MODERN ELECTROPLATING

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Acid Copper Electroplating and Electroforming

WILLIAM H. SAFRANEK

HISTORY AND DEVELOPMENT

Acid copper deposition was referred to as early as 1810 [1]. It is said that Bessemer plated small castings in 1833 [2]. A technical report by De la Rue appeared in 1836 [3] and the first patent for making electrotypes was granted to Jacobi in 1840 [4]. Smee discussed commercial copper plating processes in 1843 [1]. During the next 70 years progress was directed principally toward developing specific applications for acid copper electrodeposition. Publications during this period were reviewed by Bennett [5]. Most of these references deal with copper(II) sulfate-sulfuric acid baths, but oxalate [6], nitrate [7], acetate [7], fluosilicate [8, 9], and copper(I) chloride [8] solutions are also mentioned.

Several other acid baths were reported from 1930 to 1960, including sulfate-oxalate-boric acid [10], sulfate-oxalate [11, 12], copper(I) chloride [13], copper(I) chloride-sodium thiosulfate [14], benzene disulfonic acid [15], copper(I) iodide and bromide [16], fluoborate [17, 18], alkane sulfonic acid [19, 20], sulfamic acid [21, 22], copper (II) formate with ammonium salts [23], phosphate-sulfate [24], and fluosilicate-silicic acid [25] solutions. Copper(II) glycolate, lactate, malate, and tartrate baths were examined in 1966 [26]. At present, only the sulfate and fluoborate baths are commercially prominent.

APPLICATIONS

Electrodeposition of copper from acid baths is extensively used for electroforming, electrorefining, manufacture of copper powder, and electroplating. Refiners and electroformers, in particular, employ acid solutions because costs of chemicals and power are low and because the baths are simple and easy to control. Electroformed copper articles are produced in several important fields of industry, including electrotypes, phonograph records, band instruments, heat exchangers, and reflectors. More than 2700 metric tons of copper anodes are consumed annually in making electrotypes valued at about $100,000,000. Modern methods of electrotype molding differ greatly from the procedures of the early forties. Developments have been announced concerning the electroforming of complex shapes with reentrant angles, which cannot be made by other methods, for radar, aircraft, and other industries.

Many kilometers of steel wire are given a copper cyanide "strike" and plated with copper in acid solutions to produce a high-strength electrical cable. Thick deposits of copper (200 μm) are applied to steel rolls and then engraved for use in printing and marking paper and textiles. Stainless steel cooking vessels are copper plated in acid baths to improve the heat diffusion characteristics of outer surfaces and avoid local hot spots. Copper plating for stopping off carburizing on selected areas is accomplished by striking in a cyanide bath followed by plating in acid solutions. Acid copper plating is sometimes used for building up worn or overmachined parts, especially when copper surfaces are desired for protection against fretting corrosion.

Metal powders produced by deposition in acid baths are used for making sintered compacts and pigments. The powder is deposited from dilute solutions at high temperatures, brushed off the cathodes, filtered, washed, ground into fine particles, screened, and blended for use in manufacturing powder compacts [27, 28].

Acid copper baths containing organic brightening and leveling agents are used extensively to deposit smooth copper on rough steel, etched plastics, and unbuffed zinc die castings. For example, several million bumpers, initially given a strike in a copper cyanide or nickel plating bath, are plated yearly with about 25 μm of acid copper before nickel and chromium [29, 30]. Many die castings are plated with approximately 15 μm of leveling acid copper [31, 32], before nickel and chromium plating, to eliminate buffing before plating. Because of the excellent microthrowing power of the acid copper, pits, pores, or crevices in either steel or zinc surfaces are well filled with copper, which improves resistance to corrosion or blistering [33–35]. Copper sulfate baths have also been recommended for plating "low-density" powder compacts, to fill porosity near the surface [36].

In the electrowinning and electrorefining industries acid baths are employed exclusively. More than 80% of the domestic production of primary copper is refined electrolytically.

PRINCIPLES

The copper(II) (Cu^{2+}) salts in either the sulfate or the fluoborate bath are highly ionized except for small amounts of less ionized complex salts formed with certain addition agents. The addition of sulfuric acid to the sulfate solution, or fluoboric acid to the fluoborate bath, is necessary for obtaining acceptable deposits. Because of the high conductivity of commercial solutions, and because anode and cathode polarizations are small, voltages required for depositing copper are less for acid than for alkaline baths. Electrorefining plants employ the copper sulfate bath largely for this reason. Tank voltages for refining copper are frequently as low as 0.2 V for a cathode and anode current density of 1.6 to 2.2 A/dm^2.

Anode and cathode polarizations are nearly negligible in purified solutions used at low current densities. Even at the high cathode current density of 21.5 A/dm^2, a 6-V current source is ample when the solution is efficiently agitated. Excessive polarization of the anodes in the sulfate bath may occur when the anode current density exceeds about 5 A/dm^2. With the fluoborate bath, the anode current density can be at least 40 A/dm^2 without encountering excessive anode polarization.

