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→ ## METAL FINISHING :

Process of deposition of an adherent metallic film of a noble metal on a base metal or polymer surface.

Objectives:

- in general, a metal or alloy used for a purpose does not meet all the requirements. Metal finishing is used to improve their lacking properties.
- improving resistance to corrosion, chemical & moisture attack, scratch or abrasion and wear.
- enhancing decorative appearance
- improving hardness, thermal, optical, mechanical and electrical properties

Metal Finishing

↓ Electroplating
↓ using electricity
Electroplating of chromium

↓ Electrolessplating
↓ using reducing agents
Electrolessplating of copper

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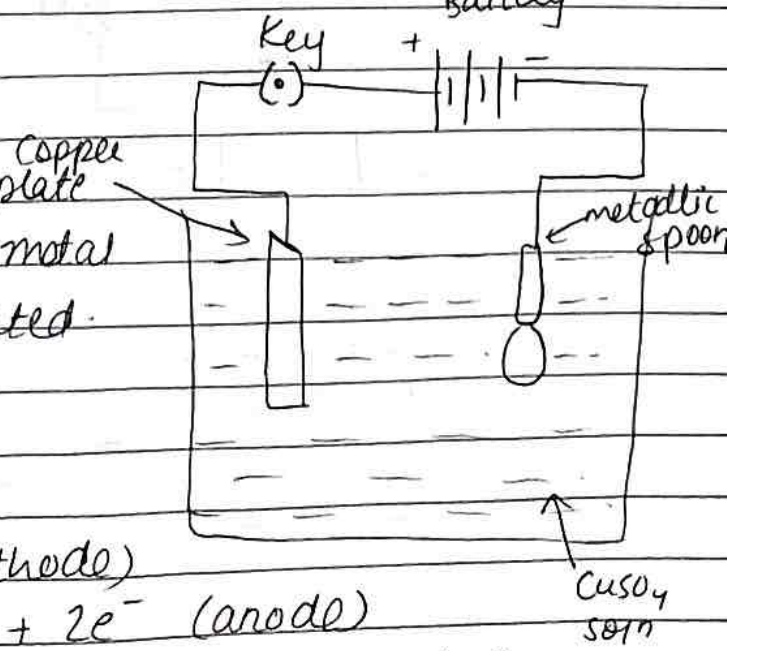
→ Electroplating:

- process in which a thin layer of coating metal is deposited on a base metal by passing d.c through an electrolytic soln., containing the soluble salt of the coating metal

- Theory of electroplating; Anode, cathode, electrolyte, direct current.

Essential Components:
A d.c electrical power source
Anode: inert material / coating metal
Cathode: article to be plated
Electrolytic bath: Solution of conducting salt, metal to be plated in a soluble form, buffer and additives.
Container: made up of rubber lined steel, wood or concrete

- Electroplating of copper



- Anode: made of coating metal
- Cathode: article to be plated.
- Electrolyte: $CuSO_4$ soln.

$CuSO_4 \longrightarrow Cu^{2+} + SO_4^{2-}$

On passing current,

$Cu^{2+} + 2e^- \longrightarrow Cu$ (cathode)

$Cu + SO_4^{2-} \longrightarrow CuSO_4 + 2e^-$ (anode)

Continuous replenishment of electrolytic salt during electrolysis. If anode is some inert material like

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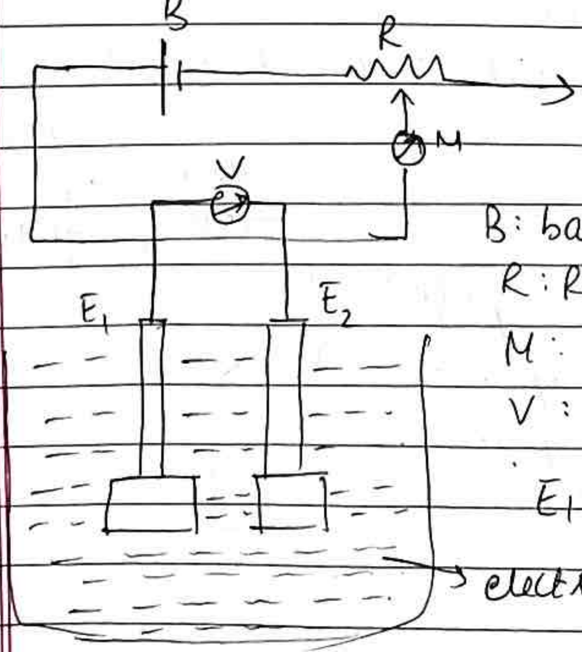
graphite, then electrolytic salt is added continuously to maintain proper coating metal ion conc.

- Factors governing Electroplating:

  - Decomposition Potential (D.P)
  - Polarization
  - Overvoltage

- Decomposition Potential:

  - Minimum external potential at which the electrolysis current begins to increase appreciably & continuous electrolysis sets in is known as decomposition potential of the electrolyte.



