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A SURVEY

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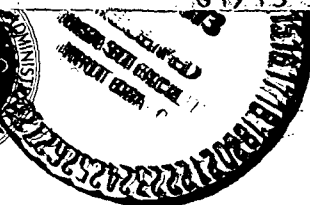
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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

PLATING METHODS

A SURVEY

By

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Prepared under contract for NASA
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Cambridge, Massachusetts



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Foreword

An important interest in plating and coating methods is found not only in NASA, but throughout industry. Improved bearing life, controlled reflectivity, corrosion resistance and improved appearance are some of the reasons for the attempts to obtain better coatings for specific purposes. Plating, as a process, has been known for many years; advances in the science and art now make it possible to finish many materials that were hitherto difficult to treat. One of the sources of this technology is a result of the space effort required to meet the extremely high standards established for space vehicles and associated hardware under severe service conditions. In this document, new progress is discussed and related to the well-known processes.

The information in this survey includes the results of a comprehensive search of the literature available, much of which has been generated by the research centers of the National Aeronautics and Space Administration and their contractors. Individuals active in the field have been contacted in gathering the information. The authors have called attention to specific areas in which applications of the technology may have potential value to industrial and other enterprises in the nonaerospace community.

From the nature of the field, numerous proprietary methods and materials are mentioned that have been used in NASA-supported research and development. This is done only to clarify the current state of the art and to indicate sources of materials and methods. There is no intent to endorse or compare and evaluate any specific product.

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Director
Technology Utilization Office

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Introduction

The electroplating industry is characterized by many small shops that are equipped to do plating, anodizing, coloring, and polishing of materials and parts supplied and owned by others. In the United States in 1967, there were 3235 independent plating plants, of which only 853 (26.4%) employed more than 20 people. The total employment in the industry in 1967 was 55 000, or an average of 17 people per plant. The total value of electroplating shipments in 1967 was \$789.8 million, an average of \$244 000 per shop.

A large segment of all electroplating is not done in small independent shops, however, but by captive or in-house ones. Captive plating output is estimated to be equal to that of the contract finishing industry in terms of dollar volume (but not in terms of number of plants or employees).

The largest and most highly automated plating plants are in the automotive and appliance industries. Many smaller metal-working companies also have their own facilities, which range from a single zinc barrel plating setup to a completely integrated finishing plant. Practically every metallic object sold to the public is subjected to some sort of final finishing operation either for decorative or functional purposes. A few of the plated products produced by the captive segment of the industry are:

- Automotive parts (bumpers alone account for a major share of the decorative nickel-chromium plating business)
- Large consumer items (such as stoves and refrigerators)
- Small appliances (such as mixers, irons, toasters, and grills)
- Assorted housewares (such as heaters, spatulas, and spoons)
- Jewelry
- Silver flatware and hollow ware
- Hardware and plumbing fixtures
- Electronic products (radios, TV's, communication equipment, and computers)
- Electrical products (such as lamps, fixtures, outlet boxes, fuses, switches, and controls)
- Wire and wire goods (pins, hooks, hangers, and cables)

- Aircraft parts
- Aerospace products
- Machine tools and heavy equipment
- Tin cans.

A small producer of metal products used to begin to think seriously about installing his own plating plant when his yearly plating bill reached \$25-\$50,000. In recent times, however, as manufacturers have become more sophisticated in estimating their own true plating costs and as the labor supply becomes more critical, they have made more use of outside vendors. This has particularly benefited the larger job shops, which are more automated and thus can do a job more economically than the manufacturer. Present trends suggest the ultimate demise of the smallest job plating shops, particularly as pollution controls become more stringent and more widely enforced.

In recent years the electroplating industry has grown in response to the demands of the electronics and aerospace industries for reliable, high-quality electroplates with well-controlled engineering properties. Traditionally, electroplating has been used to provide corrosion or oxidation resistance, wear resistance, and/or decorative surface finishes to a wide variety of consumer products and parts; today, plating is a critical step in the manufacture of computer components, space guidance systems, and communication equipment.

Classical applications of electroplating processes have generally been confined to deposition from aqueous solution of a restricted number of so-called plating metals onto a limited number of "platable" substrates. Innovations in conventional electroplating processes, discussed in Chapter 2, have been directed toward improved reliability, stringent quality control, and tailored surface properties, as required in an expanding number of engineering applications. Reliable gold-plated slip rings, for example, are a direct product of the space age. In the 1950's, the rejection rate on manufactured slip rings was as high as 75%; today, low-noise, long-life, high-reliability slip rings are achieved almost as a matter of routine.

In recent years, both the substrates amenable to electroplating and metals that can be electrodeposited have been increased in number. Plating on active-metal substrates, particularly the light-weight structural alloys of aluminum, magnesium, beryllium, and titanium, gained much impetus from the needs of the aerospace industry. The use of such alloys in industrial and consumer products is also increasing, and their applicability is enhanced when surface properties can be modified via electroplated coatings.

The major metals that cannot be deposited by conventional aqueous electroplating methods are those which lie above hydrogen in the electromotive series. However, there has been academic interest, at least, in electrodepositing such active metals for more than 75 years. Conducting solvents have been sought that contain either readily reducible hydrogen ions or no hydrogen at all. Accordingly, many organic solvents and fused-salt baths have been investigated. Perhaps the most successful nonaqueous plating system, as described in Chapter 3, is the aluminum chloride-lithium hydride-ether bath developed in 1952 by Couch and Brenner of the National Bureau of Standards (NBS) for the electrodeposition of aluminum. Under the guidance and encouragement of the National Aeronautics and Space Administration (NASA), the NBS process was developed from a laboratory curiosity to a full-scale commercial process. Today, four companies have 500-gallon tank facilities for the plating and electroforming of aluminum from modified NBS electrolytes.

The history of electroplating from fused-salt baths, outlined in Chapter 4, has been fraught with failure from the time of Michael Faraday. In 1964, Senderoff and Mellors of Union Carbide Corp. made a major breakthrough by successfully plating the refractory metals—Ti, Zr, Hf, V, Nb, Ta, Mo, and W—from carefully formulated molten salt baths. The Union Carbide process results in true electroplates and can even be extended to produce free-standing electroforms. Most fused-salt electrodeposition processes in the literature, including the *Metalliding* process recently developed by Newell Cook of General Electric Co., result in diffusion coatings, not in adherent surface plates. Both types of fused-salt coatings are under active development. The plating process is being used primarily to produce tantalum coatings and intricately shaped tantalum electroforms for applications requiring highly corrosion-resistant hardware. Columbium-plated copper seems promising for superconducting transmission lines. The electrodiffusion process has been used primarily to produce boride coatings for hardness and wear resistance, although many other types of diffusion coatings have been made and show promise for high-temperature oxidation resistance, corrosion resistance, and reduced sliding friction.

Electroforming, which is discussed in Chapter 5, has much in common with electroplating, although the electroform is deposited over a mandrel that is ultimately removed. The use of electroforming in the manufacture of consumer articles is technically well-developed but generally uneconomical. There are applications, however, for which electroforming is particularly well suited.

One is the production of nickel mirrors and reflectors, where close dimensional tolerances and exact reproduction of surface characteristics are important. Another is in the production of thin-walled objects of complicated shape, such as the rocket engine injectors for the Apollo Service Module. The latter have internal passages and orifices of variable area to maintain reproducible hydraulic characteristics and could not be made as reliably or as cheaply by conventional metalworking.

In electroplating and electroforming, the substrate is made cathodic and therefore must be an electric conductor. Plating on plastic or nonconducting substrates is a relatively new field and is based primarily on electroless deposition. In this process, which is described in Chapter 6, metals plate out from solution onto specific catalytic surfaces. Suitable catalysts for electroless nickel deposition, for example, include nickel itself and many of the other transition metals such as cobalt and manganese. In plating on plastics, a palladium catalytic surface is typically used; it is plated sequentially with layers of "electroless" copper, electroplated copper, electroplated nickel, and electroplated chromium. Tremendous growth in plated plastics is expected in automotive trim, household appliances, plumbing, printed-circuit boards, and new products.

Electroplating from gaseous plasmas (Chapter 7) is very remote from chemical electroplating in terms of equipment used and power requirements, but is quite closely related in a generic sense. While a number of gas-phase electrodeposition processes are discussed in Chapter 7, the one with the greatest immediate commercial potential is ion plating. The apparatus employed is quite similar to that used in sputtering, but the mode of operation is different. The ions in a gaseous plasma are very much more energetic than those in aqueous solutions. The discharge of highly energetic ions from the gas phase at the surface of a cathodic workpiece leads to remarkably adherent, pore-free coatings, even when the coatings are very thin, and even in systems where there is no mutual solubility. With high-precision parts that require coatings (for lubrication or corrosion resistance, for example), the high quality of an ion-plated deposit can more than justify the cost of the process.

Chapter 8 is concerned with anodizing, an old art with a continually renewed potential. The most important commercial anodizing processes are those that have been developed for aluminum and its alloys. In conventional anodizing, as in electroplating, quality control, reliability, and reproducibility of film-deposit characteristics have improved substantially in response to the

needs of the space program. The technology that has been developed is bound to have implications for industrial and consumer products. New uses for anodized aluminum that have emerged from NASA programs include hard-anodized printed-circuit boards and lightweight, hard-anodized, diamond-impregnated laps. One of the most interesting innovative applications of anodization is to pretreat active metals (Al, Ti, and Be) so that they may be subsequently electroplated.

Although process and product innovations are frequently developed in response to a particular need, ultimate applications of a new technology may be far removed from the original purpose of the invention. Thus, the anodic oxide coatings with occluded particulate matter developed by Lockheed Aircraft Corp. for thermal control purposes (see Chapter 8) might be applicable commercially to the production of colored decorative finishes on aluminum in a one-step process. Furthermore, the general concept of forming interesting and unique surface finishes by anodizing in the presence of particulate matter could probably be extended to the coating of other metals. Similarly, the techniques developed at the Jet Propulsion Laboratory (JPL) for nickel plating of a 23-ft collimating mirror (see Chapter 2) could be extended to the application of decorative or functional coatings for very large parts generally.

One of the principal reasons for electroplating is to provide corrosion and/or oxidation resistance; more generally, however, electrochemical surface treatment can be used to add special chemical or mechanical properties to the surface while maintaining the desired structural or other characteristics of the substrate. The most challenging problems of the plating industry in the years ahead will be in the development of functional rather than decorative coatings. Many new applications should emerge where improvement of some specific property other than appearance is the primary objective. Frequently, coatings will have to be developed to meet a number of specifications simultaneously—high hardness, corrosion resistance, and solderability, for example. The increasing sophistication of the plating industry, and the firm scientific base that is developing, are bringing the technology closer to the point where coatings may be tailored for specific applications.

