Electroplating

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INTRODUCTION

Electroplating is an electrodeposition process for producing a dense, uniform, and adherent coating, usually of metal or alloys, upon a surface by the act of electric current.[1] The coating produced is usually for decorative and/or protective purposes, or enhancing specific properties of the surface. The surface can be conductors, such as metal, or nonconductors, such as plastics. Electroplating products are widely used for many industries, such as automobile, ship, air space, machinery, electronics, jewelry, defense, and toy industries. The core part of the electroplating process is the electrolytic cell (electroplating unit). In the electrolytic cell (electroplating unit) a current is passed through a bath containing electrolyte, the anode, and the cathode. In industrial production, pretreatment and posttreatment steps are usually needed as well.

BACKGROUND

The workpiece to be plated is the cathode (negative terminal). The anode, however, can be one of the two types: sacrificial anode (dissolvable anode) and permanent anode (inert anode).[2] The sacrificial anodes are made of the metal that is to be deposited. The permanent anodes can only complete the electrical circuit, but cannot provide a source of fresh metal to replace what has been removed from the solution by deposition at the cathode. Platinum and carbon are usually used as inert anodes.

Electrolyte is the electrical conductor in which current is carried by ions rather than by free electrons (as in a metal). Electrolyte completes an electric circuit between two electrodes. Upon application of electric current, the positive ions in the electrolyte will move toward the cathode and the negatively charged ions toward the anode. This migration of ions through the electrolyte constitutes the electric current in that part of the circuit. The migration of electrons into the anode through the wiring and an electric generator and then back to the cathode constitutes the current in the external circuit. The metallic ions of the salt in the electrolyte carry a positive charge and are thus attracted to the cathode. When they reach the negatively charged workpiece, it provides electrons to reduce those positively charged ions to metallic form, and then the metal atoms will be deposited onto the surface of the negatively charged workpiece.

Fig. 1 illustrates a typical plating unit for plating copper from a solution of the metal salt copper sulfate ($CuSO_4$). The cathode, which is the workpiece to be plated, is charged negatively. Some of the electrons from the cathode bar transfer to the positively charged copper ions (Cu^{2+}), setting them free as atoms of copper metal. These copper atoms take their place on the cathode surface and copper plate it. Concurrently, the same number of sulfate ions SO_4^{2-} is discharged on the copper anodes, thereby completing the electrical circuit. In so doing, they form a new quantity of copper sulfate that dissolves in the solution and restores it to its original composition. This procedure is typical of ordinary electroplating processes with sacrificial anodes; the current deposits a given amount of metal on the cathode and the anode dissolves to the same extent (of the same electrical charge), maintaining the solution more or less uniformly.

ELECTROCHEMISTRY FUNDAMENTALS

When a direct electric current passes through an electrolyte, chemical reactions take place at the contacts between the circuit and the solution. This process is called electrolysis. Electrolysis takes place in an electrolytic cell. Electroplating is one specific type of electrolysis. Besides electroplating, electrolysis has also been widely used for preparation of halogens and notably chlorine, and refining of metals, such as copper and zinc. Understanding the electrochemical principles of electrodeposition is essential to the development of electroplating technologies. Some basic concepts are presented below.[3]
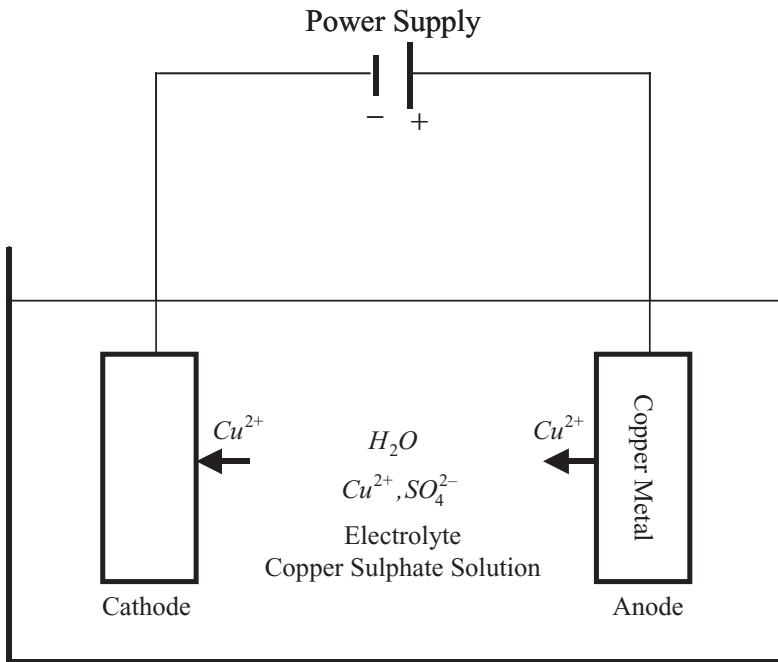
Power Supply

$-$ $+$

Cathode   Anode

Cu^{2+} H_2O Cu^{2+} Copper Metal
              Cu^{2+}, SO_4^{2-}

Electrolyte
Copper Sulphate Solution

Fig. 1 Principle of electroplating.

