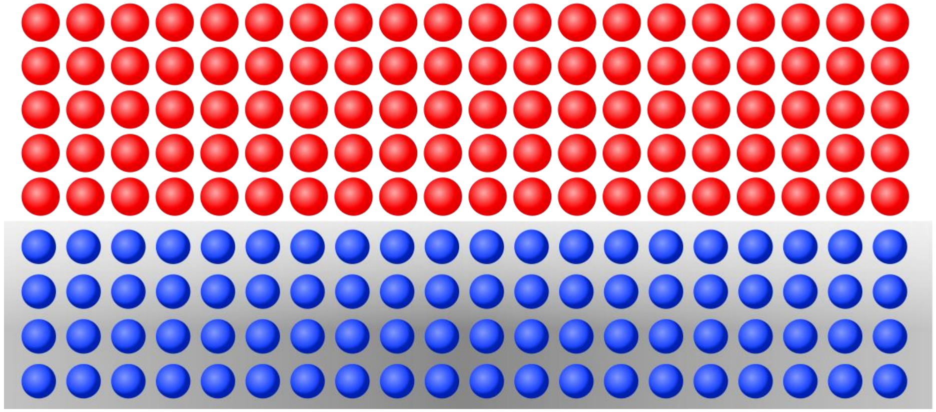
Chapter (4)

Theory of Metal Electrodeposition

Introduction

- Electro deposition is the process of coating a thin, adherent layer of one metal on top of another metal to modify its surface properties.
- Done to achieve:
  1. desired electrical resistance,
  2. corrosion resistance,
  3. Reduction in wear & friction,
  4. Improvement of heat tolerance and
  5. decoration.
- EDN is a surface coating method that forms of one metal on another.



Introduction

- Electrolytic industrial processes for metals include:

  1. the production of metals from their compounds, which is called the electrowinning of metals;
  2. the electrolytic purification of metals;
  3. electroplating of metals on conducting surfaces;
  4. electroforming of metals in different desired shapes, and
  5. recovery of spent metals and the production of metal powders and alloys.

- In all these types of electrolytic process, the reactions are mainly reduction of ions of the metal in solution in some carefully selected electrolyte.

Metal Electrodeposit

- Electrodepositive metals are crystalline in nature (Figure 4-1).
- The external appearance of the deposit depends on the rate of nucleation and the rate of growth of metal crystals.
  - If the rate of nucleation is higher than the rate of crystal growth, a smooth, fine deposit is obtained.
  - If, on the other hand, the rate of crystal growth is higher than the rate of nucleation, a coarse, rough deposit is obtained.

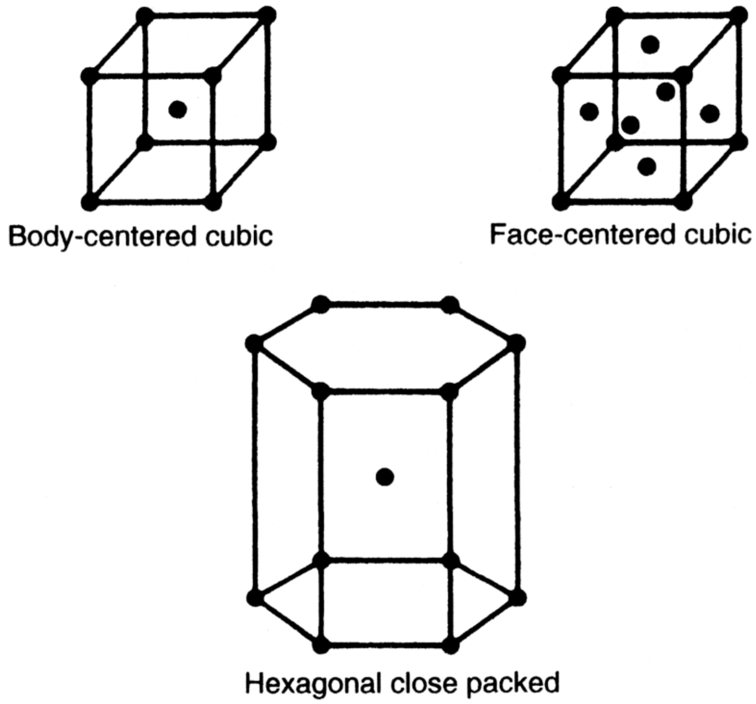

Body-centered cubic
Face-centered cubic
Hexagonal close packed

FIGURE 4-1:
Unit cells of the three most important lattices

Metal Electrodeposit

- Electroplated films almost always contain various types of impurities. These additives may be from one or more of the following origins:
    1. Added chemicals (levelers, brighteners, etc.)
    2. Added particles (for composite coating)
    3. Cathodic products (complex metal ions)
    4. Hydroxides (of the depositing metals)
    5. Bubbles (e.g., hydrogen gas)

- In general, it may be stated that deposits produced using low current densities possess higher impurity content than deposits produced using high current densities.