In the production, delivery, and testing of space-qualified hardware, NASA demanded unprecedently high standards of quality control and program management. The industry, in learning to meet rigid aerospace specifications, is in a position to emphasize better quality in commercial applications as well. In

the plating of such components as electronic gear boxes, antennas, circuit boards, slip rings, and telemetry bases for Tiros, Tetrahedral Research Satellite, OSO, Nimbus, Syncom, Oscar, Explorer, and Apollo, no aspect of finishing procedures could be taken for granted. This experience should have a profound influence on the plating industry in the years ahead.

Electroplating from Aqueous Solutions

GOLD PLATING

Gold has symbolized wealth, luxury, and power throughout history. Even today, few can afford articles of solid gold. Nevertheless, most people can derive much pleasure, at little cost, from a few microns of gold electroplated on the surface of a baser metal.

Gold plating dates back to at least 1805 (ref. 1). Until the early 1950's, the principal industrial use of electroplated gold was for jewelry and decorative insignia. As the technology of gold plating has advanced to encompass a variety of surface finishes, decorative applications have expanded. A range of attractive, fashionable gold colors can be obtained, for example, by codeposition of selected alloying elements with gold. Because of the relatively low gold content of such films, the plating operation is not expensive. Antique gold finishes are becoming increasingly popular for giving an heirloom look to relatively inexpensive jewelry. Flash gold deposits, which are less than 0.000007 in. thick, have brought "gold" trinkets within the reach of practically everyone. Recently, gold-plated tableware and serving pieces have been well received in the consumer market (ref. 2).

Gold has many useful properties apart from its beauty and intrinsic worth. It is resistant to tarnish, chemical corrosion, and high-temperature oxidation. Furthermore, gold-plated surfaces maintain low electric contact resistance and are solderable even after extended periods of storage. These engineering properties, which are almost unique, have led to increasing use of gold plate in the electronics, control, and communication industries.

The quality demanded of industrial gold coatings can be quite different from that of purely decorative coatings. Appearance is of primary importance in the latter, while mechanical and physical properties are of secondary interest. In engineering applications, such properties as surface hardness, wear resistance, and solderability can be critical. As a consequence, much effort has gone into the development of gold-plating formulations that optimize specific properties.

For space-qualified hardware, it is necessary to control deposit characteristics with absolute reliability. No aspect of the plating process can be taken for granted; surface preparation procedures, plating-bath variables, and post-plating handling procedures must all be controlled with meticulous care. Obviously, close quality control in any manufacturing operation adds to the cost of the finished product. In the space program, where defects cannot be tolerated, such costs are unavoidable; in industrial practice, they must be weighed against the cost of rejected parts. For the sophisticated electronic and communication hardware in which gold-plated contacts are used, a premium is beginning to be placed on high reliability.

Bath Compositions

There is a vast number of proprietary gold-plating formulations, each purportedly producing a different type of deposit. Before a producer starts the fabrication of gold-plated parts on a large scale, he should consult the suppliers of proprietary solutions. Commercial plating is still very much an art, and there is no substitute for prior experience. Even after a basic plating formulation has been selected, modifications in operating procedure are quite likely to be required to produce parts that consistently meet the specifications. The modifications might be as simple as controlling the bath at a particular temperature or pH within the manufacturer's recommended range; in other cases, the modifications might be very extensive, and even involve operating under conditions outside the recommended range. Nonetheless, if the desired properties are well defined, they can almost certainly be achieved by proper attention to bath composition, purity, temperature, pH, current density, agitation, and additive concentrations.

Before 1950, when gold plating was used primarily for decorative purposes, the hot cyanide bath described in table 1 was used almost exclusively (ref. 2). Unfortunately, hot cyanide gold coat-

TABLE 1.—*Hot Cyanide Gold-Plating Bath*

Gold	4–12 g/liter
Potassium cyanide	30 g/liter
Potassium carbonate	30 g/liter
Dibasic potassium phosphate	30 g/liter
Temperature	50°–65° C
Current density	Up to 5 A/ft ²
Anodes	Gold or stainless steel

ings are difficult to control, and the baths are subject to rapid contamination that seriously impairs coating reliability. Since 1950, as engineering uses of gold coatings have grown in importance, significant improvements have been made in plating formulations to meet the new demands.

For general gold-plating applications, the cold cyanide bath (table 2) is rapidly replacing the hot cyanide formulation. Cyanide decomposition products are the major contaminants in all cyanide baths, but the rate of decomposition is greatly accelerated as operating temperatures are increased. Cold cyanide baths deteriorate at a very slow rate and can be used with a minimum of maintenance for 4 or 5 years. Deposits are typically 99.9% pure or less depending on operating conditions. Gold coatings of 99.99% purity can be electrodeposited from acid citrate baths under the conditions given in table 3.

In functional or engineering-type gold coatings, a compromise must generally be made between purity and hardness. The purest gold is too soft for most contacts, and it tends to gall or cold-weld in service. On the other hand, reliable contacts can never be achieved if no attempt is made to keep impurities from depositing along with the gold. Coatings of high purity, optimized with respect to surface hardness, are usually the most desirable.

Engineering Applications

Gold-Plated Slip Rings

The recent trends in gold plating toward coatings of high reliability, controlled purity, and surface hardness for engineer-

TABLE 2.—*Cold Cyanide Gold-Plating Bath*

Gold	4–12 g/liter
Potassium cyanide	90 g/liter
Metallic brightener	0.01–0.12
Temperature	13°–25° C
Current density	Up to 6 A/ft ²
Anodes	Stainless steel

TABLE 3.—*Acid Citrate Gold-Plating Bath*

Gold	4–12 g/liter
Citrates	90 g/liter
pH	3.0–6.0
Current density	Up to 10 A/ft ²
Anodes	Carbon or platinum

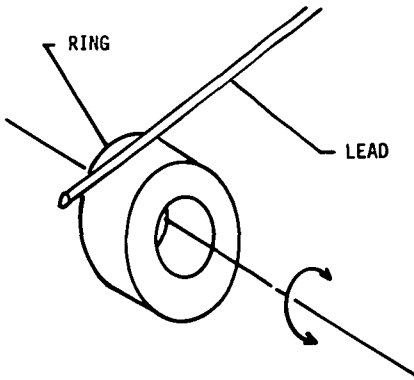


FIGURE 1.—Elementary slip-ring concept.

ing use are clearly illustrated in the history of slip-ring and brush contacts. A slip ring, in essence, is an electrically conducting ring that is rubbed by a conducting brush or lead. In an electric circuit, the ring can be rotated continuously without interruption of current flow. The elementary concept is illustrated in figure 1. In actual practice, a number of slip rings are mounted on a single shaft and are incorporated into a capsule or cartridge assembly with suitably placed brushes, bearings, and structural supports. The slip ring and brush contact is a convenient means for transmitting electric signals to or from a rotating part.

The slip-ring assemblies produced in the 1950's were so unreliable that performance data could easily vary by orders of magnitude. At one time, 75% of all slip rings manufactured were rejected for space use because of their high noise (excursions in contact resistance). While the poor quality of gold plating was not the only source of difficulty, it did present a significant barrier to high reliability (ref. 3).

The ideal slip-ring material should have high current-carrying capability and should be machinable, relatively hard, wear-resistant, and corrosion-resistant. The ideal material does not exist, but gold seems to provide the best compromise. The major problem with gold is that it is relatively soft. Fairly hard gold surfaces (up to a Knoop hardness of 200) can be obtained, however, by the proper electroplating methods.

There are many ways to manufacture slip-ring assemblies. One method is illustrated in figure 2. Lead wires are put together in a pencil shape, with terminal ends suitably placed along the axis of the cylinder. The leads are cast in plastic to hold them in place, and the plastic is grooved and drilled to expose the lead ends that will ultimately connect to the slip rings. Electroless copper is deposited at the bottom of the groove and built up to a thickness

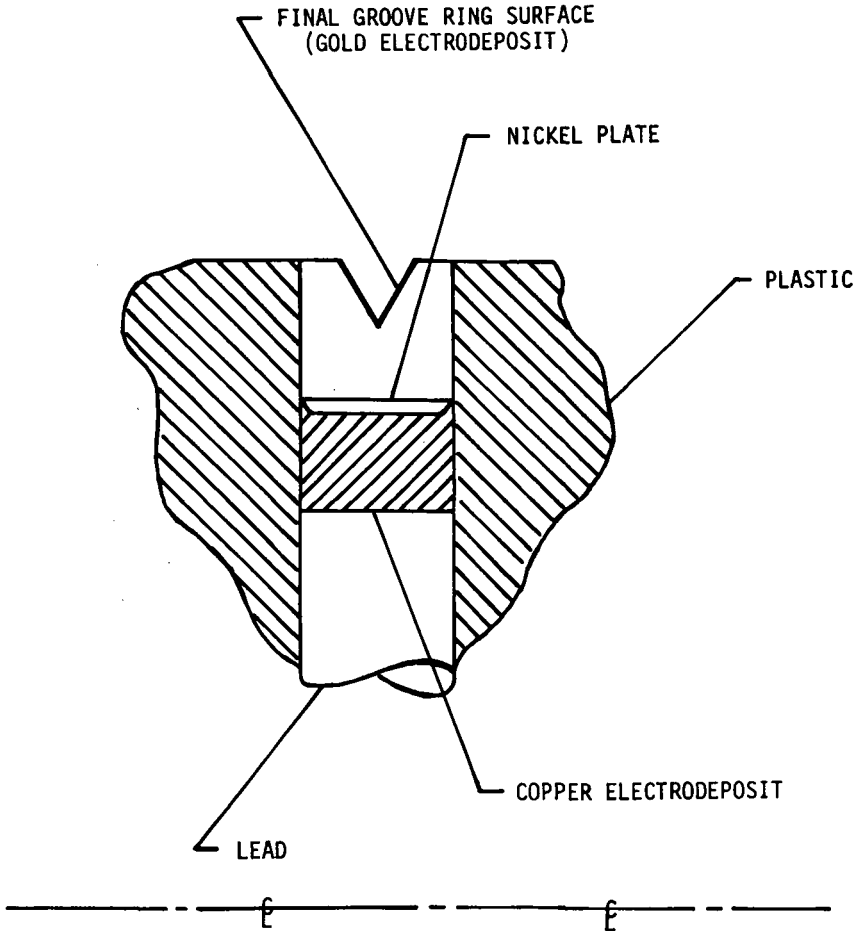


FIGURE 2.—Electrodeposited slip ring.

of 2 to 3 mils by electroplating. The copper surface is flashed with nickel, and the slip rings, 15 mils in thickness, are electrodeposited from a cold cyanide bath. The nickel acts as a diffusion barrier to prevent migration of copper out through the gold. Usually, the gold deposit is V-grooved, and a hard gold electroplate is deposited on the surface.