Because of the low cathode polarization, the acid baths do not have as good throwing power as alkaline solutions. The plate distribution closely approximates the primary current distribution; the deviation was found to be 10.8% or less for the sulfate bath [37]. This disadvantage is largely overcome in electroforming practice by appropriate current shields.

Anode and cathode efficiencies are nearly 100% at all practical current densities. The rate of deposition obtainable depends chiefly on the efficiency of agitation in preventing excessive polarization. Acceptable deposits were reported at a current density as high at 260 A/dm^2, equivalent to 3.63 mm/hr [38], with violent agitation.

The character of copper deposits is influenced by the concentrations of copper salts and of free acid, the temperature, the cathode current density, and the nature and degree of agitation. Dense deposits with good surface smoothness up to a thickness of 500 μm or more can be produced without addition agents. To brighten or harden the plate, one or more of several addition agents can be utilized, as discussed later.

FUNCTIONS OF BATH CONSTITUENTS

PRIMARY CONSTITUENTS

Copper(II) sulfate ($CuSO_4 \cdot 5H_2O$) and sulfuric acid, or copper(II) fluoborate [$Cu(BF_4)_2$] and fluoboric acid, are the primary constituents of the sulfate and fluoborate baths, respectively. The copper salts furnish the metal ions in solutions such as those given in Table 1. Copper can be deposited at very low cathode current densities from the acid-free aqueous solutions of the salts [39, 40], but at higher current densities the deposits from the sulfate bath are spongy and contain occluded salts. Plate characteristics are improved, solution conductivity is increased, and anode and cathode polarizations are greatly reduced when free acid is added to either solution [41, 17]. The acid also prevents the precipitation of basic salts.

The concentration of copper sulfate is not particularly critical, although the resistivity of the solution is greater when the concentration is increased [42]. Cathode polarization increases slightly at copper sulfate concentrations above 1 *M* (250 g/l) [43]. A concentration of less than 60 g/l copper sulfate results in a decreased cathode efficiency [44]. When very high cathode current densities are used, a high concentration of copper sulfate, within the

TABLE 1. FORMULATIONS OF COMMERCIAL ACID COPPER BATHS

Copper Sulfate Solutions[a]	"Average" Concentration	Concentration Limits
Copper sulfate, $CuSo_4 \cdot 5H_2O$, g/l	188	150–250
Sulfuric acid, H_2SO_4, g/l	74	45–110
Specific gravity, at 25°C	1.165	1.115–1.21
Resistivity, at 21°C [45], ohm-cm	4.2–4.3	
Copper Fluoborate Solutions[b]	**Low Concentration**	**High Concentration**
Copper fluoborate, $Cu(BF_4)_2$, g/l	224	448
Fluoboric acid, HBF_4, g/l	15	30
Boric acid, H_3BO_3, g/l	15	30
pH (colorimetric)	1.2–1.7	0.2–0.6
Specific gravity, at 27°C	1.17–1.18	1.135–1.36
Resistivity, at 27°C [17], ohm-cm	7.3	

[a] From 30 to 100 ppm of chloride ions is required for typical bright copper plating baths.

[b] Copper fluoborate baths are prepared by diluting a concentrated solution containing 45% $Cu(BF_4)_2$ and adjusting the pH with either fluoboric acid or copper carbonate. The concentrate contains boric acid.

limits given in Table 1, is recommended. The solubility of copper sulfate is decreased when the sulfuric acid concentration is increased [41].

To improve the throwing power of some bright copper sulfate baths used for plating printed circuit boards, a low copper sulfate concentration such as 60 g/l of $CuSO_4 \cdot 5H_2O$ is combined with 80 g/l of sulfuric acid, 30 mg/l of hydrochloric acid, and appropriate brighteners. Analogously, copper fluoborate solutions containing 56 g/l of $Cu(BF_4)_2$, 160 g/l of fluoboric acid and brighteners are also regarded as "high-throw" baths for through-hole plating. Air agitation is used for both types of solutions.

Copper fluoborate is more soluble than copper sulfate. Metal ion concentration can be more than double in the fluoborate bath in comparison with a copper sulfate solution containing 50 to 75 g/l of sulfuric acid.

Changes in sulfuric acid concentration have more influence than changes in copper sulfate concentration on solution conductivity and anode and cathode polarization. For example, specific conductivity is nearly doubled when the concentration of sulfuric acid is raised from 50 to 100 g/l [46]. An

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have been observed
cathode [62].

additional increase in free acid concentration to 200 g/l, which is the level widely used in electrorefining, reduces the resistivity from 4.2–4.3 to 1.6–1.9 ohm-cm [47]. Cathode polarization decreases when a small amount of sulfuric acid is added to a solution of copper sulfate, reaches a minimum at about 0.4 *M* (38 g/l), and increases with a further increase in sulfuric acid concentration [43]. Changes in the concentration of copper sulfate have little effect on grain size, but some grain refinement was detected as a result of increasing the sulfuric acid concentration to 1.5 *N* (72 g/l) [48].

