Handbook on Electroplating with Manufacture of Electrochemicals
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Electroplating is an electro deposition process for producing a dense, uniform, and adherent coating, usually of metal or alloys, upon a surface by the act of electric current. The term is also used for electrical oxidation of anions onto a solid substrate, as in the formation silver chloride on silver wire to make silver/silver-chloride electrodes. Electroplating is primarily used to change the surface properties of an object (e.g. abrasion and wear resistance, corrosion protection, lubricity, aesthetic qualities, etc.), but may also be used to build up thickness on undersized parts or to form objects by electroforming.

Electrochemical deposition is generally used for the growth of metals and conducting metal oxides because of the following advantages: (i) the thickness and morphology of the nanostructure can be precisely controlled by adjusting the electrochemical parameters, (ii) relatively uniform and compact deposits can be synthesized in template-based structures, (iii) higher deposition rates are obtained, and (iv) the equipment is inexpensive due to the non-requirements of either a high vacuum or a high reaction temperature. An electrochemical process where metal ions are transferred from a solution and are deposited as a thin layer onto surface of a cathode.

In recent years, developments in electronic and chemical engineering have extended the process of electroplating to a wide range of materials such as platinum, alloy, silver, palladium, rhodium, etc. The electroplating market is an application driven market, which depends largely on the net output of the manufacturing industry. The electroplating technology allows electro-deposition of multiple layers as thin as one-millionth of a centimeter which makes it an indispensable part of the semiconductor industry. Rising demand for computing devices is expected to create significant market opportunities for electroplating service providers. Growing net output of manufacturing industry, rising demand for consumer goods which mandates more surface finishing services, growth of the electronics industry are some of the key factors driving the growth of the global electroplating market.

The book gives comprehensive coverage of Electroplating Uses, Application Manufacturing, Formulation and Photographs of Plant & Machinery with Supplier’s Contact Details. The major contents of the book are Metal Surface Treatments, Electrolytic Machinery Methods, Electroless Plating, Electroplating Plant, Electroplating of Aluminium, Cadmium, Chromium, Cobalt, Copper, Gold, Iron, Lead, Nickel, Bright Nickel, Silver, Alloy, Platinum, Palladium, Rhodium, Bright Zinc, Tin and Plastics Barrel, Zinc Electroplating Brightener, Colouring of Metals, Metal Treatments, Electrode position of Precious Metals and Stainless Steel, Case Hardening, Electroless Coating of Gold, Silver, Manufacture of phosphorus. It is a very useful book that covers all important topics of Electroplating. It will be also a standard reference book for professionals, entrepreneurs, those who are interested in this field can find the complete of Electroplating. It will be very helpful to consultants, new entrepreneurs, technocrats, research scholars, libraries and existing units.

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Sample Chapter:
Electrochemical Processing

INTRODUCTION

Electrochemical processes involve the interconversion of electrical and chemical energy by means of a reaction at an electrode. Electrical charge may be fed to an electrolysis cell to induce chemical reactions (synthesis, metal winning or refining, etc), or chemical reactions may be run in a cell to generate electricity (batteries, accumulators, fuel cells) (see Batteries). Since the electrode reaction occurs at a surface, electrochemical techniques may also be used for surface treatment (electroplating (qv), electropolishing, anodizing) (see Metal surface treatments) or machining (see Electrolytic machining methods).

Electrosynthesis was first carried out by Davy in 1807 for the production of sodium and potassium, and in 1833 by Faraday who performed the first known example of the Kolbe reaction. Today this reaction remains one of the most useful in organic electrosynthesis. Generally speaking, all chemical reactions may be performed electrochemically and there are often great advantages to be obtained in doing so: electrochemical reactions allow control of selectivity and reaction rate through the electrode potential; are inherently pollution-free; have high thermodynamic efficiency; make possible reactions at ambient temperature; can often reduce the number of reaction steps; can often use cheaper starting materials; by means of electrolytic regeneration can use catalytic quantities of chemical oxidizing or reducing agents; and can often perform a synthesis electrogeneratively.

However, disadvantages are: electrochemical engineering and technology are far less developed than chemical engineering; many reaction variables may be involved with complex interdependences; long term stability of process components is often poor; and workup of product is often costly.

THE ELECTROCHEMICAL CELL

An electrochemical cell consists of at least two electrodes (anode and cathode) that dip into an electrolyte contained in a cell or reactor housing. The cell may be constructed so that the electrolytes at the anode and cathode are separated (anolyte and catholyte). One of the first cells studied was the Daniell cell and it is used as the basis of many introductions to the thermodynamics of electrochemical processes (2). It consists of a zinc anode and copper cathode dipped into solutions of their sulfates. A porous separator prevents mixing of the two solutions. Symbolically the cell is written:

\[
\text{Cu}\mid\text{Cu}^2+\mid\text{Zn}^2=\mid\text{Zn}
\]

INORGANIC

Electrochemical process involve the transfer of electrons between an electrode and a substrate in solution. The energy required is in the range 0-3.5 h eV, and depends on the electrode material and the substrate. This is a moderate energy input in comparison to photochemical or radiation activation methods. Nevertheless, it is sufficient to produce the strongest oxidizing and reducing agents known, i.e. $\text{F}_2$ and solvated electrons, respectively. It would indeed be difficult to develop manufacturing processes for chlorine, sodium, and fluorine that improve on the electrochemical ones (products; Chemicals from brine; Fluorine).

The importance of the electrochemical processing of inorganic chemicals for the production of either elements or compounds is easily appreciated from the fact that in the U.S. they consume 6% of all the electricity generated or about 16% of the electricity used by industry. Table 1 lists the most important processes that are now practiced, however, other industrial operations that involve an electrode reaction, e.g., metal refining, (see Aluminium; Extractive metallurgy), energy sources (batteries, fuel cells, electroplating (qv), electropolishing, anodizing, electrochemical machining are not discussed in this article.

Hardware for Electrochemical Processing

The distinguishing feature of an electrochemical process is the electrolysis cell and its power supply. Like many chemical processes, the feedstock must be made up by the addition of solvents/electrolytes and...
the product must be extracted or worked-up. This often involves much additional equipment as is demonstrated by the flow sheet shown in Figure 1 of a chloralkali process. However, only the electrochemical cell and its components are discussed, not the unit operations involved.