Oxidation/Reduction

In a wider sense, all electron-transfer reactions are considered oxidation/reduction. The substance gaining electrons (oxidizing agent, or oxidant) oxidizes the substance that is losing electrons (reducing agent, or reductant). In the process, the oxidizing agent is itself reduced by the reducing agent. Consequently, the reduction process is sometimes called electronation, and the oxidation process is called "de-electronation." Because a cathode is attached to the negative pole of the electric source, it supplies electrons to the electrolyte. On the contrary, an anode is connected to the positive pole of the electric source; therefore, it accepts electrons from the electrolyte. Various reactions take place at the electrodes during electrolysis. In general, reduction takes place at the cathode, and oxidation takes place at the anode.

Anode and Cathode Reactions

Electrodeposition or electrochemical deposition (of metals or alloys) involves the reduction of metal ions from electrolytes. At the cathode, electrons are supplied to cations, which migrate to the anode. In its simplest form, the reaction in aqueous medium at the cathode follows the equation:

$$M^{n+} + ne^- \rightarrow M \tag{1}$$

with a corresponding anode reaction. At the anode, electrons are supplied to the anions, which migrate to

the anode. The anode material can be either a sacrificial anode or an inert anode. For the sacrificial anode, the anode reaction is:

$$M \rightarrow M^{n+} + ne^- \tag{2}$$

In this case, the electrode reaction is electrodissolution that continuously supplies the metal ions.

Faraday's Laws of Electrolysis

In 1833, the English scientist, Michael Faraday, developed Faraday's laws of electrolysis. Faraday's first law of electrolysis and Faraday's second law of electrolysis state that the amount of a material deposited on an electrode is proportional to the amount of electricity used. The amount of different substances liberated by a given quantity of electricity is proportional to their electrochemical equivalent (or chemical equivalent weight).

In the SI system, the unit quantity of electricity charge and the unit of electric charge are coulomb (C); one coulomb is equivalent to one ampere flowing for one second ($1\,C = 1\,A\,sec$). The electrochemical equivalent of an element is its atomic weight divided by the valence change involved in the reaction. For example, for the reaction, $Fe^{2+} \rightarrow Fe^0$, the valence change is 2, and the electrochemical equivalent of iron is $55.85/2 = 27.925$ in this reaction. Depending on the specific reaction, one element may have different equivalent weights, although it has only one atomic weight.

In detail, to reduce one mole of a given metal from a metal ion with the valence charge of $n+$, n moles of electrons are required. That is, the total cathodic charge used in the deposition, $Q(C)$, is the product of the number of gram moles of the metal deposited, m, the number of electrons taking part in the reduction, n, Avogadro's number, N_a (the number of atoms in a mole), and the electrical charge per electron, $Q_e(C)$. Thus, the following equation gives the charge required to reduce m moles of metal:

$$Q = mnN_aQ_e \tag{3}$$

The product of the last two terms in Eq. (3) is the Faraday constant, F. Therefore, the number of moles of the metal reduced by charge Q can be obtained as:

$$m = \frac{Q}{nF} \tag{4}$$

The Faraday constant represents the amount of electric charge carried by 1 mol, or the Avogadro's number of electrons. The Faraday constant can be derived by dividing Avogadro's number, or the number of electrons per mole, by the number of electrons per coulomb. The former is approximately equal to 6.02×10^{23} and the latter is approximately 6.24×10^{18}. Therefore,

$$F = \frac{(6.02 \times 10^{23})}{(6.24 \times 10^{18})} = 9.65 \times 10^4 \, C/mol \tag{5}$$

On the other hand, the total charge used in the deposition can be obtained as the product of the current, $I(A)$, and the time of deposition, t (sec), if the deposition current is held constant. Or, if the current varies during the deposition,

$$Q = \int I \, dt \tag{6}$$

The weight of the deposit, W(g), thus can be obtained by multiplying the number of moles of metal reduced with the atomic weight, M_w, of the deposited metal:

$$W = \frac{M_w}{nF} \int I \, dt \tag{7}$$

Ideally, the deposition thickness, δ (cm), can be solved by:

$$\delta = \frac{W}{\rho A} = \frac{M_w}{nF\rho A} \int I \, dt \tag{8}$$

where ρ is the density of the metal (g/cm^3) and A is the area of deposition (cm^2).