B: battery
R: Rheostat
M: ammeter
V: voltmeter
E_1 and E_2: Pt electrode
electrolytic solⁿ

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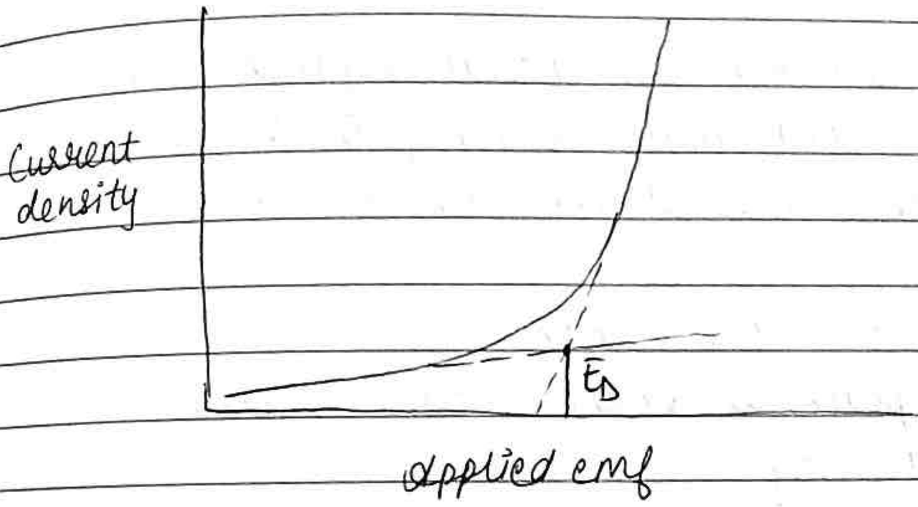

E_D - decomposition potential

- Factors affecting E_D:
  1. Strength of the current flowing through the cell
  2. Chemical & physical nature of electrodes
  3. Activity of the electrolyte
  4. Absolute temperature
  5. Uses of E_D

→ Overvoltage:

- The decomposition of an electrolyte is expected to start as soon as applied potential reaches the value of reversible emf of the cell.
- But when products discharged at the electrodes are gases, then the actual decomposition potential is invariably much higher than its theoretical reversible electrode potential.
- The excess voltage is referred to as overvoltage of the gas

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- difference between the actual applied emf to bring about continuous electrolysis & the theoretical emf needed for such electrolysis.

Factors affecting overvoltage:
- Nature & physical state of the electrodes
- Current density
- Temperature
- Nature of the electrolyte
- Nature of the material deposited

- Polarization:

- Development of over potential in an electrolytic cell is called polarization.
- Electrolytic processes occur at the electrodes of the cell.
- Polarization sets in the cell when the electrode processes become slow and irreversible.
- Magnitude of over potential is directly proportional to the extent of polarization.

Types of polarization:
- concentration polarization
- kinetic or activation polarization
  ↳ cannot be eliminated

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- Concentration polarization:

- An electrochemical reaction occurs only at the surface of the two electrodes.
- Adjacent to the electrode surface, reactant conc. decreases.
- The reactant species are transported to the electrode surface by processes like diffusion and migration from the bulk of the soln.
- Current flowing through the cell drops when the rate of transport is insufficient to match the electrode reaction.
- A potential higher than the theoretical value is required to maintain the current at the necessary level.
- can be minimized by:
  - by raising the temperature
  - mechanical agitation of the soln.

- Activation Polarization: (mostly for gas, not metal electrodes)

This is caused when any of the following steps becomes slow and need activation energy

→ Adsorption of the reactant on the electrode
→ Charge transfer across the metal-solution interface
→ Desorption of the product from the electrode
→ A higher potential than the theoretic value is to be applied to maintain current at the necessary level

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Characteristics of a good deposit:

- The deposit should be bright and lustrous.
- The deposit should be continuous, uniform, non porous and adhesive.
- It should be hard and ductile
- It should be of fine grained nature

Factors Influencing the nature of Deposit:

- Current Density:
  An optimum current density should be applied.
  If low - leads to slow process, take more time to complete the process
  results in coarse grained deposit.

  If high - more deposition, but poor adhesion
  leads to rough and brittle deposit.
  results in burnt and spongy deposit

Metal salt and electrolyte concentration:
- Moderate / low electrolyte concentration should be maintained in bath to get a better deposit.
- If concentration of metal ion is low the crystal size will be smaller and a fine adherent film may be coated
- Firm and adherent deposits.

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Low metal ion conc. can be achieved:
- by addition of a compound with a common ion
- by formation of complex compounds

- Temperature:
• It should be between 35°C and 65°C
• Lower temperature: reduces the solubility of the metal salt. reduces the mobility of the ions.
• Higher temp: increased metal dissociation, higher ionic mobility & conductance
• Crystal size increases, poor adherence affects the lining of the equipment, electrode surface and the substrate. Decomposition of organic agents and H_2 evolution.

- Agitation:

• Agitation of the solution brings up a fresh supply of metal salts to the cathode.
• It also sweeps away gas bubbles which may otherwise cause pits.
• Rapid agitation may:
  stir up the sludge.
  results in rough and porous deposits.

pH of the electrolytic bath:
• Suitable pH is maintained using appropriate buffer.
• In Ni plating, borate buffer is used to maintain pH 4.5
• At low pH more H_2 evolution takes place at cathode & burnt deposit.

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- At higher pH, precipitation of hydroxides of metal takes place

Addition agents:

- The wide range of additives are added in low concentrations, serve to electroplating bath to modify the structure and properties of the electrodeposits.

- Function:
  - makes the deposit smooth, fine grained, hard and adherent.
- Types of additives:
  - Complexing agent
    e.g: cyanide, sulphamate ions
  - brighteners:
    e.g: aromatic sulphonates, thiourea
  - wetting agents:
    e.g: sodium lauryl sulphate
  - levelers:
    e.g: cellulose derivative.

Throwing Power:

- defined as the degree of uniformity of metal distribution or evenness of deposit thickness obtained on a cathode of irregular shape.
- If distribution of the deposit is uniform throughout the surface of the article to be coated, the throwing power is considered good

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- Tendency of plating bath solution to give uniform coating irrespective of the shape of the object.