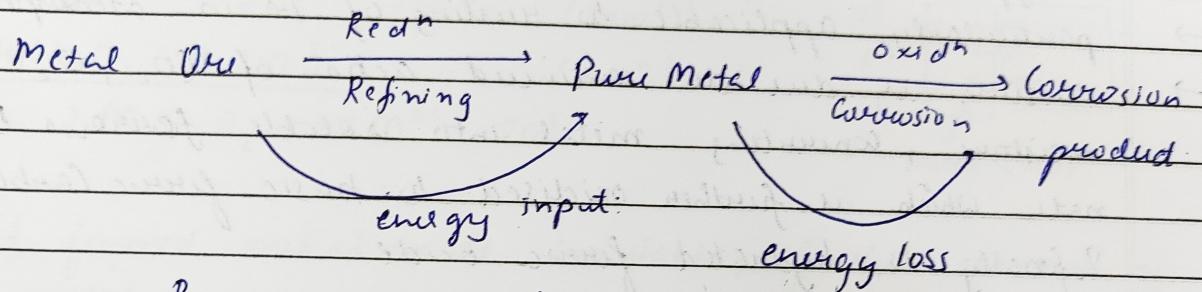


CORROSION

#

Corrosion :

- The electrochemical rxn b/w a material & its environment that produces a deterioration of material & its properties.
- degradation of material by chemical means



Reverse process of metal extraction.

#

As a result of corrosion, the metal reacts with chemicals in environment & progressively returns to combined form, rust in a form of iron oxide.

#

Effects of Corrosion :

- metallic properties are lost.
- Reduced strength
- Life time is reduced
- Wastage of metal
- Contamination
- Especially hazardous problematic for hazardous containers

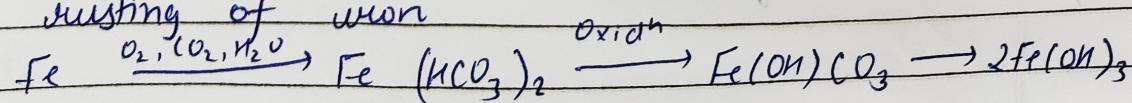
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Theories of Corrosion :

1. Acid Theory :

presence of acid is essential.

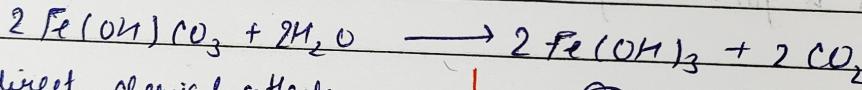
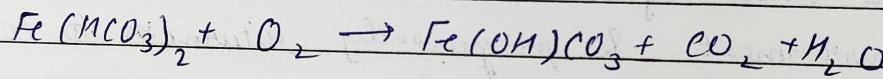
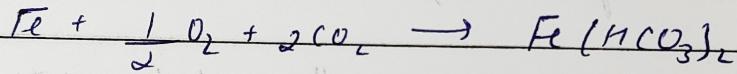
e.g. rusting of iron



2. Direct chemical attack: This theory explains so called dry corrosion.
3. The electrochemical theory: Wet corrosion based on Nernst theory.

→ Acid Theory:

→ suggests that presence of acid is essential for corrosion.
 → particularly applicable to rusting of Fe in atmosphere.
 → rusting is due to continued action of CO_2 , O_2 & moisture, converting metal into soluble ferrous bicarbonate which is further oxidised to basic ferric carbonate & finally to hydrated ferric oxide.



(i) involves direct chemical attack

Dry corrosion

- ① → Chemical corrosion.
- Oxidation corrosion.

→ Corrosion by other gases

→ liquid metal corrosion

- ② → Corrosion is uniform.
- ③ → slow process

④ involves formation of electrochemical cells.

Wet corrosion

- ① → electrochemical corrosion.

→ Electrochemical corrosion by evolution of H_2 & absorption of O_2 .

→ Galvanic corrosion

→ concentration cell corrosion.

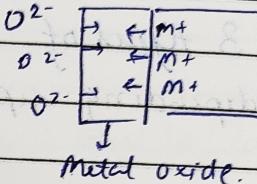
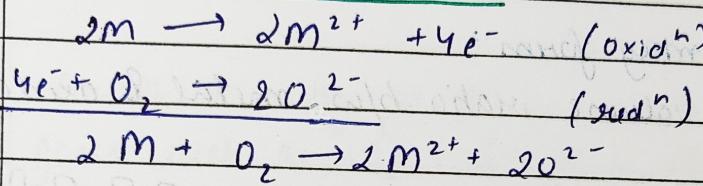
- ② → Corrosion is not uniform.
- ③ → rapid process.