In an electrochemical cell, feedstock is transported to the electrode/electrolyte interface. The design of an electrolysis cell is therefore based, among other factors, on optimization of; transport of electroactive species from the cell volume to the electrode surface; materials and topography of the electrode; and possible need to separate the products or reactants of the anode and cathode reactions. The main design possibilities of electrolysis cells are summarized in Table 2.

Industrial cells for inorganic processing seldom employ pumps to provide convection. Usually transport of the electroactive species to the working electrode is enhanced simply by the gas generation within the cell. Examples are the cells for fluorine (Fig. 2), chlorate (Figs. 3 and 4) and aluminium production (Fig. 5). Gas generation at the counter-electrode in the Krebs (Fig. 3) and Diamond Shamrock/Huron Chemicals (Fig. 4) chlorate cells are employed not only for local stirring within the electrolysis compartment but also to maintain circulation to the bulk reaction volume. The Alcoa cell for the production of aluminium by the electrolysis of AlCl₃ (Fig. 5) also relies on gas pumping of the electrolyte. In this case, the product of the secondary electrode reaction (chlorine) can exit only from one side of the electrolysis chamber. A clockwise flow of electrolyte is thereby induced.

**Electrolytic Machinery Methods**

A tool composed of a harder material is used to shape a given metallic sample of material mechanically according to a specified pattern. As in the aerospace industry, the ever-increasing development of high strength, high temperature alloys places extreme demands on the hardness of the material from which a tool may be fashioned. Consequently, one is forced to employ grinding techniques that are not only laboriously slow and highly expensive but also severely limited with respect to the intricacy of the part to be machined. It, therefore, becomes necessary to find new methods for machining these new, extremely hard alloys.

One of the promising novel machining methods is the atom by-atom removal of a metal by anodic corrosion which has been called electrochemical machining (ECM). Because the metal is removed atom-by-atom, ECM affords the opportunity to machine a given workpiece without work-hardening, burring or smearing the metal, without regard to the hardness of the metal being cut, and virtually without tool wear.

In a chemical reaction, electron transfer between the reacting species occurs by the oxidation (loss of electrons) and the reduction (gain of electrons) taking place at the same site, and the energy liberated appears as heat and possibly light. For an electrochemical reaction to occur, the oxidation must take place at a site remote from the reduction. This situation is accomplished by interposing an electrolyte between the conductor (anode) at which oxidation occurs and that (cathode) at which reduction occurs.

When iron (qv) dissolves, ferrous ions enter the electrolyte by donating electrons to the anode. Eventually, the anode become so negative that further dissolution of iron is prevented by the electrostatic attraction between negatively charged anode and the positive ions in solution. If a sink for the electrons on the anode is provided by a battery that is connected in an external circuit between the anode and cathode, continuous dissolution of the iron anode can be obtained. Current is carried in the circuit by electrons (electronic conduction), and internally by ions (electrolytic conduction) through the electrolyte. The dissolution of metal at an anode driven by an external source of current, such as a battery or rectifier, is termed anodic corrosion.

**PRINCIPLES OF THE ECM PROCESS**

In the ECM operation, the metal workpiece to be shaped is the anode, and the tool that produces the shaping is the cathode. The electrodes are connected to a low voltage source of direct current (dc). The anode and cathode are held in position by a properly designed fixture, and a solution of a strong electrolyte
is pumped between the two electrodes. If there are no side reactions, the passage of each Faraday of electrical charge (96,500 C) results in the dissolution of an equivalent weight of metal. For the ECM process to be commercially competitive with conventional machining methods with a metal removal rate of ca 0.3 cm3/s, the electrical charge must be passed at a rapid rate requiring the use of very high current densities (50–500 A/cm2). In many cases, the upper limit to the current density that can be attained is determined by the availability of high capacity rectifiers. Voltages applied between the anode and cathode is normally 5-25 V.

The Solution Gap

At these high current densities, the solution path through which the current flows must be kept small to reduce an otherwise intolerably high IR loss. The typical gap between anode and cathode for acceptable electrochemical machining is 0.05-9.3 mm. Because metal is removed during the ECM process, the gap widens during the machining operation. The current density (ie, the metal removal rate) falls to low values unless relative motion between anode and cathode (ie, the feed rate) is maintained by a mechanically driven feed system. Either the anode is fixed and the cathode is moved or vice versa. Should the feed rate, for any reason, become too large for a given metal removal rate, a possible short circuit between the electrodes results, causing catastrophic damage to the tool and workpiece by spark erosion, thermal melting, welding, and tearing of the metal. Therefore, it is necessary to incorporate a protective device based, usually, on the detection of an increasing rate of current which shuts down the current within microseconds when the gap becomes smaller than a specified, safe distance. Because there is a balance established between opposing forces of feed rate, which tends to narrow the gap, and of current density, which tends to widen it, an equilibrium or steady-state gap distance between workpiece and tool is reached quickly for a given feed rate and current density within certain boundary values.

Electrolytes

The current is conducted across the gap by the ions of a suitable electrolyte. Solutions of acids (HCl, H2SO4) have been used, but these electrolytes are very corrosive to the structural material of the machine. In addition, metal dissolved from the anode can be plated onto the cathode, thus causing the shape of the tool to change, and producing an unwanted change in shape of the workpiece. Alkaline electrolytes (NaOH, KOH) form protective anodic films on the workpiece surface and prevent metal dissolution. An exception is tungsten (qv), which can be machined only in strong alkali. The only practical electrolytes are neutral salt solutions in which a metal ion precipitates as a sludge. The most universally used salt in NaCl because of its availability and low cost. To reduce the IR drop in the gap, strong NaCl solutions of 5-25 wt % must be employed.

Any parameter that changes the conductivity of the electrolyte changes the current density, and hence, the metal removal rate.

Electroplating of Aluminium

Many metals are electroplated on aluminium to obtain various decorative and functional finishes. Aluminium has many desirable engineering properties. Aluminium has replace copper in electrical switch gear industry, because of having excellent current carrying capacity and relative cheapness. The high contact resistance of aluminium can be overcome by treating with the Alstan/Zincate process with overplating of copper/tin/silver.

Aluminium is difficult to electroplate than the common heavier metals because:

(a) It has high affinity for oxygen,

(b) Most metals used in electroplating are cathodic to aluminium, so flues in the coating lead to localised galvania corrosion. The electrodepotentials of several common metals against pure aluminium are given in Table 1.

