Deposition from Aqueous Solutions: An Overview

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1.0 INTRODUCTION

Electrodeposition, also called electroplating or simply plating, is an economical technology to protect and enhance the functionality of parts used in many diverse industries including home appliances, jewelry, automotive, aircraft/aerospace, and electronics—in both decorative and engineering applications. Although decorative applications have diminished somewhat primarily due to added expenses and problems associated with plant effluent (pollution) control and waste treatment, its applications in engineering, electroforming, and electronics have increased. The emphasis is on the latter applications, and the structures and properties of deposits.

The purpose of decorative plating is to provide a durable, pleasing finish to the surfaces of manufactured articles, so the corrosion characteristics of the deposits and their ability to protect the substrate are important factors. These and other deposit properties involved in the selection and performance of decorative coatings including hardness, wear resistance, ductility, and stress are also important to the engineering applications of plated coatings.

Engineering applications of plated coatings involve imparting special or improved properties to significant surfaces of a part or assembly and/or protecting or enhancing their function in their operating environment. Other applications include salvage of mismachined or worn parts and other types of reworking as well as material savings, use of less expensive materials, and substitution of materials more easily fabricated, Special technologies such as electroless deposition, electroforming, anodizing, thin films, magnetic coatings, and printed wiring (circuit) boards have been selected for discussion as representing specific engineering applications.

Although electroplating and vacuum deposition processes are generally considered competitive processes, there are increasing applications in which they are (or can be) highly complementary. These involve utilizing the advantages of both deposition technologies:

Vacuum Deposition

Aqueous Deposition

- Close tolerances
- Wide choice of substrates
- Wide choice of coatings
- Lower costs
- Thicker coatings
- Coating complex shapes
- Control and modification of deposit properties
- Control of residual stress

A combined process permits almost any substrate to be coated with a much wider range of deposits than either used alone. It extends the application of aqueous deposition to substrates which are difficult to coat, particularly non-metallics (ceramics) or active metals not readily or satisfactorily processed.

Examples of combined processing include the electrodeposition of such metal substrates as Mo, Ti, and Be by initially sputtering a thin Cu or Au deposit to provide substantially improved adhesion.^[1] The plating of plastics using chemical preparation is expensive, requires rigorous control, and presents formidable waste treatment problems. A pre-plate treatment using vacuum techniques to condition the surface by RF glow discharge followed by sputtering or electron beam evaporation of 1000 angstrom Ni and 1000 angstrom Cu deposits permits direct electroplating to final thicknesses.^[2]

In printed wiring board (PWB) fabrication, plasma processing is being employed to clean drilled holes and to remove drill smear. However, in some cases, this leaves undesirable interfering ash and decomposed residues requiring further chemical clean-up. Sputtering processes for depositing the initial Cu deposit on PWB's and through-hole deposition have been developed to replace the electroless Cu deposition processes.^[3] It has been predicted that such processes may replace the presently used electroless Cu systems completely.^[4]

Electrodeposition has been used to fabricate magnetron sputtering targets of well defined shapes. The advantages include deposition precisely where needed or desired, eliminating waste. Such electrodeposited targets are quite pure with a minimum of oxygen or other gases. Sputtering targets of Ag, Cr, Au, Fe, Ni, Co and alloys have been prepared by electroplating.^[5]

2.0 GENERAL PRINCIPLES

Figure 10.1 represents a simplified plating cell. A DC source, usually a rectifier or motor generator, supplies current flowing in one direction through the external portion of the circuit when a potential difference is imposed across the system. The current flow is that of electrons in the external conductors. The mechanism of electrical transfer in the solution is by means of electrically charged "particles" called ions. Positive ions (cations) travel toward the negative electrode (cathode) and negative ions (anions) travel toward the positive electrode (anode) when the potential is applied, thus completing the electrical circuit. The electrolyte usually contains other components which influence the process (see Fig. 10.7 later in this chapter).



Figure 10.1. Plating Cell

The cathode or deposition reactions are characterized as reduction reactions since electrons are "consumed," and the valence states of the ions involved are reduced. The anodic reactions are oxidation reactions wherein electrons are liberated, and the valence states are increased. Each set of reactions represents half-cell reactions and proceeds independently of the other, limited by a condition of material balance, i.e., electrons liberated in the anode reactions must equal the number of electrons "consumed" in the cathode reactions.

The above describes systems such as nickel or copper deposition from acidic solutions^{*} of their simple ions. Since these are divalent ions (Ni²⁺, Cu^{2+}), the equations shown in Fig. 10.1 would involve two electrons.

Deposition from solutions in which the metallic ions are combined with other ions or ligands as complex ions involves more complicated mechanisms. The cyanide-containing electrolytes represent the largest group of such systems. Some of these complex ions are so tightly constituted, i.e., the ionization constant of the metal ion is so small, that reduction or deposition of the metal atoms at the cathode occurs directly from the complex ions. This appears to be the mechanism involved with copper, silver and gold cyanide complex ions:

Eq. (1)	[Cu(CN) ₃] ⁼ + e	-	\rightarrow	$Cu^{\circ} + 3(CN)^{-1}$
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Eq. (2) $[Ag(CN)_2]^- + e^- \rightarrow Ag^\circ + 2(CN)^-$

Eq. (3) $[Au(CN)_2]^- + e^- \rightarrow Au^0 + 2(CN)^-$

The stability of the gold cyanide complex ion is such that it exists in mildly acidic gold plating solutions.

It should be noted that the complex ions described above and other types are anionic and would migrate to the anode during electrolysis. Yet, deposition still takes place at the cathode, indicating that mechanisms other than simple electron reactions are involved in the cathode film. These complex anions approach the cathode by convection and/or diffusion where specific adsorption effects can occur in the double layer as discussed by Wagner, citing Frumkin and Florianovich.^[6] The influence of simple cations present in the film are also involved in the reduction process.

Faraday's Laws of electrolysis (1833) are basic to electrodeposition.

^{*} Most acidic plating solutions fall into this category, involving the simple ions.

They relate the current flow, time, and the equivalent weight of the metal with the weight of deposit and may be stated as follows:

- 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.

Faraday's Laws may be expressed quantitatively:

Eq. (4)
$$W = \frac{I \cdot t E_q}{F}$$

where: W = weight of deposit in grams I = current flow in amperes t = time in seconds $E_q =$ Equivalent weight of deposited element F = Faraday, a constant, = 96,500 coulombs (approx.)

I · t is the quantity of electricity used (coulombs = ampere-seconds) and E_q , the equivalent weight of the element, is the atomic weight divided by the valence change, i.e., the number of electrons involved. If the current is not constant, then I · t must be integrated:

$$\int_{t_1}^{t_2} I dt$$

From a practical standpoint, the weight of the deposit is converted to the more meaningful thickness of the deposit using the relationship, W (gms) = volume (cm³)/deposit density, with the volume of the deposit equal to the thickness (in μ m)* times the area (in m²). The Faraday**, F, can be experimentally determined by rearranging Eq. (4):

^{*} Thickness in \propto m ξ 0.0394 = thickness in mils.

^{**} The Faraday can be derived from the fact that 1 gram-atomic weight of an element contains 6.023×10^{23} atoms (Avogadro's Number, N). If the charge on the ion is A, then Z x N electrons are required to deposit 1 gram-atomic weight, and Z x N/A = 6.023 electrons are required to deposit (or dissolve) 1 equivalent weight of an element. Since the charge on an electron is 1.602×10^{-19} coulombs, 6.023×10^{23} electrons x 1.602×10^{-19} coulombs = 96,496 coulombs.)

Eq. (5)
$$F = \frac{I \cdot t E_q}{W}$$

Rearranging Eq. (4) to

Eq. (6) It =
$$\frac{WF}{E_q}$$

permits the determination of the charge passing through a circuit by the known deposition or dissolution of an element, usually silver. Devices which utilize this application of Faraday's Laws are known as coulometers. Coulometers are used to determine the efficiency of a deposition process. They are also employed as either timers or integrators possessing "electrochemical memory" and producing sharp potential "end-points," i.e., significant changes in electrode potentials which activate electronic circuits. Figure 10.2 schematically illustrates such a device—an electrochemical cell called an E-cell as part of an electronic circuit.



Figure 10.2. Microcoulometer – E-Cell (Courtesy Plessey Electro-Products)

Faraday's Laws are absolute laws, and no deviations or exceptions have been found. Apparent exceptions can be shown to be incorrect or explained by failure to take into account all the chemical or electrochemical reactions involved at the electrode. Thus, the efficiency of an electrochemical reaction can be determined:

Eq. (7) % Electrode Efficiency = $100 \times \frac{\text{actual weight of deposit}}{\text{theoretical wt. of deposit}}$

Table 10.1 indicates typical cathode current efficiencies for some common deposits from various electrolytes. With knowledge of the actual efficiency, predicted (average) thickness of deposit can be obtained, limited by the control of the current distribution.

Deposit	Electrolyte	Range, %
Ag	CN	100
Au	Acid Neutral CN	50 - 100
Cd	CN	85 - 95
Cr	CrO ₃ /H ₂ SO 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

Table 10.1. Cathode Current Efficiencies of Various Plating Solutions

The current flowing through a conductor is driven by a potential difference or voltage, the magnitude of which is determined by the relationship expressed as Ohm's Law (1826-27):

Eq. (8) E = IR

where E = volts, I = amps, and R = ohms. This law regulates both the current flow and its paths in an electrodeposition cell. A commercial electroplating installation and operation involves a multiplicity of series and parallel electrical circuits with only the total current and applied voltage controlled. The current distribution on each individual part or portion of a part (and resulting deposit thickness and properties) depends on the electrode potentials and resistances involved in the "mini-circuits" as well as the geometry and spacing of parts. Since the resistances of the solid, metallic conductors in the circuit are several orders of magnitude lower than the electrolytic (solution) resistances, they can usually be neglected. The potentials within the electrolyte and, more importantly, the electrode-electrolyte interfaces, are fundamental controlling factors and are not as straight-forward as suggested by Ohm's Law.

When a metal is immersed in a solution containing its ions, an equilibrium condition is set up between the tendency for the metal to go into solution and the tendency for the metallic ions in solution to deposit on the metal: $M^0 \subseteq$ Mⁿ⁺+ne⁻. However, before this equilibrium is established (i.e., the exchange currents or current densities are equal $|i_+| = |i_-| = i_0$, one of the reactions may be faster than the other, resulting in a "charge separation." If the reaction proceeding to the right is faster than to the left, the metal surface would be negatively charged. If the deposition reaction (to the left) is faster, then the surface would be positively charged. This resulting potential between the metal and the solution (at unit activity) is called the single or standard electrode potential. Since this is a half-cell reaction, a reference electrode, the saturated hydrogen electrode (SHE) is used to complete the circuit and is given the arbitrary value of zero potential. In many instances other reference electrodes such as the calomel electrode are substituted with appropriate corrections. Potential measurements made in this manner (or values derived thermodynamically) result in a series known as the Electromotive Force (EMF) Series.

This origin of the electrode potential was first formulated by W. Nernst (1889). The magnitude of the potential difference between the metal and its ionic solution is given by the Nernst equation:

Eq. (9)
$$E = E^{o} + \frac{RT}{nF} = \ln \frac{a^{x} \text{ (products)}}{a^{y} \text{ (reactants)}^{*}}$$

where E = observed EMF, potential difference (volts)

$$E^{o}$$
 = standard EMF
R = gas constant, 8.314 (j · $^{o}K^{-1}$ mol⁻¹)
T = absolute temperature, ^{o}K
n = valence change (electron transfer)
F = Faraday, 96,500 coulombs (A · sec mol⁻¹)
a = activity (apparent degree of dissociation)

If the natural logarithm is converted to logarithm base 10, and T is 298° K (25° C), then Eq. (9) becomes:

Eq. (10) $E = E^{o} + (0.059/n)^{**} \log a \text{ (or } \log c \text{ approx.)}$

Thus, a tenfold change in ion concentration changes the electrode potential by 59 mV/n (a negative change makes the electrode potential less positive). This is significant when complexing agents are present since the ionic concentration can be reduced drastically with the accompanying change in electrode potential.*** For example, $E^{\circ} = -0.76$ volts for zinc. But, when zinc is complexed with cyanide:

Eq. (13)
$$Zn^{2+} + 4(CN)^{-} \rightarrow [Zn(CN)_4]^{=}$$

the electrode potential shifts to approximately -1.1volt. The standard electrode potential for the Cu^{1+}/CuM half cell is +0.52 volts which shifts to ~-1.1 volts when complexed with cyanide:

*** When complex ion reactions are involved:

Eq. (11) $M^{n+} + qX^{p-} \rightleftharpoons [MX_a]^{n-pq}$

where q is the coordination number, then the Nernst equation is modified:

Eq. (12)
$$E = E^{\circ} - \frac{RT}{nF} \ln K_{f} + \frac{RT}{nF} \ln \frac{a_{M_{q}}^{n-pq}}{a_{X^{p-1}}^{q}}$$

 K_f is the stability constant of the complex ion. Since K_f will be quite large for very stable complexes, the potential can shift substantially negatively.

^{*} Since the metal (solid) is the reactant in a plating cell, its activity is considered = 1 for all practical purposes and can be neglected. Also, as a practical approximation, the concentration in moles/L can be substituted for activities.

Eq. (14) $Cu^{1+} + 3(CN)^{-} \rightarrow [Cu(CN)_3]^{=}$

The practical significance is that a copper cyanide strike provides the best undercoat on a zinc surface since the potentials are essentially the same. Attempts to use an acid copper (Cu^{2+}) ($E^{o} = +0.34$ volts) solution would provide a potential difference of 1.1 volts, resulting in an immersion or displacement deposit with poor adhesion. The closeness of the electrode potentials for the $[Zn(CN)_{4}]^{=}$ and $[Cu(CN)_{3}]^{=}$ complexes also permits these metals to be deposited simultaneously as a brass alloy deposit from cyanide solutions.

For electrodeposition reactions to occur, an additional potential is required to overcome the equilibrium conditions discussed above, i.e., to provide a non-equilibrium, irreversible condition. Referring to Fig. 10.1, the total plating voltage is the sum of three components. E_2 represents the potential required to overcome the resistance of the electrolyte and obeys Ohm's Law; it would be the only potential required if only the single electrode potentials were involved in the electrodeposition process. E_1 and E_3 are the potentials at the electrodes required to sustain the electrolysis process when the current is flowing and exceed the single electrode potentials. The additional voltage is called polarization which usually increases as the current increases. The electrical energy is converted to heat according to Joules Law:

Eq. (15) $E_{heat} = I E t = I^2 R t$

resulting in increased temperatures of the electrolytic solutions.

Polarization, also called overpotential or overvoltage*, is an important controlling factor in electrodeposition processes. A minimum energy which the reactants must possess is a requisite for any chemical reaction to occur. For an electrochemical reaction to proceed, an overpotential is required to overcome the potential barrier at the electrode/solution interface; this is called the activation overpotential. It is the overpotential required for the charge-transfer reaction itself and is kinetically controlled. Cathodic activation overpotential shifts the energy level of the ions in the inner electrical double layer nearer to the potential barrier, so that more ions can cross it in

^{*} In more rigorous treatments, the term *overvoltage* is restricted to the excess potential required for a single reaction (usually irreversible) to proceed at a specified electrode whereas the term *polarization* is more general and includes all reactions at the electrode.

a given time, producing a deposit on the surface. Activation overpotential also exists at the anode but in the opposite direction.

Changes in the ion concentrations at the electrodes are major contributions to polarization. Figure 10.3 depicts the increased metallic ionic concentration at the anode and the decreased concentration at the cathode as a result of the dissolution and deposition processes. This results in corresponding changes in the equilibrium potentials per the Nernst equation (Eq. 9) since it changes the value of log C_E/C_S , C_E being the ionic concentration at the electrode and C_S the concentration in the bulk of the solution (see Eq. 10). This effect due to the concentration changes is called concentration polarization and is mass transport controlled.



Figure 10.3. Concentration polarization

Figure 10.4 illustrates a typical current/potential curve indicating the regions of activation polarization (η_a), concentration polarization (η_c), limiting current followed by a post limiting region (with gas evolution). The open circuit (rest) potential is indicated by (E_M)_R. Where anodic and cathodic polarization curves intersect, $|i_o|$ is indicated.

Increased anode concentration polarization ultimately results in the evolution of oxygen which reacts with the electrode to produce oxide insulating films increasing the ohmic resistance. The oxygen 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. In some processes, such as anodizing of aluminum or where insoluble anodes are involved such as in chromium plating, anode polarization is desirable.

Cathodic concentration polarization may result in the evolution of hydrogen as the competing reaction. 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.



Figure 10.4. Typical polarization curve

Hydrogen overvoltage which is the polarization for the specific reaction discharging hydrogen at a specified electrode surface involves at least two steps:

Eq. (16) $2H^+ + 2e \rightarrow 2H_{adsorbed} \rightarrow H_{2 \text{ (gas molecule)}}$

The latter step is usually the slower, rate-determining step, and a higher potential is required to discharge the gas.

The factors influencing hydrogen or oxygen overvoltage include:

- a. Electrolyte composition
- b. Type of metal electrode
- c. Nature of electrode surface
- d. Current density
- e. Temperature

Agitation and increased operating temperature of the solution help minimize concentration polarization, permitting higher current densities and faster plating rates.

The "throwing power" (TP) of a plating solution or, more properly, macrothrowing power since it indicates the degree of plate uniformity (thickness distribution) over the substrate surface contours, is an important characteristic because the deposit properties and overall quality are affected. Factors influencing deposit (plate) distribution are shown in Table 10.2. Generally, electrolytes containing free metallic ions exhibit poorer throwing power than those in which the ions are complexed or contain supporting, non-depositing, ions, the latter improving solution conductivity. The overall "geometry" of the plating system influences current distribution. Significantly increased cathode polarization at higher current densities results in decreased current efficiency, improving throwing power. Thus, cathode current efficiency-current density curves are useful in predicting the throwing power of a plating solution. If the cathode efficiency decreases with increased current density, the throwing power improves proportionately. The shape and slope of the curves are indicative of the throwing power. However, if the cathode efficiency remains high over a wide range of current densities, the throwing power is usually poor. Examples of desirable cathodic polarization are complex ion-containing solutions such as alkaline stannate (tin plating) and alkaline-cyanide (zinc plating) solutions.