4.1 Theory of Electrodeposition

A) Conditions for Starting Deposit:

- A metal starts to deposit when the cathode potential becomes equal to the value given by the equation:

$$E_{actu} = E_{theo} + \acute{\eta}_M$$

- For two metals A and B to deposit simultaneously from their salts, the following condition should be satisfied:

$$E_{A,actu} = E_{B,actu}$$

$$E°_A + (RT/zF) \ln [A^+] + \acute{\eta}_A = E°_B + (RT/ZF) \ln [B^+] + \acute{\eta}_B$$

- Examination of the above equation shows that there are three ways by which the discharge potential for the two cations may be brought together:

4.1 Theory of Electrodeposition

1) If the standard potentials are approximately equal and polarization is small, the two metals will deposit simultaneously.

2) If the standard potentials of the two metals are different, but the overvoltage vary sufficiently to compensate for this difference, the two metals will deposit together at a given concentration:

$$E^{o}_{A} > E^{o}_{B} \quad \textbf{but} \quad \acute{\eta}_{A} < \acute{\eta}_{B}$$

3) If the standard electrode potentials are not closed and polarization is not negligible, the two potentials can be made close to each other through adjusting the *metal ion concentration.*

4.1 Theory of Electrodeposition

B) Examples from Practice on the Electrochemical Deposition:

1) Lead and tin lie near each other in the electromotive series (E°, Pb = -0.126 V and E°, Sn = -0.136 V).
   - The two metals have a negligible polarization, but they can be deposited together by a slight adjustment of their ion concentration to compensate for the small difference in their E° values.

2) Zinc and hydrogen lie far apart in the electromotive series.
   - Theoretically, it is impossible to deposit Zn form an aqueous ZnSO4 solution because H2 will evolve in preference to Zn deposition (hydrogen needs less potential).
   - In practice, it is possible to deposit Zn from aqueous solutions since the difference in the standard potentials of the two elements is compensated for by the high hydrogen overvoltage on Zn.

4.1 Theory of Electrodeposition

3) Copper and zinc are far apart in the electromotive series; hence, it is impossible to deposit the two metals simultaneously from their simple source (a mixture of CuSO4 and ZnSO4).

- It was found that the two metals can be deposited together if a cyanide complex of Cu and Zn is used as discussed below.
- The degree of ionization of the Zn cyanide complex is relatively high compared with that of the Cu cyanide complex.
- Therefore, the concentration of free Zn ions will be high compared to the concentration of free Cu ions and thus, the difference in E° of the two metals will be compensated for by the difference in the ion concentrations:

- **Copper:** $K3[Cu(CN)4] \rightarrow 3\ K^{+} + \{Cu(CN)4\}^{-3}$

$$\{Cu(CN)4\}^{-3} \leftrightarrow Cu^{+} + 4\ CN^{-}$$

$$K = [Cu^{+}][CN^{-}]4 / [\{Cu(CN)4\}^{-3}] = 10^{-27}$$

- **Zinc:** $K2[Zn(CN)4] \rightarrow 2\ K^{+} + \{Zn(CN)4\}^{-2}$

$$\{Zn(CN)4\}^{-2} \leftrightarrow Zn^{2+} + 4\ CN^{-}$$

$$K = [Zn^{2+}][CN^{-}]4 / [\{Zn(CN)4\}^{-\ 2}] = 10^{-18}$$

Note:
Brown color: superscript

4.1 Theory of Electrodeposition

- The factors which affect the relative rates of nucleation and growth and hence affect the quality of the electrodeposit are discussed below.
- The morphology and composition of electrodeposits vary significantly and depending on:
  1. **Current density**
  2. **Nature of the electrolyte solution**
  3. **Concentration of electrolyte solution**
  4. **Solution temperature**
  5. **Added colloidal materials**
  6. Presence of solution impurities
  7. Physical & chemical nature of the substrate surface.