For slip rings of maximum durability and reliability in outer space, the gold deposit should be as hard as possible. Poly-Scientific Div., Litton Precision Products, Inc., under contract to NASA Marshall Space Flight Center (MSFC), found that the quality of electroformed or electroplated gold depends on the ratio of current density to the gold content of the cyanide bath (ref. 4).

If the ratio is greater than 1.2, the deposits are so hard that they crack. At ratios between 0.9 and 1.2, deposits are hard and uniform, as desired. At ratios below 0.9, the gold surface is characterized by hard bumps or cones projecting from a soft matrix. At the optimum current density/concentration ratio, the gold plate has a 125 Knoop hardness. The use of a modified nickel-hardened Technic Orotherm-ST bath can give a surface hardness consistently greater than 180 Knoop. The plate is 99.9% Au (24k) containing some nickel. The process is proprietary to the Poly-Scientific Division, Litton Precision Products, Inc. Battelle Memorial Institute has recommended the use of Au-0.1 Co electroplates (Sel-Rex Autronex CI) for short-duration applications (under 1000 cycles) requiring low wear rates, low contact resistance, low noise, and resistance to air contamination (ref. 5).

Maximizing signal-to-noise ratios in slip-ring capsule assemblies is a difficult problem. Proper lubrication of the rings is one of the most crucial factors in reducing noise, but lubrication is still something of an art. Battelle, under contract to MSFC investigated the problem of noise in slip rings and traced it to the buildup of polymeric gunk (possibly cyanide decomposition products) on low-energy gold-plated contacts (ref. 6). Because absolutely clean gold contacts freeze in service, a lubricant of some kind is necessary. It may be provided by dirt or gunk that happens to be present, or it may be introduced intentionally. Some gold plates have inherently lower friction coefficients than others. Acid gold citrate deposits are among the best, but they tend to be rather soft. Battelle found that a mixture of 75% OS-124 and 25% MC-210 (Monsanto) provided good lubrication for gold coatings and exceptionally low noise. When the lubricant was first tested, however, several slip-ring assemblies were covered with gold spatters; apparently, the oil floats the wear debris. Performance is greatly improved if the amount of lubricant is held to a minimum.

The basic principles developed for lubricated slip-ring design under NASA sponsorship have had far-reaching implications. The initial impetus for the work came from the Saturn V inertial-guidance system, but rotating contacts are an important part of any computerized communication network. Even a nominally "static" contact is subjected to vibration in service and should be appropriately lubricated. According to Gordon Gaines of Battelle Memorial Institute, Columbus, the design of the Boeing 747 guidance system took into account many of the NASA findings. Several companies have changed their hermetically sealed relay

designs to include some of the factors identified by NASA for good slip-ring design.

The lead wires used in slip rings were at one time made from Teflon-insulated, silver-electroplated copper wire. Problems were encountered when plating flaws permitted oxidation of the copper substrate to cuprous oxide, a phenomenon known as "red plague." Nickel-plated copper is not subject to this type of failure, but the resultant wire is stiffer and less flexible than the silver-plated product. Battelle has developed a silver alloy electroplate that may provide a satisfactory compromise (ref. 7).

Internally Gold-Plated Plastic Bladders

Under zero-gravity conditions, one of the best methods for metering propellants into a rocket engine thrust chamber is to use elastomeric expulsion bladders. A suitable bladder material is carboxy nitroso rubber (CNR), developed by Thiokol Reaction Motors Div. under a joint Air Force/NASA program (ref. 8). CNR is both flexible and resistant to nitrogen tetroxide, a common rocket propellant oxidizer. Unfortunately, all polymeric materials, including CNR, are permeable to liquids and gases to some extent. In the development of the Saturn V vehicle, it became clear that an impermeable bladder would have to be developed.

Thiokol, in cooperation with MSFC, developed gold-lined CNR bladders that effectively solved the problem. The general concept of forming well-bonded metal-lined plastics could be of interest for many nonaerospace applications. In fabricating the bladders, MSFC electroformed three mils of gold onto the exterior surface of an aluminum mandrel of the general size and shape shown in figure 3. Thiokol applied a CNR coating solution with an added nitroso copolymer gum to promote adhesion. The mandrel was finally dissolved out with a water solution of Oakite no. 130 at a concentration of 0.5 lb/gal. The final product was thus a gold-lined plastic bladder, of a rather intricate shape. While the production method is certainly costly, it is difficult to conceive of competitive techniques that would meet the need as well.

Thermal-Control Coatings

Electroplated gold has been used extensively in the space program to provide optical surfaces for temperature control of spacecraft. Since weight is a critical factor in all aerospace applications, the most desirable substrates are the light metals, particularly aluminum or magnesium alloys. NASA has developed

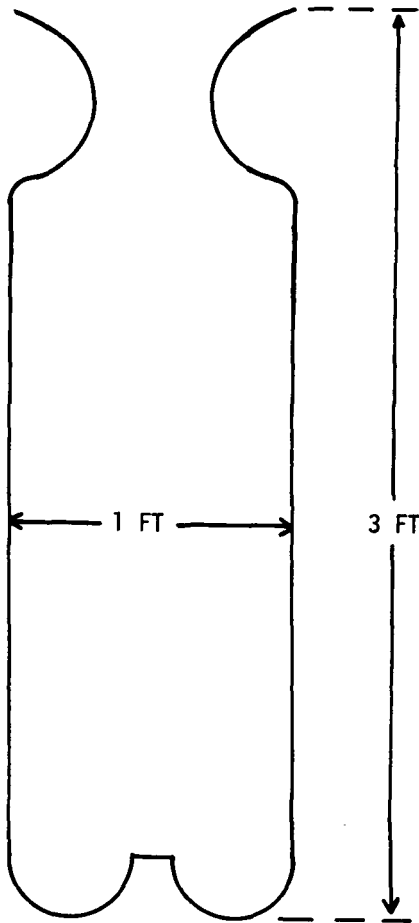


FIGURE 3.—Gold-lined elastomeric explosion bladder.

reliable procedures for depositing consistently high-emittance, high-quality gold plate on lightweight structural materials.

For the gold plating of aluminum and magnesium alloys to a mirror finish, JPL specifications call for a multilayer deposition process. A zinc coating is first applied on the alloy by the immersion process (see Chapter 6). Copper is then deposited to protect the zinc. Silver is electroplated over the copper, and finally a surface layer of gold, about 0.1 mil thick, is applied from a proprietary Sel-Rex "Bright Gold" bath. The actual process is still more complicated, since the surfaces must be meticulously cleaned and sometimes etched or activated before the multistep plating is even started. To assure adherence and a mirror finish in the final product, a few baking and buffing operations are sometimes interspersed at various points (refs. 9 and 10).

Internal Plating of Long, Narrow Tubes

Plating of the interior surfaces of small-bore tubes is generally quite troublesome. Whitfield of NASA Goddard Space Flight Center (GSFC) devised a relatively simple technique for electroplating gold onto the interior surfaces of stainless steel tubing (ref. 11). The method was developed for the Department of Agriculture for noncatalytic gas chromatography columns. The columns are normally made of stainless steel, which was found to accelerate the decomposition of certain organic compounds. The compounds were stable in contact with gold surfaces, but no commercial plating vendor was able to apply uniform, adherent gold coatings to the inside walls of the rather narrow columns.

Effective plating was achieved with inside wire anodes, sheathed in loosely woven nylon braid. The flexible braid, which is available commercially, provides insulation against short circuiting or burning, while permitting good contact between the wire and the plating electrolyte. Other technical problems, such as pumping electrolytes through the tubing and activating the stainless steel for plating, were solved in a fairly conventional manner. An ordinary laboratory pump, connected to the steel columns by Tygon tubing, transported the plating solutions. Activation of the stainless steel and application of a nickel strike that would be receptive to gold plating presented no unusual difficulties when insulated nickel wire anodes were used. For gold plating, the proprietary Sel-Rex BDT bath operated at 49° C proved most satisfactory. The anodes were nylon-sheathed, gold-plated stainless steel wires. The process, which is described in detail in reference 11, has been used to apply uniform 0.3-mil gold coatings to the inside walls of type 316 stainless steel tubing 3/16 in. in diam. and 76 in. long.

By using Whitfield's general method, it should be possible to plate the interior of any small-bore tubing with any metal or alloy amenable to electrodeposition on the surface of interest. In the chemical processing industries, for example, it might be useful to apply corrosion-resistant coatings to the interior of pipelines, while maintaining the structural properties of the base material.

Plated Seals and Joints

The Rocketdyne Division, North American Rockwell Corp. used gold plating in a rather novel way to fabricate leakproof joints for spacecraft propulsion systems (ref. 12). In a rocket engine, some parts must be capable of disassembly and cannot therefore be welded. The engine design is complicated by very

high temperatures in exhaust lines, cryogenic temperatures in liquid hydrogen and liquid oxygen propellant lines, and extremely high pressures in all lines. Hence, the development of leakproof nonwelded joints presents a significant challenge. North American Rockwell devised and patented a pressure-actuated seal known as Naflex,* which was constructed of Inco 718 and plated with 1 to 1.5 mils of silver. The seals performed effectively in service, but the silver plate was found to be blistered after hot firing, and the seals stuck to the mating flanges. The blistering was traced to oxygen diffusion through the silver at elevated temperatures and subsequent oxidation of the base metal beneath the plating. The problem was solved by preplating the seals with 0.05 mil of proprietary Sel-Rex Pur-A-Gold 401 prior to applying the silver plate. A final baking of the seals for one hour at 504° to 515° C diffused the gold into the base metal, softened the silver, and improved the adhesion of the silver plate, which completely eliminated the blistering. The plated seals still stuck to the mating Hastelloy-C flanges, but electrodeposition of 5 to 10 μ in. of Sel-Rex rhodium over the gold and silver solved this difficulty without degrading the sealing properties in any way.