Table 1: Electrode Potential of Several
Metals against Aluminium

<table>
<thead>
<tr>
<th>Metal</th>
<th>Potential (mv)</th>
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<tbody>
<tr>
<td>Magnesium</td>
<td>850</td>
</tr>
<tr>
<td>Zinc</td>
<td>350</td>
</tr>
<tr>
<td>Cadmium</td>
<td>20</td>
</tr>
<tr>
<td>Pure Aluminium</td>
<td>0</td>
</tr>
<tr>
<td>Mild Steel</td>
<td>+50 to 150</td>
</tr>
<tr>
<td>Tin</td>
<td>+300</td>
</tr>
<tr>
<td>Brass</td>
<td>+500</td>
</tr>
<tr>
<td>Nickel</td>
<td>+500</td>
</tr>
<tr>
<td>Copper</td>
<td>+550</td>
</tr>
<tr>
<td>Silver</td>
<td>+700</td>
</tr>
<tr>
<td>Gold</td>
<td>+950</td>
</tr>
</tbody>
</table>

Aluminium will protect it. Those below cause aluminium to corrode preferentially.

Hence, in order to get satisfactory deposition on aluminium, the natural oxide film which forms on its surface should be removed. It can be done either mechanically or chemically or suitably strengthened or modified.

The few common practices are given below:

1. Surface roughening or roughening plus metal deposition by immersion, before electroplating.
2. Anodic oxidation followed by electroplating.
3. Direct zinc plating before plating with other metals.
4. Immersion deposits of zinc before plating with any other metal (zincating)
5. Immersion coating of tin or nickel before any other coating (Alstan/Bondel Process)

Surface Roughening

It is done either by mechanical abrasion or by chemical etching to assist in bonding the electrode deposits to the aluminium surface. This process is used generallys for the application of hard chrome deposits to the aluminium engine parts, such as piston, etc.

Anodising

This process is also used as method of surface preparation prior to electroplating. However, the adherence of the subsequent electro deposit is limited. When subsequent plating is involved, control on anodising process is critical.

Zincating

The most widely used immersion process of coating on aluminium is Zicate process it is necessary that cleaning and conditioning treatments produce a surface of uniform activity for deposition of zinc film.

When it is ensured that the surface is free from oil/grease, by solvent/vapour degreasing, the metal is subjected to milk etching type of alkaline cleaner for 1-3 minutes.

Electroplating of Cobalt

Cobalt coatings are very similar to nickel coatings. Since coabalt metal costs several times as much as nickel the interest in cobalt plating has been relatively small and intermittent. According to forester cobalt plating replaced nickel plating in Germany during World War I but disappeared again thereafter. Berger indicates some commercial use of cobalt on printing plates because of its hardness and on mirrors and reflectors because of its high reflecting power and its resistance to oxidation. On this last point. Blum and Hogaboom state that cobalt is less resistant than nickel to corrosion attack by printing inks for example and it oxidizes more readily at elevated temperatures.

Isaac Adams, the father of commercial nickel plating, recommended double salts of cobalt with ammonium or magnesiu and laid down the same rules for the preparation and operation of cobalt baths
Because of the nickel shortage, cobalt salts were added to commercial bright nickel baths in 1968 and 1969 to produce alloy coatings containing up to 50% cobalt. These alloys have better mechanical properties than the individual metals and are said to be equivalent to sulphur containing nickel when combined with chromium for outdoor protection. Bright levelling unalloyed cobalt decoratively plated with chromium was also used successfully for some indoor and mild exposure applications.

Magnetic properties of cobalt and cobalt alloys are of interest in electronic applications such as memory drums, disks, cards and tapes, particularly in the computer industry.

Several cobalt alloys have been investigated for electroforming parts for the aerospace industry. In addition to the properties import for electroforming the low coefficient of friction and excellent wear resistance of hexagonal close-packed (hcp) cobalt and its alloys the high hot hardness of cobalt-molybdenum and cobalt-tungsten alloys the interesting mechanical properties (especially strength after heat treatment) of cobalt nickel and other alloys are opening new fields for industrial cobalt alloy plating. Dispersions of oxides (Al2O3 ThO2) or intermetallic compounds (carbides etc.) in cobalt alloy electro deposits promise a new type of material with unusual mechanical properties such as resistance to creep, high-temperature oxidation and sulfidation, wear and galling.

Principles

The baths commonly considered are the single and the double cobalt salt baths; both baths can be operated at much higher current densities than the corresponding nickel salt baths.

Baths containing fluorides instead of chlorides have been suggested with claims for better buffering and for whiter deposits than can be obtained with straight cobalt chloride baths. However, the simultaneous use of boric acid and hydrofluoric acid in a double cobalt bath results in a tendency toward pitting, pin holes and poor adherence, where as hydrofluoric acid alone without boric acid is beneficial.

Several other cobalt baths have been reported, including cobalt triethanolamine and cobalt sulfamate baths, both of which may merit further study, cobalt thiocyanate baths, which appeared discouraging, coordination compounds and fused anhydrous cobaltous chloride baths. Cobalt flakes have been prepared by adding 0.4 to 0.6 g/1Co(NH2)2 to the sulphate bath, then breaking up the deposit by impact grinding.

Electroplating of Iron

Iron plating is used principally for applications which depend on the desirable physical properties of iron and on its low cost. The early literature on iron deposition, which was concerned with both its commercial applications and its electro-refining, has been comprehensively in a monograph.

A present application is a process reported in 1930 in which intaglio plates for printing government currency and bonds are made by depositing a nickel face backed by a heavy deposit of electrolytic iron from a hot chloride bath.

Iron plating was used during World War II to make electrotypes and to coat stereotypes in order to conserve nickel and copper. During the same period the United States Rubber Company electroformed iron molds for rubber, glass and plastics. Sodering tips are plated with iron commercially and undoubtedly there are many other small-scale applications.

Electrodeposition of iron as a means of producing iron powder for powder metallurgy is an application.

There are several reasons for this persistent interest in iron plating. Iron is cheap and abundant. It can be deposited as a hard and brittle metal which by heat treatment, can be rendered soft and malleable, or as a soft and ductile metal to which surface hardness can be imparted by carburizing, cyaniding, or nitriding. The fatigue strength of surfaces prepared by case hardening electrodeposited iron has been reported equivalent to the best of commercial rolling - element bearing material. On flat or rounded surfaces that are not too deeply indented, deposits of any reasonably thickness can be produced. Electrodeposited iron can be welded readily other metals can be easily plated on it and in the soft state if has superior drawing
properties. Electrodeposited iron is relatively resistant to corrosion as would be expected from its high purity. The contrary opinion is probably due to failure to rinse deposits completely free of electrolyte traces. The throwing power of iron baths is comparable to that of nickel baths.