Current Efficiency, Current Density, and Current Distribution

Faraday's laws give theoretical prediction of electrodeposition in an ideal situation. In a real application, many factors influence the coating quantity and quality.[4]

Current efficiency

It is stated in Faraday's laws that the amount of chemical charge at an electrode is exactly proportional to the total quantity of electricity passing. However, if several reactions take place simultaneously at the electrode, side reactions may consume the product. Therefore, inefficiencies may arise from the side reactions other than the intended reaction taking place at the electrodes. Current efficiency is a fraction, usually expressed as a percentage, of the current passing through an electrolytic cell (or an electrode) that accomplishes the desired chemical reaction. Or,

$$Current \, efficiency = 100 \times W_{Act}/W_{Theo} \tag{9}$$

where W_{Act} is the weight of metal deposited or dissolved, and W_{Theo} is the corresponding weight to be expected from Faraday's laws [Eq. (7)] if there is no side reaction. Note that the cathode efficiency is the current efficiency applied to the cathode reaction, and the anode efficiency is the current efficiency applied to the anode reaction.

Current density

Current density is defined as current in amperes per unit area of the electrode. It is a very important variable in electroplating operations. It affects the character of the deposit and its distribution.

Current distribution

The local current density on an electrode is a function of the position on the electrode surface. The current distribution over an electrode surface is complicated. Current will tend to concentrate at edges and points, and unless the resistance of the solution is very low, it will flow to the workpieces near the opposite electrode more readily than to the more distant workpieces. It is desired to operate processes with uniform current distribution. That is, the current density is the same at all points on the electrode surface.

Potential Relationships

In electroplating, sufficient voltage should be provided by the power source. The voltage–current relationship

follows Ohm's law. The concepts of electrode potentials, equilibrium electrode potential, overpotential, and overvoltage are of fundamental importance.

The voltage–current relationship: Ohm's law

The current is driven by a potential difference, or voltage through the conducting medium, either electrolytic or metallic. The voltage necessary to force a given current through a conductor is given by Ohm's law:

$$E = IR \tag{10}$$

where E is the voltage (V) and R the resistance of the conductor (Ω).

Electrode potentials

The electrode potential is the electrical potential difference between an electrode and a reference electrode. The absolute potential of an electrode is not directly measurable. Therefore, the electrode potential must always be referred to an arbitrary zero point that is defined by the potential of the reference electrode.

Equilibrium electrode potential

When a metal is immersed into a solution containing ions of that metal, equilibrium is set up between the tendency of the metal to enter solution as ions and the opposing tendency of the ions to lose their charge and deposit on or in the metal.

$$M \leftrightarrow M^{n+} + ne^- \tag{11}$$

Depending on the conditions of the system, this can occur in either direction. At equilibrium, the driving forces for metal ions being discharged and metal atoms being ionized are equal. The potential difference between the metal and the solution phases under these conditions is the equilibrium potential difference.

The equilibrium electrode potential is the electrical potential of an electrode measured against a reference electrode when there is no current flowing through the electrode. It is also called open circuit potential (OCP). The equilibrium potential between a metal and a solution of its ions is given by the Nernst equation as follows:

$$E = E^0 + \frac{RT}{nF} \ln a \tag{12}$$

where E^0 is the standard electrode potential, which is a constant characteristic of the material of the electrode; R the gas constant (8.3143 J/k/mol); T the absolute temperature (K); F the Faraday constant; n the valence

change; a the activity of the metal ion. In approximation, the concentration of the metal ion can be used instead of the activity.

If numerical values are substituted for R and F, and T is at 25°C (298 K), and base 10 logarithm is used instead of base e, the Nernst equation can be expressed as:

$$E = E^0 + \frac{0.059}{n} \log a \tag{13}$$

In the above equation, if $a = 1$, then $E = E^0$. The standard potential of an electrode E^0 is the potential of an electrode in contact with a solution of its ions of unit activity. The standard potentials are always expressed against the standard hydrogen electrode, the potential of which is zero by definition. The standard potentials are a function of temperature; they are usually tabulated for 25°C. Standard electrode potential is also called normal electrode potential.