The North American Naflex seals were developed in response to a particularly difficult NASA problem. They are not likely to be used in routine applications, but as technology becomes increasingly sophisticated, today's exotic conditions become more and more commonplace. The use of high-temperature processing lines and cryogenic piping in industry is expected to expand over the next few years, and leakproof connectors can be a critical element in overall design.

Plating of Printed Circuits and Electronic Hardware

In printed-wiring boards, gold plating provides oxidation resistance, a good soldering surface, and lubrication for sliding contacts. The etched circuits, which are used in the space program, meet exceptionally high standards of quality and reliability. The procedure used at GSFC for producing etched-circuit boards to exacting specifications is described in some detail by Whitfield (ref. 13). In general, copper-printed circuits are gold-plated directly (without an intermediate metal layer) with either acid gold (Sel-Rex CI) or cyanide-free alkaline gold (Sel-Rex BDT, pH 9.4). The plate must be free from pits, dents, pinholes, blisters, and extraneous metal, and must retain reliable adhesion.

*Registered trade name.

In the manufacture of printed-circuit boards, as well as other electronic hardware, uniform gold coatings must frequently be applied through holes or into deep recesses. TRW, Inc., in the course of its spacecraft work, found that the Sel-Rex BDT* 200 noncyanide gold-plating process has exceptionally uniform throwing power for penetration into deep holes and recesses (ref. 14). The best gold coatings in terms of density, adhesion, nonporosity, and uniformity were obtained at a somewhat slower deposition rate than recommended by the manufacturer. TRW used the process to gold-plate space-qualified chassis housing assemblies, heat sinks, brackets, conductors, contacts, shields, terminals, diode holders, waveguides, and horns for the Apollo Lunar Module, Pioneer, and Explorer.

For multilayer printed-circuit boards, a number of plated holes are required to connect circuits in different layers, and to provide receptacles for auxiliary boards and leads. TRW found that BDT 200 was the only gold-plating process that gave deposits sufficiently uniform for perfect contact with plug-in fingers. Precise control of current and plating time is extremely important for accurate plating work. The control that has been applied in the plating of spacecraft hardware has greatly reduced rejects. The same kind of control, which may initially add to the fabrication expense, can in the long run effect cost economies in critical industrial components as well.

NICKEL PLATING

In industry today, nickel is the most important of all commercial electroplating materials. Both the science and technology of nickelplating methods are exceedingly well developed, and nickel plates with almost any set of desired properties can be electrodeposited on metal parts of almost any size. Numerous studies have established and codified the effects of plating-bath temperature, nickel concentration, current density, pH, agitation, and additives on the properties of electroplated nickel deposits. Many novel applications of nickel plating were brought about by the space program, and many more are to be expected as technology advances. Nonetheless, most innovations will probably involve relatively minor modifications in the state of the art.

*Registered trade mark.

*Bath Compositions***Watts Baths**

Electroplated nickel can give both a decorative surface finish and a high degree of corrosion resistance to common metallic substrates. The most extensively studied nickel-plating process is based on the Watts bath, which dates back to 1916 (ref. 15). Two basic Watts bath formulations are given in table 4 (ref. 2). In commercial practice, innumerable variations have been used to produce coatings with particular properties for given applications.

Nickel is introduced into the Watts bath primarily in the form of the sulfate. The reason is in part economic, since nickel sulfate is the cheapest and most readily available nickel salt with a stable anion. In addition, the high solubility of the sulfate provides a high nickel-ion concentration in the bath. The high salt concentration, in turn, lowers the resistivity of the bath, raises the limiting cathode-current density for sound nickel deposits, and hence reduces power costs.

The chloride ion is included for its beneficial effects on bath conductivity, cathode efficiency, and the cathode potential curve. Chloride ions also reduce anode polarization and hence facilitate anode dissolution. The use of nickel chloride, rather than another chloride salt, prevents extraneous metal contamination.

Boric acid acts as a buffer in the Watts bath to maintain the pH in the desired range. Its presence may also improve the quality of the nickel plate although excellent heavy deposits have been obtained from unbuffered, boiling electrolytes (ref. 1).

The engineering properties of electroplated nickel deposits that are frequently important in engineering applications are ductility, tensile strength, hardness, metallographic structure, and internal stress. The first three properties are not generally independent: an increase in hardness almost always implies an increase in tensile strength and a decrease in ductility. Internal contractile

TABLE 4.—*Watts-Bath Formulations*

Constituent	Low-pH bath	High-pH bath
Nickel sulfate	44 oz/gal	32 oz/gal
Nickel chloride	6 oz/gal	6 oz/gal
Boric acid	5 oz/gal	4 oz/gal
pH	1.5–4.5	4.5–6.0
Temperature	46°–60° C	46°–71° C
Current density	25–100 A/ft ²	20–100 A/ft ²

stress, which is often manifested by spontaneous fracture of the electroplated films in service, is a separate matter entirely.

By and large, electrodeposition at pH 4.5 or less leads to soft, ductile coatings. Ductility decreases rapidly as the pH of the plating bath is increased above 5. Hardness and tensile strength increase correspondingly.

At constant pH, ductility increases and hardness decreases as the bath temperature is raised toward the upper part of the operating range. The effect is more pronounced at pH 2, for example, than at pH 5 (ref. 2).

Current density has little effect on the mechanical properties of nickel electroplates from low-pH Watts baths. At pH 5, however, there seems to be some decrease in hardness and tensile strength as current density rises from 10 to 40 A/ft² (ref. 2).

The microstructure of electroplated nickel films deposited at 54° C from a bath at pH 2 is columnar or conical and tends to coarsen as the plate thickens. Grain refinement is promoted by higher pH, lower plating temperature, or higher chloride concentration in the bath.

Internal stress does not necessarily correlate with hardness or ductility, although the introduction of some ductility does permit deformation and hence reduces the danger of spontaneous cracking. Usually, specific organic agents are added to the plating bath for the express purpose of reducing internal stresses (refs. 1 and 2). The effects of the normal operating variables are not always consistent. In general, however, the pH of the Watts bath should be well below 5 to minimize internal stresses. Increase of current density or chloride content of the plating bath tends to increase internal stress.

Hard Nickel Baths

If a particularly hard nickel plate is required (for wear resistance or for salvaging of worn parts, for example), special plating baths that are quite different in composition from the basic Watts bath are generally used. The "hard nickel" bath has been used extensively for many years to build up worn or milled parts (ref. 1 and 2). The actual hardness of the nickel deposits depends critically on current density, bath pH, and temperature, all of which must be very closely controlled. More recently, it has been found that additions of sulfonated aromatic aldehydes or similar compounds (refs. 1 and 16) to the Watts bath will produce hard, compressively stressed coatings with

some ductility. These coatings have been found particularly useful for plating steel airplane propellers.

Phosphorus Acid Baths

Nickel-phosphorus deposits, which are normal in electroless nickel plating (see Chapter 6), can also be deposited by electroplating. The phosphorus content of the deposits can be varied between 2% and 15% by controlling the phosphorus acid concentration in the plating bath. Although coating hardness can be maximized by heat treatment at 400° C subsequent to plating, hot hardness remains relatively low (ref. 1).

Sulfamate Baths

Interest in nickel sulfamate and sulfamate-chloride baths has increased in recent years (refs. 1 and 16). In general, sulfamate nickel deposits are moderately hard and ductile. They have high tensile strength and relatively low internal contractile stress. As a rule, the sulfamate-chloride nickel deposits have somewhat higher internal stresses than the chloride-free deposits. It is possible to form either type deposit in compression by addition of various stress-reducing agents to the plating bath. Thus, the beneficial effects of chloride ion on plating efficiency can be retained without adversely affecting internal stress behavior.

Bright Nickel Baths

The nickel deposits electroplated from Watts baths, or from most of the specialty baths discussed above, are dull and matte-grey in appearance. They can be buffed or electropolished to obtain a bright, decorative surface finish, but the additional processing is for the most part uneconomic. Many proprietary brightening agents can be added to the standard plating baths to produce bright, lustrous deposits directly (refs. 1 and 2). Proprietary leveling agents are generally added as well to produce smooth, even deposits with good surface coverage. Nevertheless, the selection of a suitable bright nickel-plating-bath formulation is still something of an art. When organic brightening agents are added to a bath, it is generally necessary to adjust and carefully control all of the operating variables—such as current density, pH, bath composition, and temperature to assure satisfactory deposits. Surface preparation prior to bright plating is quite critical, and impurities are far more detrimental in bright than in dull plating.

The mechanical properties of bright nickel plates are not as good as might be desired. Many brighteners introduce high internal tensile stresses into the deposits. Other brighteners, which permit the formation of relatively stress-free deposits, unfortunately result in highly brittle plates. Semibright nickel plating represents a compromise between bright plating, which is prone to fracture, and dull plating, which requires buffing to obtain a decorative finish. Semibright deposits, formed from modified Watts baths, have good ductility and can be buffed readily with a minimum of effort. In practical applications, bright nickel is often deposited over semibright nickel (ref. 1).

Recent Applications

Although nickel plating is a well-developed art of considerable industrial importance, some of the plating requirements associated with the space program proved highly challenging to commercial plating vendors.

Plating of Large Parts

The JPL space simulator includes a 23-ft aluminum collimating mirror with an optically polished nickel front face. A similar 10-ft mirror has been successfully nickel-plated by the electroless Kanigen process (see Chapter 6). For the larger mirror, a nickel plate thicker than the 7 to 8 mils that can normally be obtained by the Kanigen process was desired. Furthermore, a surface hardness of 50 Rockwell C was specified, and Kanigen nickel must be heat-treated to achieve this value. The Kanigen process requires a great deal of mirror handling, which raises costs considerably.

Electroplating was ultimately selected as the optimum method for nickel-coating the 23-ft mirror (ref. 17). The task was completed successfully, although several difficult problems had to be overcome. It was found that pits up to 10 mils in diam in the aluminum substrate could be successfully plated over with 25 mils of nickel. Larger pits had to be filled with epoxy or aluminum dowel rod. A polyvinylchloride (PVC) strip (8 in. wide) was attached to the edge of the mirror with epoxy and screws to permit use of the mirror as its own tank, and thus eliminate the need for large, cumbersome separate plating tanks. Solutions were removed from the mirror-tank by positive suction through a pipe located at the center of the structure. Anodes were distributed to optimize current density over the mirror surface and were regulated by rheostats. The mirror was rotated at about 5

rpm during most of the preplating and plating steps. A standard cleaning procedure was used involving degreasing in an alkaline solution, cold-water rinsing, sulfuric acid etching, further rinsing, nitric-hydrochloric acid etching, and final rinsing.