An important problem with iron plating that has limited its usage to specialized or to high volume applications is that despite usually lower costs for anodes or solutions, the expenditures for capital equipment and maintenance may be high for iron plating that for other more commonly used plating baths. Special high temperature or corrosion resistant equipment may be required to heat, agitate, filter, or ventilate the iron plating bath. Also, unless used regularly, the solution will oxidize gradually. The time and effort required to restore the electrolyte to an operable condition may overwhelm the economics of depositing a lower cost metal.

Principles

Practically all iron is plated from acidic solutions of iron (ferrous) salts. The presence of iron in the iron (ferric) state in these baths, in an appreciable concentration, is undesirable because it lowers the cathode efficiency for depositing the metal and it may cause deposits to be brittle, stressed and pitted. In practice it is not difficult to maintain the concentration of iron ion at a harmless level. Until recently, practically all iron was plated from baths containing iron sulphate, iron chloride, or mixtures of the two. In recent years iron fluoborate and iron sulfamate baths have been used to some extent.

The Iron Chloride Bath

In rapid plating, where a hot and corrosive bath may be tolerated, the chloride bath is often used. Thick deposits can be obtained if care is exercised in the control of the bath. A finer-grained deposit could be obtained by the addition of manganese chloride to the bath. The following composition is typical.

| Table 1 : Formulation for Iron Chloride Bath |
| Ingredients | Quantity |
| Ferrous Chloride | 300 g/1 or 40 oz/gal. |
| Manganese Chloride | 5 g/1 or 0.67 oz/gal. |
| Temperature | 160 - 220°F |
| Current Density | 50 - 75 amp./sq.ft. |
| Anodes | Ingot iron |
| pH | 1.5 - 2.0 |

The bath can be easily prepared from readily soluble ferrous chloride. Commercial ferrous chloride, however, contains some ferric salts that are detrimental to the bath. In the presence of ferric ion, a rough deposit will be obtained that is unsuitable for any iron-plating application. By working the bath in the presence of a small excess of hydro chloride acid, the ferric ion can be reduced to ferrous iron. If too much acid is present, a deposit cannot be obtained on electrolysis.

But if high purity iron is hung in the bath, the acid will have a reducing action on the iron to eliminate the ferric ion. Complete reduction can be recognized by the change in colour of the bath from a brownish green to a pure green. After the bath is reduced and worked, the pH is adjusted and the bath is ready for operation. High temperatures must be used since the deposit becomes brittle with decrease in temperature.

Rubber, or plastic-lined tanks or ceramic-lined tanks must be used because this high-temperature, low-pH bath is extremely corrosive to metals.

The pH is the critical control factor in the iron chloride bath. If acid is not added frequently the pH will rise and a brittle deposit will be obtained. However, if too much acid is added, the cathode efficiency will decrease rapidly but excess acid is used up by chemical reaction with the iron anodes so that small excesses are rapidly consumed.

This variation in the rate of chemical attack with change in pH makes it practical to add acid continuously. A small amount of acid present at all times, even though the bath is not being used, keeps the
iron in the reduced state.

If the bath is operated within the recommended conditions of high temperature and controlled pH, excellent results will be obtained at high cathode efficiency.

High purity iron anodes must be used. If the carbon content of the iron is much over 0.02%, carbides will be left on the surface. The carbides will be loose, will become suspended in the bath and will eventually cause a rough plate. In any case, it is recommended that the anodes are bagged in some suitable material.

Through variation of the bath conditions, Stoddard obtained tensile strengths of 50,000 to 1,10,000 pounds per sq. inch and elongations of 6 to 50%.

Small amounts of noble metals, such as copper or arsenic will contaminate the iron bath. These can be removed by electrolysis. Organic impurities can be removed by treatment with activated carbon in the same manner as from acid baths in general.

Electroplating of Nickel
Ni coatings have long been applied to substrates of steel, brass, zinc and other metals in order to provide a surface that is resistant to corrosion, erosion and abrasive wear besides plating plastics component in order to give an attractive metallic appearance.

The importance of nickel plating industry can be gauged by the estimated 60,000 tonnes of Ni consumed each year in the western world i.e. 1 tonne in every 8 tonnes consumed in all application.

Types of Ni Solutions
Most nickel electroplating is carried out in solutions based on a mixture of NiSO4, NiCl2 and H2BO3.

Typical solution is:

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel Sulphate NiSO4 7H2O</td>
<td>240 - 30 g/l</td>
</tr>
<tr>
<td>Nickel Chloride NiCl2 6H2O</td>
<td>40 - 60 g/l</td>
</tr>
<tr>
<td>Boric Acid H3BO3</td>
<td>25 - 40 g/l</td>
</tr>
</tbody>
</table>

Operating conditions for the Watts Soln.

| Temperature | 25-50°C |
| Agitation   | Usually Air |
| pH          | 4.0-5.0 |
| Cathode Current Density | 3-7 A/dm2 |
| Mean Deposition Rate      | 40-90 µm/n |

The watts solution is relatively cheap and simple solution and is easy to control besides its ability to be relatively less affinity towards impurities.

Engineering Application
Nickel electro deposits are applied for their physical and mechanical properties and they are rarely applied brightness and leveling. Engineering Ni coatings are used on new parts and also in the reclamation of worn, corroded or mismachined parts.

Ni And Ur Plating Butterworths

Electroplating Baths used
Watts Nickel Bath
Most commercial Ni plating solution are based on the one named after Watts who first introduced a bath having the formulation:

\[
\begin{align*}
&\text{NiSO}_4\ 7\text{H}_2\text{O} : 240\ g/l \\
&\text{NiCl}_2\ 6\text{H}_2\text{O} : 20\ g/l \\
&\text{H}_3\text{BO}_3 : 20\ g/l
\end{align*}
\]

The Rame Watts bath now used to cover a range of solutions whose composition vary within the
range as shown in the table 2.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Cons. Range (g/1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiSO_4 6H_2O</td>
<td>150 to 400</td>
</tr>
<tr>
<td>NiCl_2 6H_2O</td>
<td>20 to 80</td>
</tr>
<tr>
<td>OR</td>
<td></td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>10 to 40</td>
</tr>
<tr>
<td>H_3BO_3</td>
<td>15 to 50</td>
</tr>
</tbody>
</table>

The chloride ion sometimes being introduced in the form of NaCl. NaCl being cheaper and is satisfactory for most purposes.