C) Factors Affecting the Quality of Metal Electrodeposits:

1. Effect of current density:

- At low current densities, the rate of crystal growth is higher than the rate of nucleation; so, a rough (coarse) deposit is obtained.
- At moderate current densities, the rate of nucleation becomes higher than rate of growth, and a fine (smooth) deposit is obtained.
- At high current densities, the solution at the electrode surface becomes dilute in the electroactive ion and this leads to the formation of dendritic deposit (**Figure 4.2**).
- At the limiting current, hydrogen starts to evolve and interferes with crystal growth leading to the formation of powder metal.

C) Factors Affecting the Quality of Metal Electrodeposits:

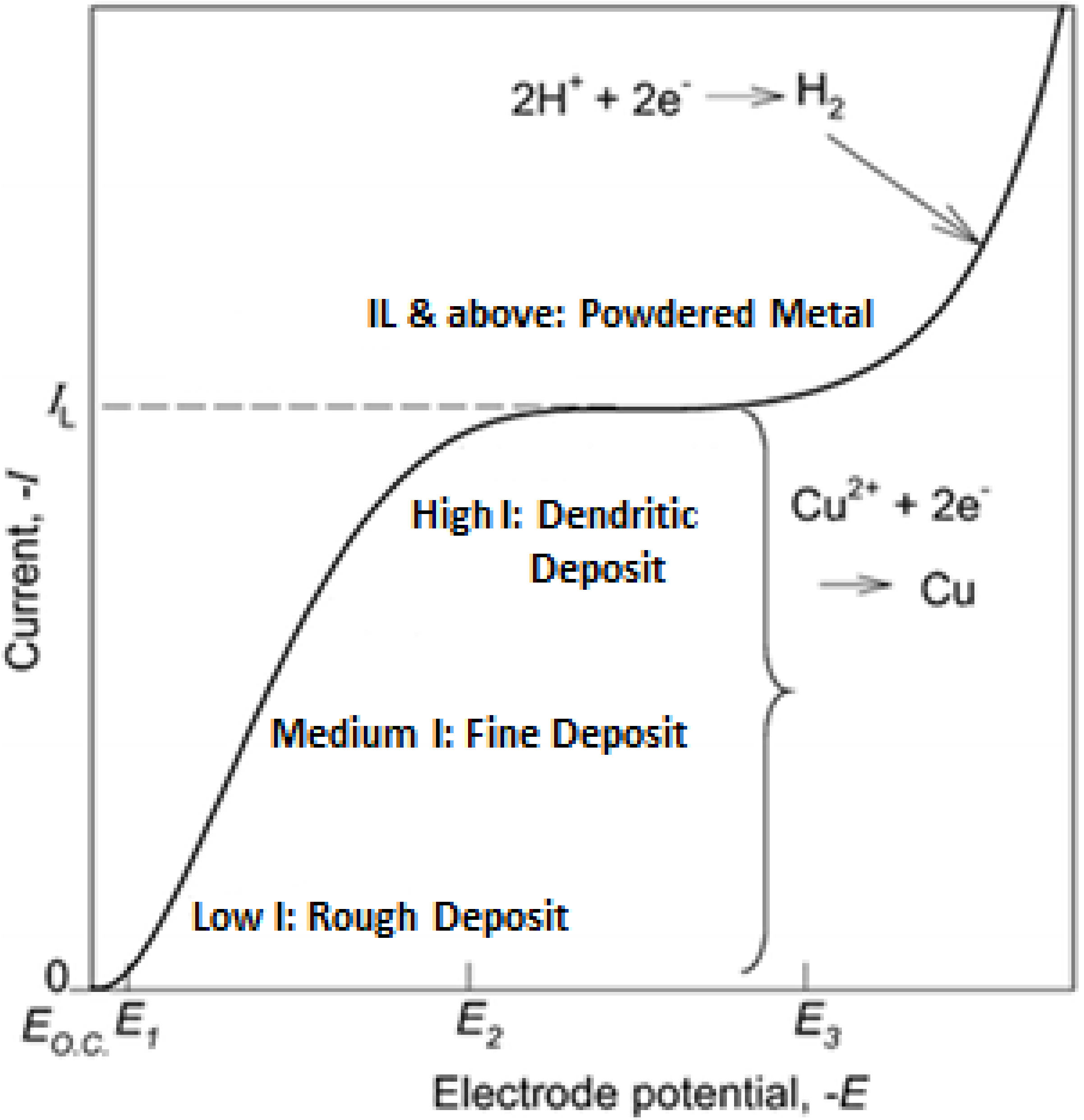


Figure 4.3: An idealized current vs. potential curve for metal deposition from electrolyte solution