Overpotential and overvoltage

The equilibrium is dynamic with metal ions being discharged and metal atoms being ionized, but these two effects cancel each other and there is no net change in the system. For the realization of metal deposition at the cathode and metal dissolution at the anode, the system must be moved away from the equilibrium condition. An external potential must be provided for the useful electrode reactions to take place at a practical rate; this external potential may have several causes.

Overpotential is the difference in the electrode potential of an electrode between its equilibrium potential and its operating potential when a current is flowing. The overpotential represents the extra energy needed to force the electrode reaction to proceed at a required rate (or its equivalent current density). Consequently, the operating potential of an anode is always more positive than its equilibrium potential, while the operating potential of a cathode is always more negative than its equilibrium potential. The overpotential increases with increasing current density. The value of the overpotential also depends on the inherent speed of the electrode reaction. A slow reaction (with small exchange current density) will require a larger overpotential for a given current density than a fast reaction (with large exchange current density). Overpotential is also referred to as polarization of the electrode.

An electrode reaction always occurs in more than one elementary step, and there is an overpotential associated with each step. Even for the simplest case, the overpotential is the sum of the concentration overpotential and the activation overpotential.

Overvoltage is the difference between the cell voltage (with a current flowing) and the open-circuit voltage (OCV). The overvoltage represents the extra energy needed to force the cell reaction to proceed at a required rate. Consequently, the cell voltage of an electrolytic cell is always more than its OCV, while the cell voltage of a galvanic cell (e.g., a rechargeable battery during discharging) is always less than its OCV. Occasionally, it is also referred to as polarization of the cell.

The overvoltage is the sum of the overpotentials of the two electrodes of the cell and the ohmic loss of the cell. Unfortunately, the terms overvoltage and overpotential are sometimes used interchangeably.

SURFACE PREPARATION

Workpieces to be plated may be put through a variety of pretreating processes, including surface cleaning, surface modification, and rinsing.[4] A schematic flowsheet of a typical electroplating plant, including surface treatment and waste treatment, is depicted in Fig. 2.

The purpose of surface pretreatment is to remove contaminants, such as dust and films, from the substrate surface. The surface contamination can be extrinsic, composed of organic debris and mineral dust from the environment or preceding processes. It can also be intrinsic, such as a native oxide layer. Contaminants and films interfere with bonding, which can cause poor adhesion and even prevent deposition. Therefore, surface pretreatment is important to ensure plating quality. Most (metal) surface treatment operations have three basic steps: surface cleaning, surface treatment, and rinsing.

Surface Cleaning

Cleaning methods should be able to minimize substrate damage while removing the contaminants, dust, film, and/or debris. Cleaning processes are based on two approaches: chemical approach and mechanical approach.

Chemical approaches

A chemical approach usually includes solvent degreasing, alkaline cleaning, (soak cleaning), and acid cleaning (acid pickling).

Solvent Degreasing. Contaminants consist of oils and grease of various types, waxes, and miscellaneous organic materials. These contaminants can be removed by appropriate organic solvents, either by dipping the workpieces in the solvent or by vapor decreasing.

Alkaline Cleaning. Workpieces are immersed in tanks of hot alkaline cleaning solutions to remove dirt and solid soil. A special type of alkaline cleaning is electrocleaning. In electrocleaning, the workpiece can be either the cathode (namely direct cleaning) or the anode (reverse cleaning). Electrocleaning adds to the chemical action of the cleaner the mechanical action caused by plentiful gas evolution at the surface of the workpiece.

Acid Cleaning. Acid cleaning can move heavy scale, heat-treat scale, oxide, and the like. The most commonly used acids include sulfuric and hydrochloric. Pickling can also be combined with current to be more effective.

Mechanical approaches

Mechanical preparations include polishing, buffing, and some variations. Polishing is to remove small amounts of metal by means of abrasives. It produces a surface that is free of the larger imperfections left by grinding, and is a preliminary to buffing. Buffing is similar to polishing, but uses finer abrasives to remove very little metal. Buffing can produce an extremely smooth surface.

Surface Modification

Surface modification includes change in surface attributes, such as application of (metal) layer(s) and/or hardening.

Rinsing

In wet plating, when workpieces are transferred from one treating solution to another, or when they leave the final treating solution, they carry some of the solution in which it has been immersed. This solution is called drag-out. In most cases, this residue solution should be removed from the workpieces surface by rinsing before the workpieces enter the next step in sequence, or come out of the final processing solution. The dirty rinse water will be sent to the wastewater treatment facilities before being discharged to a public sewage system.