Nickel cannot be plated directly over aluminum for reasons discussed below. A zinc-immersion coating was therefore deposited first from a proprietary zincate solution. When this solution was removed and rinsed off, copper anodes were mounted in position, and a copper strike was deposited from a cyanide bath to protect the zinc. It was quite important to apply the copper strike with a minimum of delay to prevent oxidation of the zinc flash and attendant loss of copper adhesion. Nickel plating was done from a sulfate solution, using nickel anodes, and required 90 hr of continuous operation. A low spot in the resultant coating was repaired by placing a nickel anode directly over the spot and electrodepositing for $4\frac{1}{2}$ hrs. Although there were some edge problems on the outer 2 to 3 in. of the mirror, the coating proved quite satisfactory. The nickel deposit was 0.033 ± 0.010 in. thick (neglecting the outer edge) and had a Rockwell "C" hardness of 50 to 58. The mirror remained mounted on the grind and polish machine throughout the plating and final optical polishing processes.

The general plating techniques developed in this project might be usefully applied to other large plating jobs. The larger the substrate, the less likely it is to be free from structural defects. A decision must be made as to which defects can be plated over and which must be repaired. Where possible, the erection of a temporary polyvinylchloride tank around the part to be plated can considerably reduce costs, particularly if different plating solutions can be readily introduced and drained out of the same tank. Principles of good anode placement and design are equally applicable to the coating of large and small parts. The successful repair of a low spot on the electroplated collimating mirror is particularly encouraging from the point of view of potential commercial applications.

Low Stress Deposits

Internal stresses in nickel-plated deposits can lead to very serious mechanical failures in service if coated parts are subjected to tensile stresses. Electrodeposits from Watts-type nickel baths are usually formed with internal stresses of 14 000 to 50 000 psi, depending on the purity of the solutions used. The lower stress levels result if the bath is very carefully prepared

and operating variables are closely controlled; however, even 14 000 psi can be objectionably high in critical applications. There are many proprietary agents that purportedly reduce the stress in Watts-type deposits. Most of these contain compounds having a ($=C-SO_2-$) group in the molecule, but little is known about how the additives actually function.

One stress-relieving agent, meta-benzenedisulfonic acid, also promotes the formation of uniformly hard nickel deposits. Munford and Whitfield of GSFC studied the effects of meta-benzenedisulfonic acid additions to Watts-type plating baths in some detail (ref. 18). The basic plating bath composition, to which various additions of meta-benzenedisulfonic acid were made, is given in table 5 (from ref. 18). Prior to its use, the bath was filtered and electrolyzed to remove impurities. The test samples were cold-rolled steel strips that were vapor-degreased, ultrasonically cleaned, and acid-cleaned in preparation for plating. The plated samples were tested for residual stress and hardness.

The effect of meta-benzenedisulfonic acid additions on the internal stress of nickel deposits is summarized in figure 4. It is seen that at low concentrations, the additions actually increase internal stresses. Additive concentrations close to 25 g/liter would be required to reduce internal stress to effectively zero. The internal stress is almost independent of current densities above 6.5 A/dm². Knoop hardness could not be correlated with internal stress, although the hardest coatings were deposited at low current density, where the stress levels were highest. As a consequence, hardness testing cannot be used as a reliable indicator of internal stress. If low stress is important, plated parts should be tested for stress directly, before being put into service. X-ray diffraction is one possible test. (ref. 18).

PLATING ON ACTIVE-METAL SUBSTRATES

In aircraft and space vehicles, weight is always at a premium; but even in terrestrial applications, the lightweight structural metals—aluminum, magnesium, beryllium, and titanium—are becoming increasingly attractive. The usefulness of these metals can be expanded greatly by applying coatings that modify surface properties in a controlled way.

Unfortunately, electroplating, which is one of the cheapest and most versatile of the common coating methods, is not directly applicable to the light metals. The basic problem stems from the high electrochemical potential of these metals in aqueous solution

TABLE 5.—*Watts-Type Plating Bath for Internal-Stress Experiments*

Constituent	Concentration, g/liter
Nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)	300
Nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$)	37.5
Boric Acid (H_3BO_3)	45
SNAP antipit wetting agent	0.37
Nickel carbonate to increase pH to 4.5	

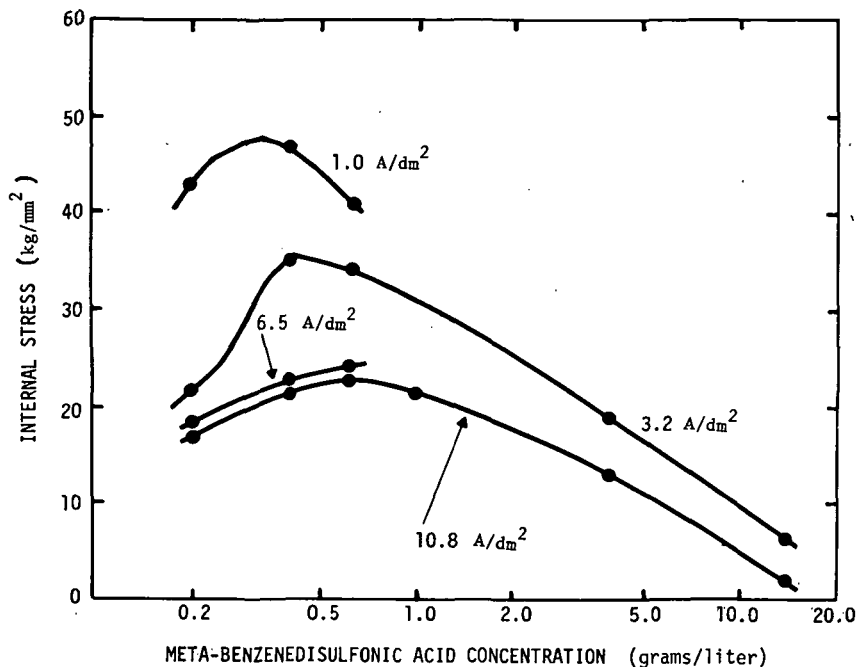


FIGURE 4.—Effect of additive concentrations on residual stress at various current densities.

and their high reactivity in air at room temperature. While aluminum, for example, is normally considered to be highly resistant to atmospheric attack, it is, in fact, oxidized very rapidly when exposed to the atmosphere initially, but the film of aluminum oxide acts as a protective coating. This highly tenacious film inhibits the adhesion of electrodeposited coatings. Similar problems are encountered with beryllium, magnesium, and titanium. In the space program, the development of reliable electroplating methods applicable to the light metals was greatly accelerated.

Plating on Aluminum

Satisfactory electroplating of aluminum alloys depends upon removing the natural oxide film and/or replacing it with a film that will not interfere with the adhesion of electrodeposited layers. Most of the practical techniques are based on predeposition of a zinc immersion coating, followed by a copper flash that prevents deterioration of the zinc plate. The resulting product behaves just like copper in any subsequent electroplating operations. Both the zinc and copper coatings must be continuous, adherent, and free from defects. Generally, aluminum surfaces are prepared for zinc immersion plating by vapor degreasing in trichloroethylene, soaking in Oakite no. 90 to remove any conversion coatings, and pickling in nitric acid. Any standard zincate bath may be used for immersion coating, but the temperature must be carefully controlled, and the bath vigorously agitated if the requisite thin, tightly adherent metallic zinc plate is to be obtained. At JPL, the copper strike that protects the zinc is applied from a cyanide copper bath with added Rochelle salt (ref. 19).

Once a satisfactory zinc-copper layered coating has been obtained, almost any of the plating metals may be deposited subsequently. Surface coatings of hard and soft gold, tin, chromium, nickel, and silver have proved most useful in industrial applications (ref. 20). For example, electroplated tin imparts good solderability to aluminum alloys and permits more extensive use of the metal in electronics. In lightweight machinery, aluminum alloys have good structural properties but poor surface characteristics; an electroplated chromium coating can provide a hard, wear-resistant surface that allows one to take advantage of the favorable strength-to-weight ratio of the substrate. Nickel-plated aluminum is used in rectifier stacks. Silver- and gold-plated aluminum are used for low-resistance contacts. The final surface finish after electroplating may be specular or dull, depending largely on the previous grinding and polishing of the substrate. In many engineering applications, a dull finish may be satisfactory. For mirrors, thermal control coatings, or decorative applications, a bright finish is normally specified.

Plating on Magnesium

The very poor corrosion resistance of magnesium virtually precludes the use of the uncoated metal in most structural applications. The most useful coating materials are nickel and tin.

To protect the magnesium, the coatings must be adherent and pore-free. Electroless nickel can be deposited on a suitably activated magnesium surface, but the coatings tend to be porous and do not provide adequate protection against corrosion in a salt spray test (ref. 21).

The main problem in electroplating magnesium and its alloys is the rapid formation of a hydroxide film in aqueous solutions. A zinc-copper preplating process, similar to that described above in preparing aluminum alloys, is the most common pretreatment. Prior to the deposition of a zinc-immersion coating, magnesium alloys are generally cleaned in an alkaline bath at pH 11 or higher, pickled in acid, and surface-activated.

Practically every magnesium alloy requires a different pickling procedure. The Boeing Co. showed, for example, that the thoriated alloy, HM21A, could be pickled in 70% to 80% phosphoric acid, while the AZ31B alloy did not respond at all (ref. 21). On the other hand, a chromic-nitric-hydrochloric acid pickling bath, which was found effective for a ZK60A alloy, proved too active for AZ31B and tended to cause surface pitting. The best compromise for AZ31B was to eliminate acid pickling altogether. In fact, most alloys should not be pickled if a mirror finish is wanted on the final product (ref. 9).

Activation of magnesium alloy surfaces, which is needed to make them receptive to zinc plating, involves replacement of oxide or hydroxide films with fluoride. A typical activator bath is a mixture of phosphoric acid and ammonium bifluoride (ref. 21).

The zinc-immersion-plating step is critical for all subsequent plating operations. Boeing found that zinc thicknesses of 5 to 15 $\mu\text{in.}$ are optimum. Immersion times, bath temperature, composition, pH, and fluoride content must be controlled fairly closely to achieve satisfactory plating quality (ref. 21).

