ChE-455/555:INTRODUCTION TO METAL DEPOSITION FROM IONIC SOLUTIONS

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Content of this presentation

- Definitions: electrodeposition? / electroplating?
  - Applications
  - Advantages
  - Plating process
- Techniques:
  - Surface preparations
  - Plating solutions
  - Plating conditions
  - Anodes
  - Mass transport requirements
  - Rinsing

Definitions

- Definition: electrodeposition? / Electroplating?
  - Process of separating metals from solutions by deposition onto a cathode
  - Depending on the physical state of the metal deposit:
    - Electroplating: fine grained crystal deposit (smooth, strong adhesion, glassy)
    - Electrodeposition/refining: coarse grained, rough, adhesive deposits (high purity)
    - Metal powder production: controlled particle size, no adherence to the cathode

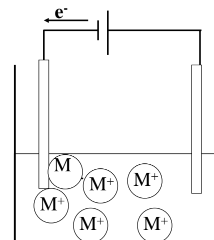
Applications

- Coatings for mechanical/ chemical properties (corrosion resistance, wear resistance,…)
- Production of electrodes (fuel cells, electrolysis, sensors)
- Refining of metals (high purity)
- Electrowinning (ionic waste removal from solution)
- Powder production (pressing, sintering)

Electrodeposition: advantages

- Control of properties
  - Chemical composition (reversibility)
  - Physical properties
  - Microstructure, …
- Some properties of deposited metals are impossible to attain by thermal processes (not predicted by phase diagrams)
- More control variables
  - Aqueous concentrations
  - Potential
  - Current density
  - Additional substances in solution (additives)
  - Substrate structure, …

Plating process



- Discharge occurs at the cathode
- Oxidation takes place at the anode

Laws and mechanisms of plating processes

- Metals plate out at different potentials

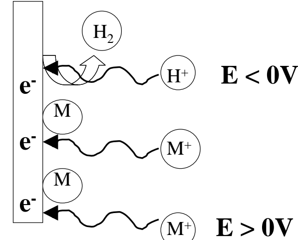
Table I - The Electromotive Force Series

Electrode	*Potential, V*	*Electrode*	*Potential, V*
$Li \rightleftharpoons Li^+$	−3.045	$Co \rightleftharpoons Co^{++}$	−0.277
$Rb \rightleftharpoons Rb^+$	−2.93	$Ni \rightleftharpoons Ni^{++}$	−0.250
$K \rightleftharpoons K^+$	−2.924	$Sn \rightleftharpoons Sn^{++}$	−0.136
$Ba \rightleftharpoons Ba^{++}$	−2.90	$Pb \rightleftharpoons Pb^{++}$	−0.126
$Sr \rightleftharpoons Sr^{++}$	−2.90	$Fe \rightleftharpoons Fe^{3+}$	−0.04
$Ca \rightleftharpoons Ca^{++}$	−2.87	$Pt/H_2 \rightleftharpoons H^+$	0.0000
$Na \rightleftharpoons Na^+$	−2.715	$Sb \rightleftharpoons Sb^{3+}$	+0.15
$Mg \rightleftharpoons Mg^{++}$	−2.37	$Bi \rightleftharpoons Bi^{3+}$	+0.2
$Al \rightleftharpoons Al^{3+}$	−1.67	$As \rightleftharpoons As^{3+}$	+0.3
$Mn \rightleftharpoons Mn^{++}$	−1.18	$Cu \rightleftharpoons Cu^{++}$	+0.34
$Zn \rightleftharpoons Zn^{++}$	−0.762	$Pt/OH^- \rightleftharpoons O_2$	+0.40
$Cr \rightleftharpoons Cr^{3+}$	−0.74	$Cu \rightleftharpoons Cu^+$	+0.52
$Cr \rightleftharpoons Cr^{++}$	−0.56	$Hg \rightleftharpoons Hg_2^{++}$	+0.789
$Fe \rightleftharpoons Fe^{++}$	−0.441	$Ag \rightleftharpoons Ag^+$	+0.799
$Cd \rightleftharpoons Cd^{++}$	−0.402	$Pd \rightleftharpoons Pd^{++}$	+0.987
$In \rightleftharpoons In^{3+}$	−0.34	$Au \rightleftharpoons Au^{3+}$	+1.50
$Tl \rightleftharpoons Tl^+$	−0.336	$Au \rightleftharpoons Au^+$	+1.68

- Complexing agents shift the potential to more negative values

Hydrogen evolution

- Protons in solution will co-deposit at potentials lower than 0V vs. SHE !!!!



