Electroplating
and
Related Processes

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INTRODUCTION

Electroplating was born from a science that demonstrated the remarkable ability of electric current to reduce metal salts to metal. It soon aided the production of beautiful objects and it became an art that was dependent on the masters who learned how to coax attractive coatings from homely solutions. But did the art of yesterday become the science of today? Or is the science of today the art of tomorrow? I think not. It will remain an art and a science. It is possible to design and operate an automatic plating process that is coldly technical. But it is not possible to remove personalities from the practice of electroplating.

Given a process, the individual will change it by science, logic, skill, intuition and art. Can anyone say that silver plating is best done with one strike, or two, or three. I prefer one. A friend prefers three. What is already known and communicated will help to understand but will not settle this difference. It is better to regard plating cycles as suggestions and plating baths as uncompleted formulations. The need for continuing experimentation is a vital part of every electroplating installation.

It is relatively easy to remove metal from solutions by the application of current, but only specific experimentally developed solutions produce useful electrodeposits.

If a metal salt is picked at random and current is applied to a solution of the salt, the results obtained will be varied. If the salt solution contains sodium chloride, only hydrogen will develop at the cathode. If a solution contains lead acetate, lead will deposit, but the deposit will appear as long crystals extending into the bath. If a solution contains stannic sulfate, the stannic ions will be reduced to stannous ions at the cathode and, at least for a short time and at a low current density, neither tin nor hydrogen will deposit. If a solution contains chromic acid, only hydrogen will develop; but if a small amount of sulfuric acid is added to the electrolyte, then chromium will deposit in addition

to hydrogen.

By experimentation with solutions of metal salts, baths can be developed that will produce satisfactory deposits. A great many experiments are usually required and often it is necessary to study the effect of a host of organic substances known as addition agents. By experimentation and study, new baths have been developed to fill specific needs. For example, a deposit that is satisfactory for electrorefining may not be satisfactory for electroforming. A deposit that is satisfactory for electroforming may not be satisfactory for electroplating.

Electroplating is a process of electrodeposition by which a thin, smooth, sound metallic deposit is produced over a basis metal. This definition sets electroplating apart from the other processes of electrodeposition even though the requirements of the definition are not met in every case.

In this book, the fundamentals of electroplating will be briefly considered. A number of plating baths will then be discussed. It is hoped that the text will aid the practices of the science and the art of electroplating.

July 1968   *J. B. Mohler*

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1. MECHANISM OF ELECTRODEPOSITION

The Electrolyte

The process of electrodeposition is one in which electric current is carried across an electrolyte and in which a substance is deposited at one of the electrodes.

The electrolyte is the medium that carries the current by means of ions. The ability of a solvent, especially water, to ionize substances dissolved in it, i.e., to split them into components that carry positive and negative charges, makes electrolysis possible. The electricity is carried across the electrolyte by the charged ions and products of electrolysis appear at the electrodes. This is a result of the positively charged ions being attracted to the negatively charged cathode while the negatively charged ions travel toward the positively charged anode. The charges of the ions are then neutralized by the charges on the electrodes and the products of the electrolysis appear at the electrodes.

The electrolyte is a conducting medium in which the flow of electric current is accomplished by the movement of matter. It is also a substance that gives rise to ions. If more than one ion is present, carrying a positive charge, several reactions are possible at the negatively charged cathode, although usually only one product of electrolysis appears. Each electrode reaction takes place at a specific voltage and the most positive metal ion will deposit at the cathode.

Any liquid or solution that contains ions can be used as an electrolyte. The large majority of commercial electrolytes, however, use water as the solvent and are therefore called aqueous electrolytes. Fused salts, which are a class of nonaqueous electrolytes, find their greatest use in the electrolytic production of metals such as sodium, magnesium, and aluminum. Fused-salt electrolytes are also used in the electrolytic cleaning of metals.

The extensive use of water as the solvent in the electroplating industry is due to its cheapness and abundance and to the fact that many com-
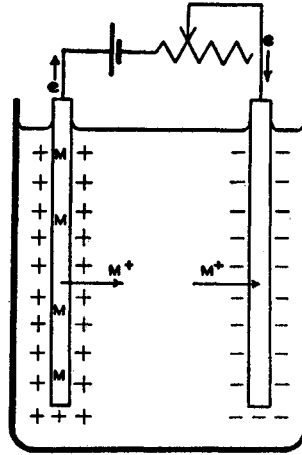
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Fig. 1   Electrodeposition.

mon salts are very soluble in water.

