **Fr** is **most reactive metal** while **F** is the **most reactive non-metal**
- ❖ **Platinum** being the **least reactive metal** cannot be oxidized in air, even at high temperatures
- ❖ **Reactivity** depends on the relative capacity of an atom, molecule, or radical to chemically react with another atom, molecule or compound

LEAST REACTIVE
↓
MOST REACTIVE

Oxidation

Oxidation is the chemical reaction that involves the transfer and transport of electrons. When iron reacts with oxygen it forms rust. The iron is oxidized and the oxygen is reduced.

For example you know the most common thing whenever we talk of chemical actions or chemical processes what immediately comes to our mind is the chemical reactivity and we are aware from our high school physics, that elements which are farthest apart in terms of their location in different different periods.

So, they basically will have very large tendencies of reacting with each other. So, for example, francium is the most reactive metal and it is in the first period and then we have fluorine which is one of the most reactive nonmetal which is the most reactive nonmetal. So, whenever you expect something at too far apart in the periodic table and they are likely to actually react with each other very strongly.

So, but then when they react this reactivity of a solid I mean this is about the pure elements, but when you talk of solids when two solids come in contact with each other there could be chemical forces acting between them and it could be a solid, it could be a solid liquid or a solid gas and eventually the surface is likely to undergo certain chemical reaction or transformation depending on its tendency of such chemical reaction.

Take the example of pure iron if you leave it in open we all are aware we all have common experience that, it develops certain covers certain compounds forming onto the surface which we call rust brownish color and this rust actually grows in with time.

Even if you do not do anything at all to the material it grows because it reacts with that and forms certain hydroxide and these hydroxide has fairly porous and structurally very different than the underlying substrate and because of which the rust or the compound actually spalls off the surface and exposes fresh one and that is how this process of degradation continues or the rusting continues.

So, any solid if it is polar in nature we will always have a tendency of dissociating, we are aware that essentially this it can actually give up electrons and then get oxidized goes into the oxidized state of oxidation state or if it actually occurs electrons, then it gets reduced. And that is how whenever electron transfer takes place between two different species one gets oxidized that again gets reduced and in the process we possibly end up forming a compound.

And this is how in most of the cases the undesirable phenomenon of oxidation takes place and this please remember that this oxidation is much more aggressive at high temperature when the mass transport is faster when the growth rate of these kind of oxides onto the surface of a metal or any other solid for that matter is much faster and uniform.

So, one does not need to always worry about whether the element belongs to a group 1 or group 2 or something. First thing is that whenever we have elements which are farther apart in the periodic table belonging to in terms of their classification on different groups they are likely to react. So, from that atmosphere if we pick up certain cations, maybe oxygen maybe chlorine or maybe some other kind of anions and if we have a metal or for that matter other solids which is ready to offer certain cations.


So, these anions and cations are likely to react immediately depending on their tendency of reaction and this rate of reaction or the degree of such reaction would be much higher at higher temperature which is what happens in case of oxidation and this leads to gradual conversion of the solid into a different form which is mostly undesirable and we need to prevent them.

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Corrosion

❖ **Corrosion** is a natural process by which solids may deteriorate because of galvanic action or oxidation that creates mixed oxides prone to spall from the base. Corrosion may occur due to various environmental factors like pH, temperature, moisture or even due to microorganisms (**microbial corrosion**)

❖ **Galvanic corrosion** occurs when two different metals have physical or electrical contact with each other and are immersed in a common electrolyte, or when the same metal is exposed to electrolyte with different concentrations



Rust

Galvanic series


Anode (Most Active) ↑

Magnesium
Zinc
Aluminum (20)
Calcium
Aluminum (175T)
Steel or Iron
Carbon
Lead - Tin solder
Lead
Nickel
Brass
Copper
Bronze
Stainless Steel (304)
Monel Metal
Stainless Steel (316)
Silver
Graphite
Gold

↓ Cathode (Least Active)

Passivation refers to the spontaneous formation of an ultrathin film of corrosion products, known as a passive film, on the metal surface that act as a barrier to further oxidation

Surface treatments like galvanization, anodization and biofilm coating is employed to protect surface from corrosion



So, in order to first be able to prevent we first should realize how this degradation is taking place and such a degradation as we just saw in case of oxidation is essentially a chemical degradation process. A similar thing can happen in terms of corrosion and this is what I was just now explaining in terms of rusting and nobody wants and should get rusted, but this is also something that is unavoidable. In fact, in the lighter vein one can say that this is how mother nature actually preserves its precious resources.

So, nobody gives you iron in its in the native form, we all get oxides or sulphides or various kinds of ores and minerals and then using our imagination and scientific knowledge we are able to win the metal value from those oxides or sulfides or nitrites. And then we use, but if you are not careful enough to actually protect them by way of either coating or something such exercise then mother nature sees that you are not caring enough for the metal.