Based on Haring-Blum %TP values, Schaefer and Pochapsky^[7] reported that conventional plating solutions generally fall into four classes: *(i)* alkaline stannate and zincate (%TP > 50), *(ii)* most other cyanide solutions (%TP = 25 to 50), *(iii)* most acid solutions (%TP > 0 to 25), *(iv)* chromium plating (%TP = -100 to 0). The wide range of "negative" macrothrowing power for chromium (from chromic acid solutions) is due to the fact that, within limits, the cathode current efficiency increases with increasing current density, thereby greatly exaggerating the non-uniformity of the deposits.

Rothschild^[8] showed substantial improvement in the throwing power of the so-called high throw acid copper sulfate plating solutions containing low metal/high acid concentrations employed for through-hole plating of printed circuits boards, 87% vs. 14% for a conventional high metal/low acid concentration solution.

Foulke and Johnson^[9] investigated the throwing power characteristics of various precious metal plating solution formulations. Percent throwing power values for both macro- and microthrowing power characteristics were reported.

The term *throwing power* is sometimes mistakenly applied to another property of plating solutions: namely, *covering power*. Covering power relates to the lowest applied current density at which a plating solution produces a deposit, i.e., it is a measure of a solution's ability to deposit into geometric recesses of an article to be plated. At very low current densities in some plating solutions, the potential required for metal deposition (sometimes referred to as the decomposition potential) may not be reached, and some other electrode reactions support the passage of current; these may include hydrogen evolution or the reduction of addition agents or other reducible species or ions. Poor covering power or the inability to deposit metal into areas of low current density can sometimes be overcome or avoided by using a high current density ("strike") to initiate plating into the recess and then reducing the current density to the normal operating range.

Table 10.2: Factors Influencing Current/Plate Distribution

Type of Electrolyte Simple "Free" lons Complex lons Supporting lons Polarization Conductivity Cathode Efficiency-Current Density Curves Geometry of Plating System Other Factors Substrate Composition and Structure Surface Preparation and Pre-treatment

Current distribution over the electrode surfaces influence plate distribution and is differentiated as primary, secondary, and tertiary. Primary current distribution involves the plating system geometry with the potential constant over the electrode surface and negligible polarization influences. Secondary current distribution involves activation overpotential (η_a), electrode kinetics, and solution conductivity. Tertiary current distribution involves concentration overpotential (η_c), the diffusion (boundary) layer, and solution agitation, i.e., mass transport is a factor.

Current and plate distributions, and methods and calculations for determining throwing power, such as the Hull Cell,^[10] the Haring-Blum

Cell,^[11] and Wagner number are reviewed and analyzed by Ibl.^[12] Shawki et al^[13] devised a method for measuring throwing power into recesses and holes using cathodes with varying tube diameters and determining plate thickness along the depth of the tubes.

The concept of microthrowing power is discussed later.

3.0 ELECTRODEPOSITION

3.1 Mechanism of Deposition

Metal deposition differs from other electrochemical processes in that a new solid phase is produced. This dynamic process complicates and introduces new factors in elucidation of the mechanisms involved in the discharge of ions at the electrode surfaces. Factors determining deposition processes include:

- The electrical double layer (~10 angstroms thick) and adsorption of ions at the surface-some 2 - 3 angstroms 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 electrocrystallization processes involved in the overall growth process.
- The energy and geometry of solvated ions-especially those involving complex ions. All metal ions are associated with either the solvent (water) molecules or complexed with other solution constituents either electrostatically or by coordinated covalent bonding. Desolvation energy is required in transferring the metal ion out of solution to the growing crystal lattice.
- Polarization effects. A symposium^[14] on Electrode Processes was held by the Faraday Society in 1947. The excellent papers pioneered the concepts upon which the modern concepts of the deposition mechanism are based. Schaefer and King^[15] compiled a chronological annotated bibliography on polarization covering the period 1875 1951.

Thus, the condition of the metal surface to be plated is a basic determining factor in the kinetics of the deposition process and the morphol-

ogy 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 electrocrystallization and growth process (Fig. 10.5).



Figure 10.5. (*a*) The distribution of ions and dipoles in the electrical double-layer. (1) Cations, (2) anions, (3) specifically adsorbed anions, (4) adsorbed additives, (5) adsorbed water dipoles, (6) electrons. (*b*) The potential as a function of distance in the double-layer [corresponding to (*a*)] measured from the metal surface.^[16]

Based on these considerations, several deposition mechanisms have been proposed.^{[16]-[21]} The basic or essential steps as shown in Fig. 10.6 include:

- 1. The aquo- or complexed metal ion is transferred or deposited as an adion (still partially bound) to a surface site. Such sites include the plane surface, edges, corners, crevices or holes with the plane surface providing the primary sites.
- 2. The adion diffuses across the surface until it meets a growing edge or step where further dehydration or desorption occurs.
- 3. Continued transfer or diffusion steps may occur into a kink or vacancy or coordinate with other adions, accompanied by more dehydration until it is finally fully coordinated with other ions (and electrons) and becomes part of the metal being incorporated into the lattice.



Figure 10.6. Diagram of the crystallization process according to the theory of Kossel and Stranski. Different atom positions: *(a)* another phase (gas phase, melt, electrolyte), *(b)* in the lattice plane [ad-atom (ad-ion)], *(c)* edge (step) site, *(d)* growth (kink) site.^[18]

Deposition of metal ions results in depletion in the solution adjacent to the surface. These ions must be replenished if the deposition process is to continue. This replenishment or mass transport of the ions can be accomplished in three ways:

1. 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 number 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.

- 2. Convection is the most effective, involving substantial movement of the solution. This is accomplished by mechanical stirring, circulation or air agitation of the solution or moving the electrodes (parts) through the solution. Any one or combination may be employed.
- 3. Diffusion is the effective mechanism for ionic migration in the vicinity of the electrode surface itself 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.^[22] The diffusion layer is much thicker than the electrical double layer (approximately 15,000 to 200,000 times thicker, depending on agitation and temperature.

Figure 10.7 illustrates the diffusion/boundary layer, differentiating the Nernst diffusion layer (δ_N) from the actual diffusion layer. The diffusion rate of the reacting species is given by:

Eq. (17)	$R = D\left(C_{s} - C_{e}\right) / \delta_{N}$	
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where:

- R = diffusion rate (moles $cm^{-2} s^{-1}$) D = Diffusion coefficient ($cm^2 s^{-1}$)
- D = Diffusion coefficient (cm² s⁻¹)
- C_s = solution concentration (bulk concentration)
- C_e = concentration at electrode

 δ_N = the Nernst diffusion thickness

The diffusion rate increases as δ_N decreases. On flat, smooth electrode areas, the diffusion layer is fairly uniform. At rough surfaces or irregularities which have a roughness profile with dimensions about equal to the diffusion layer thickness, the diffusion layer cannot follow the surface profile, being thinner at the *micropeaks* than in the *microvalleys*. The deposit may be thicker at the peaks than in the valleys, a condition characterized as poor microthrowing power. A reverse condition may also exist resulting in good microthrowing power or leveling, i.e., making the surface smoother after plating than before plating. Figure 10.8 represents the three types of microthrowing power. The plating solution composition, especially organic additives, greatly influences the character of microthrowing power and brightening.



Figure 10.7. Relation of Nernst diffusion layer (δ_{N}) to actual diffusion layer (δ) .

The limiting current (or current density) (see Fig. 10.4) can be defined* as:

Eq. (18)
$$i_{L} = nFD (C_{s} - C_{e})/\delta_{N}$$

where n = electron transfer, F = Faraday constant, D = diffusion coefficient. When the overpotential is sufficiently high, C_e can be neglected and Eq. (18) becomes:

Eq. (19)
$$i_L = nFDC_s/\delta_N$$

and D/ δ_{N} equals the mass transfer coefficient.

Increasing the current density increases the plating rate. However, the deposit deteriorates when the current density exceeds some value depending on the solution composition and operating variables. Rough, burnt, dendritic, or powdery deposits maybe obtained when the limiting current density region is approached. Landau^[23] observed that it is not the absolute value of the current density which determines the quality of the deposit, but

^{*} Electroplaters consider the limiting current density as the maximum current density which will still produce acceptable deposits. This value is generally lower than calculated values using Eqs. 18 and 19.

rather the ratio of actual plating current density to the limiting current density, i/i_L. He determined that when the ratio exceeded 0.6, rough deposits generally resulted, with the concentration overpotential, η_C , becoming appreciable. The limiting current density is higher as agitation is increased, especially in the turbulent regime.





3.2 Parameters

The parameters generally controlling the composition, structure and properties of the deposit are shown in Fig. 10.9. These are briefly reviewed.

Basic Electrolyte Composition. This includes the compounds supplying the metal ions (to be deposited) and the supporting ions. The basic functions of the supporting ions or compounds are to stabilize the electrolyte, to improve solution conductivity, to prevent excessive polarization and passivation (especially anodic), and to provide compatibility with the desired plating conditions. Supporting ions or conducting salts reduce the current shared by the metallic ions or complexes, making convection (agitation) a more significant factor.

Additives. Additives, commonly called addition agents (A.A.), are frequently added to plating solutions to alter desirably the character of the deposit. Read^[24] discussed the effects of A.A. on the physical and mechanical properties of deposits—intentional or accidental. They are usually organic or colloidal in nature although some are soluble inorganic compounds. When additives produce a specific effect, they are descriptively called brighteners, levelers, grain-refiners, stress-relievers, anti-pitters, etc.

Profound effects are produced with small concentrations, ranging from a few mg/L to a few percent. In general, the effective concentration range is of the order of 10⁻⁴ to 10⁻² moles/liter. The mechanisms by which these effects are achieved are not clear in spite of a considerable amount of research and published literature (including a voluminous patent literature, since most commercial additives are proprietary). However, the additive must be adsorbed or included in the deposit in order to exert its effect, and thus appears related to its role in the diffusion layer. Kardos^[25] reviewed comprehensively the "diffusional" theory of leveling, which, experimentally derived, provides a scientific basis to explain the phenomenon.

To date, no generally acceptable mechanism has been devised to explain satisfactorily the brightening action of addition agents. Brightness, of course, is related to the absence of roughness on a very small scale. The diffusion-controlled leveling theory may be involved for rough surfaces but becomes inapplicable on smooth surfaces or on the sustained growth of bright deposits. Kardos^[25] recognized this limitation, and for the latter favored the *selective adsorption* of inhibitor on certain growth sites without being diffusion-controlled. The selective adsorption of brightening agents on active sites (lattice kinks, crystal projections, growth steps) or random



Figure 10.9. Factors influencing the properties of deposition

adsorption to suppress crystallographic differences in the deposit represent other proposals of the mechanism, but these are still highly conjectural. Other reviews,^{[26]-[29]} with extensive references, discuss the problems associated with elucidating a brightening mechanism. It seems likely that the "trial and error" method of selecting brightening agents will remain the really effective approach—at least for the near future.

While neither leveling nor brightening may be considered "properties" of the deposit, the resulting grain size can greatly influence the physical and mechanical properties due to the inclusion of these additives or the decomposition products–especially sulfur and/or carbon–in the deposit. The corrosion characteristics of these deposits are also affected, usually adversely.

The functions of the other types of addition agents are evident. In many instances, the same addition agent performs several of these functions or acts synergistically with other solution constituents or other addition agents.

Controlled Plating Variables. The influence and effects of the operating variables are somewhat dependent upon the solution composition. They are also interdependent. All exert an influence on the structure and properties of the deposit. They are not always predictable, and establishment of optimum ranges is usually determined empirically.

The use of ultrasonic energy agitation in electroplating solutions, i.e., its effect on the polarization, the diffusion layer and properties of deposits has received considerable interest since the 1950's. Rich^[30] determined that low frequency vibrations (16 - 30 kHz) produced more uniform results, and Roll^[31] obtained best results in the frequency range 20 - 50 kHz with intensity (power) range at 0.3 - 0.5 watt cm⁻². However, Hickman^[32] found that results based only on reported frequencies and intensities provide an inadequate description and suggested the use of the limiting current method with characterization of the ultrasonic agitation intensity in terms of diffusion layer thickness. The considerable research by Russian investigators is reported by Kapustin and Trofimov.^[33] Walker and Walker^[34] reviewed the effects of ultrasonic agitation on properties of deposits and noted that the conflicting results reported in the literature may be due to the differences in frequency, intensity and methods of application. Forbes and Ricks^[35] were able to reduce the number of preparatory steps required to silver-plate aluminum bus bars from 11 to 4, using ultrasonic agitation in key operations. In this connection, ultrasonic agitation has been widely employed in degreasing, cleaning and pickling pre-plating operations.

Some of the advantages attributed to the use of ultrasonics in electrodeposition are;

- 1. Higher permissible current densities resulting in higher rates of deposition.
- 2. Suppression of hydrogen evolution in favor of metal deposition, i.e., a shift in limiting current density.
- 3. Improved adhesion
- 4. Reduced porosity
- 5. Reduced stress
- 6. Increased brightness
- 7. Increased hardness (especially in chromium deposits)

The influence of ultrasonic agitation on grain size appears to be the most important factor, controlling most of the other property changes. However, no specific effects or trends can be attributed to ultrasonics.^[34]

Walker and Holt^[36] applied hydrosonic agitation as an alternative to ultrasonic agitation. The plating solution is circulated under pressure through an hydrosonic generator, converting solution velocity to acoustical energy with a pulse waveform from 5 kHz to the ultrasonic range solely by mechanical action. Results similar to plating with ultrasonic agitation were reported without some of the disadvantages associated with ultrasonics.

Impurities. It is practically impossible to maintain a plating solution free of impurities. Common or potential sources include:

- 1. Chemicals used for make-up and maintenance.
- 2. Impure anodes.
- 3. Improperly cleaned anodes, anode bags and filters.
- 4. Rubber or plastic linings and hoses.
- 5. Rack coatings or maskants.
- 6. Decomposition of addition agents.
- 7. Improper rinsing and drag-in of solution from the previous step
- 8. Accumulated dissolution of parts during plating.
- 9. Corrosion of electrical bus bars suspended above the solution.
- 10. Improper or insufficient cleaning or preparation of parts prior to plating.
- 11. Fall-in of airborne dirt and oil particles.
- 12. Chemicals in water used for volume replenishment (e.g., hard water).
- 13. Generally poor housekeeping.

Particles suspended in the solution may become attached to the surface, resulting in rough, nodular deposits, or leave pits if they fall off; either result produces adverse effects on the integrity and corrosion resistance of the deposit. (A notable exception is the dispersion of controlled particles to be included into the deposit; see Dispersion Coatings in Sec. 5.2.)

Organic impurities generally contribute to pitting, poor covering power, poor adhesion, and harder, more brittle, stressed, darker deposits.

Metallic impurities contribute to pitting, poor throwing power, poor adhesion, lower cathode efficiency, stress and cracking, brittleness, burning and off-color deposits. These cations may co-deposit or become entrapped in the deposit, altering its structure and properties. Furthermore, the distribution of the impurity in the deposit may be current density dependent–usually more concentrated in the low C.D. areas. (*Dummying,* i.e., removal of impurities from solution by electrolysis, is a common practice in certain plating solutions–especially nickel–at C.D.'s between 0.2 and 0.5 amps/dm².) The effects and removal of metallic impurities (copper, zinc and iron) in nickel deposition were studied in detail by D. T. Ewing et al.^[37]

Current Characteristics. All plating processes–with very few exceptions–require unidirectional or direct current (DC). Current sources are motor generators or rectifiers which convert alternating current (AC) to DC, with the latter almost completely supplanting the former. At present, silicon rectifiers are the most widely used.

Depending on the number of rectifying elements, the type of AC (single or three phase), and the circuitry, the output wave form can be half wave or (usually) full wave with varying percentages of ripple, ranging from 48% to less than 4%. In most plating processes, especially from complex ion type solutions, ripple may not be too significant. However, it can be a significant factor in some plating operations, notably chromium where the ripple should be low (5 - 10%), since higher ripple may co-deposit excessive oxides and adversely affect the deposit's structure and result in dull deposits. DC rectifiers used in gold and other precious metal plating require ripple to be as low as 1% for optimum deposit characteristics.

Figure 10.10 represents examples of the modulated current forms employed in attempts to reduce the magnitude and effects of polarization and to alter the structure and properties of deposits.

Superimposed AC on DC, the earliest approach, has not had extensive application. Zentner^[38] employed this technique to raise the coercive force (Hc) and decrease remanence (B_R) in cobalt-nickel alloys developed for hard magnetics.



Figure 10.10. Examples of pulsed wave forms^[47]

Periodic reverse, or PR,^[39] under the proper conditions, produces dense fine-grain, striated, leveled and bright deposits. It has its greatest effect and applications on deposits from cyanide solutions, notably copper, permitting smooth, heavy deposits. [Copper deposits produced with DC from cyanide solutions generally become nodular when thicknesses exceed 0.075 - 0.1 mm (3 - 4 mils).] A typical PR cycle is 15 seconds plating and 3 seconds deplating; the longer the deplating (reversal) cycle, the smoother is the deposit.

The extended plating time or increased current density required by PR to deposit a given thickness led to the use of interrupted DC employing similar cycles. The interrupted or off duty segment's function is to permit the diffusion layer to be replenished.

Asymmetric AC can be considered a variation of PR. In an interesting application, Rehrig^[40] used high frequencies (500 Hz), and very high current densities [cathodic C.D. ~82.5 A/dm² - 110 A/dm² (~750 - 1000 A/ft²) and anodic C.D. at 25% of cathodic C.D.] for high speed spot plating of gold on lead frames to obtain good bonding properties. In contrast, DC current densities in excess of 33 A/dm² (300 A/ft²) produced deposits with poor bonding characteristics. Co-deposited metallic impurities were removed during the anodic phase; the degree of effectiveness was proportional to the anodic C.D. with a minimum of 22 A/dm² (200 A/ft²) required. The deposit hardness decreased and the bond pull strength increased as anodic C.D.