C) Factors Affecting the Quality of Metal Electrodeposits:

2. Effect of the nature of electrolyte:

- It was found that complex salts produce fine, smooth deposits, while simple salts produce rough deposits e.g. Ag deposited from AgNO3 is coarse, while Ag deposited from silver cyanide complex: K[Ag(CN)2] is smooth and fine.
- Similarly, CuSO4 produces a rough Cu deposit, while copper cyanide complex: K3[Cu(CN)4] produces smooth deposit.

3. Effect of electrolyte concentration: Relatively high concentrations of metal-containing electrolyte give firm, adherent deposits while dilute solutions give dendritic, loose deposits.

C) Factors Affecting the Quality of Metal Electrodeposits:

4. Effect of temperature:

- The operating temperature of the electrolytic cell has two opposing effects:
- The first effect is that increasing the temperature increases the rate of diffusion of the electroactive ion to the cathode surface.
  - This leads to the prevention of the formation of dendretic deposits which are formed at high current densities where the solution at the cathode surface is very dilute.
- The second effect is that increasing the temperature favors crystal growth, i.e., the formation of rough deposits.
  - The first effect predominates at moderate temperatures, while the second effect predominates at high temperatures.

C) Factors Affecting the Quality of Metal Electrodeposits:

5. Effect of adding colloidal materials:

- Addition of a very small amount of a colloidal material (in the order of 50 mg/L) to electroplating baths produces smooth, fine and bright deposit.
- Such colloidal materials include gelatin, agar, glue and gum.
- The mechanism of action of colloidal matter is that this material becomes adsorbed on the surface of the nuclei, thus reducing the rate of growth of these nuclei; hence, the solution is forced to form new nuclei.
- In other words, the rate of nucleation becomes higher than the rate of growth and this result in the formation of smooth and fine deposits.

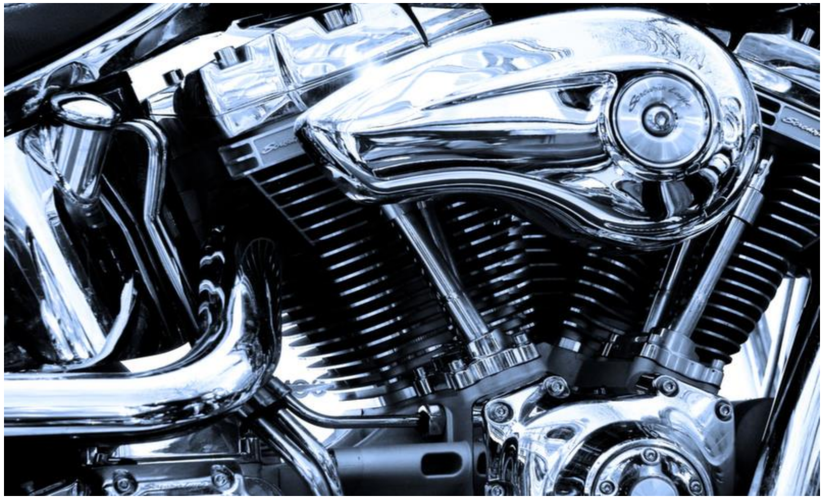
C) Factors Affecting the Quality of Metal Electrodeposits:

6. Presence of solution impurities

Varies according to the type and concentration of the impurity. Some have positive effects while others are undesirable.

7. Physical & chemical nature of the substrate surface

Some surfaces need cleaning and pretreatment before electrodeposition in order to obtain a smooth and bright deposit (plate).