CONSEQUENCE: to plate metals more negative than zinc, non-aqueous solutions are needed

Mechanism of plating

- Two-step mechanism on the surface

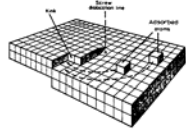


Figure 1 - Model of metal atom deposition as an adsorbed atom or adion and surface diffusion to the final location at a kink site.

- Rate of nucleation depends on the potential
- Rate of plating depends on the current density
- Amount plated: $W = ItA / Fn$ (in grams)

(FARADAY's law)

Summary on plating process

- Plating process provides control on the chemical, physical, and structural properties of deposited metals
- Each metal plates at different potential; changing the plating solution chemistry is one way to control the plating potential
- In aqueous solution, hydrogen evolution takes place for E <0V and decreases the plating efficiency
- Plating process occurs in two steps: discharge of ions followed by nucleation
- Deposition rate is given by Faraday's law

PLATING TECHNIQUES

Plating techniques: surface preparation

- Objective: obtaining a strong metal-to-metal bond

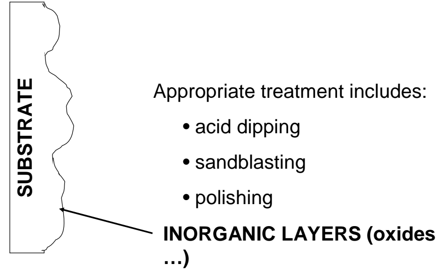
ORGANIC LAYERS

Appropriate treatment includes:

- Dilution in solvents (acetone,…)
- Saponification with alkaline cleaners
- Electrolytic cleaning

Plating techniques: surface preparation

- Objective: obtaining a strong metal-to-metal bond



Appropriate treatment includes:

- acid dipping
- sandblasting
- polishing

INORGANIC LAYERS (oxides …)

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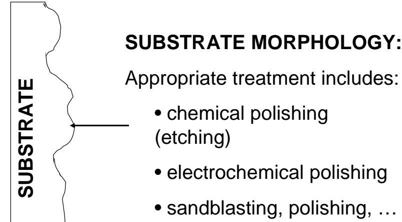
Plating techniques: surface preparation

- Objective: obtaining a strong metal-to-metal bond



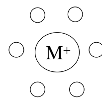
SUBSTRATE MORPHOLOGY:

Appropriate treatment includes:

- chemical polishing (etching)
- electrochemical polishing
- sandblasting, polishing, …

ChE-455/555: Electrochem. System

Plating techniques: solution preparation

- Metal deposition processes involve reduction from cations in solution:
  - Simple cations:
  - Complex ions: 
- Complex ions have different free energy/activities in solution compared to simple ions and therefore deposit at different potential:

$$\Delta G = -nFE$$

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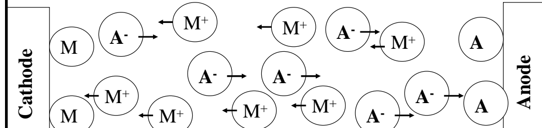
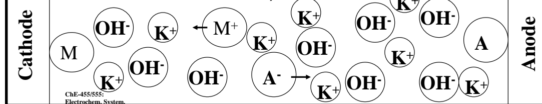
Solution preparation (continued…)

- High conductivity of the solution must be achieved to transport charges in solution either by using a high concentration of plating ions:



or by adding a supporting electrolyte (does not react at the electrode)



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Solution preparation (continued…)

- Role of anions: they determine
  - the physical properties of the metal deposit:
  - The stable valence state of the metal ions in solution
    - Eg: Cu is divalent in sulfate solution Cu^{+}

Cu is monovalent in cyanide solution Cu^{2+}

Solutions							
Sulfate and Chloride				Cyanide			Fluoborate and Fluoride
VIB	VIII			IB	IIB	IIIA	IVA
Cr	Fe	Co	Ni	Cu	Zn		
	Ru	Rh	Pd	Ag	Cd	In	Sn
			Pt	Au	Hg		Pb

Figure 2 - Metals readily plateable from aqueous solutions and bath types most often used.