Considerable work is being done applying pulsed current modification in plating, especially in electronic plating applications. Wan et al.^[41] and Puippe et al.^[42] reviewed the literature to 1979. Two symposia^[43] and a monograph, "Theory and Practice of Pulse Plating,"^[44] present current practices and applications involving pulse plating. Pulse plating may be defined as on/off DC as is interrupted DC mentioned above. The primary differences are that the on pulses are of very short duration, generally 5 - 15 milliseconds, and the off time is approximately ten times longer; much higher current densities are applied. The so-called duty cycle is the ratio of on time (T_{on}) to off time (T_{off}):

Eq. (20) Duty Cycle = $T_{on} / (T_{on} + T_{off})$

The time interval (on + off) is the reciprocal of the frequency, the on time being the product of the time interval and duty cycle.

The average current density is calculated as the peak current density times the duty cycle. The average current density in pulse plating cannot

exceed the diffusion limiting current density determined for DC plating^{[45][46]} The size of a pulse rectifier, i.e., the peak current required, is determined by the ratio of the average current to the duty cycle. The duty cycle is usually reported as percent. Each variable influences the properties and quality of the deposit and the optimum conditions are usually determined experimentally.

Osero^[47] evaluated the equipment associated with pulse current modification. Avila and Brown^[48] detail the circuitry and power requirements. They indicated that the off time is critical since it is based on and determines the requirements of the diffusion layer returning to equilibrium.

Cheh et al.^[49] indicated that the cathode current efficiency (CCE) dropped from 100% to a 93.7 - 80.4% range due to pulse plating, shorter pulses (0.5 msec) resulting in lower CCE than longer ones (2 - 10 msec). They hypothesized that this may be due to the 2-step reduction mechanism as advanced by Mattson and Bockris:^[50]

Eq. 21
$$Cu^{2+} + e^{-} \rightarrow Cu^{1+}$$

Eq. 22
$$Cu^{1+} + e^{-} \rightarrow Cu^{0}$$

where Eq. 21 is faster than Eq. 22 during the first interval of the pulse. Thus, the cuprous ion (Cu^{1+}) accumulates and during the relaxation (off) period disproportionates:

Eq. 23
$$2Cu^{1+} \leftrightarrow Cu^{2+} + Cu^{0}$$

The throwing power of copper, as measured with the Haring Cell, was somewhat reduced by pulse plating while that of gold from a citratephosphate solution was improved; however, the improvement diminished rapidly with increasing peak current densities. Using a rotating disc electrode, they found a slight improvement in the microthrowing power of the gold solution due to pulsing; however, the current densities and especially the agitation used had more significant effects.

Reid^[51] found that pulsed plating in cobalt-hardened gold deposits virtually eliminated polymer formation under low C.D. (~5 mA/cm²) and high off-to-on ratios (100 ms/10 ms). Other effects in the properties noted were:

- 1. Improved ductility without any significant decrease in hardness.
- Increased density-even in the presence of polymer-from 17.1 gm/cm³ for DC plating (1 mA/cm²) to 19.2 gm/cm³.

3. Significant reduction in electrical resistance for Co-hardened gold, from $14 \,\mu\Omega$ -cm to $6 \,\mu\Omega$ -cm, but an insignificant reduction in pure gold deposits, from $3 \,\mu\Omega$ -cm to $2.4 \,\mu\Omega$ -cm.

Effects of pulsed plating on the deposit compositions and properties of gold and gold alloys are reviewed by Raub and Knödler.^[52] They show increased alloying element content (Ni or Co) and a decrease in carbon content as a function of off-time. The tensile stresses are reduced in alloy deposits, while the hardness is about 10% higher than that of comparable DC plated alloys. The gas content (H₂, N₂, and O₂) of pulsed plated deposits is also substantially reduced. Knödler^[53] reviewed the use and effects of pulse plating of the precious metals. Hosokawa et al.^[54] found that desirable properties of gold and rhenium deposits sometimes lie within a narrow range of pulse parameters. They found that the CCE was five times greater than with DC plating when the duty cycle exceeded 50% with a pulse duration of 3 - 5 μ sec. Puippe and Ibl^[55] studied the influence of T_{on} and T_{off} on the morphology of cadmium, copper, and gold deposits. The influence of T_{off} proved to be important with regard to electro-crystallization; it also strongly influenced other properties unrelated to the morphology of the deposits.

The effect of pulse plating on current distribution and throwing power was reviewed by Dossenbach.^[56] He indicated that pulse plating does not affect primary current distribution and compared to DC plating provides a less uniform secondary current distribution whereas the tertiary distribution can be improved, especially for short duration high current density pulses.

Avila^[57] reviewed pulse plating of alloys. The pulse plating of other (individual) metals have been discussed in Refs. 43 and 44.

Fundamental aspects of pulse plating were presented by Ibl.^{[43a][58]} The influence of pulsing and the effect on the double layer at the electrode surface are discussed by Puippe and Ibl.^[59]

Some of the advantages claimed for pulse plating are:

- 1. Faster plating rates due to increased permissible current densities.
- 2. Denser deposits (less porosity).
- 3. Higher purity of deposits, less tendency for impurities to deposit.
- 4. Smoother, finer-grained deposits.
- 5. Reduced need or elimination of addition agents.
- 6 Less hydrogen evolution, providing sharper, finer lines at masking interfaces and possibly less hydrogen embiittlement.
- 7. Decreased stress in deposits.
- 8. Increased Ni or Co contents in alloy-hardened gold deposits with less polymer formation.

Some of the effects and advantages attributed to pulse plating and other modulated current wave forms are very similar to those for ultrasonic agitation. Both attempt to reduce the adverse polarization effects by decreasing the Nernst diffusion layer thickness while increasing mass transfer of the reacting species, permitting the use of higher current densities. In many instances, pulse plating has an effect similar to organic addition agents, especially as related to grain size.

A more recent approach to modification of plating processes and resulting deposits involving the simultaneous application of laser energy was first reported by von Gutfeld et al.^[60] The impingement of a laser beam on the cathode surface resulted in increased plating rates by as much as a factor of 1000. The mechanisms responsible for this deposition rate increase were investigated by Puippe et al.^[61] The absorption of laser energy resulted in localized increase in temperature at the cathode/solution interface which produced vigorous agitation *(microstirring),* a shift in the rest potential (open circuit potential), and an increase in both the charge transfer and mass transfer rates.

Gutfeld and Romankiw^[62] described the application of laser-enhanced plating to gold patterning, i.e., the selective deposition on spots and patterns or tracks with the ability to "write directly" without the use of masks as well as potential use in repair of electronic circuitry. Bocking^[63] described plating equipment and set-up combining laser-enhanced plating with high speed jet selective plating with plating rates as high as 16 \propto m/s. Pure gold was deposited on both metallic and metallized ceramic substrates without the need for any masking. Gutfeld et al.^[64] developed a method for selective pattern plating by applying a dielectric coating and utilizing a laser (Nd-YAG laser) to produce the desired pattern leaving a clean surface which could then be plated by conventional means. Gelchinski et al.^[65] found that laser-enhanced jet plating of gold increased deposit smoothness and decreased nodularity and voids with increasing laser power density; hardness of the deposits was in the range characteristic of soft gold.

Kuiken et al.^[66] indicated that laser-enhanced plating was not very effective on good heat-conducting substrates since only a limited temperature rise results. They suggested depositing an undercoat of a relatively poor heat-conducting material such as a nickel-phosphorus alloy (which is almost 1/20 that of nickel), significantly improving the effectiveness of laser-enhanced plating and reducing the need for high laser power densities.

Zahavi et al.,^[67] using a Nd/YAG laser, deposited Au and Pd-Ni alloys directly on semiconductor and polymeric substrates with conventional electroplating solutions but without external current. The deposition was highly selective and accomplished without masking or any surface preparation. The deposits exhibited Schottky contact behavior on n-type silicon and GaAs substrates.

4.0 PROCESSING TECHNIQUES

The preparation of metal surfaces for plating involves the modification or replacement of interfering films to provide a surface upon which deposits can be produced with satisfactory adhesion. The type and composition of the soils present as well as the composition and metallurgical condition of the substrate determine the "preparation cycle" and the materials used. The operations involved are designed to accomplish these objectives:

- 1. Clean the surface.
- 2. Pickle or condition the surface.
- 3. Etch or "activate" the surface.
- 4. Stabilize the surface. Strike

In some cycles, several objectives are combined in the same operation. Rinsing steps follow each treatment step.

Each of these steps is examined separately.

Cleaning. The cleaning steps serve two functions: *(i)* Removal of bulk soils (oils, grease, dirt). This may involve mechanical operations such as wet or dry blasting with abrasive media, brushing or scrubbing or chemical cleaning with solvents (degreasing) or emulsions. *(ii)* Removal of last "trace" residues. Usually chemical soak (or spray) and electrochemical cleaners are employed. These can affect the substrate and therefore should be compatible with it. Such cleaners may contain alkaline chemicals, surfactants, emulsifying or dispersing agents, water softeners, inhibitors, and chelating agents. Acidic formulated cleaners are also available.

Pickling or Conditioning. These are acid dips which neutralize and solubilize the residual alkaline films and *micro-etch* the surface. The common acid dips are either sulfuric acid (\sim 5 - 15% v/v) or hydrochloric acid (\sim 5% to full strength) and are satisfactory for most alloys. Where undesirable reactions or effects may occur, the acid dip should be formulated to be compatible with the substrate composition.

Etching or Activating. Undesirable (from the plating viewpoint) metallurgical micro-constituents are removed or rendered non-interfering; e.g., silicides in aluminum alloys or nickel, or chromium in stainless steels or super alloys, or these steps remove or reduce oxides or other passive conditions prevalent to some surfaces.

High nickel and/or chromium containing alloys usually have a tenacious oxide or passive films which must be destroyed with strong acids or anodic etching in strong acids. Solutions containing 15 - 25% v/v or more sulfuric acid are usually employed at low current densities, $2.2 \text{ A/dm}^2 - 5.5 \text{ A/dm}^2$ (20 - 50 A/ft²) for metal removal, or at high current densities, $10 - 30 \text{ A/dm}^2$ (100 - 300 A/ft²) for smut removal or oxide alteration. Both current density ranges may be employed to maximize adhesion of thick deposits.

In special cases, activation may be accomplished by cathodic treatment in acid or alkaline (cyanide) solutions. Hydrogen is deposited at the surface to reduce superficial oxide films. Solution contamination must be avoided or minimized since such contamination especially heavy metal ions may be codeposited as smut.

Stabilizing. Very active materials alloys of aluminum, magnesium or titanium tend to oxidize or adsorb gases readily, even during rinsing and transfer. These continue to interfere with adhesion of deposits. Therefore, a necessary step involving an immersion deposit of zinc or tin, electroless coating, or modified porous oxides is required to make the surface receptive to an adherent electrodeposit.

The electrodeposition of thin coatings from specially formulated solutions called *strikes* are considered stabilizing steps since they provide new, homogeneous, virgin surfaces upon which subsequent deposits are plated. These strike solutions and plating conditions are usually designed to be highly inefficient electrochemically. The considerable hydrogen gas evolution assists any final cleaning, reduction of oxides, and activation of the surface while the thin deposit covers surface defects and remaining soils (smut).

The most widely used strike is the cyanide copper strike. The pH and "free" cyanide content are varied depending on the alloy being plated. A typical formulation range is:

ai)
al)
/gal)
)

pН	10.5 - 13.0
Temperature	RT or slightly elevated, 38 - 45°C
C.D.	0.55 - 1.1 A/dm ² (5 - 10 A/ft ²)
	1.1 - 2.2 A/dm ² (10 - 20 A/ft ²)

The lower pH's and free cyanide are used for sensitive metals such as aluminum or zinc alloys; the higher pH is used for steels. The cleaning or activating ability is increased with increasing pH, free cyanide, C.D. and temperature. The deposit thickness is approximately $0.25 - 0.50 \propto m$ (0.01 - 0.02 mils); thicker deposits—1.25 - 2.5 $\propto m$ (0.05 - 0.1 mils)—are applied at slightly higher temperatures.

The second most common strike is the Woods nickel strike or its modifications. This strike is effective (and preferred) on high nickel or chromium containing alloys. A typical formulation is:

Nickel Chloride, NiCl ₂ .6H ₂ 0	O 240 g/L (32 oz/gal)
Hydrochloric Acid (Conc.):	125 ml/L (16 fl. oz/gal)
Temperature	RT (20 - 30°C)
C.D.	5 - 20 A/dm ² (50 - 200 A/ft ²)
Time	0.5 - 3 minutes

Silver or gold strikes are used prior to plating thicker deposits of these metals. Either a gold strike or the strike of the particular precious metal is used prior to plating the specific metal. These are generally formulated similar to the plating solution except that they contain approximately one-tenth the metal ion concentration. The strikes may be applied directly to the substrate or, more commonly, on the copper or nickel strikes discussed. The use of these strikes minimizes the possible contamination of precious metal plating solutions.

Unusual strikes are sometimes employed in special procedures. For example, a chromium strike appears to be most effective for plating on molybdenum alloys or an acid copper or electroless nickel strike on titanium alloys followed by a thermal diffusion treatment to obtain adhesion of subsequent deposits.

Properly designed preparation cycles and the establishment of a stable receptive surface are prime requisites for good quality deposits. However, the condition and integrity (or lack of it) of the surface prior to plating also affect the quality of the deposit; this is becoming more evident as quality and functional requirements of electrodeposits are increased.

Some plating processes require post-plating treatments. To improve the corrosion resistance of zinc or cadmium deposits or the tarnish resistance of silver, chromate conversion coatings are applied by chemical or electrochemical treatments; these gel-like films also improve adhesion of paint films.

Since most preparation and plating processes generate hydrogen which can be occluded and can migrate into the substrate, possibly causing

hydrogen embrittlement, stressed articles or high-strength materials are usually given a stress relief bake in air at 190° C ($350 - 400^{\circ}$ F) for 3 - 24 hours within 3 - 4 hours after plating.

Procedures for the preparation of difficult-to-plate substrates have been prepared as "Standard Recommended Practices" by ASTM. These are listed in Appendix A. The "Standards" reference the literature upon which they are based. Included in the Appendix is a discussion of preparation of less common metals.

5.0 SELECTION OF DEPOSIT

5.1 Individual Metals

Only nineteen or so of all the known individual (single) metals are presently of practical interest in aqueous electrodeposition. Of these, only ten have been reduced to large scale commercial practice. These are indicated in Table 10.3 with the most widely used ones underlined. Holt^[68] reviews the electrodeposition of "uncommon" elements from aqueous, organic and fused salt media.

Alloy deposition, electroless deposition and deposition with dispersed particles *(inclusion plating)* extend the practical use of aqueous coating systems considerably. These are discussed separately.

In order to make a proper selection of a deposited coating, one must be cognizant of the fact that these coatings can vary widely in structure and physical and chemical properties, depending on the electrolyte composition and operating conditions as discussed above. For example, the hardness of as-plated chromium deposits can be varied from 350 to 1100 DHN, and nickel from about 150 to 650 DHN. The corrosion protection afforded by a coating depends upon its electrochemical relationship to the substrate, its thickness, continuity (porosity), and the environment as well as its overall quality. The important factors to be considered in the selection of a deposit are the purpose of the deposit and the use (function) of the finished article. Other factors which must be considered are the size, shape, and expected useful life of the article and the costs and environment involved.

Table 10.4 comprises a list of various engineering functions of deposited coatings and the deposits usually employed. Table 10.5 gives "representative" hardness values for various deposits in relation to some common materials and hardness scales. Spencer^[69] discusses selection factors for coatings, their properties and characteristics, and uses.

LIGHT METALS		Electro Config	on → 1 1 ← Atomic Number uration H ← Symbol 100797 ← Atomic Weight		
		HEAVY	METALS	NON METALS	² 2 He
² 3 2 4 Li Be 6.939 90127	, BRITTI	F		V III A IV A V A VI A VI A 3 5 2 6 3 7 2 8 3 9 B C N O F 10.811 12.01115 14.0067 15.9994 18.9944	4 0026 2 10 Ne 20 183
² 11 ² 12 ¹ Na ² Mg ^{22 9898} 24.312	111 B 1V B V B		VIII 18	2 13 2 14 2 15 2 16 2 17 3 Al 3 H 8 26 5815 28 086 30 9738 32 064 35 453	2 18 Ar 39.948
² 19 ² 20 K 2 Ca 39 102 40 08	2 21 2 22 2 23 2 Sc 10 Ti 11 V 44.956 47.90 50.942	24 25 13 Cr 13 Mn 51.996 54 9380	2 26 2 27 2 28 2 29 12 Fe 12 Co 12 Ni 14 Cu 55.847 58.9332 58.71 63.54	29 2 30 2 31 2 2 33 2 34 2 35 20 12 Zn 15 Ga 14 Ge 15 As 16 Se 15 F F 69.72 72.59 74.5216 78.96 79.909 79.909	36 Kr 83 80
2 37 2 38 16 Rb 1 Sr 1 85 47 87.62	² 39 ² 40 ² 41 ¹ Y ¹ Zr ¹ Nb [*] ² 88.905 91.22 92.906	² 42 ² 43 ¹⁸ Mo ¹⁸ Tc ¹³ 95.94 (99)	2 44 2 45 2 46 2 47 1 Ru 1 Rh 1 Pd 1 Ag 101.07 102.905 106.4 107.87	17 2 48 2 49 2 50 2 51 2 52 2 53 18 12 10 1 1 1 50 1 1 1 1 1 10 112.40 14 18 18.69 121.75 127.60 126.5044	2 54 Xe 131 30
2 55 2 56 3 Cs 1 Ba 1 132 905 2 137.34	57-71 2 72 2 73 <u>str</u> 10 Hf 10 Ta LANIMANIOL 10 2 178.49 2 180.941	2 74 2 75 10 W 10 Re 32 183.85 2 186.2	2 76 2 77 2 78 2 79 10 Os 10 Ir 10 Pt 10 Au 12 190.2 15 192.2 15 195.09 1 196.96	79 2 80 2 81 2 2 83 2 84 2 85 Au 13 Hg 13 TI 15 Pb 15 Bi 15 Po 15 At 947 2 200.59 3 204.37 2 207.19 5 201.940 4 (210) 7 (210) (210) (210)	2 86 Rn (222)
² 87 ² 88 ³² Fr ³² Ra ¹ (223) ² (227)	89-103 ² 104 ⁵¹⁷ ¹³² ¹³² ¹³² ¹³² ¹³² ¹³² ¹⁰⁴ ¹⁰⁵	NTHANIDE 257 SERIES 18 LA ARE EARTH LEMENTS) 2 136 91	2 58 2 59 2 60 2 61 2 62 1 Ce 10 Pr 12 Nd 13 Pm 12 Sm 2 100 12 2 100 10 1 14 74 2 (15) 2 100 3	22 2 63 2 64 2 65 2 66 2 67 2 68 2 69 2 70 m]; Eu]; Gd]; Tb]; Dy]; Ho]; Er]; Tm]; Yt os 2 111 14 2 117 3 2 114 174 2 14 193 2 16 19 3 2 14 19	2 71
An atomic weight given mass number of the i Atomic weights correct international committe on carbon 12	in parentheses denotes the	ACTINIDE 289 SERIES 32 AC INSURANIUM 12 LEMENTS) 2 (227)	90 91 92 93 94 Th 17 Pa 19 U 17 Np 19 Pu 2000 2010 2010 204 00 2000 2000 2000 200	14 95 96 97 98 99 100 110 10 10 20 1 Am 1 Cm 1 Bk 1 Cf 1 Es 1 Fm 1 Md 1 N 40 1 Am 1 Cm 1 Bk 1 Cf 1 Es 1 Fm 1 Md 1 N 41 1 Am 1 Cm 1 Am 1 Am 1 Am 1 Am 1 Am 1 A	2 103 5 12 Lw

(*) Also known as Columbium, Cb

Enclosed area contains "metallic" elements which have been deposited from aqueous solutions.

