Vékonyrétegek előállítása és alkalmazásai

2010. december 6.

Dr. Geretovszky Zsolt

Externally driven plating

Electrolytic anodization:

An oxide film is formed ***from the substrate***, i.e. the *anode* reacts with negative ions originating from the electrolyte in solution and becomes oxidized.
Generally an oxide or hydrated oxide coating is formed, while hydrogen gas evolves at the cathode.
Adherent, nonporous oxide films can only be formed on certain metals, e.g. **Al**, Ta, Nb, Ti, Zr and Si.
Films are mainly used as corrosion-resistant and/or decorative coatings (using dyes as additives) on Al and its alloys, or as an insulation layer for electrolyte capacitors made of Al and Ta.

Electroplating or plating:

In electroplating a metallic coating is electrodeposited *on the cathode* of an electrolytic cell. The cell consists of a positive electrode (anode), a negative electrode (cathode) and an electrolyte solution (containing the metal ions to be deposited) through which electric current flows.
When the layer is very thick the method is called electroforming.

History of plating

Luigi Valentino BRUGNATELLI
1761-1818

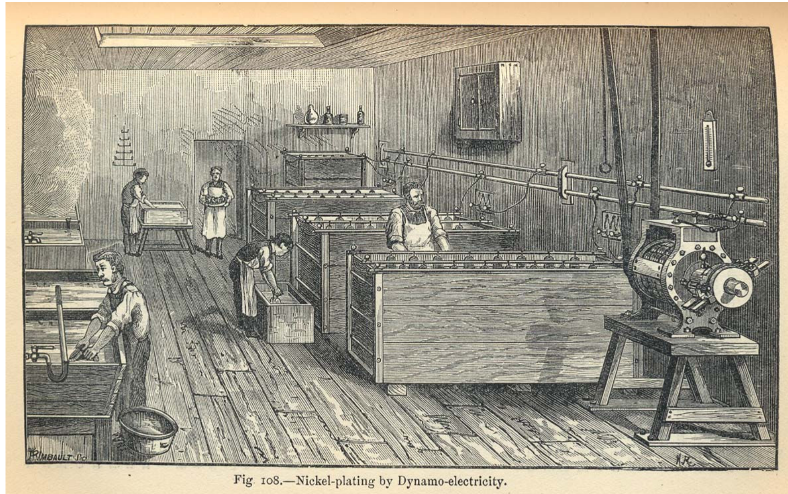


Fig 108.—Nickel-plating by Dynamo-electricity.

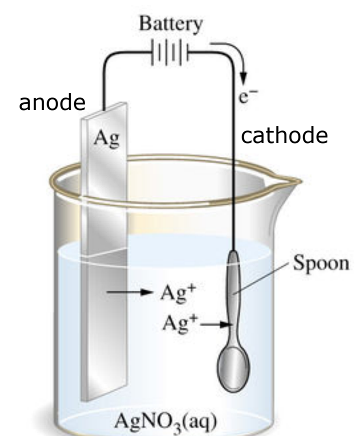
Modern electrochemistry was invented by Italian chemist L.V. *Brugnatelli* in 1805. The first modern electroplating plant started its production in 1876. (Norddeutsche Affinerie, Hamburg)

Source: Arnold Philip: The Electro-Plating and Electro-Refining of Metals, 1911. (D. Van Nostrand Company)

Electroplating

Electroplating is a plating process that uses electrical current to reduce cations of a desired material from a solution and coat a conductive object with a thin layer of the material, such as a metal.

The process used in electroplating is called *electrodeposition*. It is analogous to a galvanic cell acting in reverse. In one technique, the anode is made of the metal to be plated on the part. In this manner, the ions in the electrolyte bath are continuously replenished by the anode. Other electroplating processes may use a nonconsumable anode such as lead. In these techniques, ions of the metal to be plated must be periodically replenished in the bath as they are drawn out of the solution.



Faraday's laws

Michael_FARADAY
1791–1867

Faraday's laws of electrolysis (1833) forms the are basis of electrodeposition.

1. The amount of chemical change at an electrode is directly proportional to the quantity of electricity passing through the solution.