ELECTROLYTIC METAL DEPOSITION

There are three types of electrolytic metal deposition processes: direct current electrodeposition, pulse plating, and laser-induced metal deposition.[2]
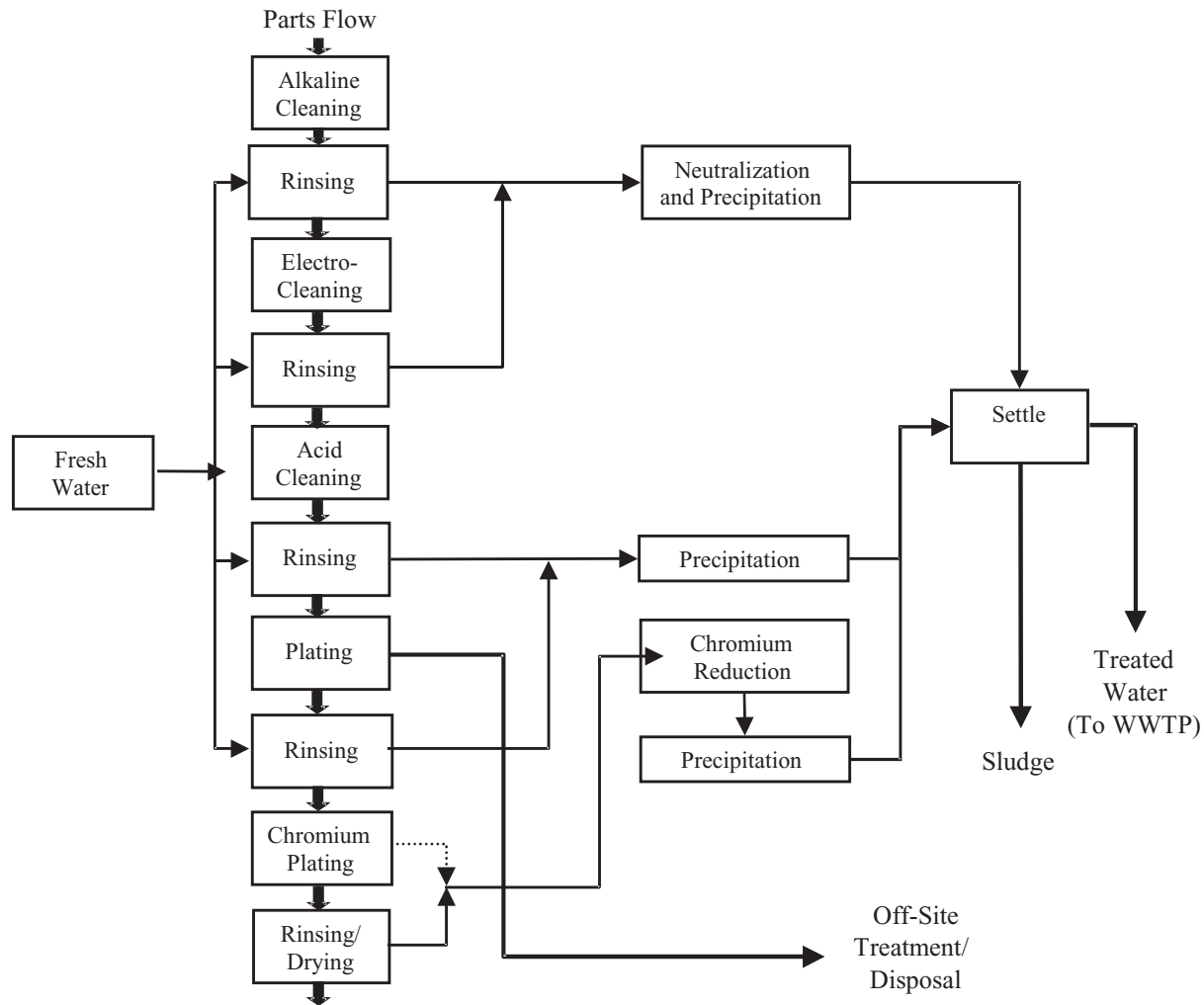
Parts Flow

Alkaline
Cleaning

Rinsing → Neutralization
and Precipitation

Electro-
Cleaning

Rinsing

Fresh
Water → Acid
Cleaning

Rinsing → Precipitation

Plating

Chromium
Reduction

Rinsing

Precipitation

Chromium
Plating

Rinsing/
Drying

Settle

Treated
Water
(To WWTP)

Sludge

Off-Site
Treatment/
Disposal

Fig. 2 Process flowsheet of a typical electroplating plant.