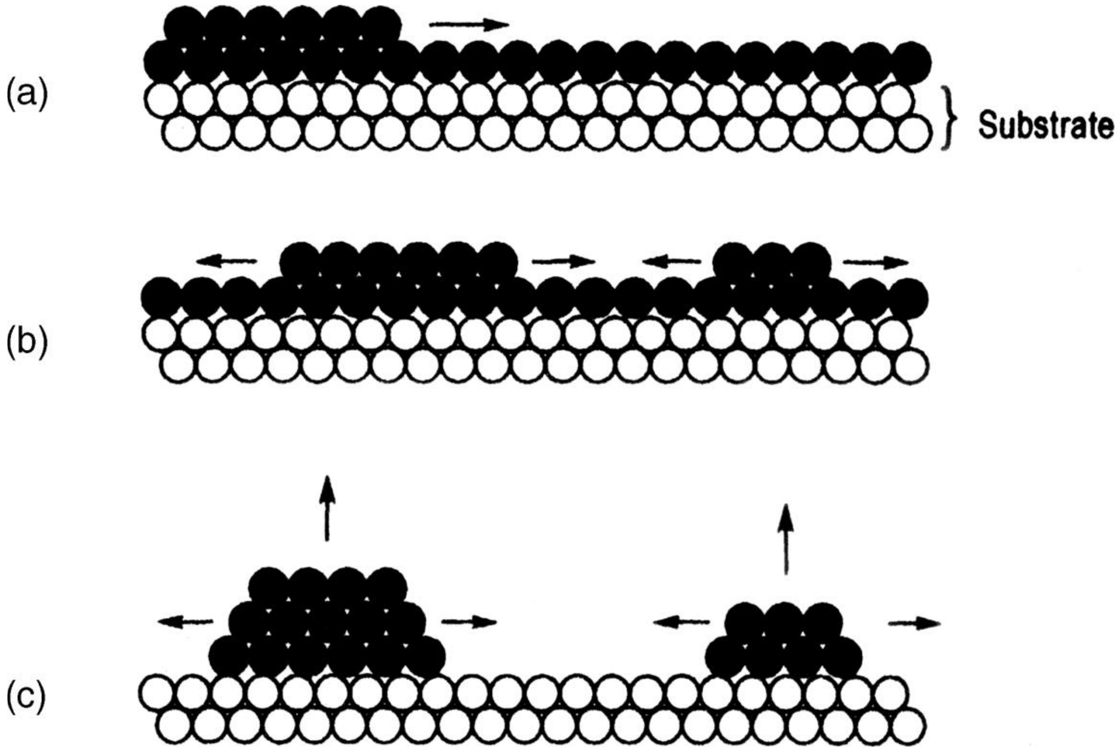
Cathode Efficiency

- The ratio of the weight of metal actually deposited to the weight that would have resulted if all the current had been used for depositing it is called the cathode efficiency.
- Cathode efficiency in electrodeposition (e.g. plating) depends on:
    1. Electrolyte or bath composition
    2. Concentration of chemical component
    3. Solution pH
    4. Agitation
    5. Current density
- The current efficiency varies widely in metal deposition.
    - For example, in Ni plating is close to 100% , while in Cr plating it is approximately 20%.

Electrodeposit Growth Mechanism

- There are two basic mechanisms for formation of a coherent deposit: layer growth and three-dimensional (3D) crystallite growth (or nucleation–coalescence growth). A schematic illustration of these two mechanisms is given in **Figure 1.16**. coarser grains at greater distances from the substrate.

FIGURE 1.16
Schematic representation of layer growth (a, b) and the nucleation–coalescence mechanism (c).



Electroanalytical

1. The most common use of electrodeposition is known as *electrogravimetry.*
2. The electrodes are weighed prior to the deposition and afterwards.
3. The increase in mass on the cathode is the amount of that material present.

Sample Problem:

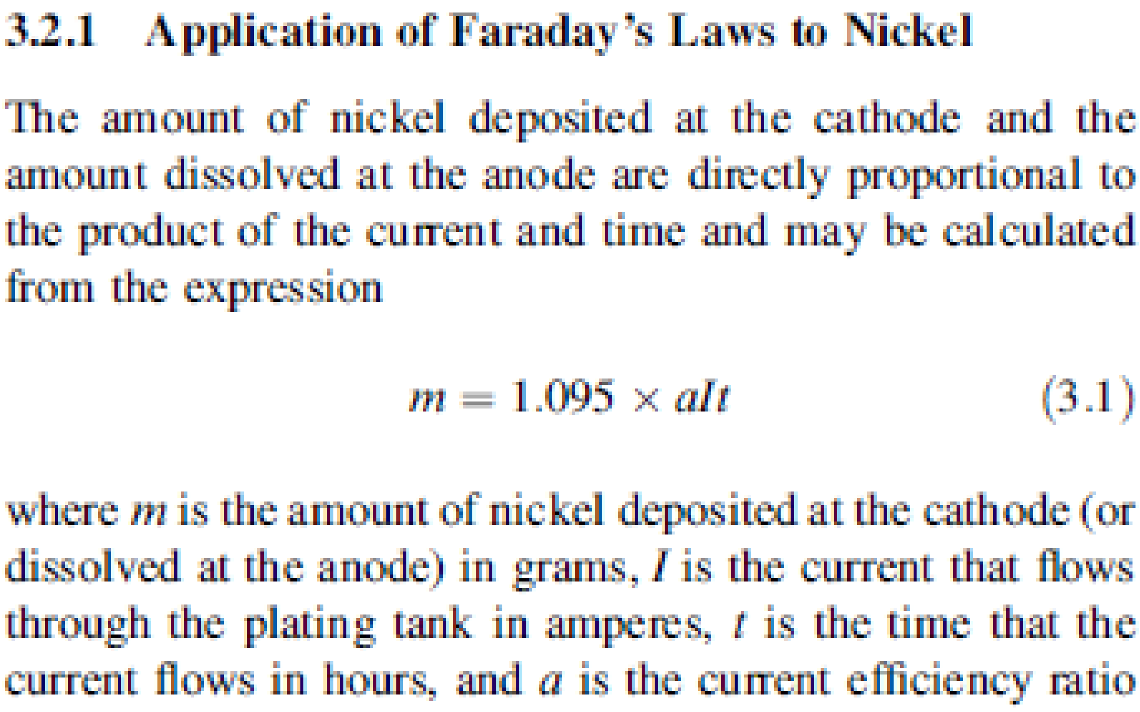
A 1.2563 g sample containing copper was analyzed by dissolving it in sulfuric acid and carrying electrolysis. The cathode weighed 22.3165 g before electrolysis and 22.5433 g afterwards.

What is the % copper in the original sample?

- mass of Cu = 22.5433 – 22.23165 = 0.2268 g
- % Cu = (0.2268/1.2563) x 100 = 18.05%

Electroanalytical

Deposit Thickness:
Nickel as an Example

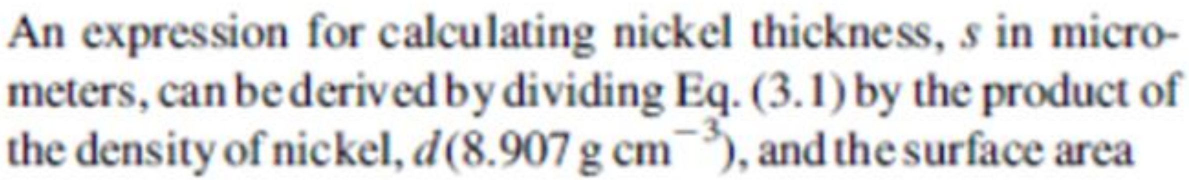


3.2.1 Application of Faraday's Laws to Nickel

The amount of nickel deposited at the cathode and the amount dissolved at the anode are directly proportional to the product of the current and time and may be calculated from the expression

$$m = 1.095 \times aIt \qquad (3.1)$$

where m is the amount of nickel deposited at the cathode (or dissolved at the anode) in grams, I is the current that flows through the plating tank in amperes, t is the time that the current flows in hours, and a is the current efficiency ratio