If the acid concentration in the fluoborate bath is too low (pH more than 1.7), deposits are dull, dark, and brittle. Boric acid is added to stabilize the bath and prevent decomposition of copper fluoborate; this increases resistivity slightly. In a bath with concentration of more than 15 g/l fluoboric acid or 220 g/l copper fluoborate, an increase in the concentration of either the salt or the acid lowers the resistivity.

ADDITION AGENTS

Addition agents for brightening, hardening, grain refining, surface smoothing, increasing the limiting current density, and reducing trees are frequently added to the acid copper sulfate bath, but the use of a particular addition must be evaluated for each application, because undesirable characteristics can then be avoided. For example, many of the addition agents proposed result in embrittlement of the plate. Deposition potentials are generally higher when addition agents are added. Cathode polarization is greatly increased by adding gelatin (0.2 g/l) [48, 49] or glue [43, 50]. These additions result in grain refinement, but this is chiefly unidirectional, because the structure remains columnar and becomes more fibrous [48]. Gelatin additions to the sulfate bath introduce porosity, organic inclusions [39, 51, 52], or both.

The effects of glycine, one of the amino acids formed by the hydrolysis of gelatin, are similar to the effects of gelatin [53]. Cystine and methionine, like gelatin, are cathode-polarizing agents [54]. On the other hand, dicarboxylic amino acids appeared more effective than monocarboxylic [55].

Phenolsulfonic acid is used in the electrotyping industry, but results with it depend on the sulfonation and purification procedures [56]. Deposits become harder and smoother after a bath has been electrolyzed or dummied for a short time following an addition of phenol or phenolsulfonic acid [57].

The smoothing and grain-refining tendencies of addition agents are sometimes associated with the formation of complex ions with copper or of colloids at or near the cathode interface. Gelatin or glycine, for example, forms complex ions with copper [58–60] and also exists in colloidal form [61]. Particles of colloids arising from additions of selenious and arsenic oxides have been observed by ultramicroscopic examination to concentrate at the cathode [62].

With 0.14 to 0.42 mg/l selenious oxide and 0.0065 to 0.13 mg/l arsenious oxide, grain structure was refined, surfaces were smoothed, and density was improved. Nevertheless, the ability of a colloidal or ionic addition agent to improve the deposit cannot be conclusively predicted in advance on the basis of a general knowledge of its ionic or colloidal behavior in electrolytes. Thus, in a copper(II) nitrate bath colloidal addition agents were effective as cathode polarizers, but did not always result in surface smoothing or grain refining [63].

Brightening Agents. Thiourea additions brighten copper deposited from acid sulfate baths. A 1951 patent disclosed the use of 0.002 to 0.005 g/l [64]. An appreciable grain-refining effect was reported for a concentration of 0.003 g/l or more [65]. The grain-refining and brightening effects of thiourea are attributed to its adsorption in copper deposits and the resulting effect on crystal nucleation [66].

Sulfide ions created when thiourea decomposes reduce the ductility of copper deposits [67–69]. Combined with dextrin [62, 70, 71], molasses [72–74], lignosulfonates [75], mercaptobenzimidazoles [76], naphthalene sulfonic acid [77–79], or tribenzylamine [80] and other organic agents [71], small concentrations of thiourea were once employed for brightening purposes, but have been largely superseded by better brighteners that have little or no harmful effect on ductility.

Sulfonated acetylthiourea or sulfonated aryl and alkyl substitution products of acetylthiourea were developed for bright copper plating from acid baths [81]. Another process utilized the sulfonation products of sulfurized aromatic compounds prepared by the reaction of toluene with sulfur chloride or thionyl chloride in the presence of anhydrous aluminum chloride and sulfuric acid [82, 83]. Acetyl cyanamide was proposed as a brightener for either the sulfate or the fluoborate bath [84]. Several complex amines were patented as brightening agents in 1958 [85–87]. In 1959, a patent disclosed a combination of thiohydantoin (a thiourea derivative) and a multiringed aromatic amine [88]. A substituted amino benzene sulfonic acid was disclosed in another patent for brightening copper deposited from the copper sulfate bath [89]. Polyacrylamides [90, 91], the reaction products of aminothiozole [92], acrylamines with a high molecular weight [93], tertiary amines [87], thiocarbamates [94, 95], thiocarboxylic acid amides [96], tetrahydropyranyl amides [97], homopolymers of 1,3-dioxolane [98], and a combination of phenol polyglycols and thiosemicarbazones [99] are also included among the brightening agents patented since 1955.

Some of these brightening agents also induce leveling. For example, a surface finish of 0.46 μm (rms) can be smoothed to only 0.18 μm with 12.5 μm of good leveling bright copper or to only 0.1 μm with 25 μm [32]. Such

processes deposit copper with a leveling power much higher than typical bright nickel deposits.