Dry corrosion :-

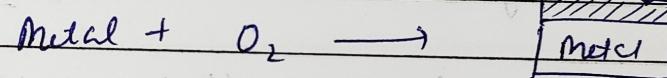
direct chemical attack on the atmospheric content on the metal surfaces in absence of moisture.

1. Oxidatⁿ corrosion \rightarrow Direct action of O₂ at higher or lower temp.
2. Corrosion by other gases \rightarrow Attack of gases like SO₂, CO₂, H₂S, Cl₂, F₂, metal surfaces.
3. Liquid metal corrosion \rightarrow Attack of inorganic liquid metals on solid metallic surfaces

1. Oxidation corrosion:



\rightarrow if formed metal oxide is stable, further corrosion of metal is prevented.

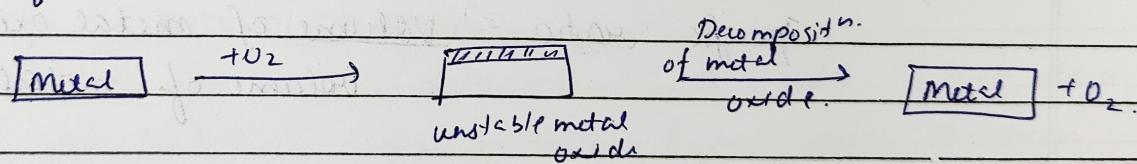


metal oxide layer.

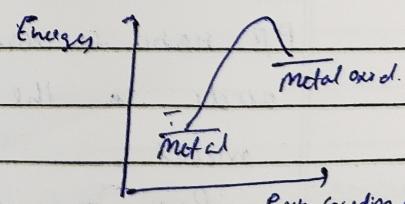
no corrosion

e.g Al, Sn, Pb, Cu, Bronze.

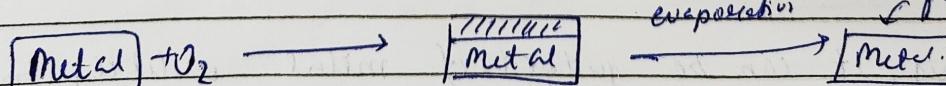
\rightarrow if formed metal oxide is unstable, corrosion does not occur.



e.g Au, Pt, Ag



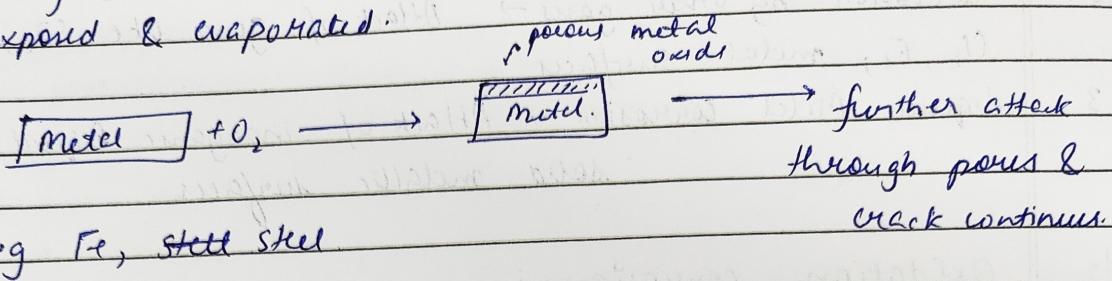
\rightarrow if formed metal oxide is volatile, surface is rapidly exposed & evaporated.



fresh surface exposed for attack.

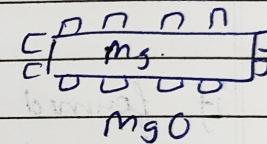
e.g Mo

→ If formed metal oxide is porous, surface is rapidly exposed & evaporated.

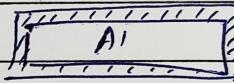


⇒ 3 types of oxides may form depending upon the volume ratio b/w metal & oxide.