The copper strike used to protect the zinc coating is applied in the Boeing laboratory from a high-fluoride copper solution or from a Rochelle salt solution. As usual, some special technique is involved: for best results, a free-cyanide concentration of 0.75 oz/gal is maintained continuously. A potential of $\frac{1}{2}$ to 1 V imposed on parts before immersion in the copper bath helps to prevent gas evolution, which can damage the zinc plate. Current density must be closely controlled during the entire copper electroplating procedure. Deposition of 200 to 300 $\mu\text{in.}$ of copper appears to be optimum. If the zinc-copper coating is satisfactory, a final corrosion-resistant surface of nickel, tin, or gold, for

example, can be electrodeposited by standard plating techniques.

While the plating of any magnesium alloy is far from straightforward, the plating of magnesium-lithium alloys is next to impossible. Lowery and Mitchell of MSFC found that common acid-pickling solutions and activators did not adequately prepare the surfaces of LA-141 and LAZ-933 Mg-Li alloys for subsequent zinc-immersion treatment and plating (ref. 22). The alloys responded well, however, to pickling in a 6% solution of nitric acid. Treatment in a modified "Dow" zincate bath at pH 7.5 to 8.0 then resulted in an adherent zinc plate. A copper strike was applied from a cyanide bath. Finally, a coating of gold, cadmium, or nickel was electrodeposited. Although adherent coatings were obtained, porosity proved troublesome. In salt-spray tests, galvanic corrosion was apparently initiated at pore sites. This problem might be alleviated by deposition of corrosion-resistant films more than 2 mils thick.

Plating on Beryllium

Beryllium, like aluminum, is rapidly coated with a thin, tightly adherent oxide skin when it is exposed to air at room temperature. The oxide, which interferes with normal plating operations, may be removed by light etching in a solution of 45% to 50% nitric acid and 1% to 3% hydrofluoric acid at 32° C for 1 to 2 min. The etched surface is receptive to a zinc immersion coating. The usual copper strike can be applied from a cyanide solution, and other metals may be subsequently deposited over the copper (ref. 23). At MSFC for example, copper from a pyrophosphate solution and nickel from a Watts bath were successfully deposited by electroplating. The electroplated surfaces might provide a means for brazing beryllium to itself or to other metals (refs. 23 and 24).

Plating on Titanium

Titanium and its alloys are particularly difficult to electroplate successfully, not only because of the tenacious natural oxide film, but also because of the susceptibility of many titanium alloys to hydrogen embrittlement. A zinc-immersion preplate, which allows subsequent electroplating of aluminum, magnesium, and beryllium alloys, cannot be deposited satisfactorily on titanium alloys. Apparently, a titanium oxide film forms more rapidly than the zinc plate in the aqueous solution.

Battelle Memorial Institute reviewed the available methods for

plating various metals onto titanium surfaces for MSFC. Pretreatment procedures to remove the natural oxide or to replace it with a film that does not interfere with adhesion are, of course, critical to successful plating. The most common pretreatments include (1) anodic etching and zinc-strike plating, (2) acid pickling, and (3) electroless deposition of nickel on vapor-blasted surfaces. No routine procedures are effective for all titanium alloys.

Titanium surfaces can be prepared for plating by anodic etching (see Chapter 8). A zinc strike may then be applied by electrodeposition from an essentially nonaqueous solution of hydrofluoric acid, zinc fluoride, and ethylene glycol (ref. 25). Pretreatment of the alloys to remove surface oxides is mandatory if a satisfactory zinc strike is to be obtained. Zinc, of course, provides a suitable underplate for electrodeposition of many other metals.

Acid pickling in hydrofluoric-nitric acid mixtures has been used to prepare several titanium alloys for chromium and copper plating (ref. 25). Pickling in hot concentrated hydrochloric acid permits subsequent electrodeposition of cyanide gold or platinum coatings on some titanium alloys. Titanium does not catalyze electroless nickel deposition, but surfaces may be cathodically activated to initiate nickel plating. The resultant coatings are not adherent, and are usually heat-treated to diffuse the nickel into the substrate.

Significant practical applications for titanium alloys have emerged only in the last few years. Advances in plating technology will become critical as use of the alloy becomes more widespread.

HYDROGEN EMBRITTLEMENT

It is characteristic of advanced materials technology that the solution to one problem generates several others at least as difficult to solve. High-strength steels and titanium alloys have been developed for structural applications where the strength-to-weight ratio is critical. The developmental effort has concentrated on optimization of mechanical properties, and within that context it has been highly successful. For many applications, however, high-strength materials must be coated to assure adequate corrosion and/or oxidation resistance. Electroplating, if applicable, is one of the best and most economical coating-deposition methods. Unfortunately, no electroplating method deposits metal with 100% efficiency, and some hydrogen is codeposited with most metals. Even in trace amounts, hydrogen is quite incompatible

with many high-strength materials: if it diffuses into the alloy matrix, it can cause mechanical failure of various kinds, which are known collectively as "hydrogen embrittlement" (ref. 26). In general, the higher the strength of a material of a given class, the more severe the embrittlement problem can be.

Battelle, under contract to MSFC, investigated the tendency of several common electroplating processes to induce hydrogen embrittlement in susceptible alloys. The Watts-bath plating process, the hard-chromium plating process, the Wood's nickel strike, several cadmium electrodeposition processes, and the Ti-Cd (Delta) process were evaluated. These deposits would ordinarily provide satisfactory corrosion protection in commonly encountered environments. The hydrogen embrittlement susceptibility of plated alloys was determined by means of sustained-load experiments with notched tensile specimens. Similarly prepared specimens were analyzed for hydrogen. Results depended upon the alloy substrate as well as the plating method used.

Electroplating in a Watts bath resulted in hydrogen-stress-cracking failures of AISI H-11 tool steel and AISI 4340 alloy steel, but caused no detectable damage to 18 Ni(250)-maraging steel (ref. 26). All three of these alloys picked up large quantities of hydrogen and developed serious failures as a result of hard chromium plating.

The Wood's nickel strike was evaluated on four stainless steels (17-7 PH, 17-4 PH, AM-335, and AISI Type 410). Only 17-7 PH exhibited delayed failure after plating.

Conventional cadmium-cyanide plating proved detrimental to all five high-strength steels that were evaluated (AISI H-11, AISI 4130, AISI 4340, AISI E 8740, and 18 Ni(250)-maraging steel). More hydrogen was introduced during plating than during the initial cleaning processes. However, the anodic alkaline cleaning and pickling in inhibited HCl did introduce sufficient hydrogen to cause delayed failure in AISI 4130, AISI 4340, and AISI E 8740 steels. Dull cadmium plating was found to be somewhat less embrittling than bright plating.

A number of cadmium electroplating processes have been developed specifically to minimize hydrogen embrittlement. These include a nonaqueous dimethyl formamide (DMF) process (ref. 27), a stable cyanide process (no free cyanide) (ref. 28), a proprietary low hydrogen embrittlement (LHE) process (Selecons, Ltd.), and a cadmium acetate-methanol process (ref. 29). In the Battelle work, the DMF and cadmium acetate-methanol process did not result in hydrogen embrittlement, in the sense

that high-strength steels survived a 100-hr delayed failure test at applied stresses of 75% and 90% of the average notched-bar tensile strength of unplated specimens. Protection is not perfect, however, since random failures were observed when the test was extended beyond 200 hr with DMF plated specimens (ref. 26). The stable cyanide bath did induce hydrogen-stress-cracking failures, although delayed failure times were longer than those observed with conventional cadmium cyanide plating. The LHE process was designed for brush plating, and Battelle could not establish appropriate conditions for bath plating that would yield adherent deposits. The Cd-Ti (Delta) process appeared not to be hydrogen embrittling in the Battelle work, at least for specimens baked at 200° C for 12 hr subsequent to plating.

The cleaning and pickling procedures commonly used prior to electrodeposition can also cause hydrogen embrittlement in particularly sensitive alloys. Inhibited HCl pickling is one of the more culpable operations. A number of organic inhibitors, however, can alleviate the problem (ref. 26).

A final baking is frequently recommended for relieving hydrogen embrittlement stresses introduced as a result of plating. A 24-hr bake at 190° C seems to be effective for many cadmium-electroplated high-strength steels and for Watts-bath electroplated steels; AISI 4340 steel is an exception. Baking was not as effective for hard-chromium electroplated steels.

Since hydrogen embrittlement is not well understood and problems of a catastrophic nature can arise in service, any projected plating process for high-strength materials should be scrutinized closely for possible embrittling tendencies. Unfortunately, however, laboratory tests do not always adequately reflect behavior in the field. One must be constantly alert to the potential magnitude of the problem. An example of the type of difficulty that can occur was the failure of cadmium-plated cup screws used on the midstrike locking mechanism of Saturn 5/S-1C engine actuators. The Boeing Co. traced the difficulty to hydrogen embrittlement caused by inadequate or no baking of the screws after plating (ref. 30).

Electroplating from Nonaqueous Solutions

STATE OF THE ART

As an electroplating medium, water has the distinct disadvantage that active metals (those above hydrogen in the electro-motive series) cannot be plated from aqueous solutions. That is, hydrogen ions in water are much more readily reduced at the cathode than the active-metal ions. One obvious solution to the problem, at least in principle, is to plate from a conducting solution that has no easily reducible hydrogen ions. A stable organic solvent is one possibility, provided some salt of the metal to be plated can be dissolved in it to form a transportable ion that will discharge properly at the cathode. Fused salts, discussed in Chapter 4, are another possibility.

The first active metal to be satisfactorily plated from a nonaqueous solution was lithium. It was electrodeposited as a coherent coating from lithium chloride solutions in acetone or pyridine by Laszynski in 1895 (ref. 31). Although there is little commercial demand for coatings of lithium or, for that matter, any of the alkali metals, this old process should not be overlooked for specialized applications such as battery plaques, electron emitters, or surface modification.

The active metals of most interest as coatings are aluminum, titanium, magnesium, and beryllium. Beginning in 1902, many attempts were made to plate aluminum from organic solvent baths, but a practical method did not appear until 1952 (ref. 32). Spurred by the needs of the aerospace industry, aluminum and aluminum-alloy plating and electroforming from modified Brenner baths were developed into commercial processes in the 1950's and 1960's. Abortive attempts were made during the same period to plate beryllium and magnesium from nonaqueous solutions, but definitive processes are yet to be devised. Titanium plating from organic solvent baths is in a still more primitive state of development.