2. The amounts of different substances liberated at an electrode by a given quantity of electricity are proportional to their chemical equivalent weights.

$$m = \frac{I \cdot t \cdot m_{eq}}{F}$$

where:
m: weight of deposit in grams
I: current flow in amperes
t: time in seconds
m_{eq}: equivalent weight of deposited element
F = 96,496 coulombs, Faraday constant

The equivalent weight of the element, is the atomic weight divided by the valence change, i.e. the number of electrons involved in reduction.

if the current is not constant, then $$Q = \int_{t_1}^{t_2} I dt$$

Electrode efficiency

Faraday's laws are absolute laws. Apparent exceptions are explained by failure to take into account all the chemical reactions or electrochemical processes taking place at the electrode.

$$Electrode\ efficiency = \frac{actual\ weight\ of\ deposit}{theoretical\ weight\ of\ deposit} \times 100$$

With knowledge of the actual efficiency, predicted (average) thickness of deposit can be obtained.

Deposit	Electrolyte	Range, %
Ag	CN	100
Au	Acid Neutral CN	50 - 100
Cd	CN	85 - 95
Cr	CrO_3/H_2SO_4 CrO_3/SO_4-F	10 - 15 18 - 25
Cu	Acid SO_4 CN (low eff.) CN (high eff.) P_2O_7	97 - 100 30 - 45 90 - 95 ~100
Fe	Acid	90 - 98
In	Acid or CN	30 - 50
Ni	Acid	93 - 98
Pb	Acid	95 - 100
Rh	Acid	10 - 50
Sn	Acid Alkaline	90 - 95 70 - 95
Zn	Acid CN	~95 50 - 80

Cathode Current Efficiencies of Various Plating Solutions

Electrode potential

Walther Hermann NERNST
1864–1941

The magnitude of the potential difference between the metal and its ionic solution is given by the Nernst equation (1889):

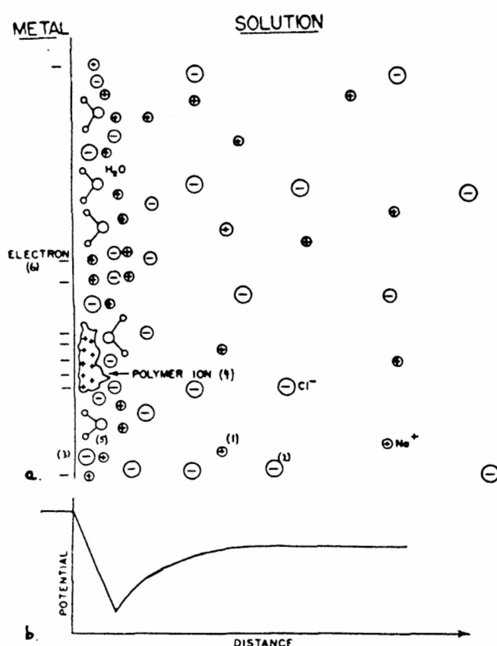
$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{a_{red}}{a_{ox}}$$

where:
- E: observed EMF, potential difference
- E^{o}: standard EMF
- T: absolute temperature
- R: universal gas constant
- n: electron change in redox reaction
- F = 96,496 coulombs, Faraday constant
- a_{red}: activity of reduced species
- a_{ox}: activity of oxidised species

For electrodeposition reactions to occur, one need to apply a voltage that overcome the equilibrium EMF of the two electrodes plus the potential drop in the electrolyte which obeys Ohm's law.

http://en.wikipedia.org/wiki/Nernst_equation

The deposition process



Factors affecting deposition processes include:

1. The electrical double layer (~10 Å thick) and adsorption of ions at the surface some 2 - 3 Å away. At any electrode immersed in an electrolyte, a double layer of charges is set up in the metal and the solution ions adjacent to the surface. At solid electrode surfaces, which are usually heterogeneous, the character and constitution of this double layer may exhibit local variations, resulting in variations in the kinetics of the deposition process. This could affect the electro-crystallization processes involved in the overall growth process.

2. The energy and geometry of solvated ions – especially those involving complex ions. All metal ions are associated with either the solvent molecules or complexed with other solution constituents either electrostatically or by coordinated covalent bonding. Desolvation energy is required for transferring the metal ion out of solution to the growing crystal lattice.