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Solution preparation (continued…)

- Microthrowing/macrothrowing power:

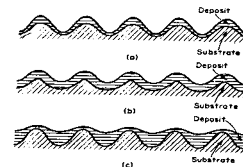


Figure 3 - Types of microthrowing power: (a) negative microthrow, (b) geometric leveling, (c) true leveling.

The microthrowing/macrothrowing power of the solution will depend on the bath composition (anions) AND the addition of inorganic/organic additives

ChE-455/555: Electrochem. System

Plating techniques: plating variables

- Objective: achieve the optimum deposit quality (to be defined) at as high a rate as possible
- Plating temperature: usually above ambient (+/- 5°C is acceptable)
- Solution pH (unless bath is strongly acidic or alkaline) ⇒ use of buffers
- Current density: an optimum current range exists:
  - Too high ⇒ "burned", dull, and rough deposits (under mass transfer limitation)
  - Too low ⇒ long plating times, coarse, dull plating
- Overpotential: high η favor macrothrowing power and uniform metal deposition

Plating variables (continued…)

- Rate of metal deposition is related to the electrode overpotential:

$$i = -i_0 \exp\left(\frac{\eta\alpha nF}{RT}\right)$$

Butler - Volmer equation

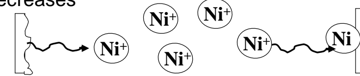
- An independent determination of i_0 and α can predict the dependence between η and i
- Usually high exchange current densities i_0 are sought for a corresponding low overvoltage η (exception: Ni, Fe, Co)

Plating variables (continued…)

- Cases where high overvoltage is beneficial:
  - Reducing surface oxides
  - Enhance hydrogen evolution and benefit from its reducing power
  - The "strike" technique (very high current densities and low solution concentrations) to improve adhesion of metal-metal bonds on "hard-to-plate metals" (eg. Ni strike on stainless steel)

Plating techniques: anode requirements

- Objective: maintain constant the concentration of metal ions in solution during the plating process and avoid formation of oxidation products
- Two types of electrodes:
  - Solubles: they dissolve as the bath concentration decreases



  - Insoluble: usually made or coated with noble/inert metals (Pt, carbon) to prevent the formation of oxides

Plating techniques: mass transport

- Fact: for most electrodeposition with high exchange current densities, the process is limited by the supply of metal ions to the cathode surface
- Mass transport occurs by:
  - Convection
  - Diffusion
  - Migration
- Limiting current is given by:

$$i_l = \frac{nFDC}{\delta}$$

Mass transport (continued…)

- Some numbers:
  - Still solutions: δ = 500μm
  - Vigorously stirred baths: δ = 10μm
- A good rule of thumb for plating is (1 e^- transfer reaction):
  - 1 mA/cm^2 for each cm/s of flow rate across the cathode
- Mass transfer limited electrodeposition prevents from obtaining bright and smooth electrodeposits
- It is under mass transfer limitation that the formation of dendrites and powders is possible

Plating techniques: rinsing

- Rinsing should ALWAYS be provided (as important as surface preparation) to obtain a clean, active, and stable metal deposit
  - High purity water is best if affordable
  - Rapid water movement is preferable (spraying) for impurities removal (dust, powder,…)
  - Heated water is needed to dissolve deposited salts

REMEMBER: the conductivity of your rinsing water is a good parameter to estimate the cleanness of your electrode

Summary on plating techniques

- Pre-treat your cathode (organic / inorganic layers removal and shaping of the surface)
- Prepare your plating solution (select a salt (anion), ligands, supporting electrolytes, organic/inorganic additives)
- Select your anode (soluble or non-soluble)
- Set the hydrodynamics of your cell (strong mixing for high current densities)
- Set your plating variables (T, pH, i, and η)
- Rinse your electrode thoroughly

READY TO GIVE IT A TRY?