In this book, the aqueous electrolytes alone will be considered. The term electroplating will occasionally be simplified to "plating."

The Cathode

The plater is primarily interested in the reaction that takes place at the cathode since this is where deposits are produced. The potential at which this reaction takes place is called the deposition potential. This potential can be measured readily in the laboratory, but it is neither convenient nor desirable to measure it in the plating tank. The reaction at the cathode is much easier to follow by a knowledge of the quantity of current that reaches the cathode. If, in addition, the plater has some knowledge as to the distribution of the current over the cathode, he may then have some idea of how the plated article will be coated with metal. He will be able to predict the time required to produce a desired thickness of deposit and also have an idea of how the thickness will vary from one area to another.

Unfortunately, it is difficult to make accurate predictions regarding the distribution of metal over the cathode. In practice, the quantity of current is controlled and the current is allowed to flow for a definite period of time, after which the local thickness of metal on the plated piece is measured. If an undesirable distribution of metal is obtained, adjustments are made in the racking or positioning of the pieces or of

the anodes. In some cases, chemical adjustment of the electrolyte may improve the metal distribution.

The current allowed to flow to the cathode is in proportion to the area being plated, so that the current is expressed as current density or quantity of current per unit area. In commercial plating, the current density is expressed as amperes per square foot.

Occasionally, a plating tank is controlled by voltage. This procedure is less satisfactory than control by current density, since the tank voltage is affected by many factors other than the reaction taking place at the cathode. Tank voltage, however, is very easily measured and often gives information about changes in the plating process, such as a reduction in conducting salt content, or polarization of the anode. Plating control by tank voltage is satisfactory when the cathode area is difficult to measure, such as in barrel plating.

The Anode

The reactions taking place at the anode are almost independent of the reactions occurring at the cathode. The position of the anodes naturally has much to do with the distribution of current at the cathode, but the anodes usually operate best at a range of current densities that can be changed independently of the cathode current density by changing the anode area.

The Balanced Bath

A plating bath can be operated successfully for long periods of time if the composition of the bath is not changed too rapidly. Such changes are primarily due to:

1. Chemical decomposition.
2. Incomplete electrode reactions.
3. Drag-in or drag-out.

The bath stability can best be illustrated by consideration of several typical baths.

An acid copper bath is relatively easy to control because there is very little tendency for chemical decomposition and the reactions at the electrodes are essentially complete. This means that the electrolyte is chemically stable and that for every chemical equivalent of copper

dissolved at the anode there is a chemical equivalent of copper deposited at the cathode. Nevertheless, the bath cannot be continuously operated without control, since solution is lost from the system by drag-out every time a rack is removed. Control is further complicated in that glue is generally added to the bath to produce a finely crystalline deposit. The glue is not stable and must be controlled. This bath is typical of many acid baths where the major factor in control is the addition agent used—in this case, the glue.

An alkaline tin bath is not a typical alkaline bath, but it is a good example of a bath where care is required to maintain solution balance.

In the alkaline tin bath, the electrode reactions are not complete, i.e. the anode and cathode efficiencies are less than 100%. In addition to depositing tin, hydrogen is evolved at the cathode. And in addition to tin being dissolved, oxygen is given off at the anode. To make the problem more complex, the bath undergoes continuous chemical decomposition and the anodes must be maintained with an oxide film at all times. If the oxide film is not present or is too thick, troubles set in that throw the bath out of balance or even cause a deposit to form that is not acceptable. The bath can be controlled by regulation of bath temperature, cathode-current density, anode-current density, and by chemical analysis and proper chemical additions. The bath voltage is responsive to changes at the anodes; and since the bath is sensitive to anode changes, the voltage may be used as an aid to bath control.

A plating bath should always be kept within prescribed chemical limits whether or not the bath composition is difficult to maintain. The bath should also be used in such a way that a minimum of chemical additions is required. It is very rare that a bath does not require frequent additions, although this condition is approached when the anode efficiency is slightly higher than the cathode efficiency. Such a bath would be a perfectly balanced bath, but even in this case, drag-out would eventually remove a sufficient amount of one of the essential chemicals so that chemical additions would be required. Since additions are required to all baths, it is best to make them frequently and in small amounts, so that chemical limits are easily held. Addition of large quantities of chemicals to the plating bath often leads to trouble. For example, with a large addition of chemicals, a small error in chemical analysis is liable to result in a concentration exceeding the chemical limits on the bath. Moreover, the chemicals often contain impurities that are not harmful for small additions but that require elec-

trolysis with dummy cathodes before the bath may be used, if the additions are large.