3. Polarization effects. The change of potential of an electrode from its equilibrium potential upon the application of a current. $E_a > E_{a0}$ and $E_c < E_{c0}$

The condition of the surface to be plated is a basic determining factor in the kinetics of the deposition process and the morphology and properties of the final deposit. The presence of other inorganic ions and organic additives in the double layer or adsorbed on to the surface can greatly modify the growth process.

Polarization

The potential changes (polarization) arise as the result of current flowing across a metal-solution interface to which the following three basic processes may contribute:

Activation Polarization

This is the change in potential that is required just to make the reaction go faster. This phenomenon can be analyzed in terms of the energy barrier between the reactant and the product states, and this gives rise to a relationship between current and potential of the form:

$$E = a + b \log i$$

A reaction for which activation polarization dominates is referred to as *activation controlled*.

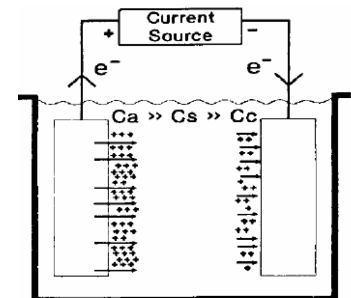
Concentration Polarization

Many electrochemical reactions produce or consume species in the solution. The rates of reactions involving dissolved species which participate as reactants in the rate-determining step (that stage in the reaction which controls its rate) will be dependent on the concentration of the dissolved species. As the dissolved species are consumed by the reaction, so a greater change in potential will be required to maintain the current, and this is known as concentration polarization. A reaction for which concentration polarization dominates is referred to as *mass-transport or diffusion controlled*.

Resistance Polarization

Solutions of electrolytes generally have a rather poor conductivity compared to metals, particularly for dilute solutions. If the solution has a high electrical resistance this will give rise to a potential difference between the anodic and cathodic sites, which is known as resistance polarization. If resistance polarization dominates a reaction, it is referred as *resistance or IR controlled* (the latter term arises from Ohm's Law, V = IR).

Polarisation



During electroplating the concentration of the ions changes around the electrodes.
→ concentration polarisation

Increased *anode concentration polarization*

- ultimately results in the evolution of oxygen which $2H_2O = O_2 + 4H^+ + 4e^-$
- may react with the electrode to produce insulating oxide films and hence increase the ohmic resistance. (In some processes, such as anodizing of aluminum or where insoluble anodes are involved such as in chromium plating, anode polarization is desirable.)
- may also react with various solution constituents such as organic compounds or cyanides, thereby consuming them and/or converting them into other compounds which may be detrimental to the electrodeposition process.

Cathodic concentration polarization

- May result in the evolution of hydrogen as the competing reaction. $2H_2O + 2e^- = 2OH^- + H_2$
- The pH of the cathode film increases and hydrates or hydroxides may precipitate and be occluded in the deposit.
- The co-deposition of hydrogen may result in brittleness of the deposit and, by migration and diffusion into the substrate, result in hydrogen embrittlement.