Elements most commonly plated commercially

- --- Elements less frequently plated commercially
- ···· Elements infrequently plated commercially

540

Primary Function of Coating	Most Widely Used Coating	Representative Application
Corrosion Resistance	Zn, Cd Sn Ni, Cr	Sacrificial coatings, fasteners, hardware fittings Food Containers Food processing equipment (wear resistance required)
Decorative	Cu/Ni/Cr composite, Brass (Cu-Zn)	Household appliances, automotive trim
	Ag, Au, Rh	Jeweiry
Dielectrics	Anodized oxide coatings of Al & Ti, Ta	Condensers Capacitors Coatings
Electroforms	Ni, Cu, Fe, (Cr) Co, composites	Radar "plumbing," screens, bellows, containers, molds
High temp. oxidation resistance Diffusion Barrier	Cr, Rh, Pd, Pt, Au, Ni	Air and space craft Electronic devices
Maskant	Cu, Sn Bronze Sn, Pb-Sn	Selective carburizing, nitriding Etch Resists
Reflectors	Ag, Rh, Cr Au	Visible light reflectors Infra-red reflectors
Salvage	Cu, Ni, Cr, Fe	Mismachined, worn parts
Soldering, Bonding	Pb, Sn, Sn-Pb Cu, Ag, Au Sn-Ni, Cd, Ni	Containers, printed circuit and other electronic assemblies and chassis
Wear Resistance	Ni, Cr, E-Ni, Hard Anodizing Rh, Au, Au alloys	Air and space craft, hydraulics Electronic contacts

Table 10.4. Selection of Deposits
Table 10.5.
 Comparison of "Normal Hardness" of Commonly Deposited

 Coatings in Relation to Hardness Scales



Approximate Comparison of Hardness Scales, Substrates and Deposits.

(Modified and based on Metal Progress, p. 131, Sept. 1959)

5.2 Alloy Deposition

Alloy deposition extends the availability and applicability of coatings from aqueous solutions. It is an area of increasing research and development, although most of the systems have not attained commercial application. An extensive literature has developed. Brenner's two-volume comprehensive, definitive monograph^[70] details compositions, operating conditions, structures and properties of the deposits, covering developments up to 1960. A Russian monograph^[71] details their extensive research in this area. Brenner^[72] updated the state of the art to 1964. Krohn and Bohn^[73] reviewed the literature to 1973 with a count of more than two hundred binary alloys; Fig. 10.11 summarizes the binary alloy combinations reported to June, 1972. Over one thousand abstracts on alloy deposition were reported in Chemical Abstracts between 1964 and 1972. Sadana et al.^[74] annually review developments in alloy plating.



Figure 10.11. Binary alloys which have been electrodeposited form aqueous solution: ℜ indicates alloys reported up to 1960, ● indicates alloys electrodeposited for the first time between 1961 and 1964, and • indicates alloys reported since 1964.^[73]

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.

The electrodeposition of tungsten alloys^{[75]-[78]} of Fe, Ni and especially Co is commercially feasible but has remained largely experimental although their properties should be of sufficient interest for engineering applications. While the as-deposited hardness is lower than chromium or Ni-P, these alloys can be precipitation hardened. One drawback is the high optimum temperature (600°C) for the Co-W alloys, which can be detrimental to the substrate. The deposits retain hot hardness similar to the Stellites.

Binary and ternary alloys of Fe, Ni and Cu have been produced almost as stainless steel coatings^{[79]-[83]} other studies^{[22][73][84]} include reviews. Machu^[85] investigated the problems with anodes especially oxidation to higher valence states and the use of insoluble anodes, alone and in combination with soluble anodes. Other work with ternary alloys has been with gold alloys to increase hardness; Au-Ag-Sb alloys^[86] reportedly showed wear resistances 25 - 33 times greater than pure Au. Srivastava^[87] reviewed the electrodeposition of ternary alloys with special reference to solution compositions and characteristics and applications.

Amorphous coatings, i.e., coatings exhibiting no x-ray diffraction patterns, have been produced by electrodeposition and electroless deposition. Aqueous deposition possibly is the best means for producing amorphous metals and alloys since low operating temperatures are involved and rapid solidification (as with metallurgically produced alloys) is not involved. Iron, nickel and cobalt-based alloys containing sufficient phosphorus or boron are generally amorphous in the as-plated condition. Thick amorphous electroforms of Ni-P have been produced.^[88] The deposition of amorphous alloys is not restricted to alloys containing these light non-metallic elements. Amorphous single metal electrodeposits have also been produced, e.g., amorphous chromium deposits.^[89] Amorphous deposits are generally hard, and corrosion and wear resistant.

Methods other than co-deposition have been developed to produce alloy coatings. These include diffusion of sequential deposits, dispersion of particles or fibers in deposits (electro-composites), electrophoretic phenomena, and mechanical plating.

Diffusion coatings. These processes involve the deposition of coatings sequentially similar to the composite; Cu under Ni under Cr for decorative finishes, followed by a thermal diffusion treatment. Such techniques have been applied to improve the adhesion of deposits on difficult-toplate substrates (diffusion bonding). They have not, however, been extensively applied to producing alloy coatings by deposition possibly due to temperature requirements and the formation of intermediate diffusion zones with undesirable properties (brittleness, etc.).

A proprietary alloy of Ni-Zn called "Corronizing"^[90] was used commercially as an improved corrosion resistant coating. (Subsequently, codeposited Ni-Zn alloys were developed.) The substitution of Cd for Zn by Moeller and Snell^[91] produced a corrosion preventive coating for jet engine parts, permitting the use of low alloy steels operating at temperatures up to $535^{\circ}C(1000^{\circ}F)$. The coating consisted of $5 - 10.2 \propto m (0.2 - 0.4 \text{ mils})$ Ni plus $2.54 - 5 \propto m (0.1 - 0.2 \text{ mil})$ Cd diffused at $332^{\circ}C(630^{\circ}F)$ (M.P. of Cd = $321^{\circ}C$ ($611^{\circ}F$)). The satisfactory function of this diffused alloy coating is dependent on the quality and characteristics of the Ni component.^[92]

Sequentially deposited coatings of Co-W alloy and Cr diffused in air and in a carburizing atmosphere are shown in Fig. 10.12 to illustrate the potential of producing unique alloy coatings by controlled heat treatments.



Figure 10.12. Diffused Co-W/Cr/Co-W composite coatings. (a) H.T. in air, 1680°F, 10 hrs (500x) (unetched), (b) H.T. in carburizing atmosphere, $1680^{\circ}F$, 10 hrs (500x) (unetched), (c) H.T. in atmosphere, $1680^{\circ}F$, 10 hrs (500x) (etchant: hot Murakami).

Dispersion Coatings. One of the common problems in electroplating is roughness of the deposit, the primary cause of which is the presence and suspension of discrete particles in the solution with subsequent entrapment in the deposit. To overcome this problem, continuous or periodic filtration is part of the operation for many types of plating solutions; so it is not difficult to include foreign material into a deposit. The purposeful addition of a second, dispersed phase of controlled particle size into a plating solution, is referred to variously as: dispersion, inclusion, occlusion, composite or electrophoretic plating, deposition or coating.

The requirements are simple:

- 1. The particles must be insoluble (or only slightly soluble) in the solution.
- 2. The particles must be compatible with the solution, i.e., not produce any detrimental effects.
- 3. The particles must be dispersed either "naturally" (as colloidal size particles) or mechanically (stirring, agitation) in order to contact physically the surface being coated.
- 4. The particle size is usually in the colloidal range (~0.005 0.2 ∝m) or slightly larger, usually less than 0.5 1.0 ∝m although there are exceptions for certain applications.

The possibilities are numerous. Satin nickel deposits^[93] were developed to reduce glare on automotive trim, also providing improved corrosion characteristics. Kilgore^[94] described various applications including: (*a*) non-galling Ni deposits containing 1000 mesh silicon carbide for pistons and cylinder walls on internal combustion engines, (*b*) inclusion of Cr in Ni deposits producing nichrome by subsequent heat-treatment, (*c*) 120 grit diamond dust in nickel to produce permanent abrasive grinding wheels. The hardness and wearability of Cd deposits from acid baths were improved by inclusion of corundum or boron carbide particles.^[95]

An important, desired result of dispersion plating is the improved strength, hardness, creep and other properties of the deposit, including the retention of strength after thermal treatments. Sautter^[96] reported increased yield strength from 8 kg/mm² (11,375 psi) for pure Ni deposits to 35 kg/mm² (50,000 psi) for dispersed alloys containing 3.5 - 6.0 volume percent (v/o) Al₂O₃; the particle size ranged from 0.01 - 0.04 \approx m to 0.3 \propto m and the plating parameters other than agitation had little or no effect. Electroformed lead and lead alloys were strengthened only by additions of

TiO₂ (0.01 - 0.03 \propto m) although Al₂O₃, BaSO₄, Pb₃O₄ and W additions were also studied,^[97] indicating the possibility of specificity with respect to the dispersoid. Greco and Baldauf^[98] found 2 - 15% of Al₂O₃ to be the effective range for dispersion-hardening of Ni deposits from a sulfamate bath. The increase in hardness appeared to be linear to the square root of the volume fraction of the dispersoid with Al₂O₃ showing a higher slope than TiO₂. The deposits contained three times (v/o) more TiO₂ than Al₂O₃ at the same solution concentrations and plating conditions; the particle size averaged 0.074 \propto m Al₂O₃ (0.013 - 0.339 \propto m range) and 0.2 \propto m TiO₂ (0.037 - 0.313 \propto m range).

Table 10.6 indicates the variations in mechanical properties of particledispersed nickel alloys due to the dispersoid material and the plating solution composition.

Electrophoresis is the term used to describe the migration, by virtue of the electric charge on their surfaces, of colloidal or near-colloidal particles in a suspending medium when a potential is applied. This migration is analogous to ionic migration through a solution. The electrical double layer of charges discussed above is involved. The process has been applied to the deposition of a variety of materials including metal powders, oxides, cermets and other particles to metal substrates. Usually the particles ranging in size between 0.5 and 45 m are suspended in a non-conducting (or poorly conducting) medium and a high potential (50 - 1000 V) is applied to the electrodes. High rates of deposition are obtained and coating thicknesses can be varied by controlling voltage, electrode spacing, suspension concentration and time. The coating is air dried and baked to remove the solvent medium. The coating is nonadherent and must be processed further by compression and/or sintering or by subsequent electrodeposition to bond it to the substrate. Electrophoretic deposition has been applied to produce Ni, Ni-Cr, Ni-Cr-Fe coatings to base metals as well as inclusion of such dispersoids as molybdenum disulfide or silicon carbide.^[99] Ortner^[100] applied electrophoretic deposition of TaC-Fe-Ni coatings onto graphite, sintered at 2300°C (4170°F) for the protection of rocket nozzle inserts and oxidation resistant coatings for refractory alloys.

A mechanical method of applying a coating involves peening soft metals (Cd, Zn) and alloys onto a substrate with glass beads in an aqueous medium in a tumbling operation. The equipment is similar to a cement mixer. "Alloys" of Cd-Sn deposited in this manner exceeded two thousand hours in salt fog corrosion tests.

		Tensile Strength		Yield Strength			Modulus of Elasticity		,
Dispersed Material(a)	Plating Bath	kg/sq mm	psi	kg/sq mm	psi	Hardness, kg/sq mm	kg 'sq mm	psi × 10*	Reference
Alumina, 1.0%	Sulfamate (50 C)	77(6)	110,000(b)	52.5(6)	75,000(6)	270 to 320 ^(b)	<u></u>		1
Alumina, 1.7%	Watts (50 C)	45(+)	64.000(*)			-			2
Alumina, 2%	Watts (50 C)	21(4)	30,000(4)		-	514(*)		_	4
Alumina, 2.5%	Chloride (50 C)	<u> </u>		35(1)	50,000(1)		_		3
Alumina, 4.5%	Watts (50 C)	68	97,000	45	64,000	350		_	5
Alumina, 6.0%	Watts (50 C)	75	107,000	56	80,000	380	22.000(=)	31(4)	5
Alumina, 9.4%	Watts (50 C)	70	100,000	45	64,000	400	22,000(#)	31 (2)	5
Silicon carbide, 3.2%(b)	Sulfamate	174	249,000	_		_		- <u>-</u>	6
Silicon carbide, 3.6% ^(b)	Sulfamate	202 to 229	288,000 to 327,000		_		31,500	44	6
Silicon carbide, 5.6%	Watts (50 C)	85	121,000	60	86,000	4 10	21,000(*)	30 ^(g)	5
Silicon carbide, 9.6%	Watts (50 C)	74	105,000	55	79,000	450	21,000(#)	30 ^(x)	5
Titanium dioxide, 5%	Sulfamate (50 C)	81 (6)	115,000%)	55%)	78,000(6)	300 to 420 ^(b)	-		1

Table 10.6. Mechanical Property Data for Nickel-Particle Composites^[122]

(a) Weight percent.

(b) The effects of heat treating are summarized in Table 14.2.

(*) Tensile strength was 32 kg/sq mm (46,800 psi) after heat treating at 1100 C. The 100- to 500- angstrom particles formed 2500 angstrom clusters during heat treating.

(d) Tensile strength was 2.3 kg/sq mm (3,300 psi) at 1095 C. Elongation at 1095 C was 34%.

(*) Hardness decreased to 205 kg/sq mm at 260 C and 74 kg/sq mm at 425 C.

(1) Yield strength for alloy deposit after heating to 750 C. The yield strength of nickel containing no alumina, which was deposited in a similar solution, was only 8 kg/sq mm (11,400 psi) after a similar heat treatment.

(s) The modulus of the matrix nickel was 18,000 kg/sq mm (26,000,000 psi).

(b) Whiskers about 1 µm in diameter were incorporated in the deposit.

From The Properties of Electrodeposited Metals by W.H. Safranek, Elsevier Publishing Co., 1974.⁸⁰ Reprinted with permission

Alloy deposits, however produced, offer certain advantages over single metal deposits:

- 1. Increased corrosion resistance due to greater density and finer grain structure.
- 2. Combination of properties of the individual constituents.
- 3. New properties, unlike the individual constituents.
- 4. "Tailor-made" properties by proper selection of the constituents.

The limitations include the greater control required, the difficulty of reproducing the alloy composition, the greater attention to the anode systems used and their effects on the solution constituents and complexes.

6.0 SELECTED SPECIAL PROCESSES

6.1 Electroless Deposition

Electroless plating processes differ from electroplating processes in that no external current source is required. Metal coatings are produced by chemical reduction with electrons supplied by a reducing agent (R.A.) present in the solution:

Eq. (24) $M^{+n} + ne^{-}$ (supplied by R.A.) $\rightarrow M^{o}$ (+reaction products) surface

The uniqueness of the process is that the reduction is catalyzed by certain metals immersed in the solution and proceeds in a controlled manner on the substrate's surface. The deposit itself continues to catalyze the reduction reaction so that the deposition process becomes self-sustaining or autocatalytic. These features permit the deposition of relatively thick deposits. Thus the process is differentiated from other types of chemical reduction: (*a*) simple immersion or displacement reactions in which deposition ceases when equilibrium between the coating and the solution is established (e.g. copper immersion on steel from copper sulfate solutions), and (*b*) homogeneous reduction where deposition occurs over all surfaces in contact with the solution (e.g. silvering-mirroring).

To prevent spontaneous reduction (decomposition), other chemicals are present; these are generally organic complexing agents and buffering agents. Other additives provide special functions as in electroplating solutions: additional stabilizers, brighteners, stress relievers. The reducing agents most widely used are:

Sodium hypophosphite (for Ni, Co)

Sodium borohydride (for Ni, Au)

Dimethylamineborane (or other substituted amine boranes) for Ni, Co, Au, Cu, Ag)

Hydrazine (for Ni, Au, Pd)

Formaldehyde (for Cu)

The process was reported by Brenner and Riddell^[101] in 1946 for nickel and cobalt coatings and has enjoyed very active interest since, resulting in extension* to electroless plating of copper, gold, palladium, platinum, silver and a variety of alloys involving one or more of these metals. Comprehensive reviews^{[102]-[108][175]} with extensive bibliographies cover the considerable technology, solution composition and operating conditions, and literature (including patent) which have accumulated. Representative solution formulations are given in Appendix B.