NiSO_4 is the principle ingredient. It is used as main source of nickel ion because it is readily soluble, relatively cheap commercially available and is a source of uncompleted nickel ion.

In Ni plating solution the activity of the nickel ions is governed by conc. of nickel salts in solution. The presence of chloride has two main effects. It assist anode corrosion and increase the diffusion coefficient of Ni ions thus permitting a higher limiting C.D. Boric acid is used as a buffering agent in watts Ni solution in order to maintains the pH of the cathode at predetermined value. Boric acid solutions of the strength used in watts solution have pH of about 4.0 due to the Ni-ions.

Hard Watts Bath

This is mainly used for engineering proposes. The increase in hardness in achieved at the expense of other properties. The incorporation of ammonium ions or organic additions in the plating solution results in modification of structure and certain properties such as ductility are adversely affected. On the other hard this solution does provide a melens of producing a hard deposit when this is the most important feature required for a particular purpose.

Nickel Sulphate Bath

A simple solution of NiSO_4 in water has little commercial application, but sound deposits can be produced at reasonable efficiency if boric acid is added as buffer. However, for commerical application the sulphate plus chloride soln. of the watts type is superior in performance, except with inert anodes.

Nickel Sulphonate Bath

Small volumes of plating solution based on Ni salts other than Ni sulphate and Ni chloride are used for certain purposes and the commonest of these is the Nickel sulphate solution. The advantages of this soln. are in the high rates of deposition possible and low in the deposit. It is more expensive plating solution than sulphates but is used where the aforementioned properties are important for purpose such as electrotypes in the printing industry and for making gramophone record stampers.

The process is mainly used for heavy Ni deposition and electro forming. The essential features of the solution are similar to those for nickel sulphate the pH of the bath being between 3 and 5 and most often between 3.5 and 4.5

Electroplating of Alloy

Electroplating - It normally indicates depositing of one metal one substrate metal. The deposit is of high quality rather of high purity. But sometimes the phenomenon of deposition of more than one metal takes place termed as alloy plating. To avoid rusting NiFe, Ni-W, CD-Zn and Zn-Sn alloys are used.

The most important and characteristics factor in the alloy plating is the metals with common electrochemical properties can only be employed and electroplating of alloys is much difficult.

Alloy plating for solution of simple ions is limited because of the deposition potential of the metals. These potential can be changed to certain extent by changing concentration, acidity, temperature, current density etc.

In alloy plating one metal is termed as noble metal i.e. one metal deposits more readily than the other.
It is necessary then to use the term noble metal in the potential system and is independent of the cone ration of the two metals. Potential system obtains the percentage of metals in the deposit is dependent on the ratio of metal in the soln.

In alloy plating there are certain problems which are not in the single metal plating. For alloy plating in solution salt of both metals are mixed with different quantities e.g. Cu and Zn make an alloy called brass and its chemical equivalent are different. Due to slight from the process can lead either of the metal getting deposited. Similar difficulties may arise while selection of anode.

Electrodeposition of Zinc-Iron Alloy

In recent years, many developments have taken place in production of galvanised coatings on steel and efforts have been made from time to time to enhance the corrosion resistance of the coating. Zinc-Iron alloy is such development. These alloys were mainly deposited from sulphate or chloride baths. It has been reported that a Zn alloy containing 15-25% iron has good weldability and corrosion resistance and is electroplated commercially on steel strip. For automobile application Further Zn-alloy containing 50% or more iron provided better paissntablity.

Table 1: Bath Composition

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrous ammonium sulphate (g/l)</td>
<td>350</td>
</tr>
<tr>
<td>Zinc chloride (g/l)</td>
<td>21-105</td>
</tr>
<tr>
<td>Glycine (g/l)</td>
<td>10</td>
</tr>
<tr>
<td>Citric acid (g/l)</td>
<td>2</td>
</tr>
</tbody>
</table>

Operating Conditions:

<table>
<thead>
<tr>
<th>pH</th>
<th>2-2.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>323-328°K</td>
</tr>
<tr>
<td>Current density</td>
<td>0.5-1.5 KA/m²</td>
</tr>
<tr>
<td>Anode:</td>
<td>Equal areas of zinc and iron.</td>
</tr>
</tbody>
</table>

For electroplating conventional sequence of plating operations are. The electrolyte is prepared. With the rise in the zinc ion content, the brightness was decreased and ceased after 20 gpl of zn. The bright range is present only for PHZ and is wider at the temp. of 323°K.

Lead-Tin Plating

The process is same as in case of tin plating. In this tin is added to the solution and tin-Pb anodes are used to control composition.

<table>
<thead>
<tr>
<th>Tin</th>
<th>11 gm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>200 gm</td>
</tr>
<tr>
<td>Fluobric acid</td>
<td>80 gm</td>
</tr>
<tr>
<td>Gelatine</td>
<td>5 gm</td>
</tr>
<tr>
<td>Water</td>
<td>1 lit.</td>
</tr>
</tbody>
</table>

Current density of the anodes is maintained at 10-40 amp./sq.ft. Rubber lined tanks are used. Tin is not stable in acid and oxidises to starric tin.

Speculum Plating

Due to the less copper and tata cyanide and increase in the Sn of the bronze solution alloys having 50-60% copper may be obtain. The deposit is bright which attractive and decorative.

The solution used is:

<table>
<thead>
<tr>
<th>Sodium stannate</th>
<th>90 gm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single copper cyanide</td>
<td>11 gm</td>
</tr>
<tr>
<td>Sodium cyanide</td>
<td>28 gm</td>
</tr>
<tr>
<td>Caustic soda</td>
<td>12½</td>
</tr>
</tbody>
</table>
Ammonia : 1 ml

In one it, of distilled water 9/10 of the water is heated to 60ºC and all the content ammonia are added to it the rest 1/10 of water is added. The NH3 is gradually mixed in this solution to get the good reaction, NH3 is mixed in 5 ml water then used in the solution. While plating temp, is maintained at 60-55ºC and the limit should not be increased.

Electroplating of Bright Zinc

Processes, centering round the production of bright zinc deposits have been developed and commercially operated on a considerable scale as a result of intensive research which has resulted in much technical progress in this field during the last 10 to 15 years. The interest in bright zinc plating is directly connected with the economics entering into the two competing metal finishing processes, cadmium plating as opposed to zinc plating applied primarily for the prevention of corrosion of ferrous material.