An expression for calculating nickel thickness, s in micrometers, can be derived by dividing Eq. (3.1) by the product of the density of nickel, d (8.907 g cm^{-3}), and the surface area

s (thickness) = volume/area

= mass/ density/ area

= 1.095 (a. I. t) /(8.907 A) in cm

= 1.095 (a. I. t) .10000/ (8.907 A) in µm

Electroanalytical

Deposit Thickness:
Nickel as an Example

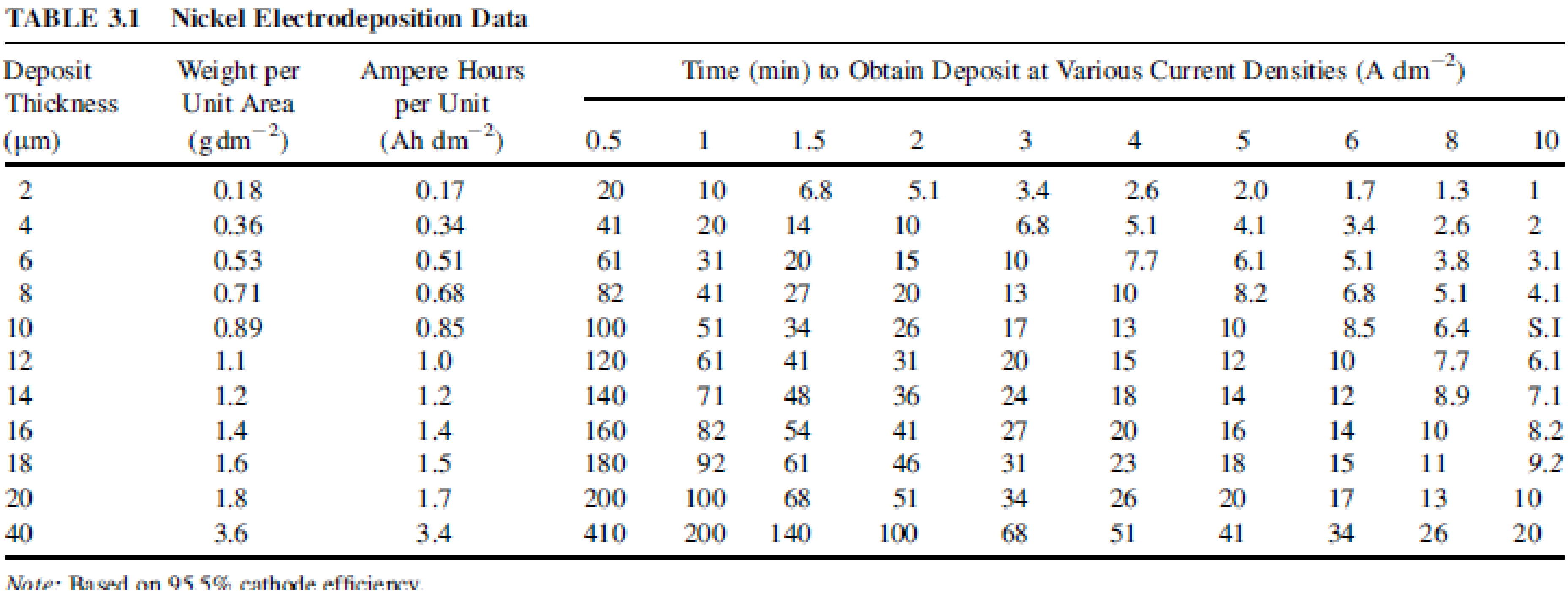


TABLE 3.1 Nickel Electrodeposition Data

Deposit Thickness (μm)	Weight per Unit Area (g dm^{-2})	Ampere Hours per Unit (Ah dm^{-2})	Time (min) to Obtain Deposit at Various Current Densities (A dm^{-2})									
			0.5	1	1.5	2	3	4	5	6	8	10
2	0.18	0.17	20	10	6.8	5.1	3.4	2.6	2.0	1.7	1.3	1
4	0.36	0.34	41	20	14	10	6.8	5.1	4.1	3.4	2.6	2
6	0.53	0.51	61	31	20	15	10	7.7	6.1	5.1	3.8	3.1
8	0.71	0.68	82	41	27	20	13	10	8.2	6.8	5.1	4.1
10	0.89	0.85	100	51	34	26	17	13	10	8.5	6.4	5.1
12	1.1	1.0	120	61	41	31	20	15	12	10	7.7	6.1
14	1.2	1.2	140	71	48	36	24	18	14	12	8.9	7.1
16	1.4	1.4	160	82	54	41	27	20	16	14	10	8.2
18	1.6	1.5	180	92	61	46	31	23	18	15	11	9.2
20	1.8	1.7	200	100	68	51	34	26	20	17	13	10
40	3.6	3.4	410	200	140	100	68	51	41	34	26	20

Note: Based on 95.5% cathode efficiency.