Three reviews of electroplating in nonaqueous media, made over a period of 75 years, are good summaries of the state of the art. The early work covering the technology from its begin-

nings in 1895 to 1931 was reviewed by Audrieth and Nelson (ref. 33); Brenner (ref. 34) covered the entire period up to 1959, and Clay et al. (ref. 35) gave a detailed review of developments in aluminum plating from 1952 to 1969. The most important events are summarized in table 6.

ALUMINUM PLATING

Numerous nonaqueous aluminum electroplating baths based on a variety of organic solvents were investigated for over 50 years. Highlights of this effort are listed in table 6 and appropriate references are cited. None of the processes, however, could be

TABLE 6.—*Highlights of Developments in Nonaqueous Plating.*

Ref. no.	Investigator	Year	Metal plated	Electrolyte
31	Laszynski	1895	Li, K	LiCl ₂ in acetone or pyridine, KSCN in pyridine
37	Kahlenberg	1899-1900	Li, Ag, Pb, Sb	Chlorides or nitrates in aniline, benzonitrile, quinoline, acetone, pyridine or methyl alcohol
38	Plotnikov	1902	Al	AlBr ₃ in ethyl bromide
39	Patten and Mott	1904-1909	Cd, Sn, Sb, Bi, As, Zn, Li	Chlorides in acetone
40	Röhler	1910	Zn, Cd, Pb, Sn, Co, Ni	Chlorides, bromides, iodides, cyanides, or nitrates in formamide
AlCl ₃ in acetonitrile	41	Lalbin	1917	Al
42	Williams	1920	Al	Al ₂ (SO ₄) ₃ in conc. H ₂ SO ₄
43	Müller et al.	1922-1924	Ag, Mg, Ca, Zn, Cu, Fe, K, Na, Li	Chlorides, bromides, iodides, thiocyanates, nitrates in pyridine
44	Keyes et al.	1928	Al	Ethyl Al iodides in ether
45	Taft and Barham	1930	Pb, Ni, Cd, Cu, Ag, Zn	Nitrates in liquid ammonia
33	Evans	1930	Mg	Mg Grignard reagent in ether

TABLE 6.—*Highlights of Developments in Nonaqueous Plating.*—
Continued.

Ref. no.	Investigator	Year	Metal plated	Electrolyte
33	Yntema and Audrieth	1931	Zn, Cd, Sn, Pb, Ni, Co, Ti	Chlorides, bromides, iodides, cyanides, acetates in acetamide
33	Nelson, Smith, and Audrieth	1931	Sb, Bi, Sn, As	Chlorides in glacial acetic acid
46	Blue and Mathers	1933-1936	Al	Bromides in ethyl bromide and benzene
47	Hurley and Wier	1951	Al	Aluminum chloride and ethyl pyridium bromide in toluene or benzene
48	Safranek, Schickner, and Faust	1952	Al	Hurley and Wier bath and additives
32	Couch and Brenner	1952	Al	Aluminum chloride, lithium aluminum hydride in ether (NBS bath)
36	Conner and Brenner	1956	Al	Further developments of NBS bath
49	Wood and Brenner	1957	Be, Be-B, Be-Al	Be hydrides, alkyls and aryls in ether and other solvents
50	Reid, Bish, and Brenner	1957	Ti, Zr	Halides, hydrides, borohydrides and organometallic compounds in ether and many nonaqueous media
51	Connor, Reid, and Wood	1957	Mg, Mg-B, Mg-Al	Halides, aluminohydrates, borohydrides, and Grignard reagents in ether
52-53	Heritage and Balmer	1955-1957	Al	NBS bath and chlorinated ethers
54	Elze, Lange, and Meyer	1959	Al	NBS bath and additives
55	Cooke and Kritzer	1959	Al	Plating Al on Mg in NBS bath
56-58	Schmidt, Hess, Buschow, Esola, and Kreitz	1965-1969	Al	Scale-up of NBS bath for electroforming large mirrors and aluminum composites

TABLE 6—*Highlights of Developments in nonaqueous Plating—*
 Concluded.

Ref. no.	Investigator	Year	Metal plated	Electrolyte
59-60	Lui, Guidotti, and Klein	1965-1967	Al, Mg, Be	Modified NBS bath for electroforming hardened Al, plating of Mg and Be
61	Carlson	1966-1969	Al	Modified NBS bath for electroforming solar panels
35	Clay, Harding, and Stimetz	1967-1969	Al	Scale-up and further investigation of NBS bath
62	Beach, McGraw, and Faust	1968	Al	Low-volatility NBS bath by addition of quaternary ammonium salts

scaled up to commercial size until 1952, when Couch and Brenner at the National Bureau of Standards (NBS) developed a formulation based on aluminum chloride and lithium hydride (or lithium aluminum hydride) dissolved in diethyl ether (ref. 32). Continued research at the NBS, reported in 1956, resulted in a bath with greater stability, longer life, and the ability to deposit thick coatings (ref. 36). The NBS bath was further studied and modified by several other investigators in laboratory experiments between 1955 and 1959. Between 1963 and 1969 the process was scaled up to commercial size by two separate groups under programs sponsored by the NASA Langley Research Center (LaRC). Schmidt and his colleagues at General Electric Co. electroformed 30-in. diam aluminum mirrors, while Lui and co-workers at Electro-Optical Systems, Inc., produced electroformed aluminum hollow-core solar panels 5 ft square in a 200-gal modified NBS bath.

The National Bureau of Standards Bath

Coherent aluminum coatings up to 0.5 mm thick were electro-deposited by Brenner and his colleagues at NBS in diethyl ether solutions containing 2 to 3 moles/liter (265 to 400 g/liter) of anhydrous aluminum chloride (AlCl_3) and 0.5 to 1.0 mole/liter (4 to 8 g/liter) of lithium hydride, or an equivalent amount of lithium aluminum hydride (LAH). The latter hydride was pre-

ferred, since it dissolved more readily and extended the bath life. A composition 3M in AlCl_3 and 0.13 to 0.4M in LAH was used in a number of experiments designed to test the life of the bath.

The plating solution can be made up most easily by first preparing separate concentrated stock solutions of 5 moles of AlCl_3 and LAH in ether. For making up small baths, the ether may be added to AlCl_3 ; however, due to the high heat of solution, an uncontrolled temperature rise may occur if large quantities are involved. Therefore, it is preferable to add solid AlCl_3 to the ether, using a container with cooling coils. A 2M solution of LAH was made by refluxing the solid in ether for 4 to 6 hr, filtering the mixture, and concentrating the filtrate by vacuum evaporation.

Because the bath is decomposed by oxygen, carbon dioxide, or moisture-laden air, the plating is generally conducted in an atmosphere of dry nitrogen or argon. Electrolytic decomposition of the solution at the anode, however, was found to be the chief reason for bath degeneration. The bath would tolerate up to 3.7 g/liter of water and still produce a deposit. Later, Clay et al. (ref. 35) found that up to 50 g/liter of water did no harm, provided hydride was added to compensate for its loss by hydrolysis. Factors cited by Brenner (ref. 36) that could increase the life of the bath from about 2.3 to 30 faradays/liter were:

1. The use of LAH instead of lithium hydride
2. Isolation of the anode by a coarse paper diaphragm
3. Replacement of the solution in the anode compartment with fresh plating solution when the bath voltage began to increase
4. Addition of solid AlCl_3 to the bath when LAH failed to regenerate it.

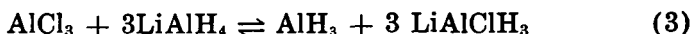
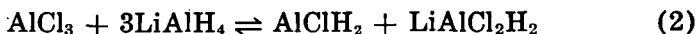
Aside from the need for an inert atmosphere over the solution and for using safety precautions because of the flammability of the ether, the bath is operated quite analogously to aqueous baths and responds to operating variables in the same way. Good deposits are produced up to 5 A/dm² and temperatures up to 60° C. However, there appears to be no net advantage in operating above room temperature, because at higher temperatures there are significant losses of ether. At the preferred current density of 2 A/dm², about 25 μ of aluminum are deposited per hour at a cathode efficiency of about 90%.

Brenner (ref. 36) found that the maximum amount of aluminum that would plate out as a good deposit was about equal to the aluminum present as AlCl_3 , even though the anode apparently corroded at 100% efficiency and the AlCl_3 remained at 3M. The experience of subsequent investigators, however, suggests an al-

most unlimited life for the hydride bath, provided it is well filtered and chemically maintained. It has also been established that the anode replaces the deposited aluminum in equivalent amounts in excess of the original amount present as AlCl_3 .

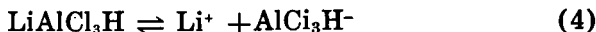
The electrochemistry of the hydride bath has been studied but not completely defined. The reactions of a 3.4M AlCl_3 -0.4 LAH bath were summarized by Clay et al. (ref. 35) as follows:

The mixing of ethereal solutions of AlCl_3 and LAH can give several reactions, depending upon the relative proportions of the reactants.



As there is a large excess of AlCl_3 in the aluminum plating solution, reactions (2) and (3) do not occur to a significant extent. Infrared studies confirm that, with an excess of AlCl_3 , only the monohydride of reaction (1) is formed.

In a plating bath, the AlCl_3 and the AlCl_2H are present as etherates. The LiAlCl_3H ionizes as follows:



and the Li^+ is also etherated.

Since ethereal solutions of AlCl_3 have some conductivity, there must be some interaction of the AlCl_3 , possibly that given in the following equation:

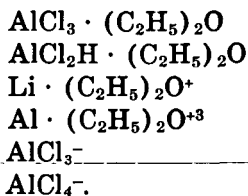


The following equilibrium is probably also established:



The existence of an anion containing hydride was confirmed by Couch and Brenner (ref. 32).

In summary, the plating solution probably contains the following chemical species:



It is likely that the $\text{Li} \cdot \text{etherate}^+$ is the principal current-carrying ion.

General Electric Co. Experience

In its continued search for lightweight components for use in space flight and space satellites, LaRC contracted with General Electric Co. to develop the technology necessary for electroforming 30-in. diam, .020 in. thick nonmagnetic aluminum paraboloidal solar concentrators (mirrors). The NBS ether hydride bath was chosen as the most promising process after the initial evaluation of samples prepared in this bath indicated that the physical properties of the deposit could meet the requirements noted in table 7.