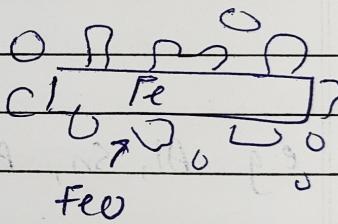
a) Magnesium produces a porous oxide film



b) Al form a protective, adhesive adherent, non porous oxide film.



c) Fe forms an O₂ film that spills off the surface & provides poor protection.



Pilling-Bedworth rule

$$\text{Specific ratio} = \frac{\text{Volume of metal oxide}}{\text{Volume of metal}}$$

PB ratio is ratio of volume of elementary cell of metal oxide to the volume of elementary cell of corresponding metal.

$$P-B = \frac{\text{Volume of the elementary cell of metal oxide}}{\text{Volume of elementary cell of metal}}$$

→ Using this it can be judged if metal is likely to passivate in dry air by creation of protective O₂ layer.

$$R_{PS} = \frac{V_{oxide}}{V_{metal}} = \frac{M_{oxide}}{n \times M_{metal}}$$

eg. Mg, Co

(< 1 , coating layer is too thin, non protective effect. e.g. Al)

(> 1 , the oxide layer provides protection)

2.

Corrosion (by gases):

→ Gases such as O_2 , SO_2 , H_2S , Cl_2 , Fe , etc. come in contact with metal surface corrosion occurs.

→ Extent of corrosion depends on chemical affinity b/w the metal & gas concerned.

→ Whether the layer of corrosion product is protective or non-protective.

- If formed corrosion is protective, metal is prevented.
- If formed corrosion is non protective, the corrosion occurs non-stop.

3.

Liquid metal corrosion

The chemical action of following liquid metal at high temp, on a solid metal or alloy produces liquid metal corrosion.

Reasons for corrosion:

- Dissolution of solid metal by liq. metal.
- Internal penetration of liq. metal into solid phase, weakening solid metal.

Eg. Na liq. used as coolants in nuclear plants then cause cadmium corrosion.

#

ELECTRO CHEMICAL

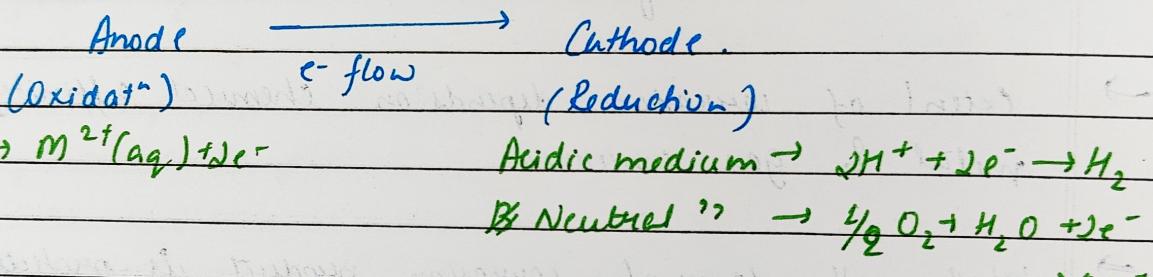
WET CORROSION

→ metal surface undergoes electrochemical rxn with moisture & oxygen in atmosphere.

Mechanism

① Anodic Rxn (Oxidn of metal) : (corrosion)

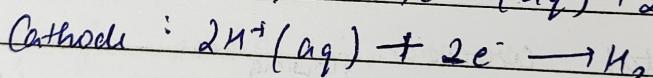
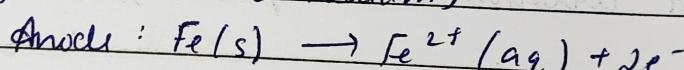
② Cathodic Rxn (Consump. of $O_2 e^-$)



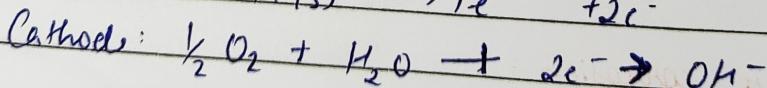
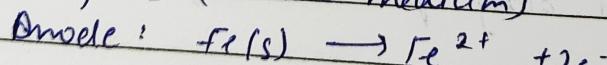
→ Mechanism:

Evolution of H_2 :

① 1) Evolution of H_2 (acidic medium)



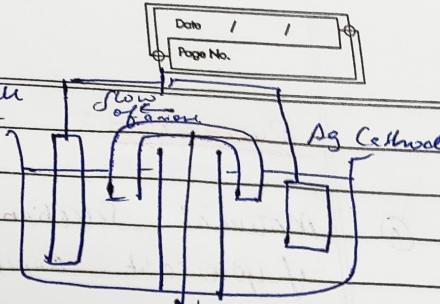
2) Absorption of O_2 : (Neutral medium)



→ Salt speeds up the process.