OPERATING CONDITIONS

Temperatures may vary from 18 to 60°C; however, a temperature between 32 and 43°C is common, since it can be maintained economically with little or no heating or cooling. An increase in the temperature results in a higher conductivity and reduced anode and cathode polarization [48]. Decreasing the temperature from 35 to 15°C brought about a considerable grain refinement in plates deposited at 3 A/dm^2 [48]. A temperature below 30°C is recommended for plating bright copper in acid baths to maintain good leveling power. These solutions are customarily agitated with air.

Current density and agitation must be balanced in order to obtain deposits having the desired properties. For producing electrotypes, cathode current densities of 16 to 22 A/dm^2 are generally employed when using the sulfate bath agitated with air. Fast-moving, endless wire can be plated at 50 A/dm^2 [100]. Still higher current densities are used when sufficient agitation can be supplied. Impinging of jets of electrolyte on the surface of the cathodes is said to permit a current density of 215 A/dm^2. When movement of the work is impractical or when air agitation fails to provide good mixing at all significant surfaces, the current density is usually kept at 3.7 to 5.4 A/dm^2. It is claimed that higher current densities are practical with the fluoborate bath when agitation is the same as for the sulfate bath [17, 18]. Acceptable deposits 25 μm thick were obtained without agitation at 38 A/dm^2.

In either the sulfate or the fluoborate bath, an increase in current density results in increased cathode polarization (but not to the extent noted for many other solutions). Cathode films become more depleted in copper(II) ion and more concentrated in sulfate ion when the current density is increased [101]. Clear evidence has been reported of grain refinement produced by increasing the current density [102–104]. An increase in current density from 1 to 7 A/dm^2 reduced grain size to about one-third [105]. It was reported that high current densities resulted in grain refinement but promoted nodules and tree growth [48].

Periodic current reversal is patented for promoting leveling in copper plate deposited from copper sulfate baths containing 15 g/l zinc or cadmium [106]. A recommended PR cycle includes 2 sec plating and 0.4 sec deplating at 11 and 16 A/dm^2, respectively. Directing ultrasonic waves with a frequency of 1000 kHz and an acoustical intensity of 100 w/cm^2 to the cathode resulted in a colloidal suspension of copper instead of an adherent deposit [107].

MAINTENANCE AND CONTROL

The concentration of copper sulfate or copper fluoborate can be approximated by specific gravity measurements, but the contribution of sulfuric acid to the specific gravity of the sulfate bath must be taken into account. The acid concentration of fluoborate baths is controlled by measuring pH, using colorimetric pH papers.

The concentration of addition agents is usually controlled by empirical methods, such as evaluating the appearance of deposits on special bent or sloping cathodes immersed in beaker samples of the plating solution. An analytical method based on a bromination reaction [57] was developed for determining the concentration of phenol or phenolsulfonic acid.

Filtration requirements depend on the dirt load of the air, any dirt brought in by the work, and the amount of detached anode sludge particles. If the cathodes are steel and if they are incompletely protected with a copper or nickel strike, particles that become detached from immersion deposits will also contribute to the filtration requirements. Although it is possible to maintain acceptably smooth deposits with only occasional batch filtration, continuous filtration is usually preferred. Cellulosic filter aids are satisfactory, but siliceous filter aids should be avoided when the fluoborate solution is filtered; filter papers are satisfactory.

EFFECTS OF IMPURITIES

Acid copper baths are more tolerant of ionic impurities than many other plating solutions. Many metallic ions introduced regularly by carryover with the work, by dissolution of impurities in the anode, or by dissolution of the basis metal (for example, iron, nickel, or zinc) can be expected to accumulate in the bath, because conditions are usually not satisfied for effecting codeposition of such metallic impurities (nickel, cobalt zinc, iron) with copper. For example, less than 2 ppm nickel was codeposited with copper in a sulfate bath containing 15 g/l nickel [108].

Nickel and iron reduce the conductivity of the sulfate bath to the same degree as an equivalent increase in copper [109]. The deposition potentials of arsenic and antimony are apparently near that of copper in the sulfate bath, since codeposition was reported to occur [110]. Arsenic and antimony in concentrations of 10 to 80 g/l and 0.02 to 0.1 g/l, respectively, embrittled deposits and roughened surfaces. Additions of gelatin or tannin, however, effectively inhibited codeposition of these impurities and prevented roughness and embrittlement caused by them. Antimony readily codeposits with copper, but only small amounts of arsenic could be detected [111]. Bismuth, like arsenic and antimony, caused granular deposits [112].

Antimony and bismuth are believed to form insoluble complex compounds with arsenate [113].

Small concentrations of alkali metal and alkaline earth salts were found to smooth copper deposits [8]. Tin salts were also reported to smooth deposits and were, at one time, purposely added to the sulfate bath for this reason [8]. Lead is completely precipitated as sulfate, and silver partly. If silver is a contaminant, a small amount will be codeposited with copper. A high current density favors the codeposition of silver [108]. Silver chloride caused pitting in semibright copper plate [114].

Between 2 and 35 mg/l chloride is added in the form of hydrochloric acid to electrorefining solutions to precipitate silver and avoid "sandy" deposits [113]. From 30 to 100 mg/l of chloride is recommended for bright copper plating with many modern brighteners.