Nickel deposits produced with hypophosphite or the boron-containing reducing agents are alloys containing the element P or B. They are very fine polycrystalline supersaturated solid solutions or amorphous metastable alloys^{[109]-[111]} with hardness ranging approximately 500 - 650 VPN and can be precipitation hardened, being converted to crystalline nickel and nickel phosphide (Ni₃P) or boride (Ni₃B). Maximum hardness ranging from 900 -1100 VPN is obtained at 400°C (750°F) for 1 hour (Fig. 10.13). The effects of heat treatment at various times and temperature on the hardness of electroless Ni-P have been extensively investigated.^{[109][112]-[114]} Johnson and Oaburn^[115] supplement more fully previous work, showing the influence of phosphorus contents and the specific heat treatments on the range of hardness obtained (Fig. 10.14). Higgs^[116] investigated the effects of heat treatments on the hardness and structure of the deposits reporting the presence of several NixPv compounds present other than the usually reported Ni₃P. Alloys containing more than 7 wt. % P do not exhibit ferromagnetism in the as-plated condition. Schwartz and Mallory^[117] found differences in the increasing ferromagnetism of alloys from various solutions as a result of heat treatments.

The phosphorus content of the deposit increases as the hypophosphite concentration increases and the pH decreases in the solution. The boron

^{*} These are commercially available. Other electroless processes for iron, chromium, cadmium, and tin have been reported but either not confirmed or commercially applied. Undoubtedly, new developments will continue to be reported.



Figure 10.13. Hardness of electroless Ni alloys as a result of heat treatments (1 hr).



Figure 10.14. Hardness of Ni-P alloy: ● as-plated, X after 8 hrs at 200°C, O after ½ hrs at 400°C.^[115]

content in Ni-B systems is generally similar. The complexing agents in the solution influence deposition rate^[118] (along with pH) and may also have an effect on the as-plated deposit; Mallory^[119] related differences in salt fog corrosion tests to this factor. It appears that the properties of the deposit may vary considerably depending on the phosphorus content which, in turn, is determined by the solution used and its operating pH. Graham et al.^[110] observed abrupt changes in structure, strength and ductility of deposits at a phosphorus content of about 7 w/o with both strength and ductility increasing with increasing phosphorus content. They also observed that the lamellar banded structure was 10 times broader (5 ∞ m = 0.2 mils) in deposits from alkaline solutions than in acid solution deposits (0.5 ∞ m = 0.02 mils).

Parker and Shah^[120] determined that the stress in electroless Ni-P alloys varies from tensile to compressive as the phosphorus content of the deposit increases. They also observed variations in stress depending on the thermal expansion coefficient of the substrate. However, increased thickness reduced the stress on most substrates. Baldwin and Such^[121] indicated that zero stress can be obtained by adjustment of solution pH and that any desired value between 11.25 kg/mm² (16,000 psi) (tensile) and 5.6 kg/mm² (8,000 psi) (compressive) is achievable; maximum ductility was obtained with a 5.5 w/o P alloy from a solution at pH 5.6 \pm 0.2. The least wear of hardened electroless Ni-P vs. quenched annealed steel was obtained with deposits containing 8 - 12 w/ o P and the maximum and minimum values of average friction coefficient were 0.43 and 0.57, respectively, compared to 0.63 - 0.64 for pure nickel.^[114]

Thus, it is evident that the compositions, structures and properties of electroless deposits can vary widely and are dependent on many factors. Safranek^[122] reviewed those for electroless nickel and cobalt, and Okinaka^[123] those for electroless gold. Saubestre^[124] studied various reducing agents for electroless copper, concluding that formaldehyde was the most suitable. He also studied the effects of inhibitors or stabilizers to extend the useful life of the solution.^[125]

The costs of the complexing and reducing agents used in electroless plating solutions make them non-competitive with electroplating processes. The application of electroless plating is usually based on one or more of the following advantages over electroplating:

 Deposits are very uniform without excessive build-up on corners or projections or insufficient thickness in recessed areas. Internal surfaces are also evenly coated. The uniformity is limited only by the ability of the solution to contact the surface and be replenished at the surface.

- 2. Deposits are usually less porous and more corrosion resistant than electroplated deposits (of equal thickness).
- 3. Almost any metallic or non-metallic, non-conducting surfaces, including polymers (plastics), ceramics, glasses can be plated. Those materials which are not catalytic (to the reaction) can be made catalytic by suitable sensitizing and nucleation treatments (see Sec. 6.4, Plating on Plastics).
- 4. Electrical contacts are not required.
- 5. The deposits have unique chemical, mechanical, physical and magnetic properties.

The disadvantages of electroless plating compared to electroplating include;

- 1. Solution instability
- 2 More expensive
- 3. Slower deposition rates
- 4. Frequent replacement of tanks or liners
- 5. Greater and more frequent control for reproducible deposits.

Properties and Trends of Electroless Nickel Deposits. Tensile strength increases from 40 to 60 kg/mm² for deposits containing 5 - 7% P to as high as 85 kg/mm² for deposits containing more than 9% P. Ductility also increases with increasing P content but decreases with increasing hardness. Ductility is reduced ~75% by heat treatment at 400°C (750°F). Severe strain or impact results in cracking with no plastic deformation.

Heat treatment above 250°C (480°F) causes recrystallization and precipitation of Ni₃P or Ni₃B and other phases in a Ni matrix, resulting in increased hardness. Figures 10.13 and 10.14 show the effect of heat treatment on hardness of the deposits. Heating at 400°C (750°F) for 1 hour produces maximum hardness for most compositions.

High internal stress is reported for thin deposits (\leq 1500 angstroms) in the range of 28 - 35 kg/mm², tensile. Stress values for thicker deposits vary considerably, from -10.8 (compressive) to +15 kg/mm² (tensile). High tensively stressed deposits usually contain \leq 7% P. Generally, stress values vary inversely with the phosphorus content. Deposits containing \geq 9% P are usually compressively stressed. Heat treatment increases stress tensively, compressively stressed deposits becoming tensively stressed even after heating at 200°C (390°F) or less for several hours.

Wear test data vary greatly since many factors are involved, making comparisons and trends difficult. Some of the variables include: type of

solution and operating conditions, % P and thickness of deposit, heat treatment temperature and time, and the kind of wear test used. Figures 10.15 and 10.16 indicate some trends in the wear resistance of electroless Ni coatings. Abrasion resistance as measured by the Taber Abraser Test indicates that heat treatment improves resistance. However, the hardest deposits do not necessarily provide the greatest abrasion resistance. Generally, NiB deposits are superior to NiP deposits.

The excellent wear resistance of electroless nickel coatings may be due, in part, to the presence (and amount) of P which may improve the (dry) lubricity of the coating and prevent seizure or galling except at high loads or sharp impact conditions. However, the deposits do not break off as discrete particles under heavy loads as do chromium deposits, the latter causing excessive scoring. Although electroless nickel and chromium deposits have similar hardness ranges, they perform well as a wearing combination.

The coefficient of (dry) friction for NiP varies from approximately 0.3 against grey iron, to 0.38 against steel, to 0.43 against chromium, with only slight differences due to phosphorus content or heat treatment. NiB deposits generally show higher values than NiP deposits.



Figure 10.15. Wear of electroless Ni in Taber Wear Test. Adapted from Ma and Gawne.^[126]





Composite Electroless Nickel Coatings. Electroless nickel coatings are readily produced containing dispersed inert particles from highly stabilized solutions (to minimize solution decomposition) in which the particles are mechanically dispersed. Parts are usually rotated to obtain uniform particle distribution. The particles are physically entrapped and not co-deposited. Particle size range from 0.5 to $10 \propto m$. Hard particles such as diamond, boron carbide, silicon carbide, tungsten carbide, titanium carbide, aluminum oxide, and chromium have been used to produce composite coatings with the particles constituting up to 30 volume % of the coatings.

Applications include metal forming dies, molds for plastics, oil well equipment, textile (yarn) spinning equipment, and friction disks. The asplated coatings are rough and dull but can be polished and lapped to provide smooth, semi-bright finishes.

Heat treatment increases hardness and wear resistance as it does for deposits without particles. However, such treatments should not exceed 400°C (750°F) for composites containing carbides since nickel carbide is produced and hardness and wear resistance are greatly reduced.

Other applications involve the incorporation of soft or polymeric particles such as PTFE (polytetrafluoroethylene) into the electroless nickel deposits. These provide excellent lubricating characteristics, wear resistance and corrosion resistance. PTFE composites containing between 18 and 25 volume % are commercially produced for many wear, mold release, and corrosion resistance applications.^[127] Figure 10.17 shows the reduced wear resistance of PTFE-composite coating over conventional electroless nickel with extended testing.

Parker^[128] has compiled literature data on hardness, wear resistance, coefficient of friction, stress and other properties and characteristics of electroless nickel coatings with and without dispersed particles.

6.2 Electroforming

Electroforming is defined^[129] as the "production or reproduction of articles by electrodeposition upon a mandrel or mold that is subsequently separated from the deposit." (Occasionally the mandrel may remain in whole or in part as an integral functional part of the electroform.) The mandrels used are classified as permanent or expendable. The choice, composition, design considerations, preparation cycles, and methods of removal of mandrels are probably the most vital aspects of electroforming.^{[129]-[132]} Various types of mandrels are given in Table 10.7.



Figure 10.17. Taber wear test on as-plated PTFE-electroless nickel composite coatings.^[127]

Since the electrodeposits, called electroforms, are used as separate structures, they are usually substantially thicker than plated coatings. The fixturing or tooling of the mandrel and the anode positioning are quite critical. These determine the current distribution and resulting thicknesses of the deposit. A wide range of current densities produces changes in the structure, concentration of impurities and properties of the deposit which, in view of the function as an electroform, now are of paramount interest.

Braddock and Harris^[133] reported increases in carbon content of nickel deposits from 0.004 w/o to 0.008 w/o and sulfur contents from 0.0002 w/o to 0.0014 w/o when the C.D. was reduced from "normal" (537 A/m² \equiv 50 A/ft²) to very low C.D. (21.5 A/m² \equiv 2 A/ft²). Dini et al.^{[134][135]} discussed the effects of variations in carbon and sulfur contents of nickel electroforms from sulfamate solutions; these are shown in Figs. 10.18 and 10.19. Sulfur in nickel deposits causes embrittlement and cracking, limiting high temperature applications (370°C \equiv 700°F max.) (Fig. 10.20).

Nickel, copper and iron are the most widely used electroforming deposits. Knowledge of the solution compositions, operating conditions and resulting structures and properties of deposits makes it possible to specify a given solution and the desired results. These are tabulated by DiBari.^[130]

Table 10.7. Comparison of Mandrel Materials (from Spencer, Ref. 131)

Туре	Material	Advantages	Disadvantages
Permanent	Carbon steel	Availability, low cost	Attacked by some plating solutions, such as acid copper and hot ferrous chloride.
	Carbon steel, chromium or silver plated	Improved hardness and/ or corrosion resistance. Coating may be stripped and renewed.	Chromium coatings may be pitted by hot chloride type baths.
	Stainless steel	Inert to most plating solutions.	Costly. Soft surface of non-hardenable types is easily scratched.
	Inconel	Natural oxide film prevents adhesion of most deposits.	
	Invar Kovar	Low temperature coefficient of expansion facilitates removal from electroform. Non- adherent.	Costly, poor machinability.
	Brass, Ni Cr, Ag plated	Good machinability, low cost.	Surface easily scratched.
	Glass, Quartz	Close tolerance, high finish.	Costly, fragile and requires a conductive coating.
	Wood, plaster, plastic, etc.	Low cost. Moldable. Flexible types can be withdrawn from undercuts.	Large tolerances. Requires a conductive coating and/or sealing.
Soluble	Aluminum	Good machinability. Good finish. Close tolerances can be held in complex n o n - w i th d r a w a b l e shapes. Soluble in sodium hydroxide.	Costly. Surface easily scratched.
	Zinc and zinc base alloys	Can be die-cast	Acid stripping solution more likely to attack electroform than caustic solution used for dissolving aluminum.
	Plastics	Moldable. Low cost. Fairly close tolerances.	Cannot be used in hot plating baths. May swell in some baths. Requires conductive coating.
Fusible	Low melting alloys (Pb-Sn-Bi types)	Can be cast at low cost.	Difficult to remove from electroform completely.
	Waxes	Can be cast or molded at low cost.	Easily scratched. May deform by creep. Requires a conductive coating.

Electroforming with fiber re-inforced composites and methods used are described by Withers and Abrams^[136] and Wallace and Greco.^[137] Representative fibers or filaments included tungsten, boron, carbides and borides. Greco et al.^[138] investigated the bond strength characteristics of electrode-posited nickel on boron and silicon carbide filaments.

Electroforming is very costly and is a very slow method for producing parts. It finds application when:

- 1. Producing parts by mechanical or other means is unusually difficult or costly.
- Extremely close dimensions and tolerances must be held, especially on internal dimensions or surfaces with irregular contours.
- 3. Very fine reproduction of surface details is required.
- 4. Thin walls are required.
- 5. Unusual physical, chemical and/or mechanical properties are required in the part.

6.3 Anodizing

Anodizing is an electrochemical process in which the part is made the anodic (positive) electrode in a suitable electrolyte. Sufficiently high voltage is deliberately applied to establish the desired polarization to deposit oxygen at the surface (O_2 overvoltage). The metal surfaces or ions react with the oxygen to produce adherent, oxide coatings, distinguishing the process from electrobrightening or electropolishing processes.

Industrial anodizing processes are confined mainly to aluminum and to a much lesser extent to magnesium and titanium alloys. Anodized tantalum is used in capacitors. Anodic coating applications include:

- 1. Protection corrosion, wear and abrasion resistance.
- 2. Decorative clear coatings on polished or brightened surfaces, dyed (color) coatings.
- 3. Base for subsequent paint or organic coating.
- 4. Base for plating an aluminum.
- 5. Special based on some specific property or the coating, e.g., thermal barrier films, refractory films, electrolytic condensers, capacitors (dielectric films).

Anodizing of aluminum has been investigated intensively. Wernick and Pinner^[139] definitively discuss the various processes and the nature and properties of the oxide coatings produced.



Figure 10.18. Influence of carbon on tensile strength: full curve, all data[134]



Figure 10.19. Influence of sulfur content on impact strength of electroformed nickel.^[135]



Ductile fracture (~ 100 ppm sulfur)

Brittle fracture (~ 200 ppm sulfur)

Figure 10.20. Fracture surface of part with sulfur content varying from 88 to 210 ppm $(x \ 1000)$.^[135]

The anodic films are classified according to the solvent action of the electrolyte. The films produced in sulfuric or chromic acids are porous type films. Phosphoric acid has even greater solvent action, resulting in oxides with a greater degree of porosity; these coatings are used for adhesive bonding and for plating on aluminum processes to provide deposit adhesion by mechanical locking in the enlarged pores. On the other hand, less aggressive mild electrolytes such as tartaric acid, ammonium tartrate, boric acid, borate compounds, citric acid, etc., have little or no ability to attack the anodic oxide. These films are essentially non-porous and thin (approximately $0.5 \propto m = 20 \propto in$) and are considered barrier type coatings. Due to their unique electrical characteristics, the barrier type films are used for such applications as electrical capacitors; they arealso applied as protective

coatings ("overlays") for vacuum deposited aluminum on precision mirrors for optical equipment.

Specification MIL-A-8625 (see latest revision), used for both military and non-military applications, describes the most widely used processes and the expected requirements and tests for quality coatings. Three types of anodized coatings are called out:

Туре І	from chromic acid solutions
Type II	from sulfuric acid solutions
Type III	from cold sulfuric acid processes (plus additives), producing thicker deposits (12.7 - 127 μm) (0.5 - 5.0 mils). primarily for wear and abrasion resistance. (Table 10.8 presents the most widely used pro- cesses in the U. S. A.)

Types I and II are usually sealed with a 5% (w/v) sodium dichromate solution (Class 1) or after absorption of a dye (Class 2) with a nickel (or cobalt) acetate solution. Typical processing cycles are illustrated in Figure 10.21.

The advantages and limitations of these three types of anodizing processes are analyzed in Appendix C.

ASTM Specification B 580-73 designates seven types of anodizing:

		Minimun	n Thickness
Туре	Description	μm	mils
Α.	Hard Coat	50	2.0
В.	Architectural, Class I	17.5	0.7
C.	Architectural, Class II	10	0.4
D.	Automotive - exterior	7.5	0.3
E.	Interior - Moderate Abrasion	5.0	0.2
F.	Interior - Limited Abrasion	2.5	0.1
G.	Chromic Acid	1.2	0.05

The chemical composition of unsealed sulfuric acid anodized films is approximately:

80% aluminum oxide 18% aluminum sulfate 2% water* + traces of alloying elements

The coatings can probably be considered as approximating $2AI_2O_3 \cdot H_2O$ and after sealing convert to $AI_2O_3 \cdot H_2O$ with accompanying increased volume, providing enhanced corrosion resistance. Hot sealing reduces the hardness of the coating as much as 40%.

^{*} The water content may vary between 1 - 6 %, probably entrapped.



Figure 10.21. Anodizing Aluminum – Sequence of Operations

Conditions	Alumilite	Martin	Hardas	Sanford
Solution Composition	12 w/o Sulfuric Acid + 1/w/o Oxalic Acid	15 w/o Sulfuric Acid, saturated with CO ₂	Sulfuric, Oxalic Acids	Sulfuric, Organic Acids
Temperature (%	C) 9-11	-3.9 - 0	0	-17.8 to -9.5
C.D. (A/dm²)	4	2.7 - 3.2	10.8 - 32.4	1.3 - 1.6
Voltage*	10 - 60 (or higher)	10 - 75	DC or DC/AC in various proportions	15 - 150
Film Growth Rate	25 µm/hr	25.4 μm /40 min	25.4 μm /5-10 min	25.4 μm /10-20 min
Alloy Limitations	4% Cu 7% Si 7 - 9% Cu+Si	5% Cu	?	?

Table 10.8: Aluminum Hard Anodizing Processes^[141]

* At a film thickness of approximately 50 μm, voltage requirement is approximately 40 - 45 volts.

Typical Properties of Hard Anodize Coatings^[140]

Hardness: usually ranges between 350 - 450 DPH (35 - 55 Rc). Abrasion resistance (Taber): 30,000 - 40,000 cycles/ μ m. Porosity: 5 - 15% Heat resistance: to approximately 400°C (750°F). Break-through voltage: 7 - 10 v/ μ m.