Replenishment of precursors

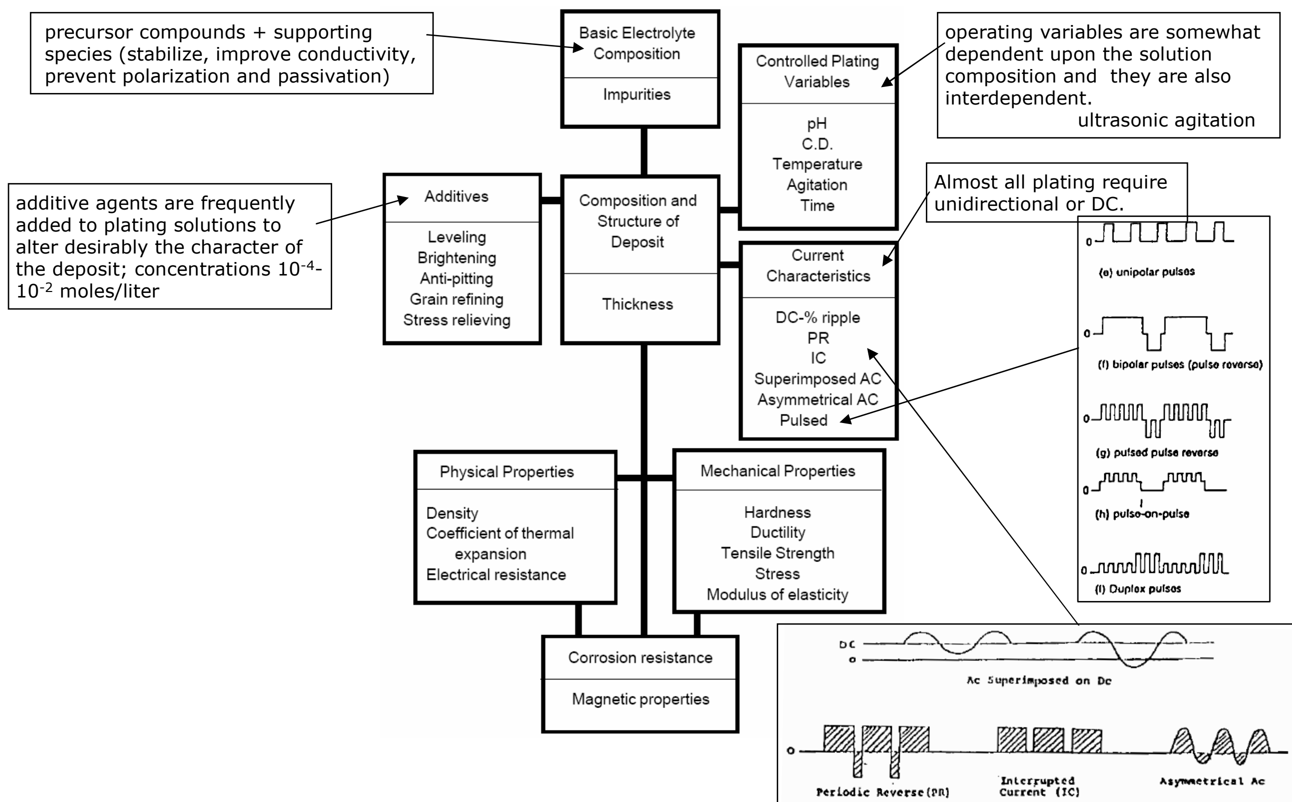
Replenishment (mass transport) of the ions can be accomplished in three ways:

1. **Convection** is the most effective.
This is accomplished by mechanical stirring, circulation or air agitation of the solution or moving the electrodes (parts) through the solution. Any, or a combination of these may be employed.

2. **Ionic migration** is least effective.
The mobility of the metal ion is very low, its migration rate being dependent on the current and the *transport/transference/Hittorf number* (i.e. the fraction of the total current carried in a solution by a given ion) which is usually less than 0.5. When other conducting salts, are added, these conduct most of the current, reducing the metal ion migration approaching zero. In the case of complex ions where the total charge is negative (complexed as anions) the migration is actually in the reverse direction.

3. **Diffusion** is the effective mechanism for ionic migration in the vicinity of the electrode surface where convection becomes negligible.
The region near the electrode surface where the concentration of the ions differs from that of the bulk of solution is called the diffusion or boundary layer. It is defined, somewhat arbitrarily, as the region where the concentrations differ by 1% or more. The diffusion layer is much (approximately 15,000 to 200,000 times) thicker than the electrical double layer, and depends on agitation and temperature.

Control parameters



Metals electroplated from aqueous solutions

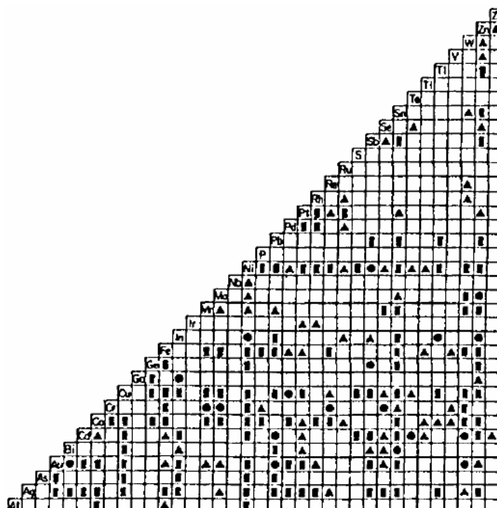
Periodic Table of the Elements

Colour codes:

Elements most commonly plated commercially
Elements less frequently plated commercially
Elements infrequently plated commercially

Alloys 1/2

Alloy deposition extends the availability and applicability of coatings from aqueous solutions.