Nitrates were reduced to ammonia at the cathode in copper sulfate baths [115]. A reduction product of the sulfate ion, which is said to have a grain-coarsening effect, can be removed by heating the bath and adding an oxidizing agent [65], but oxidizing agents such as hydrogen peroxide or potassium permanganate are said to reduce throwing power [114].

In the fluoborate bath, lead is the only metallic impurity known to interfere with the deposition of ductile plates; it can be precipitated by adding sulfuric acid. Besides lead, metals like silver, gold, arsenic, and antimony might be codeposited with copper, but the effects of such impurities are not known.

Organic impurities originating from decomposition of addition agents or leaching of elastomeric tank linings sometimes embrittle deposits, but can be removed by treating the solution with an appropriate activated carbon, followed by filtration. α-Naphthylamine was identified as an injurious contaminant leached from certain rubber tank linings [116]. As little as 10 mg/l α-naphthylamine caused an irregular pattern of uneven copper plate having ridges and valleys. Treatment with activated carbon is desirable when a new bath is being prepared—especially the fluoborate bath, which may be contaminated with impurities leached from rubber shipping drums. An instance has been reported of embrittlement traceable to impurities leached from wood tanks [117].

ANALYTICAL METHODS

Methods for determining copper and sulfate concentrations and a method for determining iron and aluminum in copper sulfate baths are described by Langford [118], who also presents procedures for determining copper and fluoboric acid concentration. Methods for determining trace amounts of lead [119], nickel [120], chromium [121], and chloride [123] have been reported.

ANODES

Copper anodes in sulfate and fluoborate baths usually become coated with films containing finely divided copper and copper oxide particles. A copper oxide film is believed to cause intergranular corrosion, which promotes disintegration of surface layers into fine copper particles [112]. Some, however, have attributed the films to copper particles formed by the disproportionation of copper(I) ion to copper(II) ion and metal [123]. The films on the anodes in the sulfate bath also contain insoluble impurities such as arsenic, selenium, tellurium, lead, and silver.

Anode film particles often become detached from the anodes. Air agitation promotes the detachment, causing some particles to be dissolved by the free acid. If the work is racked so that cathode shelves lie in a horizontal plane, particles will settle out on these areas and roughen the plate. In such cases, the anode sludge can cometimes be decreased and the deposits made smoother by raising the bath temperature or increasing the acid concentration. In one series of tests, less copper was found in anode films formed in fluoborate baths than in those from sulfate baths [17].

Fine copper particles can be prevented from reaching the cathode by bagging anodes with woven Dynel or polypropylene. To allow good mixing of the solution adjacent to the anodes, bags can be made in the form of envelopes, enclosing several anodes placed edgewise to the cathodes.

Rolled and cast bars and electrolytic copper sheets have been employed as anodes in sulfate and fluoborate baths. Anode sludge is decreased by using oxygen-free, high-conductivity copper [124]. On the other hand, the tenacity of the anode film is improved and the number of particles that become detached from anode surfaces in air-agitated baths is decreased by adding 0.02 to 0.04% phosphorus to cast copper [123, 125]. The films on phosphorized copper anodes are responsible for the slight polarization of about 0.5 V [124]. Rolled copper anodes containing at least 0.004% phosphorus are customarily recommended by the vendors of brighteners for plating bright copper in copper sulfate solutions. Chunks of phosphorized copper are frequently used in titanium anode baskets.

To avoid excessive polarization at any anode in the copper sulfate bath, the anode current density should not be more than about 5 A/dm^2 in unagitated baths. With vigorous air agitation, the limiting anode current density is more than 17 A/dm^2. The anode current density in an unagitated fluoborate bath can be as high as 40 A/dm^2, and with air agitation, it can be increased to 55 A/dm^2.

Small amounts of silver, sulfur, lead, tin, nickel, and other elements are common impurities in rolled, cast, and electrolytic copper [124]. Silver as an impurity in the anodes employed in sulfate and fluoborate baths is of much

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less consequence than it is in cyanide baths. OFHC° and electrolytic copper were found to have a lower impurity content than rolled or ordinary cast anodes. The metallic impurities in OFHC and electrolytic copper totaled about 0.006%.

Grain size is considered inconsequential [124, 125]. Two batches of high-purity anodes with average grain sizes of 10 and 0.01 mm performed similarly [124]. On the other hand, high density is a desirable characteristic, because it promotes uniform anode dissolution.

An instance is reported of a preference for continuously using insoluble, conforming anodes in order to improve deposit thickness distribution [126]. Copper was replenished by circulating the solution through an auxiliary electrolytic tank connected in series with the electroforming tanks. The electrolytic corrosion tank was equipped with soluble copper anodes and scrap. On each side of a rotating disk cathode were microporous rubber diaphragms, which inhibited the diffusion of copper ions into the catholyte and kept the cathode efficiency low. The insoluble anodes in the electroforming tanks were made with silver-lead alloy (1% silver).

Lead containing 3% tin and 3% antimony has been proposed as an insoluble anode for facilitating the plating of printing rolls [127].