Bright Zinc-plating Processes

While most of the electrolytes producing bright zinc are of the cyanide type, more recently solutions have been advocated based on the acid-zinc sulphate electrolyte. Bright zinc plating may be obtained from a weak acid electrolyte of the following composition:

ZnSO4 7H2O : 430 gm/litre
A12(SO4)3 18H2O : 30 gm/litre
Na2SO4, 10H2O : 50-150 gm/litre

To this is added some three or five grams per litre of 2,6 or 2,7 sodium naphthalene disulphonate, while thiourea is another useful additional agent which may be added to the solution.

The pH of this solution is maintained at between 4 and 4.5 and the current density employed at a bath temperature which is below 25ºC varies from 30 to 80 amps, per sq.ft.

The brightening agent does not appear to help the notoriously poor throwing power of the acid-zinc electrolyte and this is one of the drawbacks of the process.

Most of the cyanide solutions contain the three essential components of this type of electrolyte, namely, zinc-cyanide, sodium cyanide and caustic soda, the brightening agent being additional: a wide range of “brighteners” occurring in the literature. The latter for example, may be one of the colloids commonly employed in brightening deposits e.g. of the gelatin, dextrin, glucose, etc. class, or complex aromatic or aliphatic organic materials have been specified. For example, a recent patent advocates on aromatic aliphatic ether containing an aldehyde group. Another suggests the use of a condensation product of a phenol and an aldehyde, together with a soluble compound of one of a number of metals, which include molybdenum, chromium, cobalt, manganese etc. A further patent utilises as the brightening agent an oxygen containing heterocyclic compound e.g. piperonol. Another suggests the addition of approximately 0.25 gram per litre of vanillin, veratraldehyde, anisaldehyde, 2,3-dimethyl oxybenzaldehyde, or 0-methoxy benzaldehyde and a soluble metallic salt, particularly compounds of such metals as molybdenum, chromium, manganese, cobalt, nickel etc. The range of possible brightening agents thus seems to be extensive.

Chemical Control

While the addition agent is present in relatively small quantity, one of the most essential features in maintaining a bright deposit is the careful control and progressive adjustment of the concentrations of the sodium cyanide, metallic zinc and caustic components respectively. It is particularly important to maintain a constant ratio of the total sodium cyanide to the metallic zinc, this being a critical factor.

Electroplating of Barrel

Barrel plating has been developed specially for handling small articles in quantities and in many cases this process has a number of advantages over the original suspended anode method. The anode insulated by a vulcanite cover is situated at the base of the barrel.
The barrel itself is made of welded steel internally lined with vulcanite and is mounted on a swivel arrangement, which permits immediate removal of the work by dumping it into a suitable container for transfer to the drier. Electrical contact is made through an insulated rod passing through the centre of the shaft and directly connected to the anode the current returning to the plating dynamo or rectifier by way of the barrel and framework of the machines.

An important feature of this type of barrel is that it can be relined with vulcanite at very small cost and it is also easily and quickly rinsed for different kinds of plating or barrelling.

The use of barrels for electroplating small articles in bulk is the most efficient and economical means of dealing with those goods which are of suitable size and shape for this method of plating (such as screws, studs and buttons) - having no parts which are liable to “bind” or “mass” together when the barrel revolves. No wiring up is necessary in barrel plating and the elimination of this operation is a great advantage: nevertheless its absence entails the need of care in loading. A plating barrel should never be loaded above the capacity stated by the maker, nor should articles of unsuitable shape be loaded. In either event the goods will either mass or mask one another and perfect deposition will be impossible.

Barrels are constructed for all plating processes - the containers vary for different solutions - and selection depends upon the particular process of electrode position and the required capacity. Incidental advantages of barrel plating are that while the articles are receiving the deposit of metal, they are rubbing together and become highly burnished and the deposit, mechanically closed by the continual rubbing, is close grained and durable. These advantages would be nullified by overloading or loading with unsuitable goods. Several types of barrels are made to meet the requirements of different industries, for plating any of the metals usually electro-deposited on goods of sizes and shapes ranging from gilded wedding rings to copper (and oxidised) door handles. The solution to be used determines the material for the vat, whether timber, glazed stone-ware, or iron, the latter in some cases rubber lined. Timber vats are used for nickel and acid zinc only: an iron tank is required for cyanide, copper, cyanide zinc, brass, cadmium and tin. Rubber-lined tanks may be used for any solution. Barrels are also made without centre spindle through the container for plating wire goods in straight lengths.

In one type of plating barrel the mechanical gear is arranged independently of the vat and as the container for the good’s is made of non-metallic material without metallic fittings, perfect insulation is obtained. Incidental, this gets rid of the objection of the growth of deposit on metallic fittings in the old types. Articles require swillings out and drying after barrel plating and a swill vat is usually attached to the barrel, with the exceptions referred to latter.

In one form, the barrelling machine does not require a separate vat, the plating solution being contained in the outer vessel and remaining their undisturbed when the goods container is lifted out for swilling and emptying.

Electropolishing of Stainless Steel

Electrolytic polishing of a metal is a method of imparting smartness and brightness to a metal surface by removal of a thin surface layer. The degree of smoothness and brightness obtained on the electropolished surface depends on the initial surface roughness. Electropolishing produces bright surfaces not usually attainable by other mechanical methods. One very important advantage of electrolytic polishing over the buffing burnishing methods is that the surface is not cold worked. The surface is metallurgically clean after electropolishing, free from zones and fresh foreign inclusions due to cold working and abrasive particles respectively.

Application

Refrigerator, shelves, springs wire assemblies like baskets, chains fabricated light sheet material parts like table ware, kitchen tools, surgical instruments and the like are more advantageously and economically polished by the electrolytic techniques.
Baths

The recommended bath compositions and operating conditions are given in Table 1 (i to vi).

The baths have some serious limitations and do not fulfill the conditions for an ideal electropolishing bath such as:

(a) Stability,
(b) Simplicity.
(c) Low power consumption i.e. low operating voltages and low current densities.
(d) Wide current density range to get the same finish all over.
(e) Ease of maintenance i.e. no frothing or sludging or decomposition of the bath constituents and,
(f) Low operating costs.