The oxide coating consists of two different structures: an inner (nonporous) barrier or dense structure, and an outer, thicker, porous cell-like hexagonal structure.^[142] The barrier layer is approximately 250 angstroms thick and constitutes about 1 to 2% of the total anodic film thickness. The pore diameter may range from 100 angstroms to 300 angstroms, depending on the electrolyte, operating temperature, and voltage. The porosity of the coating is very high; a coating which exhibits 15% porosity contains approximately 62 x 10⁹ pores/cm² (400 x 10⁹ pores/in²).

Spooner^[143] emphasized the importance of sealing methods, operating conditions (temperature and time), water quality, and the detrimental effects of contaminants in the water seal on the quality of the sealed coating, especially corrosion resistance. The suggested maximum contaminant levels in the sealing solution are:

Sulfate (SO ₄) ⁼	250 ppm
Chloride (Cl) ⁻	100 ppm
Silicates (SiO ₃) ⁼	10 ppm
Phosphates (PO	₄)= 5 ppm
Fluorides (F) ⁻	5 ppm

In the 1980's, cold sealing (temp. 20 - 30°C) processes, claimed to be equivalent to conventional hot sealing, were developed. These processes are based on heavy metal salts (e.g., Ni), fluorides or silicates in water/ various alcohol mixtures. Apparently, the pores are sealed by "plugging" with precipitated compounds; the term "impregnation" is considered more appropriate by some. Wernick^[144] reviewed the development of cold sealing processes; Short and Morita^[145] discussed the mechanism(s) involved.

Since the oxide film is a growth film at the expense of the aluminum substrate (and not simply an add-on-film as in electrodeposition) the dimensional changes depend on the equilibrium set up between film growth and the dissolving action of the electrolyte. For Type I and II films, it may be assumed that the dimensional increase per surface is about one-third the actual thickness of the film. For Type III, Hard Anodized coatings, the dimensional increase per surface is about one-thickness. Thus, stripping and re-anodizing would require approximately twice the original film thickness to meet the same dimensional requirements. This could present serious problems in salvaging rejected parts.

The wear resistance of Hard Anodized coatings may vary significantly with coating thickness and alloy composition. George and Powers^[146] proposed a more concentrated modified Alumilite (Alcoa's Hard Anodizing process) solution which appeared to provide improved wear characteristics for difficult-to-coat alloys.

Some of the trends of the effects of operating conditions on the properties of the coatings are summarized in Table 10.9. The following observations are noted:

- 1. Recesses of parts receive lower current densities (at least initially) resulting in softer coatings.
- Conversely, projecting surfaces, especially sharp corners, receive higher current densities which produce harder coatings, resulting in cracking.
- 3. Cracking can occur at either concave or convex corners due to stresses.

Condition	Limiting Film Thickness	Hardness*	Corrosion Resistance	Porosity	Adhesion/ Dye Absorption
Temperature increased	\checkmark	\checkmark	\rightarrow	\uparrow	\uparrow
Current Density increased	\uparrow	\mathbf{T}	\rightarrow	\checkmark	\checkmark
Anodizing time increased	\checkmark	\checkmark	\uparrow	\checkmark	\uparrow
Acid concentratior increased	n ↓	\checkmark	\rightarrow	\uparrow	\uparrow
Use of less aggressive electrolyte	\uparrow	\uparrow	\rightarrow	\checkmark	\checkmark
Alloy homogeneity increased	\uparrow	\uparrow	\checkmark	\checkmark	\checkmark

Table 10.9. Effect of Operating Conditions on Anodic FilmCharacteristics (from Wernick and Pinner, Ref. 147)

 \uparrow = increases, \downarrow = decreases, \rightarrow = passes through a maximum

* Hardness of sealed coatings is approximately 60% of unsealed coatings. Sealing time also affects hardness, inversely; increased sealing time results in decreased hardness.

Notes: – Effects on hardness and dye absorption ability of coating are usually in opposite directions.

- Voltage requirements increase for all above conditions.

- 4. Coatings which grow laterally as the dielectric film spreads are softer than coatings formed rapidly.
- 5. Properties of the coatings are influenced by the geometry of the parts as well as the alloying constituents or the electrolyte and its operating conditions.

Additions of certain organic acids* to sulfuric acid anodizing solutions produce integral colored anodized coatings, ranging from a light bronze or gold to black. These have been used in architectural applications.^[148]

Another approach to coloring anodized coatings involves a 2-step process.^[149] After the anodizing step, the parts are immersed in a solution containing nickel or tin salts and after one minute immersion, current is applied at 10 to 18 volts. The desired colors are produced by varying either the time (voltage constant) or the voltage (time constant). The colors produced range from light bronze (in 10 - 15 sec) to black (in 15 min). The advantages over the more widely used organic dyed coatings include better light-fastness and better protection since the precipitated inorganic deposits are at the base of the pores prior to subsequent hot sealing.

Pulsed current modifications have been applied to both conventional and hard anodizing.^[150] Superior coatings produced at slightly lower voltages in shorter times are claimed for more alloys. Konno^[151] reviewed these processes for aluminum, magnesium, and zinc.

The anodizing of magnesium alloys has not found extensive use, possibly because it is somewhat more difficult than anodizing aluminum. Magnesium oxide (MgO) is more water-soluble and considerably softer than aluminum oxide (Al₂O₃). The anodizing processes are similar and sealing is also required. The primary purpose is as a preparatory coating for painting or for corrosion and abrasion resistance. The older processes are referred to as Dow 12, Dow 14, and Manodyzing; these are AC or DC low voltage processes. The "newer" processes are fluoride-containing solutions and include Dow 17, CR 22 and HAE (Hardcoat). These are high voltage (from 80 V up to 320 V) processes. CR22 and HAE processes require alternating current. Solution formulations and operating conditions can be found in the referenced Handbooks.^{[107][130][152]}

Titanium and its alloys are anodized to provide:

1. Protection from galvanic corrosion when assembled or in contact with dissimilar metals by reducing or minimizing potential differences.

^{*} Sulfosalicylic acid, Kaiser Aluminum & Chemical Company, U.S. Patent 3,031,387 (April 24, 1962) and Sulfophthallic acid, Aluminum Company of America, U.S. Patent 3,277,639 (June 4, 1966).

- 2. Anti-galling, anti-fretting properties to the surfaces of parts in moving assemblies.
- 3. Part identification using a range of integral colors produced by the particular anodizing process.

Both acid and alkali solutions have been used. Table 10.10 indicates typical solution formulations and operating conditions. The colors produced due to variations in current densities and voltages are also indicated.

Table 10.10. Representative Titanium Anodizing Formulations andOperating Conditions (153)

Composition g/L	H₂SO₄ 150 - 180	H ₂ SO ₄ - 100 H ₃ PO ₄ - 800	NaOH 50
Temperature, °C	18 - 24	20	90 - 95
Current Density (A/dm²)	0.2 - 0.4	3.0 - 5.0	5
Voltage	20 - 25	30 - 110	35 - 40
Color Range	Blue to Blue-Violet	Blue to Opaque Grey	Dull Grey

Colors Produced on Pure Titanium Anodized in 15% H₂SO₄

Color	C.D. (A/dm ²)		Volts
Yellow	0.15	5 - 12	
Violet to 0. Blue-Violet	3	13 - 22	
Dull Blue	0.75	23 - 30	

6.4 Plating on Plastics

Commercial plating on plastics became feasible with the development of electroless plating processes–especially the low temperature electroless nickel and copper processes. Large scale, high production automatic decorative (Cu/Ni/Cr) plating on plastics is increasing on automotive trim, houseware and other articles. The technology for manufacturing printed circuit (PC) boards is another development of electroless plating. This discussion is limited to these developments.

The plastics most widely plated today for decorative applications are (in decreasing order and increasing difficulty): Acrylonitrile-butadiene-styrene (ABS), polyphenylene-butadiene-stryene (Noryl), polysulfones, polypropylenes, nylons and polytetrafluoroethylene. It should be noted that most of these plastics are "filled", i.e., they contain mineral fillers, additives, modifiers, or are co-polymers or mixtures of co-polymers. ABS is a mixture of acrylonitrile-styrene and butadiene-styrene; polysulfones generally contain ABS; nylons are mineral-filled. In the etching step, one or more of the components is selectively etched, providing a non-uniformly roughened surface for improved mechanical bonding of the deposits (with possible chemical bonding).

The plating cycle^{[154]-[156]} for decorative coatings (may) include:

- 1. Surface deglazing-mechanically or chemically
- 2. Etch
- 3. Neutralize
- 4. Activation (catalyze)
- 5. "Accelerate" (remove residual tin hydroxide)
- 6. Electroless Deposit (Cu or Ni)
- 7. Racking (if above steps done in bulk)
- 8. Clean (if required)
- 9. Strike (if required)
- Plate: Bright acid copper Bright nickel or dual nickel Chromium, microcracked preferred (Note: Rinses are critical between various steps.)

The etch step is a critical one. Usually chromic acid, either supersaturated*, or mixed with sulfuric acid or with sulfuric-phosphoric acids^[156] is employed. An alternative etching technique involves the use of plasmas.^[157]

^{*} L. Kadison, U.S. Patent 3,668,130 (June 6, 1972), (assigned Crown City Plating Company).

The adhesion of the deposits is also related to the activation of the surface. The most widely used system is the stannous chloride $(SnCl_2)$ /palladium chloride $(PdCl_2)$ 1- or 2-step treatment based on the redox reaction:

Eq. 25
$$\operatorname{Sn}^{+2} + \operatorname{Pd}^{+2} \to \operatorname{Sn}^{+4} + \operatorname{Pd}^{0}$$

The 2-step activation involves first adsorption of $SnCl_2$ on the etched surface, followed by the redox reaction in a solution of $PdCl_2$. The 1-step or mixed catalyst system includes both components and is considered either a complexed chloride of Sn and Pd or a colloidal mixture. There is considerable controversy regarding the nature of the system.^[158]

Perrins^[156] determined that the adhesion of electroless nickel and electroless copper (on polypropylene co-polymers) was dependent on the amount of palladium deposited. Low palladium gave high copper adhesion and low nickel adhesion. High palladium initially gave low adhesion to both which improved, peaking, with 3 - 5 week aging. Accelerated aging at 70°C for 1.5 hours gave a 70% improvement over control values. (Improved adhesion by heating is also found with other plastics.) An oxidation mechanism at the deposit/polymer interface is suggested as being responsible for increased adhesion.

Selective plating of plastics^[159] can be accomplished by applying an organic stop-off which remains on the surface as a finish coat. Deposition is prevented on the stop-off film by use of a chromating treatment after etching.

6.5 Plating Printed Circuit Boards

The printed circuit board (PCB), also called printed wiring board, has made rapid advances since its development in the late 1930's. It is a pre-determined electrical conducting design or path, on a non-conductive base, whose primary function is to carry an electronic impulse or signal. The non-conductive base or board can be made of a wide variety of materials including wood, masonite, or resins such as epoxy, epoxy-glass, phenolics (flame-retardant or paperreinforced), polybutadienes, polyimides, and ceramics. Presently, the most popular materials seem to be phenolics, epoxies (and glass), and polyimides.

The types of PC boards fabricated today include:

1. Print-and-Etch*

^{*} Print-and-Etch involves no plating. A (photo) resist is applied exposing unwanted copper (on a copper-clad board) which is etched away. Holes are drilled and eyelets inserted for connecting circuitry.

- 2. Plate-and-Etch
- 3. Plated-Through-Hole (PTH)
 - a. Panel Plate
 - b. Pattern Plate
- 4. Multi-Layered (MLB)*
- 5. Additive Circuits
- 6. Integrated Circuits
- 7. Flexible Circuits

The pre-plating preparation steps involve alkaline cleaning, acid etching as do other plating cycles. Additional steps such as abrasive cleaning or honing to remove smeared polymer in the drilled holes and "etch-back" (of polymer) to expose the intermediate layers of copper in MLB's (Fig. 10.22) are required. Also required for through-hole plating is the SnCl₂/PdCl₂ activation treatment discussed above. After activation, electroless copper is deposited over the exposed outer circuits and through the hole. This is followed by electrodeposited copper.

Rothschild and Schwartz^[160] and Smith^[161] describe fabrication and plating operations. A trouble-shooting chart^[162] and manual^[163] identify possible sources of trouble and their rectification or suggested cures.

Rothschild and Kilgore^[164] discuss the problems of plate distribution (throwing power, T.P.) in MLB's and relate T.P. to the ratio of surface to minimum hole thickness (S/H) and the ratio of total board thickness (hole length) to hole diameter (B/D). They also discuss fabrication and plating steps, the choice of deposits (Au, Sn-Pb, Sn-Ni), solderability and diffusion and/or migration problems.

Copper plating is used for through-hole plating. Acid sulfate and acid fluoborate plating solutions possessing high throwing power have been developed. These are low-metal ion, high acid concentration formulations (to promote desirable polarization at high current density surfaces) with grain refiners to eliminate columnar structures which may develop cleavage planes at corners, resulting in cracking. The pyrophosphate copper solution is the other type of solution employed. (Cyanide copper formulations damage the board due to the high alkalinity and cyanide content.) Which solution is the preferred plating solution is a moot question and invokes considerable controversy among the "practitioners of the art." However, the "high throw" bright acid copper sulfate solutions are the most widely used; they are easier to control and are more economical.

^{*} This is similar to Plated-Through-Hole except two or more PCB's are bonded together using an epoxy/glass pre-preg. Interconnections are made by drilling holes after laminating layers. The individual layers are referred to as details or inner layers.



Figure 10.22. Through-Hole solderplate on multilayer printed circuit board (x 50) (Courtesy of B. F. Rothschild.)

A high-throw Sn-Pb, solder plate, has also been developed for throughhole plating.^[165]

Other electrodeposited coatings used on PCB's include: Sn-Pb, Sn-Ni, Sn, Ni, Au with various functions as etch resists and to provide solderability, corrosion resistance, wear resistance, or low contact resistance.

7.0 STRUCTURES AND PROPERTIES OF DEPOSITS

The structure and properties of a deposit are related to the deposition parameters and deposit thickness (Fig. 10.9). Changes in these parameters may produce significant differences in a deposit, making generalizations difficult, if not misleading. Some investigators have omitted indicating important plating parameters or deposit thickness or testing conditions when reporting property measurements, making these data at least suspect. Further, extrapolation from a narrow set of conditions and data could also be misleading. Figures 10.18, 10.19, and 10.23 emphasize the influence of impurities and thickness on properties of nickel from sulfamate solutions. They also illustrate the importance of taking measurements in a thickness range related to the intended application of the deposit. There appears to be a certain degree of specificity, yet trends have been established that correlate structure with deposition parameters and properties. Weil^[166] reviewed how nucleation and growth, including epitaxy, twinning, and dislocations determine deposit structure and properties. A few examples and data for copper, nickel and chromium deposits are used in an attempt to illustrate these points.

Since approximately 1947, the American Electroplaters' and Surface Finishers' Society (AESF) has initiated and supported research programs at various institutions on structure and properties of electrodeposits. These studies and other published data (about 1500 references) have been "compiled and systematized" into a single source book by Safranek.^[122] Dini provides a comprehensive materials science approach relating deposition parameters to structure, texture, properties of deposits, and the interrelationship between deposits and substrates. Test methods and data to evaluate deposit properties and performance are presented.^[176] Most of the data presented here are based on these sources.

The structures of electrodeposits are classified as:

Columnar Fibrous Fine-grained (usually equiaxed) Banded (or striated or lamellar)



Influence of Thickness on Tensile Strength For Flat Electrodeposited Nickel Specimens

	Thic	kness	Yield Stre	ngth ^c , d	Ultimate Tensi	le Strength	Elongation	RAS
_	(mm)	(mils)	(MN/m ²)	(psi)	(MN/m ²)	(psi)	(%)	(%)
(D. 14 ^a	5.5	302	43 700	588	87 400	-	-
	D. 21ª	8.3	265	38 400	556	80 700	-	-
). 38ª	15	-	-	532	77 100	10.9 ^e	90.8
(0. 51ª	20	-	-	530	76 800	12.1 ^e	93.9
). 74 ^a	29	274	39 600	515	74 700	12.6 ^e	94.4
1	l. 4 ^a	54	267	38 700	488	70 900	-	-
:	2. 3 ²	91	229	33 200	490	71 000	31.8 ^e	90.8
:	3. 7 ^a	144	270	37 600	489	70 900	29. 2e	88.4
:	3. 2 ^b	125	274	39 600	524	75 900	22. 5 ^f	89.7

INFLUENCE OF THICKNESS OF SULFAMATE NICKEL DEPOSITS ON TENSILE AND DUCTILITY PROPERTIES

^a Flat tensile specimens 242 mm (9.5 in.) long with a reduced section of 64 mm (2.5 in.).

 $_{Round tensile bars with a reduced section 19 mm (0.75 in.) long and 3.2 mm (0.125 in.) in diameter, machined from a plate 6.4 mm (0.250 in.) thick.$

 $^{\rm C}All$ values for yield, tensile strength, elongation, and RA are the average of at least two specimens. Strain rate was 1.1 x 10^-3 s^-1.

^dDetermined by 0.2 percent offset.

^eIn 44.5 mm (1.75 in.).

^fin 12.7 mm (0.5 in.).

^gDetermined by measuring the reduced area with the aid of a microscope at 10% or greater magnification.

Figure 10.23. Influence of thickness on mechanical properties of deposits.[167]

Columnar structures are characteristic of deposits from solutions (especially acid solutions) containing no additives, high metal ion concentration solutions at low deposition rates. They usually exhibit lower tensile strength, percent elongation and hardness than other structures; they are generally more ductile. Such deposits are usually of highest purity (high density) and low electrical resistivity.

Fibrous structures represent a grain refinement of columnar structure. Stress relieving additives (such as saccharin or coumarin) promote such refinement as do high deposition rates. These may be considered intermediate in properties between columnar and fine-grained structures.

Fine-grained deposits are usually obtained from complex-ion solutions (such as cyanide) or with certain addition agents. These deposits are less pure, less dense and exhibit higher electrical resistivities due to presence of foreign material.

Banded structures are characteristic of bright deposits (as a result of brightening addition agents—usually S-containing organic compounds which result in small amounts of S and C in the deposit) and some alloy deposits. These deposits generally possess higher tensile strength, hardness, and internal stress and decreased ductility than other structures. The use of plating current modifications (PR, IC, pulse) favors the conversion of structure from a solution to a banded structure.