An insoluble anode that has been used in copper electrowinning was made of an alloy of copper, silicon, iron, and lead [44]. Graphite is the only electrically conductive material known to be insoluble as an anode in the fluoborate bath. When used as an anode, graphite produces a sludge of finely divided carbon particles.

EQUIPMENT

Steel tanks lined with rubber or plastic are preferred for large acid copper baths, but glass-fiber-reinforced plastic tanks are used for small volumes of solution. Lining materials that are generally suitable for either the sulfate or the fluoborate bath are properly formulated natural hard rubber, neoprene rubber, polyethylene, or plasticized vinyl chloride polymers. Air lines can be made of hard rubber or polymerized vinylidine chloride. Special grades of carbon pipe and tubing make efficient heat exchangers or cooling coils. Lead is, however, satisfactory in the sulfate bath and is less expensive. Rubber or rubber-lined filters are used for continuous filtration, but stainless steel is satisfactory for short periods.

Graphite is recommended for use as heat exchangers for copper fluoborate solutions [128]. For further details, see reference 129.

°Trademark, American Metal Climax Inc.

PREPARATION OF BASIS METALS

Because loose, nonadherent displacement films of copper are formed on steel and zinc when these basis metals are immersed in acid copper baths, a cyanide copper or nickel strike plate is required before plating in acid baths. If the basis metal is completely covered, the strike plate can be as thin as 1.3 μm, but 2.5 μm is sometimes preferred for parts of complex shape. After plating in the cyanide bath, the work should be thoroughly rinsed, dipped in a dilute solution of hydrochloric or sulfuric acid to neutralize any undissolved alkaline material, and rinsed again before plating in the acid bath.

Nickel or nickel alloys, when appropriately surface-activated by cathodic treatment, reverse current etching in sulfuric acid, or other method, can be plated directly in an acid copper bath. Contact should be made to the work before immersion. Stainless and chromium steels are plated in acid baths with adherent copper deposits by first striking in a solution concentrated in sulfuric acid but dilute in copper sulfate: 240 g/l sulfuric acid and 112 g/l $CuSO_4 \cdot 5H_2O$ [130].

The usual procedures for plating on aluminum are described in Chapter 3. An acid pyrophosphate bath for plating copper adherently on aluminum was described in 1958 [131].

MOLDS AND MANDRELS FOR ELECTROFORMING

Metallic and nonmetallic materials are used as molds or mandrels for electroforming. Surface passivity characteristics make chromium alloy steel, aluminum, magnesium, tantalum, and chromium-plated metals useful as metallic mandrels that require neither a surface treatment for providing conductivity nor a separating film for providing ready removal of the electroform. Surface-passive metallic mandrels can be used repeatedly without intermediate surface treatments, although a thin film of graphite is sometimes applied before each use to facilitate the final separation of the deposit. A mixture of graphite and wax has been utilized as a parting medium in the electroforming of tubing that was subsequently drawn into trombone slides [126]. A thin suspension of graphite in kerosene is sometimes used.

Temporary mandrels are used only once and are then deformed or destroyed when deposition is completed. Low-melting alloys containing lead, tin, bismuth, cadmium, or mercury, or combinations of these, are melted out and recast. In electroforming Pitot-static tubes, low-melting mandrels were employed [132]. Aluminum and zinc can be cast or machined into mandrels and subsequently chemically dissolved.

Nonmetallic materials used for mandrels are asbestos, asphalt, cloth,

gelatin, glass, paper pulp, plastics, plaster, pottery and other ceramics, rubber, wax, and wood. Each of these must be made surface conductive by one of the procedures discussed in Chapter 28 after molding is completed. Plaster, wood, and ceramics require sealing to fill pores near the surface before the application of the conductive film.

Thermoplastic sheet, such as vinyl acetate and vinyl chloride copolymer, has found wide acceptance in the electrotyping industry as a molding medium. Impressions of printing surfaces are made in the heated plastic sheet, which is then cleaned, sensitized with a stannous chloride solution, and silvered by simultaneously spraying an ammoniacal silver nitrate solution and a solution of a reducing agent such as hydrazine sulfate, formaldehyde, or hydroxylamine hydrochloride [133]. Such molds largely replace the graphitized wax and lead molds used formerly. Copper is deposited on the silver (using a low current density for a few minutes) until the metal film is thick enough to carry a higher current. Then the current density is raised to about 22 A/dm^2 or more for another 40 to 70 min until a shell 180 to 380 μm thick is deposited. Flexing the plastic mold releases the shell. Edges of the electrodeposited shell are trimmed, and the back is tinned in preparation for backing up with electrotype metal, a lead alloy containing 3% Sn and 3% Sb. Fidelity of reproduction of the final electrotype is good enough to duplicate photoengravings containing more than 264 dots/mm^2 in 133-screen halftone subjects.