Table 1: Various Electropolishing Baths

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Bath Composition</th>
<th>Conditions of Operation</th>
<th>Reference No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Phosphoric Acid (1.75)</td>
<td>64% by vol.</td>
<td>32-40 amp/dm²</td>
</tr>
<tr>
<td></td>
<td>Sulphuric Acid (1.84)</td>
<td>13% by vol.</td>
<td>45°C (i)</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>23% by vol.</td>
<td>2-6 volts</td>
</tr>
<tr>
<td>2.</td>
<td>Sulphuric Acid</td>
<td>40% by vol.</td>
<td>112 amp/dm²</td>
</tr>
<tr>
<td></td>
<td>Glycerine</td>
<td>46% by vol.</td>
<td>82°C (ii)</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>14% by vol.</td>
<td>4-25 volts</td>
</tr>
<tr>
<td>3.</td>
<td>Phosphoric Acid (1.75)</td>
<td>47% by vol.</td>
<td>72 amp/dm²</td>
</tr>
<tr>
<td></td>
<td>Glycerine</td>
<td>49% by vol.</td>
<td>110-1120°C (iii)</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>4% by vol.</td>
<td>14 volts</td>
</tr>
<tr>
<td>4.</td>
<td>Phosphoric Acid (1.75)</td>
<td>100% by wt.</td>
<td>16 amp/dm²</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40-95°C</td>
<td>5 minutes</td>
</tr>
<tr>
<td>5.</td>
<td>Sulphuric Acid</td>
<td>19% by wt.</td>
<td>8-64 amp/dm²</td>
</tr>
<tr>
<td></td>
<td>Citric Acid</td>
<td>76% by wt.</td>
<td>50-120°C (iv)</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>5% by wt.</td>
<td>½-3 minutes</td>
</tr>
<tr>
<td>6.</td>
<td>Phosphoric Acid</td>
<td>40-45% by wt.</td>
<td>40-70 amp/dm²</td>
</tr>
<tr>
<td></td>
<td>Sulphuric Acid</td>
<td>34-37% by wt.</td>
<td>70-80°C (v)</td>
</tr>
<tr>
<td></td>
<td>Chromic Acid</td>
<td>3-4% by wt.</td>
<td>5-15 minutes</td>
</tr>
<tr>
<td>7.</td>
<td>Phosphoric Acid</td>
<td>50% by wt.</td>
<td>12-45 amp/dm²</td>
</tr>
<tr>
<td></td>
<td>Sulphuric Acid</td>
<td>50% by wt.</td>
<td>40-60°C (vi)</td>
</tr>
<tr>
<td></td>
<td>Lactic Acid</td>
<td>30-45 ml/L</td>
<td></td>
</tr>
</tbody>
</table>

From the literature, survey made, it appeared that the sulphuric acid phosphoric acid-glycerol bath closely approaches the ideal conditions. But details of operating data were not available.

Lead and Its Compounds

Discovery

Lead was known to mankind from pre-historic times and it was one of the seven metals recognized from the very earliest times. It was known to the Egyptians in 1200 B.C., while Romans and Greeks mined lead in considerable quantities in 200 B.C. The alchemists represented lead by the symbol of Saturn.

Mineralogy

Lead occurs chiefly as the sulphide or galena, PbS, which is hydrothermal in origin. Lead ores are found in veins and lodes or in fissures which are of magnetic sources. Other ores which occur in quantities sufficiently large to be mined include: Anglesite, PbSO₄, Cerussite, PbCO₃; Matlockite, PbCl₂. PbO, Lead occurs in the Northern Shan states in Burma and is worked upon by the Burma Corporation Ltd.
Extraction—Two principal methods are used for the extraction of lead from its ores. Smelting may be carried out in a blast furnace or in a reverberatory furnace, the latter method is gradually becoming obsolete.

Smelting in a Blast Furnace

Concentration—The ore is concentrated by the froth-flotation process. This consists in suspending the finely ground ore in water with a required quantity of oil, and stirring the mixture vigorously with a blast of air. The gangue particles which are wetted by the water sink to the bottom and are rejected. The sulphide ore is wetted by oil and the froth that rises up carries the ore and is skimmed off.

Roasting—The ore is mixed with lime and the mixture is roasted in a massive crucible. Inside the crucible a blast of air is passed through a grating at the bottom as represented in Fig. 1. The crucible is mounted on a trunnion closed with a conical hood provided with a suction to remove the fumes. The former arrangement enables the contents to be discharged at the end of the process. At the bottom of the crucible is a layer of fuel—generally coal, and above that a mixture of the ore and lime is charged. The fuel is burnt and the blast of air switched on. The sulphur present in the ore burns to sulphur dioxide and the sulphide ore is converted to the oxide.

\[
S + O_2 \rightarrow SO_2
\]

\[
2PbS + 3O_2 \rightarrow 2PbO + 2SO_2
\]

A part of the ore may be converted to lead sulphate.

\[
PbS + 2O_2 \rightarrow PbSO_4
\]

The lime acts as a flux. It allows free excess of air into the ore, and prevents the mass from becoming a lump before the oxidation is complete.

Chemistry of Sodium

Mineralogy

Sodium like other alkali metals does not occur free in nature but in combined state, it forms about 2.36 per cent, of the earth’s crust. The important compounds of sodium in order of commercial importance are given in the sequel.

- Sodium chloride, NaCl.
- Sodium nitrate, NaNO3
- Sodium carbonate, Na2CO3
- Borax, Na2B4O7. 10H2O.
- Soda-fersper, NaAlSi3O8

Metallurgy

Sodium is obtained on a commercial scale in two different processes: (a) Down’s Process—by the electrolysis of sodium chloride; (b) Castner’s Process—by the electrolysis of sodium hydroxide.

Down’s Process—Electrolysis of Sodium Chloride

This is the cheapest method of getting sodium and the additional advantage is that chlorine is obtained as the by-product. At the same time it should be remembered that there are certain difficulties encountered in this process viz., it is more difficult to keep sodium in a state of complete fusion than is the case with sodium hydroxide, since the former melts at 800°C, while the latter at 318°C. At the working temperature of the plant, sodium chloride, sodium and chlorine exert a fairly high corrosive action on the materials of construction. In the vicinity of 800°C. sodium forms a metallic fog or a colloidal solution with molten sodium chloride, so that the removal of the metal is rendered almost impossible.

Down’s process embodies certain unique attempts to solve some of the above difficulties. It consists of an iron vessel arranged as represented in Fig. 1. The carbon anode is stout and situated at the bottom, while the cathode is of copper or iron. The sodium generated at the cathode, being lighter than fused salt,
rises quickly to the surface and is collected in the sodium collector which stands just above the cathode. The collector delivers the sodium to a closed compartment from which it is drawn out at intervals. Fresh salt is added from time to time and the process is continuous.