The Equilibrium Potential

It is well to settle a few points regarding the equilibrium potential before considering some of the details of the plating process.

The well-known series of potentials for electrochemical reactions is shown in Table 1. This series has also been called the electrochemical series or the electromotive force series of elements. It is a reliable point for reference; however, it can be highly misleading if it is used as a definite guide. These potentials are equilibrium potentials. They were measured under conditions where no current was flowing and with definite quantities of dissolved salt present and at a standard temperature to obtain comparable valves.

Hydrogen is taken as the reference point on the electrochemical scale and is arbitrarily assigned a value of zero. The metal ions whose voltage is listed as positive are more reactive than the hydrogen ion when they are present in equivalent chemical quantities, whereas the metal ions having a negative voltage are less reactive than the hydrogen ion. Thus, as we go up the scale, the metal ions become more and more reactive at the cathode, i.e. they become more electropositive (attracted to the cathode), or they deposit more readily. As we go down the scale to more negative electrode potentials, the metals become more electronegative, or they go into solution more readily

Table 1   Electrochemical Potential Series

Ion	Voltage
Au^+	$+1.5$
Ag^+	$+0.7995$
Cu^+	$+0.0528$
Sn^{++++}	$+0.003$
H^+	0
Pb^{++}	-0.1264
Sn^{++}	-0.1406
Ni^{++}	-0.231
In^+	-0.336
Cd^{++}	-0.4024
Cr^{+++}	-0.509
Zn^{++}	-0.762
Na^+	-2.7125

(anodic metals).

With reference to this scale, it has been said that any metal on the scale will displace from solution all those metals that appear above it. This is true for the conditions under which the potentials were measured, but it cannot be taken as a general rule. According to this rule, if a piece of copper is immersed in a solution containing silver ions, silver will deposit on the copper. This will occur in acid solutions even though the solution contains a very small quantity of silver. However, the opposite reaction can be made to take place. That is, if silver is immersed in a concentrated acidic solution of copper, copper will deposit on the silver. In other acid solutions tin can be deposited on copper[1] even though tin is below copper on the electrochemical scale. These apparent exceptions occur because the conditions under which the experiments are carried out differ greatly from those under which the potentials were measured. However, the metals in the series are arranged according to their relative reactivity. The metals below hydrogen can be dissolved readily in acids and those very low in the table will react with water. The metals above hydrogen can only be dissolved in acids under oxidizing conditions. Thus, the table indicates chemical reactivity, but if it is to be applied to new or unusual conditions, it will be necessary to experiment or measure the potential under the new conditions. When the potential is measured during plating, it is measured under dynamic conditions and is called a deposition potential.

The Deposition Potential

The potential of an electrode and of a solution of its ions may be measured during plating. This deposition potential varies with the concentration of metal ions in the bath and is also greatly affected by the current density. As the current density is increased, polarization at the electrode increases, resulting in conditions more favorable for deposition of metals low in the electrochemical scale. Thus, it becomes possible to deposit zinc from acid solutions, whereas zinc normally dissolves in acids. One might expect that zinc could not be deposited in the presence of hydrogen ions, and under some conditions it is difficult to achieve this. If polarization does not exceed the hydrogen overvoltage, hydrogen will develop exclusive of zinc. This can take place even during the electrolysis of copper from a copper nitrate solution. Such

an electrolysis is carried out in the presence of nitric acid, and by continued electrolysis, the copper can be deposited completely from the solution. However, if the solution is heated while copper is depositing, a point will be reached where the tendency for the copper to dissolve will be greater than its tendency to plate. At this point the copper will go back into solution in the nitric acid even though the current is flowing. The behavior of copper in nitric acid solutions and that of zinc in acid solutions illustrate that to study the mechanism of deposition the measurement of deposition potentials is helpful. These potentials direct attention to the importance of polarization, overvoltage, chemical reactivity, and ability to plate in the presence of other ions.

REFERENCE

1. U.S. Patent 2,369,620.

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