So, the it converts the metal into oxides and take it back to the condition under which it can be very easily saved and stored forever. And this happens because of one very important reason and that is what I wanted to actually point out now I did mention earlier that all systems in the universe always tends to minimize its Gibbs energy because that is the that is how it can improve its stability.

In order to actually reach that stabler form we have to wear options, which is more stable like I was describing the example between iron and iron oxide. And if you have

these two lying side-by-side in open atmosphere; obviously, according to the thermodynamic conditions the oxide would be stabler than the pure metal. A that is exactly the reason why there is a natural tendency always for any metallic systems to undergo either corrosion or oxidation which essentially are very similar electrochemical processes only oxidation occurs at usually of course, at high temperature whereas, corrosion can happen in the presence of an electrolyte at room temperature.

But whenever we have metals of dissimilar nature for example, if you look at this series here these are called galvanic series and they are actually created in terms of the galvanic potential or real criminal potential of these metals and these. So, in this series actually they are arranged in terms of their electrochemical potential and it clearly shows that the metals which are high above into this series are much more reactive and that is why they are called anodic whereas, the ones which are at the bottom of the series are cathodic.

So, these metals which are at the top of the series are very prone to donating electrons and get oxidized and if there is an electrolyte which actually can conduct either the electrons or the species the ionized species, then it reaches the other end and donates the electrons or the electrons are required by the cathodic part of the of the cell and that is how the transfer of electron leads to gradual degradation of these metals into another form.

In order to prevent this we actually need to create a passivation layer and this passivation is possible only when we actually create an oxide layer normally we do not want to convert a metal into an oxide, but in certain cases we actually prefer to create an oxide layer only difference is this oxide layer actually has to be very adherent and stable and non-porous. So, that further ionic transport across this oxide is prevented or stopped and hence the process actually stopped or and further degradation cannot take place.

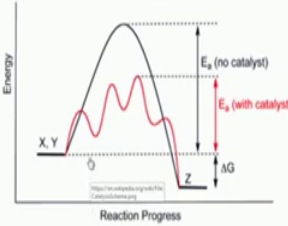
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Catalysis

- ❖ **Catalyst** increases the rate of a chemical reaction
- ❖ This increase in the rate of chemical reaction is known as **Catalysis**
- ❖ With a catalyst, reactions occur faster and require less activation energy
- ❖ Catalysts are not consumed in the catalyzed reaction
- ❖ The effect of a catalyst may vary due to the presence of other substances known as **inhibitors**, that reduces the rate of a chemical reaction

APPLICATIONS:

- Petroleum refinery
- Chemical and Fine Chemicals
- Food processing/hydrogenation
- **Enzymes** are protein based bio-catalyst which play important role in metabolism of living beings



So, catalysis is another such phenomenon I mean its very simple to for us to understand the way the catalysis works that if you actually imagine a hump like this such a big hump. So, it actually shows that you have a large barrier to cross. So, instead of this big hill if you have smaller helix to actually cross which is going to be much easier and that is exactly what happens when you do catalysis.

So, essentially you need certain extraneous agent which act as catalysts which actually accelerate the process and this acceleration of the process is called catalysis. But on the other hand if you do not want such reaction to take place, then we apply the opposite which are called inhibitors which actually reduces the rate of the chemical reaction fine.

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Points to ponder (recapitulation):

1. What is the origin of surface dependent physical and chemical properties?
2. Why are such surface dependent physical and chemical properties important for engineering applications?
3. What are the equipment, protocol and units for the assessing surface dependent chemical and physical properties?
4. Are these properties intrinsic or extrinsic?
5. How can surface dependent properties be tailored/improved by surface engineering?

So, now its time that we sum up. So, just like the way we discuss the various surface dependent properties under mechanical activation, here we discuss surface dependent properties under physical and chemical activations and we try to understand, what are the origin of various surface dependent properties.

For example when you excite the surface with certain photon if that surface is photosensitive enough, it can emit electrons and that is what is known as photo electricity. On the other hand if you expose a surface to certain chemical reagents or certain ions and if it leads to chemical reaction and gradual formation of a compound then that is corrosion and that is essentially through a chemical activation.

So, these surface dependent properties of coming from physical or chemical activation are very important because as we discussed in the previous lecture that they actually determine the life the reliability the safety the utility overall utility of the component in the long run. We should be aware of the various kinds of equipments and protocols used for assessing the surface dependent properties.

For example how do we measure corrosion property, how do we measure physical properties and so on some of these properties are intrinsic in nature, but not always. So, the activation some something can happen from within. So, we call them intrinsic or something happens because of extraneous influences which are extrinsic. So, both kinds of varieties are possible in these categories and what actually we should now try to focus

upon in the future lectures is how we can actually tailor the surface properties by way of changing their micro structure and composition of the near surface region.

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So, we need to discuss a little more of fundamentals about the strengthening mechanisms of various types both for metals and nonmetals before we start discussing the processes for which are typically called surface engineering techniques, but before that in the next lecture we will discuss about classification of various surface engineering approaches.

Thank you very much.