② Galvanic corrosion: when one metal corrodes preferentially to another when both metals are in contact & immersed in electrolyte.

→ Results from diff. in oxidⁿ potentials of metallic ions b/w two or more metals. The greater is diff in oxidⁿ pot., the ↑ the galvanic corrosion.



Salt bridge NaNO_3 .

→ less noble will corrode → Anode
more noble will not corrode → Cathode.

→ the best known of all corrosion types is galvanic corrosion, which occurs at the contact point of two metals or alloys with diff. electrode potential.

→ **Galvanic Series**: determining nobility of metal & semi-metals. When two noble are submerged in electrolyte, while electrically connected, the less noble experience the galvanic corrosion.

Rate of corrosion determined by

- electrolyte
- nobility difference

⇒ Galvanic vxn is principle upon which batteries are based

Severity of Galvanic corrosion depends on:

① Amount of separation in galvanic series

② Relative surface areas of two.

Severe corrosion if Anode is small & Cathode is large

does not depend on:

Amount in contact

Mass

Volume.

(Big cathode +
small anode
↔ big trouble)

Prevention:-

- ① Material Selection: Do not connect dissimilar metals or if you can't avoid it, try to electrically isolate one from other.
→ Make anode large & cathode small.
→ better option - Aluminium siding with steel fasteners

- ② Eliminate electrolyte
- ③ Galvanic of anodic protection

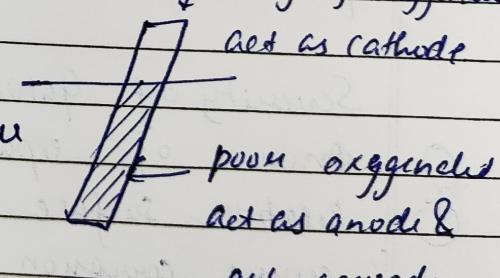
- ③ Concentration of cell corrosion:-
because of differential aeration, the concn' of O_2 is varied & causes oxidation of metal.

→ poorly oxygenated paint act as anode.

Water line corrosion:-

When water is stored in metallic tank, it is observed that metal below waterline get corroded.

→ O_2 deficient areas acts as anode, therefore cracks were as four for corrosion.



→ Corrosion is accelerated under accumulation of dirt sand, scale & other contamination.

→ Metal exposed to ag. media under blocks of wood or piece of glass, which screen that portion from O_2 .

(b) Pitting Corrosion:

It is extremely localised corrosion leads to creation of small holes in metal.

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(c) Crevice Corrosion:

- Here corrosion take place in crevices because solutions retained at this place & takes longer time to dry out.
- Corrosion in crevices is due to deficiency of O_2 , acidity changes.

Measures to reduce Pitting & Crevice Corrosion:

1. Fully understand the environment.
2. Control the environment to low chloride content & low temp. if possible.
3. Use alloys sufficiently high in Cr, Mo & or N to ensure resistance.
4. Design & fabricate to avoid Crevices.
5. Prepare surfaces to best possible finish. Mirror finish resists pitting best.
6. Design & fabricate to avoid trapped & pooled liquids.
7. Remove all contaminants.

(d) Stress corrosion:

It is combined effects of static tensile stress & the corrosive environment on metal.

For This to occur:

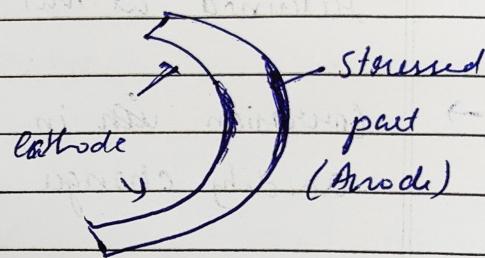
1. presence of tensile stress
2. A specific corrosive environments
e.g. caustic alkali & strong soln for mild steel.