Electro- and electroless deposits generally conform to the Hall-Petch relationship.

Eq. 26	H (or YS) = σ_0 + kd ^{-1/2}	
where	H = hardness of the de YS = yield strength of th d = grain size	posit e deposit
	σ_{o} , k = constants	

That is, factors which decrease grain size increase hardness, yield and tensile strength of the deposit. In aqueous deposition, grain size of the deposit decreases as:

- Current Density increases
- · Cathode potential increases
- Solution agitation increases
- Solution temperature decreases
- Metal ion concentration decreases
- Addition agents are added
- · Complexing agents are present

Also, the brightness and smoothness of the deposit increase as grain size decreases.

Grain size can vary widely from 100 to 50,000 angstroms; the grain size of fine-grained or banded deposits is usually between 100 and 1000 angstroms. Read^[168] observed that frequently the grain size of electrodeposits is much larger than indicated by etched specimens (the metallographic procedures usually used) and that x-ray techniques are more reliable, especially for measuring larger grain sizes. As indicated previously, certain deposits, especially alloys, show no grain structure, i.e., are amorphous.

Some metals (notably Cu, Ni, Co, and Au) can be deposited in all four types of grain structures depending on the solution composition and plating conditions. This is shown in Figure 10.24 for copper deposits. Typical properties of these structures are given in Table 10.11.

Zentner, Brenner, and Jennings^[169] (AESF Research Project No. 9) studied the structure-property relationships of nickel electrodeposits to plating solution composition and operating variables. The effect of current density, pH, temperature, and chloride content on deposit structure are shown in Figs. 10.25 - 10.28. The trends appear to be:

- 1. Grain structure changed from fine-grain to coarse-grain as temperature increased.
- Significant structural changes occurred at both low and high current densities. Typical columnar structure is obtained between 2 and 25 A/dm² (20 - 250 A/ft²) in Watts-type solutions. The structural changes at low C.D. may be explained by the increased sulfur and carbon contents of the deposit as shown in Table 10.13. Thus, low C.D. produced a banded structure similar to bright nickel deposits.
- There is essentially no structural change in Watts-type deposits in the pH range 1 - 5. At pH's above 5 there is a distinct change from columnar to fibrous or fine-grained which is probably due to inclusion of basic material (Ni(OH)₂?).
- 4. Deposits from Watts solutions produced the coarsest, columnar deposits. Increasing the chloride content of the solution results in finer-grained deposits. All-sulfate (no chloride) solution showed a somewhat finer columnar structure than a Watts deposit, with some evidence of a banded structure.

A good correlation was found to exist between structure and properties as shown in Fig. 10.29. Typical values of the mechanical properties of nickel deposited from various engineering electroplating solutions are given in Table 10.12.


Figure 10.24. Structure of copper deposits (x 500) (etchant: ferric chloride). Structures are typical for: *a*)acid sulfate (no A.A.); *b*)acid sulfate with A.A. (gelatin + phenolsulfonic acid; *c*) acid sulfate with brighteners or pyrophosphate solution; *d*) cyanide solution with PR.^[22]



Figure 10.24. (Cont'd)



(A) 30°C (86°F)

S_{III}C₁ at pH 5.0 (B) 55°C (131°F)

(C) 80°C (176°F)



⁽D) 30°C (86°F)

Figure 10.25. Effect of temperature of the plating solution on the structure of nickel deposited at 5 A/dm² (46 A/ft²). Cross section x 250. Etchant: glacial acetic and nitric acid.^[169]

S_{III}C₁ at pH 1.5 (E) 55°C (131°F)

⁽F) 80°C (176°F)



(G) 30°C (86°F)

(H) 80°C (176°F)

Figure 10.25. (Cont'd)



Figure 10.26. Effect of current density on the structure of nickel deposited from the $S_{III}C_{I}$ solution at 55°C (131°F), and a pH of 3.0. Cross section x 250. Etchant: glacial acetic and nitric acid.^[169]



20 amp/dm² (186 amp/ft²) (G)

25 amp/dm² (230 amp/ft²) (H)

50 amp/dm² (460 amp/ft²) (I)

Figure 10.26. (Cont'd)



(A) pH 1.0

(B) pH 1.5

(C) pH 3.0



(D) pH 4.0 (E) pH 5.0

(F) pH 5.5

(G) pH 5.7

Figure 10.27. Effect of the pH of the plating bath on the structure of nickel deposited from the $S_{III}C_{I}$ solution at 5 A/dm² (46 A/ft²)and 55°C (131°F). Cross section x 250. Etchant: glacial acetic and nitric acid.^[169]



(A) Bath S

(B) Bath S_{III}C_I

(C) Bath SICI



(D) Bath S_IC_{III}

(E) Bath C

Figure 10.28. Effect of increasing chloride content of the solution on the structure of nickel deposited at 55°C (131°F), 5 A/dm² (46 A/ft²) and a pH of 3.0. Cross section x 250. Etchant: glacial acetic and nitric acid.^[169]

		Modu Elan	ha of icity	Ter Stre	ndik ngth	Yi Şure	eld ngth				
Plating Solution	Structure	kg/nq mm	304 pei	kg/m num	kpói	kg/kg mm	kpei	-Elongation, percent (2 in.)	Dennity, g: cu cm	Electrical Resetutity, nucrohm-can	Hardness, KHN ₂₀
Amine (=)	Fine- grained	-	1	42	හ	31	44	•	8.906	2.10	36974
Cyanide Low Cu cone. and low recuperature ⁽¹⁾	Columnar	11,000	16	31	44	-	-	7	8 900	1.80	144
Low Cu conc. and High temperature ¹¹	Fine- grained	11,000	16	55	78	-	-	6	8.912	1.79	131
High Ou cont. and high temperature ⁴⁹	Dine		-	26	37	-	-	22	8.919	1.80	114
Ditto with 2 gl KSCN ⁽¹⁾	-	12,000	17	60	86	40	57	10	8.917	2.02	144
Fluoborate ^(a)	Fibrous	8,500	12	26	37	81	16	31	8.926	1.73	56
Pyrophesphate ^(b)	Fine- graintd	12,000	37	28	40	15	22	33	8.926	1.74	92
Sulfate ⁽¹⁾	Coarse, columnar	10,000	14	21	50	6	9	24	8.922	1.72	53
Sulfate with 10 ⁻⁴ g/l Se ⁽¹⁾	Fibrous	11,000	16	35	50	20	25	20	8.928	1 75	108
Sulfate with 3.5 g/l triisopropanal- amine ^(h)	Fine- grained	10,500	15	50	71	30	43	7	8.913	1 89	144

(*) Solution at 53 C containing 100 g/l OuSO4-5H/O, 20 g/l (NH1)-SO, 4 ml/l NH2OH and 80 ml/l ethylene diamine.

(b) Hardness of copper deposited in a similar bath at a slightly lower temperature was 140 to 150 kg/sq mm. (70)

101 Solution at 40 C containing 40 g/l CuCN, 6 g/l free NaCN and 30 g/l NarCO; with a pH of 11.7 to 12.8.

41 Solution at 80 C containing 40 g/l CuCN, 10 g/l free NaCN and 30 g/l NarCO1 with a pH 11 8 to 12.8.

** Solution at 80 C containing 75 g/l CuCN, 10 g/l free KCN and 40 g/l KOH with a pH of 13.6.

(1) Copper deposited at 6 amp/sq dm.

(e) Solution at 30 C containing 177 g/l Cu(BFs)s, 12 g/l HBFs and 12 g/l HsBOs

(1) Solution at 50 C containing 90 g/l CurP.Or 3H,O, 350 g/l K.P.O. 80 g/l K.P.O. 15 ml/l KNO1 and 2 ml/l NH, with a pH of 8 5.

40 Solution at 30 C containing 187 g/l CuSO+5H/O, and 39 g/l H/SO+. In comparison with data for these deposits, commercial electrolytic copp

(produced with addition agents) exhibited a tensile strength of 28 to 34 kg /sq mm (40,000 to 48,000 psi). (71)

⁽¹⁾ Solution at 30 C containing 187 g/l CuSO+SHsO, 74 g/l HsO+ and 10-1 g/l Se (2 amp/sq dm).

(13 Solution at 30 C containing 187 g/l CuSO, SH₂O, 74 g/l H₂SO, and 3.3 g/l triisopropanolamine (5 amp/ng dm).

Table 10.11. Comparison of Structure and Properties of Copper Deposited at 4 A/dm² in Several Different Copper Solutions.^[122] (From The Properties of Electrodeposited Metals & Alloys by W.H. Safranek, published by AESFS, 1986. Reprinted with permission.)

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Table 10.12. Nickel Solutions for Heavy Plating^[22]

					Cathode			_	Properties		
Туре	ingredients ^a	Concen- tration, g/l	pH (electro- metric)	Temper- ature, °C	Current Density, b A/dm ²	Hardness, Vickers	<u>Tensile</u> kg/cm ²	Strength.	Elun- gation.	Resid	ual Stress.
Wates	Nichel sulfate, NiSO4 = 6H2O	330	1.5-4.5	4565	2.5-10	140-160	3850	55,000	30	1260	15,000
	Nickel chloride, NiCl2 6H2O	45									
	Boric acid, H3BO3	38									
Hard	Nickel sulfate, NiSO4 + 6H2O	150	5 6-5.9	4360	2-10	350500	10,500	150.000	5-6	1080	44.000
	Ammonium chloride, NH4Cl	25						100,000		30000	44.000
	Borie seid, H3BO3	30									
Chloride	Nickel chlande, NiCl2+6H2O	300	2.0	50-70	\$ 5-10	230-250	7000	100.000	-	8900 3500	
	Boric acid, H3BO3	38						100,000	20	2000-3300	40,000-30,000
Chloride -	Nickel sulfate, NiSO4 + 6H9O	200	1.5-2.0	45	2 5-10						
Sulfate	Nickel chloride, NiCl2-6H2O	175			2.0-10						
	Boric acid, H3BO3	40									
Chloride-	Nuckel chloride, NiCl2+6H2O	135	4.5-4.9	30-30	9-10	750	14 000				
Acetate	Nickel acetate, Ni(C2H3O2)2-4H	2O 105					14,000	200,000	10		
Nickel-	Nickel sulfate, NISO4 + 6HpO	240	4.7	40		450 500					
Cobalt	Nickel chloride, NiCl2+6H2O	22.5			· ·					1030-1190	15,000-17,000
	Borac acid, H3BO3	30									
	Ammonium sulfate, (NH4)2504	1.5									
	Nickel formate, Ni(CHO2)2*2H20	D 15									
	Cobalt suffate, CoSO4+7H2O	2.6									
Fluoborate	Nickel (as fluoborate)	75	2.0-3.5	40-80	6 -10	187	5850	78.000	18.30	1100	16 600
	Free Subboric acid, HBF4	3.7-37.5 ((colorimetric)					13,000	13-30	1120	10,000
	Free boric acid, H3BO3	30									
Sulfamate	Nickel sulfamate, Ni(NH2SO3)2	450	3.0-5.0	40-60	8-30	450.350	6300	~ ~ ~ ~ ~	An an		
	Boric acid, H3BO3	30					12.36.81	90,000	20-30	35	300
Sulfamate-	Nickel sulfamate, Ni(NH2SO3)2	300	3.5-4.2	28-60	0_05	100	-540	100.000			
Chloride	Nickel chloride, NiCl2-6H2O	6				380	1.000	106,000	15-30	105	1500
	Borsc acid, H3BO3	30									

*An antipitting agent is normally used in these baths. **Brigher current densities can be used with increasing rate of agitation**.

Table 10.13. Results of Elemental Analysis of Nickel Electrodeposits^[133]

Type of Nickel	Carbon	Copper , (Weight P	Iron ercent)	Sulphur
As deposited nickel produced at 21.5 A/m ²	0.008	0.046	0.04	0.0014
Nickel produced at 21.5 A/m ^a and annealed in mass spectrometer experiments	0.007	0.054	0.02	0.0012
As deposited nickel produced at 537 A/m^2 Nickel produced at 537 A/m^2 and appealed	0.004	0.058	0.03	0.0002
in mass spectrometer experiments	0.003	-	0.03	0.0004
Nickel anode material used for both low and high C.D. deposits	0.009	-	-	-



Figure 10.29. Range and trend of physical properties of nickel deposited from 5 different types of solutions, each point is the average of the properties of 5 or more deposits obtained under various conditions of plating.^[169]

1 equals a, b, c, d, e, f, OB, and OBT solutions. Bright nickel.

- 2 equals $S_i C_{iii}$, C, Ac, C (-4N) solutions. Chloride nickel.
- 3 equals S₁C₁ solution.
- 4 equals S and oS solutions.

5 equals $S_{\mu}C_{\mu}$, $oS_{\mu}C_{\mu}$, $S_{\mu}C_{\mu}$ (-1N), NH_4 , Na and F solutions. Watts nickel.

 Table 10.14.
 Recommended Basis Metal Hardness and Chromium-Plate

 Thickness for Various Applications^[22]

Application	Recommended Rockwell C Hardness of Basis Metal	Thickness of Chromium, μm
Drills	62-64	1.3-13
Reamers	62-64	2.5-13
Burnishing bars	60-62	13-75
Drawing plugs or mandrels	60-62	38-205
Drawing dies	62 inside,	
	45 outside	13-205
Plastic molds	55-60	5-50
Gages	48-58	2.5~38
Pump shafts	55-62	13-75
Rolls and drums		6-305
Hydraulic rams		13-100
Printing plates (engraved steel)	_	5-13

Table 10.15. Coefficient of Friction for Various Metal Combinations^[22]

	Static	Stiding
Metal	Coefficient	Coefficient
Chromium-plated steel on chromium- plated steel	0.14	0.12
Chromium-plated steel on babbitt	0.15	0.13
Chromium-plated steel on steel	0.17	0.16
Steel on babbit	0.25	0.20
Babbitt on babbitt	0.54	0.19
Steel on steel	0.30	0.20
Bright chromium plate on cast iron		0.06
Bright chromium plate on bronze		0.05
Bright chromium plate on babbitt		0.08
Hardened steel on cast iron		0.22
Hardened steel on bronze		0.11
Hardened steel on babbitt		0.19

Properties of chromium deposited under a wide variety of plating conditions and solution compositions were extensively covered by Brenner, Burkhead and Jennings.^[170] The deposits especially the bright deposits are very fine-grained, as small as 10 angstroms on the basis of x-ray data. They concluded that the oxide content of the deposit had far greater influence on the properties than crystal orientation or structure. Increased plating temperature from 10°C to 100°C caused reduction of oxygen content from ~1 w/o to~0.1 w/o. The hydrogen content of the deposit also decreases with increasing plating temperatures.

The hardness of chromium is probably its most important engineering property. The oxygen content to the deposit is one of the most important factors affecting its hardness. Above 0.12 w/o O_2 , the hardness ranges between 850 - 1000 KHN (Knoop Hardness Number) and when below 0.12 w/o O_2 , the hardness ranges from 625 to 325 KHN. However, it was noted that hardness values may fluctuate as much as 200 points KHN for the same oxygen content. It also appears that bright deposits are hardest. The hardness of chromium deposits, therefore, is probably the result of oxide inclusion, small grain size and internal stress.

The hardness of the substrate along with that of the deposit is an important factor in the application for improved wear resistance of various tools (Table 10.14). In other wear applications the coefficient of friction is a factor; Table 10.15 gives values for various combinations.

Different etching techniques reveal interesting structural characteristics in chromium deposits.^[171] In fact, no single etchant reveals all possible features and it is advisable to use several techniques. Structures which have been observed include: fibrous texture, banded or striations associated with the crack pattern (and not found in crack-free deposits), bands delineating changes in plating variables (C.D. and temperature) during deposition.

The internal stress, negative coefficient of thermal expansion (initial shrinkage) and the effect on fatigue strength of the substrate are properties (besides hardness) of interest in engineering applications. These are adequately covered in references already cited.^{[22][122][170]} The reported stress values for chromium deposits cover a very broad range, from highly tensile to compressive in microcracked deposits (>1000 cracks/linear inch). It is influenced by the solution composition and concentration, C.D., temperature, deposit thickness and probably other factors. The high tensile stress and resulting cracking lower the fatigue* limits of substrates (primarily steel, but possibly also aluminum and titanium).

^{*} The higher the stress (in tension) of the deposit, the greater the reduction in fatigue strength.

No ductility was found for chromium deposits from aqueous solutions. In general, the physical properties of electrodeposits approach those of metallurgical wrought metals as the purity increases. Observations regarding the physical properties are:

- 1. The density is related to pores, voids and impurities in the deposit. Corrosion and high temperature characteristics can be significantly affected by low density.
- 2. The coefficient of thermal expansion is also affected by impurities in the deposit. Thermal properties are not too well established for electrodeposits. Most deposits expand with thermal cycling, notable exceptions being chromium and cobalt-tungsten alloys. Deposits which expand appreciably develop voids on thermal cycling and could not be considered for high temperature service since they would exhibit decreased corrosion and oxidation resistance.
- Electrical resistivity is quite sensitive to the presence of small concentrations of impurities. Most deposits, therefore, exhibit higher values than wrought counterparts. Impurities such as oxides, sulfides, hydrates or inclusions tend to concentrate at grain boundaries especially after a thermal treatment or annealing.

With respect to mechanical properties, the relationship of hardness to strength is not always similar to wrought metals where a constant relationship exists. Although the generalization that the strength of a deposit increases with hardness and ductility varies inversely with strength and hardness holds in many cases, the exceptions are too numerous to make it reliable. Other observations regarding mechanical properties of deposits are described below.

Hardness. Hardness (microhardness) of the deposit is the most widely measured property (probably due to the ease of measurement). It may also be the most abused. The literature is replete with inconsistencies and contradictions. This may be due, in part, to techniques of specimen preparation, methods of measurement, differences in deposit thickness, plating solution differences, quality of deposit, inadequacy in reporting data, neglect to indicate load applied*, type and condition (hardness) of substrate, and other factors.

^{*} Hardness values should be reported with designated loads, e.g., VHN_{100} , or KHN_{25} , where 100 and 25 (as subscripts) represent the load in grams. Loads less than 25 grams are subject to serious errors and are undesirable due to poor reproducibility.