Direct Current Electrodeposition

In the direct current (DC) electrodeposition, the current source is. A power source in the form of a battery or rectifier (which converts alternating current electricity to regulated low-voltage DC current) provides the necessary current.

Electroplating is performed in a plating unit. Electrodes, immersed in the electroplating bath (electrolyte), are connected to the output of a DC current source. The workpiece that is to be plated acts as a negatively charged cathode. The positively charged anode(s) completes the electric circuit. This type of circuit arrangement directs electrons (negative charge carriers) into a path from the power supply (rectifier) to the cathode (the workpiece to be plated).

The geometric shape and contour of a workpiece to be plated affect the thickness of the deposited layer. In general, workpieces with sharp corners and features will tend to have thicker deposits on the outside corners and thinner ones in the recessed areas. The cause of this difference in the resulting layer thickness is that the DC current flows more densely to sharp edges than to the less accessible recessed areas. In other words, the current distribution is not uniform. Therefore, a judicial placement of the anode(s) as well as modifications of the current density are required to overcome the thickness irregularity effects.

Pulse Plating

Electrodeposition using pulsed currents is known as pulse plating. The pulsed currents can be unipolar (on–off) or bipolar (current reversal). Pulses can be used along or be superimposed on a DC feed. By using the bipolar pulse, metal deposition occurs in the cathodic pulse period, with a limited amount of metal being

redissolved in the anodic period. This repeated deposition and partial redissolution could improve the morphology and the physical properties of the deposit.

Laser-Induced Metal Deposition

In laser-induced metal deposition, a focused laser beam is used to accelerate the metal deposition. Experiments have shown that the deposition rate can be increased by 1000 times. The plating equipment mainly consists of a laser head with focusing optics and the electrolytic cell. The focused laser beam can pass through a hole in the anode through the electrolyte and impinge on the cathode surfaces.

ELECTROLYTE

Different metals may need different types of electrolyte. The composition and properties of the electrolyte is very important for the coating quality.

Types and Components

Types of electrolytes include water solutions of acids, bases, or metal salts, certain pure liquids, and molten salts. Gases may act as electrolytes under conditions of high temperature or low pressure. In addition to metal salts, electrodeposition electrolytes usually contain a number of additives for various purposes. Some agents are used to increase electrolyte conductivity (supporting electolytes). Others may be used for increasing bath stability (stabilizers), activating the surface (surfactants or wetting agents), improving leveling or metal distribution (leveling agents), or optimizing the chemical, physical, or technology properties of the coating. These coating properties include corrosion resistance, brightness or reflectivity, hardness, mechanical strength, ductility, internal stress, wear resistance, or solderability.[2]

Properties of Electrolyte

The properties of electrolyte are usually characterized by electrolytic conductance, covering power, macrothrowing power, and microthrowing power.[4]

Electrolytic Conductance

Electrolytic conductance is different from electrical conductance in metal. Electronic conductance is called a ''Class I'' conductor, while electrolytic conductance is a ''Class II'' conductor. Both inorganic and organic salts, acids or alkalis can be used to increase the electrolytic conductance. The conductivity of an electrolyte is a function of the degree of dissociation, the mobility of the individual ions, the temperature and viscosity, and the electrolyte composition.

Covering Power

Covering power describes the extent to which an electrodeposition electrolyte can cover the entire surface of a workpiece being plated, with reasonable uniform thickness. Covering power is influenced by the nature of the substrate surface, the electrolyte composition, the temperature and viscosity, and the current density.

Macrothrowing Power

Macrothrowing power predicts the ability of an electrolyte to lay down as nearly as possible a uniformly thick deposit across the surface of a workpiece. A good covering power is a prerequisite for good macrothrowing power. Other factors that affect macrothrowing power include the current distribution and current density, electrolyte composition, electrolytic conductance, and electrolyte agitation.

Microthrowing Power

Microthrowing power indicates the extent to which metal electrodeposition occurs at the outer plane of the substrate or at the base of valleys or cracks. Microthrowing power can be improved by activating the surfaces at the base of valleys or cracks to promote electrodeposition there, while inhibiting the outer surfaces by using inhibitors preferentially. In many cases, microthrowing power is inversely related to macrothrowing power.