Tensile stress is caused by:

1. Deformation during fabrication.
2. Unequal rate of cooling from a high temp.
3. Internal stress rearrangement involving volume changes.
4. Stress induced by rivets, bolts & shrink fits.
5. Eliminating high stress areas prevent this type of corrosion.

→ Caustic embrittlement:

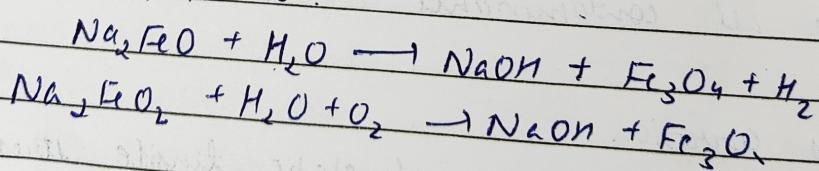
- very dangerous form of stress corrosion
- occur in mild steel exposed to alkaline solⁿ at high temp & stresses.



→ In steam boiler & heat transfer equipment, water of high alkalinity attacks the mild steel plates, particularly at the crevices near rivets.

→ Boiler water usually contain Na_2CO_3 for water softening.
In high pressure $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{NaOH} + \frac{1}{2}\text{CO}_2$.

→ NaOH make water alkaline in nature. & this flow into the minute hair-cracks & crevices by capillary action. then it dissolves Fe as.



Prevention →

- Material selection for a given environment.
- Reduce applied or residual stress.
- Use corrosion alloy inhibitors.
- Apply protective coatings.

#

Factors affecting the rate of corrosion:-

1. Nature of metal:

- Position in the Galvanic series
- Relative areas of cathodic & anodic parts
- Volatility of corrosion product
- Solubility of " "
- Purity of metal.

2. Nature of corroding environment

- Temperature
- Humidity of air
- suspended impurities
- pH value of medium
- presence of impurities in atmosphere

3. Solution pH

- nobles are not affected by pH.
- H^+ ions capture e^- & promote anodic corrosion.
- amphoteric metals dissolve rapidly in either acidic or basic solⁿ. e.g Al & Zn.
- Metal such as Fe dissolve rapidly in acidic solⁿ. Corrosion rate is controlled by rate of transport of O_2 .

4. Oxidising agents:

- They accelerate the corrosion of one class of materials, whereas retard another class.
- Oxidizing agent retard corrosion due to formation of surface oxide films, which makes the surface more resistant to chemical attack.

5. Temperature:

- TP corrosion ↑
- Temp ↑ solubility of O₂ ↓ corrosion ↑
- Temp ↑ phase change, corrosion ↑

6. Velocity:

- High velocity of corrosive medium ↑ corrosion.
- Corrosion products are formed rapidly & are brought to surface at high rate
- accumulation of insoluble film on metallic surface is prevented. So corrosion resistance of these films ↓.
- Corrosion products shifted & carried away & exposure of new surfaces for corrosion.

7. Surface films:

- Oxide films are formed on surface, delay time of drying & ↑ corrosion.

#

Corrosion Control methods:

1. Proper design

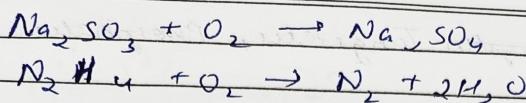
- Minimal contact with medium
- Welding
- prevent uneven stress
- paint cathodic portion
- protection from moisture

2. Modifying the environment

The corrosive nature of environment can be reduced either.

1) By removal of harmful constituents

2) By adding specific substances which neutralize the effects of corrosive environment



3. Cathodic protection

method of protection given to metal by forcibly making it to behave like cathode.

(i) Sacrificial Anodic protection

The metallic st. to be protected called "base metal" is connected to more anodic metal through a wire.

(ii) Impressed current cathodic protection.

current is applied in app. direct to nullify the corrosion current, thus the anodic corroding metal becomes cathodic & protected from corrosion.

→ A Sacrificial Mg anode assures that the O.C. make the pipeline cathode. e.g. Mg sacrificial anode of an iron storage tank.

Anodic protection

technique to control the corrosion of a metal surface by making it the anode of an electrochemical cell & controlling the electrode potential in a zone where the metal is passive.

e.g. zinc is attached to the steel hull of vessel.

4. Corrosion Inhibitors.

When added to aq. corrosive environment, effectively stops the corrosion.