Although sodium chloride fuses at 800ºC, the cell is operated at a lower temperature viz., 600ºC. This is successfully carried out by the addition of certain substances such as calcium chloride to the bath. The current efficiency is over 80 per cent and the cells are so constructed as to take 20,000 amps. The operating voltage lies between 7 to 8, while the decomposition voltage of sodium chloride at 600ºC is 3.53.

Details regarding the Downs sodium cell and the economic prospects for the sodium industry is discussed by Hardie.

Castner’s Process (From fused sodium hydroxide)

The electrolysis of sodium hydroxide is carried out just above its melting point (318ºC), whereby sodium in hydrogen are liberated at the cathode and oxygen at the anode. The theory of reaction may be symbolised as follows.

\[
\text{NaOH} \to \text{Na}^+ + \text{OH}^-.
\]

At the cathode, the reduction of the cations occurs:

\[
\text{Na}^+ + \text{E} \rightarrow \text{Na}.	ext{ and } \text{H}^+ + \text{E} \rightarrow \frac{1}{2} \text{H}.
\]

At the anode, the oxidation of the anion takes place:

\[
\text{O}^- \rightarrow \frac{1}{2} \text{O}_2 + 2\text{E}.
\]

Aluminium and Its Compounds

Mineralogy

Aluminium occurs in fairly good quantities in nature coming next to oxygen and silicon, and constituting about 7.5 per cent of the earth’s crust. The chief minerals of aluminium are classified below:

1. Silicates: Potash Felspar, K2O. Al2O3. 6SiO3
   Potash Mica, K2O. 3Al2O3. 6SiO2. 2H2O. Kaolin, Al2O3. 2SiO2. 2H2O.
2. Oxide: Bauxite, Al2O3. 2H2O. (The most important source).
   Al2(SO4)3 4Al(OH)3 Cryolite, Na3AlF6.

The most important aluminiferous minerals from the commercial point of view are Bauxite and Cryolite.

A detailed survey of the distribution of bauxite in India indicate that it occurs in Behar, Bombay, Central Provinces, Mysore, Madras and Kashmir. The total resources of Indian bauxite are estimated to be about 250 million tons.

Indian bauxites and some activated aluminas have been tested for their activity and specificity in the dehydration of ethanol to ethylene.

Extraction

1. Purification of Alumina—The main impurities of bauxite are ferric oxide and silica which have to be eliminated since these render the metal brittle and liable to corrosion. The removal of the impurities may be achieved by two different methods:

   a. Bayer’s Process—This process is suited for the treatment of bauxite which contains more of ferric oxide (red bauxite). The ore is ground finely and digested with a strong solution of caustic soda in an autoclave whereby aluminium oxide passes into solution as sodium aluminate and partly as colloidal alumina, while ferric oxide remains undissolved. The solution is diluted with water, and filtered to remove ferric oxide. Now, a small quantity of hydrous, aluminium oxide (from the previous operation) is added to the liquid to provide nuclei for the precipitation and the mixture is agitated for several hours when, aluminium oxide is precipitated. Finally it is washed, dried and ignited to obtain pure alumina.

   \[
   \text{Al}_2\text{O}_3 + 2\text{NaOH} \rightarrow 2\text{NaAlO}_2 + \text{H}_2\text{O}.
   \text{2NaAlO}_2 + \text{H}_2\text{O} + 2\text{NaOH} + \text{Al}_2\text{O}_3
   \]
Serpeck’s Process—Serpeck’s process is employed for purifying bauxite which contains much of silica. The ore is first powdered, mixed with carbon and heated to 1800°C, in a current of nitrogen so that aluminium nitride is formed. The silica of the bauxite is reduced to silicon and being volatile the latter escapes as vapour. The product containing aluminium nitride is decomposed by water, to obtain aluminium hydroxide which is then ignited. The reactions taking place in Serpeck’s process are summarised in the sequel.

\[
\begin{align*}
\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 & \rightarrow 2\text{AlN} + 3\text{CO}. \\
\text{AlN} + 3\text{H}_2\text{O} & \rightarrow \text{Al(OH)}_3 + \text{NH}_3. \\
\text{SiO}_3 + 2\text{C} & \rightarrow 2\text{CO} + \text{Si}. \\
2\text{Al(OH)}_3 & \rightarrow 3\text{H}_2\text{O} + \text{Al}_2\text{O}_3
\end{align*}
\]

Metallurgy

In aluminium production the first stage is alumina. A comprehensive account of the modern methods of production of aluminium is discussed elsewhere. Aluminium is extracted from pure alumina obtained as above, by the electrolytic process. Alumina is dissolved in molten cryolite and electrolysis earned out in an iron tank lined with carbon which forms the cathode. The anodes consist of a row of carbon rods attached to copper clamps, Fig. 1. To start the plant, the cryolite is melted by the arcs struck between the lining and the carbon rods. (At temperature of 875º-950ºC and a voltage of 5.5 volts is maintained.) The anodes are then raised and a calculated quantity of the alumina is added and also some coke is thrown in to cover the surface of the electrolyte and thereby keep off the blinding glow produced by the vigorous action of oxygen liberated at the carbon anodes. A low resistance charge-control lamp L, is connected in parallel with the electrolyte cell so that the current’s in them are in the inverse ratio of their resistance. When the concentration of alumina in the bath falls below a certain critical point, the resistance of the cell increases correspondingly and the amount of current flowing through the lamp increases to make it glow bright—the signal helps the operator to know the time for addition of fresh alumina. The process is continuous and fused aluminium which collects at the bottom is tapped off once in three or four days.

Purification of Aluminium, Hoope’s Process—The molten aluminium from the electrolytic cell is carried to the refining furnace, Fig. 2. It consists of three liquid layers of different specific gravities. The uppermost layer consists of molten, aluminium which acts as a cathode, while the anode is an alloy of copper, aluminium and silicon forming the lowermost layers. The middle layer acts as the electrolyte and consists of a fused mixture of fluorides of sodium, aluminium and barium. The current causes aluminium ions from the fused salt to be discharged and aluminium collects at the top. Meanwhile, the equivalent quantity of aluminium from the crude alloy at the bottom goes into solution in the middle salt layer. Crude aluminium is added from time to time which accumulates along with the lower layer.