Original, master phonograph records are cut in wax or lacquered aluminum disks and then metalized by cathode sputtering gold or copper, or by silvering; chemical reduction methods like that used in the electrotyping industry [134] are employed. After electroforming and separating the mother negative from the original master recording, a metal master is electroformed on the negative and subsequently used as a mold for electroforming the number of record stampers needed for production of the record. To facilitate the separation of record stampers from the metal master, the master is dipped in a solution of potassium dichromate (15 g/l) before electroforming is started.

Gravure cylinder shells are examples of electroformed articles that are detached from their mandrels after their service life is completed. An immersion nickel or silver deposit, or other separating film, is applied to copper-plated steel cylinders. A 150- to 200- μm thick copper layer is deposited on the cylinder and etched through a resist of carbon tissue or pigment paper to produce the printing surface [135]. After the shell is no longer serviceable because of excessive wear, it is removed mechanically and replaced with a new shell. The shells are deposited from both sulfate and fluoborate [136] baths.

In addition to those mentioned, many other kinds of molds, parting

media, and methods for making surfaces conductive have been used [137].

Electroless copper or nickel has become popular for metalizing plastic or other nonconducting mandrels used for electroforming.

TESTS OF DEPOSITS

The thickness of copper on zinc die castings is measured on magnified microsections, or by anodic dissolution in accordance with coulometric principles [138]. Magnetic instruments can be used for measuring the thickness of copper deposits on steel. See Chapter 30.

Copper-plated steel wire for electrical cable is tested for thickness and thickness uniformity, electrical conductivity, and tensile strength. Electroformed shapes are frequently given physical tests, in order to control strength and ductility, by determing such properties as hardness, tensile strength, elongation, and resistance to impact or denting.

PHYSICAL PROPERTIES AND STRUCTURE

Data on the physical, mechanical, and electrical properties of electrodeposited copper were comprehensively reviewed [139]. Table 2 summarizes the ranges for high-strength, hard, lowly stressed, good leveling, or thermally stable electrodeposited copper. The high-strength copper was deposited from copper sulfate baths containing triisopropanolamine [140] or molasses and thiourea [68] and in copper cyanide baths containing potassium thiocyanate, operated with periodically reversed current [141]. Hard deposits also were produced in the copper cyanide-potassium thiocyanate solution with PR current and in the copper sulfate bath containing naphthalene disulfonic acid and thiourea [142] or several other addition agents.

The deposits with a low electrical resistivity were obtained in copper fluoborate and sulfate baths at 30°C, wich contained no addition agents [68, 141]. These deposits also were thermally stable to 400°C, changed very little in density, and exhibited low stress, less than 3.0 kg/cm^2. The properties for the good-leveling copper were measured for specimens deposited [68] in a copper sulfate bath containing a sulfonated compound and an azo dye [143]. The influence of modifying the bath formulations and the operating conditions on the properties and structure of copper electrodeposits is described in references 68, 139, and 141.

The grain structures of copper deposits usually correspond to one of four types, shown in Figure 1. Deposits from the sulfate baths containing no addition agents are columnar (Figure 1*a*). Additions of gelatin, phenolsulfonic acid, and many other agents cause the fibrous structure shown in Figure

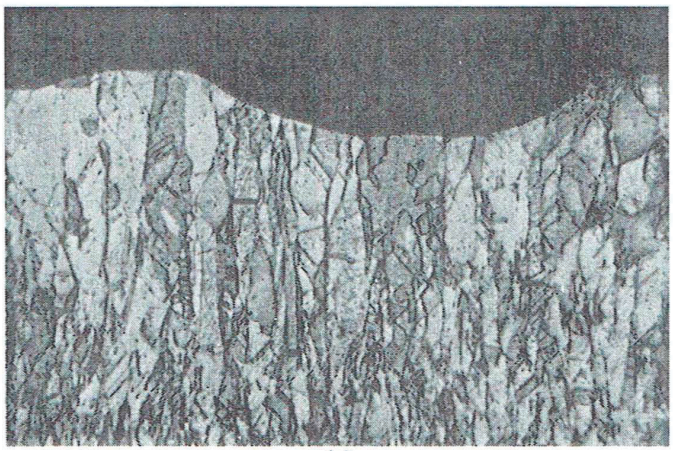
Table 2. Properties of Copper Electrodeposits Useful for Diverse Applications