TYPES OF ELECTROPLATING PROCESSES

Depending on the size and geometry of the workpieces to be plated, different plating processes, including mass plating, rack plating, continuous plating, and in-line plating, may be adopted.[2]

Mass Plating

Mass plating is used for small workpieces to be plated in large quantities, such as nuts and bolts, but it is not used for delicate workpieces. The most widely used mass plating system is called barrel plating, where the workpieces are loaded into a plating barrel. Other mass plating containers include plating bells and vibratory units.

Rack Plating

Some workpieces cannot be mass plated because of their size, shape, or special features. Rack plating means workpieces are mounted on a rack for the appropriate pretreatment plating and posttreatments. Racks are fixtures suitable for immersion in the plating solution. Rack plating is sometimes called batch plating.

Continuous Plating

Continuous plating means the workpieces to be plated move continuously passing either one row or between two rows of anodes. Continuous plating is usually used for a workpiece of simple and uniform geometry, such as metal strip, wire, and tube.

In-Line Plating

In-line plating is used to integrate the plating and finishing processes into a main production line. The benefit of in-line plating includes exclusion of pretreatment steps and a significant reduction in material, chemical and energy consumption, and waste discharge.

TYPES OF METAL COATINGS

Plating metals can be roughly classified into the following categories with the typical applications.[4]

Sacrificial Coatings

Sacrificial coatings are primarily used for the protection of the base metal, usually iron and steel. Another name for sacrificial coating is anodic coating, because the metal coatings are anodic to the substrate metal, so the coatings sacrifice themselves to protect the base metal from corrosion. Zinc (Zn) and cadmium (Cd) coatings can be used as sacrificial coatings. Because of high toxicity, cadmium plating is now forbidden by law in many countries.

Decorative Protective Coatings

Decorative protective coatings are primarily used for adding an attractive appearance to some protective qualities. Metals in this category include copper (Cu), nickle (Ni), chromium (Cr), zinc (Zn), and tin (Sn).

Engineering Coatings

Engineering coatings (sometimes called functional coatings) are used for enhancing specific properties of the surface, such as solderability, wear resistance, reflectivity, and conductivity. Metals for engineering purpose include precious gold (Au) and silver (Ag), six platinum metals, tin, and lead (Pb). The six platinum metals are ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), and platinum (Pt). These six metals are noble, i.e., with positive electrode potentials and they are relatively inert.

Minor Metal Coating

Minor metals here refer to iron (Fe), cobalt (Co), and indium (In). They are easily plated but have limited applications in electroplating.

Unusual Metal Coating

The unusual metals are rarely electroplated and can be divided into the following categories: 1) easily platable from aqueous solutions but not widely used, such as arsenic (As), antimony (Sb), bismuth (Bi), manganese (Mn), and rhenium (Re); 2) platable from organic electrolyte but not aqueous electrolyte, such as aluminum (Al); and 3) platable from fused-salt electrolyte but not aqueous electrolyte, including refractory metals (named because of their relatively high melting points), such as titanium (Ti), zirconium (Zr), hafnium (Hf), vanadium (V), niobium (Nb), tantalum (Ta), molybdenum (Mo), and tungsten (W). The periodic table in Fig. 3 shows that the metals that can be electrodeposited from aqueous solutions are those inside the frame.

Alloy Coatings

An alloy is a substance that has metallic properties and is composed of two or more chemical elements, at least one of which is a metal. The elements composing the alloy are not distinguishable by the unaided eye. Examples of alloy coating include gold–copper–cadmium, zinc–cobalt, zinc–iron, zinc–nickle, brass (an alloy of copper and zinc), bronze (copper–tin), tin–zinc, tin–nickle, and tin–cobalt. Alloy coatings are produced by plating two metals from the same solution.

Multilayered Coatings

Multilayered coatings are produced by plating different metals from the same solution at different potentials. A pulse train-shaped potential is enforced, resulting in the multilayer deposition. For example, multilayered coatings based on copper, nickle, chromium, in that order, can be applied to either metal or plastic components for visual appearance, corrosion and wear resistance, and weight saving.