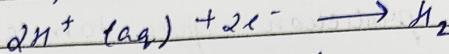
Anodic Inhibitors:

they avoid the corrosion rxn occurring at anode, by forming sparingly soluble compounds. A protective film is formed. as a barrier which reduce corrosion rate.

Eg → Chromate, Tungsten Tungstate, Phosphate.

Cathodic Inhibitors:

→ In acidic medium, corrosion may be reduced by



1. Slowing down the diffusion of H^+ ions by organic inhibitors like amines, mercaptans etc.
2. ↑ the voltage of H evolution by adding inhibitors like Antimony & As oxides.

→ In neutral $O_2 + H_2O + 2e^- \rightarrow OH^-$

1. Eliminating O_2 from corrosion by addition N_2, SO_3, Na_2S .

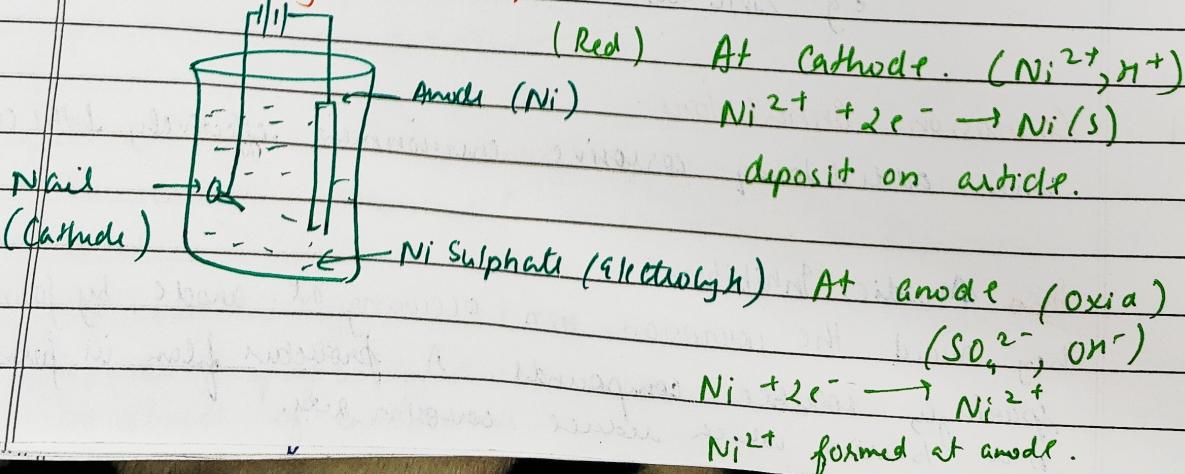
5. Electroplating

process of depositing a thin layer of a fine & superior metal (like Cu, Zn, Ni, Au etc) over the article of a base & cheaper metal (like Fe) with current.

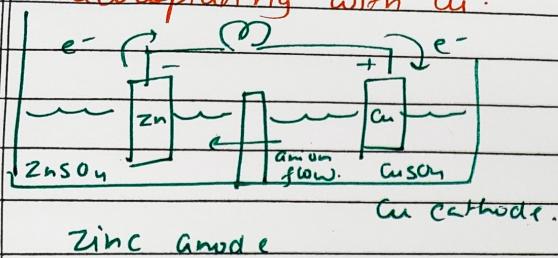
Two Methods \rightarrow by Ni
 \rightarrow Cu.

→ Cathode to electroplate & pure metal as Anode.

Electroplating with Ni



Electroplating with Cu:



6. Metals Coating:

- Coatings of metals that are susceptible to differential corrosion will protect them from further corrosion.
- best → galvanised steel. (steel coated with Zn)

Why Zn is a good choice?

- ① It forms passive layer that prevent further corrosion
- ② It is anodic when compared to steel, so in the event of underlying steel becoming exposed the Zn will still corrode to protect the steel.

Dating Methods

Hot dipping
Metal

↓ cleaning
acid

↓ dipped in
coating material
which is melted.

Electroplating
involves use of
an electric current to
deposit a layer of
protective metal onto
surface;
metals used → Ag, Au,
Cr.

Spraying
Zn powder is
deposited onto a
heated obj; used
when H.D may clog
fine details.

Electrode potential: p.d b/w electrodes developed when a electrode is place in a solⁿ containing ions of that element.