	Hardness (VHN$_{200}$)	Internal Stress, a	Elongation, %	Electrical Resistivity

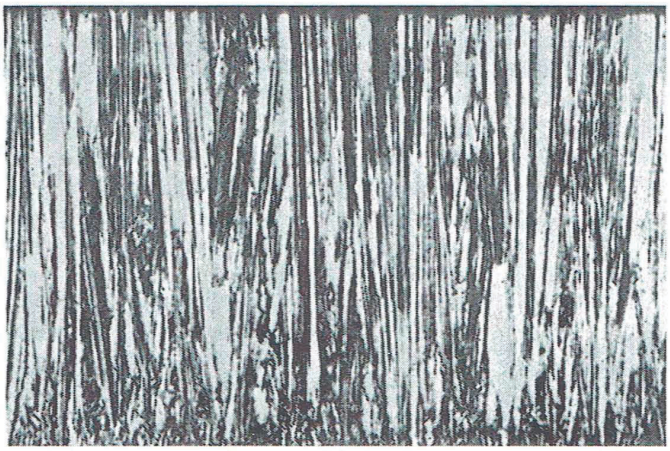
Table 2. PROPERTIES OF COPPER ELECTRODEPOSITS USEFUL FOR DIVERSE APPLICATIONS

Outstanding Characteristic	Tensile Strength, kg/mm^2	Elongation, % (5cm)	Internal Stress,[a] kg/mm^2	Hardness (VHN200), kg/mm^2	Electrical Resistivity, microhm-cm
High strength	45–63.5	4–18	−4.2 or 3.6 to 5.5	131–159	1.75–2.02
Hardness	3.5–55.5	0–10	−4.2 or 3.0	193–350	1.96–4.60
Low electrical resistivity	18.5–27	15–41	−0.5 to −1.6	48–64	1.70–1.73
Near zero stress	14–16	8–24	−0.08–0.06	56–57	1.71–1.72
Good leveling	36–36.5	14–19	2.0	128–137	1.82
Thermal stability[b]	22.5–30	26–39	0.5–2.9	55–106	1.73–1.76

[a]Negative values indicate a compressive stress.
[b]Deposits that changed less than 0.02% in length after heating to 400°C.



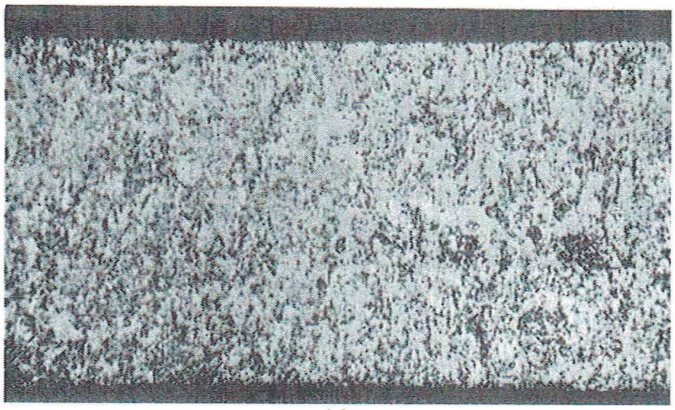
(a)



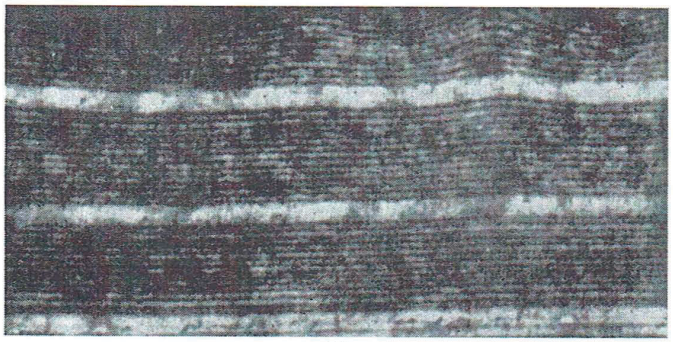
(b)

Fig. 1 Structure of copper deposits—cross-sectional views (about 500×) after etching with ferric chloride reagent. (*a*) Columnar; (*b*) fibrous; (*c*) fine-grained, equiaxed; and (*d*) banded.

1*b*. Such copper usually is 15 to 20% harder than columnar copper. The fine-grained deposit in Figure 1*c* is characteristic of copper deposited in copper cyanide solutions at high temperatures (70–80°C), copper pyrophosphate baths, copper sulfate solutions containing triisopropanolamine or other amines, and copper sulfate solutions containing popularly used



(*c*)



(*d*)

Fig. 1 (Continued)

brighteners. The banded copper in Figure 1*d* is characteristic of copper deposited with periodic current reversal from cyanide baths containing brighteners.

Copper is deposited from the sulfate bath as fcc crystals that are randomly oriented [144], unless deposited at less than 1.5 A/dm^2, when the basis metal can exert an influence on the structure so that crystals in the basis metal and plate are oriented similarly [145]. Hardness has generally been associated with fine grains [102, 105], yet it can be increased by introducing crystal orientation in the absence of grain refinement.

Grain continuity from the basis metal into sulfate-copper deposits has

been detected by many investigators [104, 146, 147]. Thus the structure of the deposit is often influenced by that of the basis metal. The basis metal structure was reproduced in the copper plate when the copper substrate was cleaned and immersed in an acid solution before plating [148, 149], but was not reproduced when the basis metal was cleaned but not dipped in acid solution before plating [149]. The grain size of the substrate appeared to influence the reproduction of the basis metal structure in the copper deposit [149]. The structure of copper electrodeposited from sulfate solutions was not influenced by dislocations such as etch pits in the substrate surface, unless the etch pits contained oxides or sulfides [150]. Oxide and sulfide particles in the surface layer of the substrate behaved as nucleation sites.

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