To obtain reasonably reliable microhardness measurements:

- 1. The deposit thickness should be at least ten times the depth of the indent. For the same load, the depth of a Knoop indent is approximately 1/7 that of a Vickers indent.
- 2. The distance of the indent from the substrate interface should be at least 1/2 the diagonal of the indent (the short diagonal for the Knoop indent) to minimize the "anvil" effect.
- 3. When taking multiple measurements on the same specimen, a transverse track should be followed with the distance between indents as in 2.

Vickers microhardness measurements are less sensitive to errors arising from elastic properties than are Knoop measurements and result in less serious errors as loads are increased.

It appears that too much value is sometimes placed on hardness measurements. The assumed relationship between hardness and strength was discussed above. The same may be said to some degree for the correlation of hardness to wear resistance. The excellent wear resistant characteristics of chromium deposits are related to the low coefficient of friction (Table 10.15) as much as to hardness. The wear resistant characteristics of electroless nickel alloys is related to the presence of phosphorus (or boron) as well as to the hardness.

Despite these comments, hardness measurements are useful in evaluating deposits and predicting their usefulness. They are especially useful in evaluating alloy deposits since changes in hardness reflect (possibly) changes in structure or composition of the alloy deposit.

It is not unexpected that the hardness values of deposits (of the same metal) vary greatly (Fig. 10.30). Noteworthy are the great ranges reported for chromium and iron deposits and the ability of some alloy deposits to undergo precipitation hardening.

Tensile strength. In many instances, the tensile strengths of deposits exceed those of annealed metallurgical counterparts (Table 10.16). The primary reason is the finer-grain structure of electrodeposits. Coarser grained or columnar structures may exhibit lower strengths.

Ductility. The ductility of electrodeposits may equal metallurgical counterparts but is usually lower in the as-plated condition.

Stress. The mechanism of internal (residual) stress in electrodeposits is not completely understood, but undoubtedly a distorted atomic lattice is involved. If the deposited atoms are closer together than normal lattice spacing, the tendency is for the atoms to "push" further apart, pulling on the substrate and resulting in tensile stresses. Conversely, if the depositing

atoms are farther apart than they should be in a normal lattice spacing, they tend to pull closer together, exerting a compressive stress on the substrate.

Stress measurements are subject to variations in testing procedures and conditions and are generally not reproducible. A particular stress measuring instrument or technique is useful in controlling a plating solution and its operating conditions as well as in predicting the quality of the deposit within parameters experimentally established and observed. Weil^[172] reviewed the various methods used to measure internal stress of electrodeposits and discussed the reasons for possible variances between measured values and those actually present in plated parts. He also made a comprehensive analysis of the various types of stresses encountered in electrodeposits.^[173] The various mechanical methods and calculations (formulas) used to measure macrostress were examined critically (microstresses can be measured only from broadening of x-ray diffraction lines). It contained an extensive review of the literature dealing with stress, including the various theories proposed on the origin of stresses in electrodeposits.

Stress Corrosion. The tensile strength and ductility and internal stress of the deposit are interrelated in determining the degree of resistance to stress corrosion cracking when deformation may be involved or anticipated.

Magnetic Properties. Magnetic properties of deposits are usually restricted to ferromagnetism and characterized by B-H hysteresis loops, where H is the applied field and B the induced magnetic flux density. Magnetic materials are classified as soft or hard, depending on the value of the coercive force, Hc, which is the magnitude of H when B = O, i.e. the force required to cause random orientation to the domains.

If Hc is small, the magnetic material is considered "soft". These are generally materials which are mechanically soft, i.e., they have a low yield strength. Permalloy (80 Ni, 20 Fe) is such an alloy. If Hc is large, usually>200 oe, the material is considered a hard magnetic material, useful in fast switching computer memory components. Alloys of Co with P and other constituents are usually of this type.

The saturation flux density (B_S) is a physical property determined by the chemical composition of the material. The remanent flux density or retentivity (B_R) and Hc are structure-sensitive properties. The composition, microstructure (grain size and orientation and defects), stress, thickness and impurities of the deposit affect these properties. Romankiw and Thompson^[174] reviewed the magnetic properties and applications of plated magnetic films as well as methods of measurements.





				Maximum h Tensile Strength			Wrought Metal ^(a)			
		Tensile Strength					Tensile Strength			
Metal	Plating Bath	kg/sq mm	psi	kg/sq mm	psi	percent	kg/sq mm	psi	Elongation, percent	
Aluminum	Anhydrous chloride- hydride-ether	7.7	11,000	21.7	31,000	2 to 26	9.15	13,000	35	
Cadmium	Cyanide		_	7.0	10,000		7.2	10.300	50	
Chromium	Chromic acid	10	14,000	56	80,000	<0.1	8.4	12,000	õ	
Cobalt	Sulfate-chloride	54	76,500	121	172,000	<1	26	37,000	_	
Copper	Cyanide, fluoborate, or sulfate	18	25,000	66	93,000	3 to 35	35	50,000	45	
Gold	Cyanide and cyanide citrate	12.7	18,000	21.2	30,000	22 to 45	13.5	19,000	45	
Iron	Chloride, sulfate, or sulfamate	33	47,000	109	155,000	2 to 50	29	41.000	47	
Lead	Fluoborate	1.4	2,000	1.6	2.250	50 to 53	1.85-2.1	2,650-3,000	42 to 50	
Lead-TiO2 composites	Fluoborate	3.2	4,500	4.1	5,800	7 to 15	3.2%)	4,500 ^(b)	18 ^(b)	
Nickel ^(e)	Watts, and other type baths	35	50,000	107	152.000	5 to 35	32.2	46.000	30	
Silver	Cyanide	24	34,000	34	48,000	12 to 19	16-19	23.000-27.000	50 to 55	
Zinc	Sulfate	4.9	7.000	11.2	16,000	1 to 51	9.1	13.000	32	

(a) Annealed, worked metal.

(b) Powder compact prepared with 1.5% PbO particles.
(c) Data do not include values for nickel containing >0.005% sulfur.

Epitaxial Growth. If the lattices of the substrate and deposit are similar, the substrate structure can be extended into the deposit. This is called epitaxial growth. High rates of deposition, the presence of addition agents and impurities tend to break down epitaxy. If the lattices differ, then the initial epitaxial growth shifts toward the structure of the deposit. The thickness of the epitaxial transition zone may vary from 0 to>5 μ m before the deposition variables control growth. Also, certain crystal faces grow more rapidly than others, resulting in grain orientation. These factors may be significant for thin film applications such as semiconductor or magnetic applications.

8.0 SUMMARY

Aqueous deposition is a complex process; the structure and properties of the resulting deposits depend on many factors (see Fig. 10.9). It is the oldest deposition technology and is receiving renewed and increasing interest. Research and new applications are providing increased understanding of electrode processes and solution chemistry with the development of new alloy and multilayered coatings and films. Electro- and electroless deposition are much more suitable than other deposition technologies for depositing films on complex geometric surfaces and into through-holes and blind recesses (vias).

It has a wide and varied range of applications (see Table 10.4). Continued development of the newer techniques will undoubtedly result in further engineering and electronic applications of strip line, very high speed plating, improved selective and maskless plating. These include current modifications; laser, ultrasonic, and jet enhanced deposition; new cell designs; computer-controlled processes, solution analyses, and chemical additions.

Improved and new processes and techniques to control, treat, minimize, and recycle plating solutions, wastes, and effluents are being studied and developed. These may result in near-zero discharge from plating processes and installations.

APPENDIX A - Preparation of Substrates for Electroplating

ASTM Recommended Practices*

Number	Title
B 177-68 (73)	Rec. Practice for Chromium Plating on Steel for Engineer- ing Use
B 183-72	Rec. Practice for Preparation of Low-Carbon Steel for Electroplating
B 242-54 (71)	Rec. Practice for Preparation of High-Carbon Steel for Electroplating
B 253-73	Rec. Practice for Preparation of and Electroplating on Aluminum Alloys by the Zincate Process
B254-70	Rec. Practice for Preparation of and Electroplating on Stainless Steel
B 281-58 (72)	Rec. Practice for Preparation of Copper and Copper-Base Alloys for Electroplating
B 322-68 (73)	Rec. Practice for Cleaning Metals Prior to Electroplating
B 343-67 (72)	Rec. Practice for Preparation of Nickel for Electroplating with Nickel
B 431-69	Rec. Practice for Processing of Mandrels for Electroplating
B 450-67 (72)	Rec. Practice for Engineering Design of Electroformed Articles
B 503-69	Rec. Practice for Use of Copper and Nickel Electroplating Solutions for Electroforming
B 480-68	Rec. Practice for Preparation of Magnesium and Magnesium Alloys for Electroplating
B 481-68 (73)	Rec. Practice for Preparation of Titanium and Titanium Alloys for Electroplating

^{*} Book of ASTM Standards, Vol. 2.05, Sec. 2, revised annually. Also approved by the American National Standards Institute.

B 482-68 (73)	Rec. Practice for Preparation of Tungsten and Tungsten Alloys for Electroplating
B 488-71	Spec. for Electrodeposited Coatings of Gold for Engineer- ing Uses
B 558-72	Rec. Practice for Preparation of Nickel Alloys for Plating
B 580-73	Spec. for Anodic Oxide Coatings on Aluminum

Preparation for electroplating of less common substrates including those used in nuclear, electronic or high temperature alloys of Fe, Co, Ni or Cr usually requires activation treatments* in order to obtain satisfactory adhesion. Other techniques involve diffusion bonding with thermal treatments.

Beach and Faust** and Friedman*** review procedures for light metals and for high temperature applications including plating on refractory metals– U, Mo, W, Th, Zr, Nb and Si.

For plating Cr on previously plated Cr, the following procedure has been satisfactory:

- 1. If Cr is oiled (due to grinding), degrease and polish lightly. Then clean in alkaline cleaner by immersion or scrubbing, or clean cathodically.
- 2. Provide a light etch anodically in alkaline, sulfuric or chromic acid solutions.
- 3. Immerse in Cr plating solution and allow parts to reach solution temperature.
- Plate at low C.D. (77.5 mA/cm², ~0.5 A/in²) to deposit only hydrogen to activate the surface, for 0.5 - 3 minutes approximately.
- Slowly increase C.D. to (0.5 1.0 A/cm², ~3 6 A/in²) for 15 30 seconds to guarantee coverage, then reduce to normal plating C.D. (0.15 0.5 A/cm², ~1 3 A/in²).

^{*} See C. Levy, *Proc. AES*, 43, 219 (1956) for activation for Cr plating and W. W. Sellers and C. B. Sanborn, Ibid., 44, 36 (1957) for Ni and Ni alloys prior to Ni plating for detailed formulations.

^{**} *Modern Electroplating,* 3rd ed., Ch. 27, 618, (F. Lowenheim, ed.), John Wiley & Sons (1974)

^{***} Plating, 54 (No. 9), 1035 (Sept., 1967)

APPENDIX B - Representative Electroless Plating Solution Formulation

1.	Nickel-Phosphorus				
	(See reference below)	(a)	(a)	(a)	(b)
	Nickel sulfate Sodium hypophosphite Sodium bydroxyacetate	35 g/L 10 10	35 g/L 10	30 g/L 10	25 g/L 25
	Sodium acetate	10	10		
	Sodium citrate			100	
	Sodium pyrophosphate				50
	Ammonium chloride			50	
	рН	4.5 - 5.5	4.5 - 5.5	9.0 - 9.5	10 - 10.5
	Temp. °C	90 - 95	90 - 95	90 - 95	25 - 75
	w/o P in deposit	7 - 9	7 - 9	5 - 7	4 - 6
2.	Nickel-Boron	(c)			
	Nickel chloride	30 g/L			
	Dimethylamine borane	3.5			
	Malonic acid	34			
	pН	5.5			
	Temp. °C	77			
3.	Cobalt-Phosphorus	(d)			
	Cobalt sulfate	24 g/L			
	Sodium hypophosphite	20			
	Socium citrate	70			
	Ammonium sulfate	40			
	Sodium laurylsulfate	0.1			
	рН	8.5			
	Temp. ^o C	92			

4.	Copper	(e)		
	Copper sulfate Sodium	29 g/L		
	potassium tartrate	142		
	Versene T	17		
	Sodium hydroxide	42		
	Sodium carbonate	25		
	Formaldehyde (37%)	167 ml/L		
	Temp. °C	25		
5.	Palladium	(f)		
	Palladium chloride	5.4 g/L		
	(as ammino complex)	33.6		
	Ammonium hydroxide	350		
	Hydrazine	0.3		
	Temp. °C	80		
6.	Gold	(g)	(g)	(g)
	Potassium cvanoaurate	5.8 a/L	0.86 a/L	5.8 a/L
	Potassium cvanide	13	6.5	1.3
	Potassium hydroxide	11.2	11.2	45
	Potassium borohydride	21.6	10.8	
	Dimethylamine borane			23.6
	Temp. °C	75	75	85
7.	Silver	(h)		
	Sodium silver cyanide	1.83 g/L		
	Sodium cyanide	1.0		
	Sodium hydroxide	0.75		
	Dimethylamine borane	2.0		
	(thiourea	0.25)		
	Temp. °C	55 - 65		

8.	Platinum		(i)
	Sodium platinate		10 g/L
	(Na ₂ Pt(OH) ₆)		
	Ethylamine	10	
	Hydrazine (as sulfa	te)	as required for reduction
	Sodium hydroxide		as required for pH 10
	Temp. ^o C		30

REFERENCES (for Appendix B)

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- (h) Pearlstein, F. and Wightman, R. F., *Plating*, 58:1014 (1971)
- (i) Rhoda and Vines, U.S. Patent 3,486,928 (1969)
- Note: (1) Some of the above formulations are protected by U.S. Patents. Their listing here does not imply any right to infringe.
 - (2) See Ref. 175 for additional solution formulations.

APPENDIX C - Comparison of Aluminum Anodizing Processes (Types I, II and III)

Advantages of Type I coatings

- 1. Corrosion resistance of coatings are as high (if not higher) than Type II coatings.
- 2. Provide excellent bond for organic coatings.
- 3. Chromic acid is a corrosion inhibitor, therefore it is not essential to assume (or provide for) complete removal from crevices, joints or recesses due to spot welding, riveting, bolting or blind holes.
- 4. It has practically no effect on the fatigue strength of the part.
- 5. Although thinner, less porous, and somewhat opaque due to pick up of chromate ion and alloying constituents, the coating is capable of absorbing dark dyes for Class 2 requirements.
- It is preferred as a maskant for selective Hard Anodize since it is less porous than Type II films, especially for assemblies with joints or recesses.

Limitations of Type I coatings

- 1. A smaller increase in abrasion resistance is obtained as compared to Type II coatings due to lower thickness and structure differences.
- 2. Limited to alloys containing less than 5% copper or 7% silicon.
- 3. Higher voltage is required with extended time as compared to Type II coatings.
- 4. Under conditions used for wrought alloys, casting alloys tend to use excessive current and "burning" may occur. In such cases, conditions might require changes to 30 - 35 volts at 90°F with compensating increase in time to obtain adequate coating thickness.
- 5. Alloys in the annealed condition do not anodize satisfactorily, Heat treatable alloys should be tempered by solution heat treatment and approved aging.

6. Wrought and cast alloys with high alloy content (such as 7075) tend to develop thinner coatings and may behave erratically or poorer in salt spray tests.

Advantages of Type II coatings

- 1. Less expensive (compared to Type I coatings) with respect to chemicals involved (and waste treatment thereof), heating and power costs, length of time to obtain required coating.
- 2. More alloys can be treated
- 3. Coatings are harder than Type I coatings.
- 4. Coatings may be slightly more corrosion resistantafter sealing than Type I coatings (due to thicker and more porous coating).
- 5. Clear coating permits dyeing with greater variety of colors.

Limitations of Type II coatings

- 1. Cannot be used where possibility of solution entrapment exists, especially joints, laps or recesses since any sulfuric acid residue may be corrosive.
- 2. Reduces the fatigue characteristics of the alloy.
- Difficult to control where small dimensional changes are desired or required since coatings grow faster and are thicker for corrosion resistant requirements as compared to Type I coatings. (Thus, Type I coatings should be considered on close tolerance parts such as threads.)

Characteristics of Hard Anodize Coatings

- 1. Corrosion resistance is excellent, several thousand hours in salt spray tests have been reported (after proper sealing).
- 2. Abrasion and wear resistance excellent.
- 3. Chemical resistance is poor as compared to calcined aluminum oxides; will not resist alkalies or acids as well.

- 4. Coefficient of thermal expansion is different from that of the aluminum alloys and spalling may result at temperatures above 200 300°C.
- 5. Film crazing As part temperature increases from formation temperature (-4 0°C = 25 32°F) to room temperature or the higher sealing temperatures (93 99°C = 200 210°F) or post honing temperatures, the coating may craze or fracture since it is tensively stressed; this phenomenon becomes aggravated as film thickness increases. Sometimes this crazing seems to disappear after aging.
- "Chalking"–This refers to a white film which sometimes appears on the surface after drying. It is not considered detrimental and is usually not noticed unless (or until) surface is wiped. The mechanism is not understood; it may possibly be a bleed-out phenomenon.

Effect of Alloying Elements on the Hard Coating.

1. Thicker coatings are obtained with the purer or higher conducting alloys containing magnesium or zinc:

 Purer alloys
 EC, 1100, 3003

 Al-Mg alloys
 5005, 5050, 5052, 5252

 Al-Mg-Si alloys
 6061, 6063

 Al-Zn alloys
 7075

- 2. Copper-containing alloys produce intermetallic compounds (after HT) which increase the ohmic resistance resulting in thinner coatings. Type III Hard Anodize is restricted to those alloys containing less than 5% Cu.
- 3. High silicon-containing alloys also produce intermetallic compounds and do not anodize readily. These involve most castings which depend on reduction of the alloy's melting point by the eutectics formed with the silicon (even less than 7% Si). The Si or silicides do not anodize, being "inert" and acting as inclusions, depending on "bridging" for continuity of coating.
- 4. Since copper and silicon constituents may result in poorer coatings, a total of 7 9% of the combination of these two elements is usually considered as a maximum in an alloy to be hard anodized.
- 5. The color of the Hard Anodize Coating reflects the alloying constituents.

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