The Nernst equation is also significant when complexing agents are present in the electrolyte since ionic concentration can be reduced drastically with the accompanying change in electrode potential.

E.g. co-deposition of Zn and Cu from cyanide solutions

Alloys 2/2

The most widely used plated alloys are:

Cu-Zn	brasses ranging from red brass to white brass, primarily decorative and for rubber bonding.
Cu-Sn	bronzes, decorative, antiquing and as corrosion resistant undercoats substituting for a copper strike.
Sn-Pb	compositions ranging from 5% Sn to 65% Sn. Applications include bearings, corrosion resistant coatings, solderable coatings and etch-resists in electronic assemblies.
Au-Co	hardened gold alloy deposits used for electronic contacts Au-Ni and wearing surfaces.
Sn-Ni	for corrosion resistance and solderability.
Ni-Fe	as substitute for nickel plating (decorative), soft magnetics on computer heads (Permalloy).
Ni-P	deposited either electrolytically or (more prevalently) electrolessly for its hardness, wearability and corrosion resistance and as non-magnetic undercoat on computer hard disks.
Co-Ni	for decorative plating, magnetic applications electroforming (molds for plastics).
Co-P	for hard magnetics, sometimes as ternary alloys containing Ni, Fe, Zn, W, Mo, etc.

Internal plating 1/2

Electroless, electroDEless deposition or autocatalytic plating

is a selective process in which metal ions are reduced to a metallic coating by a reducing agent in solution. It takes place on suitable catalytic surfaces, which include substrates of the same metal being plated (hence autocatalysis). The deposit itself catalyses the reduction so the process becomes self-sustained. (→ thick films) It is an appealing heterogeneous process due to its selective nature (patterned deposition), but is limited to a few metals and alloys, e.g. Ni, Cu, Co, Au, Pd, Pt, Ag and a variety of alloys. Typical reducing agents are sodium hypophosphite (for Ni, Co), sodium borohydride (for Ni, Au), hydrazine (for Ni, Au, Pd), dimethylamineborane (for Ni, Co, Au, Cu, Ag) and formaldehyde (for Cu).

Pros and cons with respect to electroplating

Advantages	Disadvantages
Uniform deposits. Internal surfaces are also coated evenly.	Solution instability.
Less porous deposits (more corrosion resistance)	More frequent control for reproducible deposits.
Almost any surfaces (even non-conducting) can be plated. They can be made catalytic by sensitizing and nucleation treatments.	Slower deposition rates.
No electrical contacts are required.	Frequent replacement of tanks or liners.
	More expensive.

Internal plating 2/2

Immersion plating or displacement deposition

Deposition of a metal film from a dissolved salt of the coating metal by chemical displacement without external electrodes. Generally the less noble (more electronegative) metal displaces from solution any metal that is more noble. Actually, different localised regions of the surface become anodic and cathodic, resulting in thicker films in the cathodic areas. Industrial use is limited to Sn coatings on Cu and its alloys.

Electrophoretic deposition

is based on deposition of a film from a dispersion of colloidal particles onto a conductive substrate. The dispersion in a conductive liquid dissociates into colloidal particles and ions and the colloidal particles migrate to the substrate, become discharged and form a film. E.g. black oxides on steel, Cu, Al, chromate conversion on Zn, Cd, Ag, Cu, Al and Mg. Phosphate conversion uses phosphoric acid containing salts of Fe, Zn and Mn.

Chemical reduction plating

is based on reduction of a metal ion ***in solution*** by the reducing agent, added just before use. Reaction is homogeneous! Ag, Cu, Ni, Au and some sulfide films are readily plated. Not too much of use.