Period / Group**	1 IA 1A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIII	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 vIIIA 8A
1	1 H 1.0088																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.47	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	57 La* 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 190.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.5	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (210)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 Ac~ (227)	104 Rf (257)	105 Db (260)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 --- ()	111 --- ()	112 --- ()		114 --- ()		116 --- ()		118 --- ()

	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
Lanthanide Series*														
Actinide Series~	90 Th 232.0	91 Pa (231)	92 U (238)	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (257)

Fig. 3 Periodic table (metals inside the frame can be electrodeposited from aqueous solutions). *(View this art in color at www.dekker.com.)*

Composite Coatings

Composite materials can be defined as coatings consisting of minute second-phase particles dispersed throughout a metal matrix. The size of the second phase particles may range from 10 μm down to nanoscale and the particles can be inorganic, organic, or occasionally metallic. The presence of fine particles in a metal matrix generally improves its mechanical and chemical properties, resulting in a wide range of applications. Composite coatings with an electrodeposited metal matrix and nonmetallic inclusions have excellent wear resistance and permit emergency dry running of machinery.

Conversion Coatings

Conversion coatings are formed by a reaction of the metal on the surface of the substrate with a solution.[5] For example, chromate coatings are formed by the reaction of water solutions of chromic acid or chromium salts. The chromate coatings can be applied to aluminum, zinc, cadmium, and magnesium. The coatings usually have good atmospheric corrosion resistance. Chromate coatings are widely used in protecting common household products, such as screws, hinges, and many hardware items with the yellow-brown appearance.

Anodized Coatings

Anodizing is produced by electrochemical conversion. In an anodizing process, the metal workpiece to be plated is the anode in a suitable electrolyte. With the electric current passing through the electrolyte, the metal surface is converted to a form of its oxide. An anodizing process is usually used on aluminum for protection and cosmetic purposes. The electrolyte provides oxygen ions that react with metal ions to form the oxide, and hydrogen is released at the metal or carbon cathode. Anodizing differs from electroplating in two aspects. In electroplating, the workpiece to be plated

is the cathode, and the metallic coatings are deposited on the workpiece. In anodizing, the workpiece is the anode, and its surface is converted to a form of its oxide.

RELATED PROCESSES

The related processes for metal deposition include electroless deposition, immersion plating, and electroforming.[4] They follow the basic principles of electrochemistry.

Electroless Deposition (Autocatalytic Plating)

A special type of electroplating is called electroless deposition, autocatalytic plating, or "chemical deposition." In electroless plating, there is no external power source. The deposited metal is reduced from its ionic state in solution by a chemical reducing agent. The reducing agent supplies the electrons for the following reaction:

$$M^{n+} + ne^- \rightarrow M \tag{14}$$
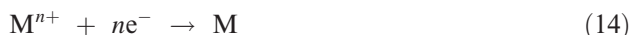
This reaction takes place only on a catalytic surface. Therefore, once deposition is initiated, the metal deposited must itself be catalytic for the deposition to continue.

Not all metals can be plated autocatalytically. The reducing agents are usually more expensive electron sources as compared with the electric current. The major advantages of electroless deposition are as follows:

1. It can be used to deposit metal on nonconductive surfaces, such as plastics, glass, or ceramics. Some proper pretreatment steps are needed to activate these surfaces. The metallizing of printed circuit board is one such example.
2. The throwing power is perfect. Deposits are laid down on the surface with no excess buildup on projections or edges.

Immersion Plating

Immersion plating is the deposition of a metallic coating on a substrate by chemical replacement from a solution of salt of the coating metal. It requires no electric circuitry or source of power, but it differs from autocatalytic plating in not requiring a chemical reducing agent to reduce the metal ions to metal. Immersion deposition stops when the substrate is completely covered by a layer of coating.

The major advantages of immersion plating include simplicity, minor capital expense, and the ability to deposit in recesses and on the inside of the tubing. But, the applicability of immersion plating is limited.

Electroforming

Electroforming is to produce or reproduce a metal workpiece by electrodeposition in a plating bath over a base form (mold) or mandrel, which is subsequently removed. In some cases, the mandrel or mold may remain within the finished metal workpiece. A mandrel is a form used as a cathode in electroplating.

The advantage of the process is that it faithfully reproduces a form of mandrel exactly, to within one micrometer, without shrinkage and distortion associated with other metal forming techniques, such as casting, stamping, and drawing. Because the mandrel is machined as an outside surface, close dimensional tolerances and high surface finishes can be held and maintained on complex interior configurations. The disadvantage of electroforming includes slow production, relatively high cost, design limitations of the geometry, and the separation of workpieces from the mold or mandrel.

CONCLUSIONS

The electroplating industry has been experiencing continuous innovations and also facing significant challenges from economic and environmental perspectives. The purpose of electroplating is to produce a qualified coating with the desirable attributes. Based on the specifications of the coating and the substrate, one may select a specific electroplating process for a given application.

ACKNOWLEDGMENTS

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