TABLE 7.—*Physical Properties of Deposit in NBS Ether Hydride Bath*

Properties	Electroformed Al, 3-sample av	1100 Aluminum, nominal
Modulus of elasticity, psi	7.98×10^6	10.0×10^6
Ultimate tensile strength, psi	11 050	13 000
Tensile yield strength, psi	7810	5000
Elongation, %	26	35
Linear coefficient of thermal expansion, μ in./in./° C	24.5	22-23.6
Density, g/cm ³	2.66	2.71
Stress, psi	< ± 80	—

The composition of the bath and plating conditions used by Schmidt et al. to electroform 2.5-, 5-, 7-, and 30-in. aluminum solar concentrators is given in table 8 (ref. 56).

The process was scaled up successively from a 1.5-liter laboratory-size bath to 3.5, 5.5, and 7.5 liters and finally to a pilot plant facility of 200 gallons. Filtration was important to avoid the formation of rough nodular deposits, particularly with thick films. Roughness or nodular growth on the back of the electroform tended to show through to the front optical surface and to distort the quality of the mirror. On 30-in. mirrors, the use of continuous filtration and rotation of the rack assembly carrying the mandrel eliminated the need for periodic current reversal.

The bath was operated intermittently over a 30-month period and was controlled by chemical analysis. $AlCl_3$ and LAH were added periodically to keep the bath composition in balance. Absorbed water above about 0.25% was detrimental to the properties of the deposit; stress increased and ductility decreased as water accumulated. A simple monitoring procedure for water content allowed the periodic addition of hydride to compensate for the increased moisture (ref. 62). The method involved the use of

TABLE 8.—*Composition of Bath and Plating Conditions Used by Schmidt at General Electric Co.*

Bath composition	3.4M AlCl ₃ , 0.4M LiAlH ₄ in diethyl ether
Bath volume	2 to 200 gal
Cathode CD	2 A/dm ² (20 A/ft ²)
Anode	1100 Aluminum (conforming and bagged in glass cloth)
Anode: cathode surface area ratio	1.1:1
Electrode spacing	6.3–10.2 cm (adjustable to 25.4 cm)
Cell voltage	12–18 V
Agitation	Solution agitation and rotating cathode or magnetic stirring (on small mirrors)
Filtration	Continuous or intermittent
Temperature	20° to 30° C
Deposition rate	1 mil/hr
Periodic reverse	Plating—494 sec @ 2A/dm ² ; deplating—6 sec @ 3A/dm ²
Mandrel material	Electroformed nickel or optical ground glass

an oscilloscope to measure the time of depolarization of the cathode, which increased as moisture content increased.

Glass containers were used for laboratory investigations, but larger cells must generally be made of metal to avoid the hazards of breakage. A number of metals and plastics were found to be compatible with the ether hydride bath. They included Inconel, AISI type 301 stainless steel, nickel, silver, copper, brass, Teflon, rigid PVC, lined fiber glass, and Synthesine coating. Rubbers, plasticized PVC, aluminum alloys, carbon steel, and polyethylene were discolored, swollen, or attacked by the bath. The smaller baths were operated in a laboratory-type glove box under an atmosphere of dry nitrogen. The 30-in. mirrors were produced in a specially designed 200-gal cell provided with a superimposed access chamber that was also continuously purged with dry nitrogen.

Plating and storage tanks were fabricated from nickel-clad steel and provided with cooling coils. The plating tank was lined with Teflon to prevent any stray current plating on the walls. Filter tanks, piping, fittings, and valves were of stainless steel. A cross-sectional sketch of the 200-gal plating compartment with the glove box in position is shown in figure 5.

In electroforming the 30 in. mirror, adhesion to the master had to be controlled to prevent premature parting or lifting during plating, and yet allow the relatively thin deposit to be stripped from the mandrel or master without distortion. Schmidt

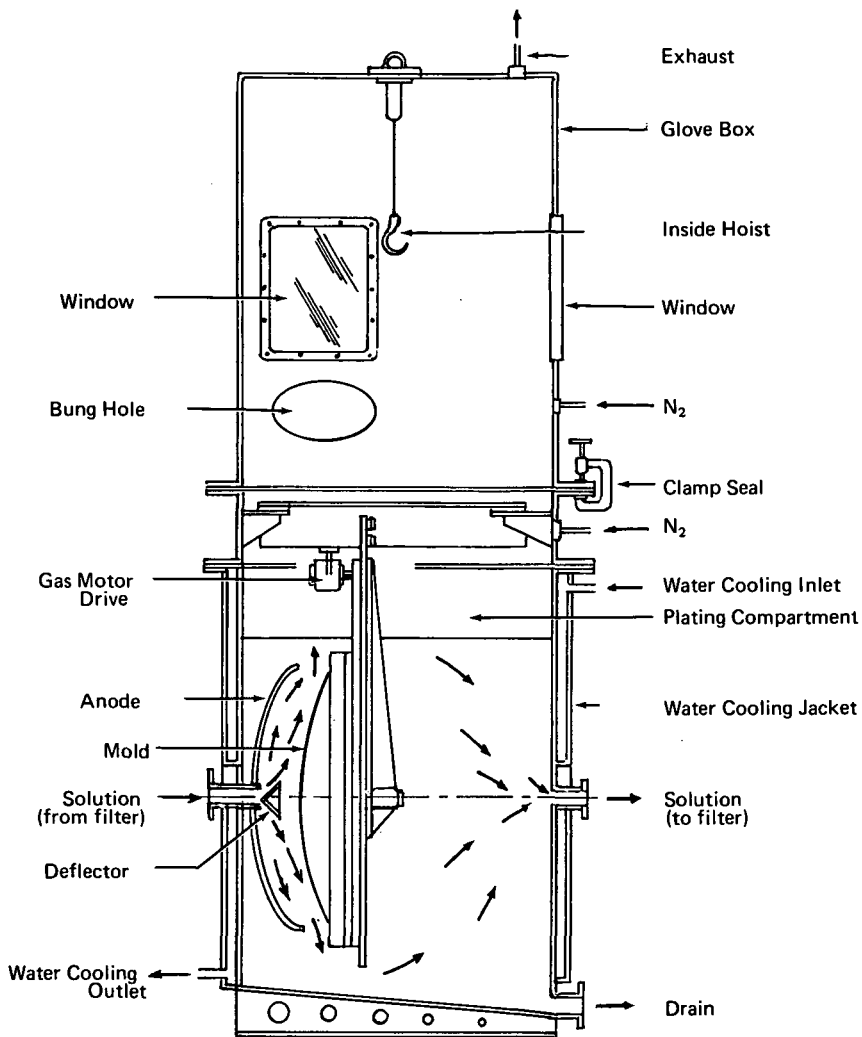


FIGURE 5.—Cross-sectional sketch of plating compartment with glove box in position.

developed a combination of a thin, chemically reduced silver film and an oleic-acid solution treatment that enabled the successful separation of aluminum mirrors from nickel mandrels (ref. 56). On later work with glass masters, a thin, spray-reduced silver film was applied, followed by the electrodeposition of 1 mil of silver and a treatment by an organic acid to control adhesion.

For normal coating applications, however, the deposit must adhere well to the substrate. Special treatments involving a

variety of acid and anodic etches and a final dip in an ethereal solution of an organic acid were reported by Brenner for obtaining good adhesion to aluminum, titanium, copper, brass, chromium, silver, and steel (ref. 36).

The work at General Electric for LaRC resulted in the scale-up and successful operation of a 200-gal facility in which six electroformed aluminum mirrors 30 in. in diam were produced during the initial contract. Later, six more mirrors of this size were made, three all-aluminum, two containing codeposited hollow silica microspheres, and one with codeposited glass fibers (ref. 57). Investigation of the codeposition of various fibers, whiskers, microspheres, or powders with aluminum was directed toward developing high-strength, lightweight electroformed structures. The strengthening effect of incorporating such materials into aluminum electroforms is illustrated in table 9. The fine fibers or powders were added directly to the ether-hydride plating bath, and agitation of the solution kept them suspended. The codeposition mechanism was primarily a random entrapment of fibers as they impinged and lodged on the plating surface. In the case of graphite fibers, an electrophoretic migration to the cathode was induced by treating the fibers ultrasonically in an ether solution containing an anionic dispersant prior to adding them to the plating bath.

On the basis of the experience in electroforming mirrors 30 in. in diam, a preliminary design of a plating cell for electroforming solar concentrators 10 ft in diam was developed as well as an improved plating cell for codeposition of fibers.

Another aluminum electroforming task, carried out for NASA Lewis Research Center in the General Electric facility, was the production of 10 cylindrical aluminum tank liners. They were 7.5 in. in diam and 22 in. long with wall thicknesses of 4 mils.

TABLE 9.—*Strengthening Effect of Codeposition*

Codeposited	Maximum ultimate tensile strength, psi	Yield, 0.2% Offset, psi	Elongation, %
All-aluminum	11 050	8450	26
Glass fiber	20 700	18 300	—
Silica microspheres	15 100	—	16.5
Iron Powder	11 595	—	20
0.3-mil W wire	10 850	—	7
Nickel fibers	10 425	—	18
Graphite fibers	32 400	—	—

Specifications called for the elongation to exceed 12% and for the walls to be gastight. The liners were made into high-strength, low-weight, gastight bottles by filament winding techniques. The most important result of this work was that large-scale aluminum electroforming in the ether-hydride bath was demonstrated to be feasible and practical. The 200-gal bath was operated without any serious consequences, even though mishaps occurred such as inadvertent shorts, sparking, spillage of solution, and vapor leakage.

Electro-Optical Systems, Inc., Experience

Langley Research Center supported several projects at Electro-Optical Systems (EOS), covering the development of electroformed hardened aluminum and aluminum alloys and the production of electroformed aluminum hollow-core solar panels 5 ft square (refs. 59 to 61).

A mixed anisole-ether bath (refs. 59 and 63) was developed by EOS for electroforming much harder and stronger aluminum deposits than could be deposited in prior ether-hydride-type baths. The mixed-ether bath, in which one-third of the diethyl ether normally used was replaced with anisole, was only half as volatile as an all-ether bath, thus greatly reducing health and fire hazards as well as evaporation losses. The mechanical properties of aluminum electroformed in the mixed-ether bath are compared with those of deposits prepared in the all-diethyl-ether bath in table 10.

The yield and ultimate tensile strength of the deposits made in the mixed-ether bath, particularly at the higher temperature, represented a significant advance over aluminum electroformed in the NBS bath. The deposits were very pure (at least 99.9%

TABLE 10.—*Comparison of Mechanical Properties in NBS and Mixed-Ether Baths*

Properties	NBS bath	Mixed-ether bath	
		47° C	30° C
Yield strength, psi	8200	21 400	17 600
Ultimate tensile strength, psi	10 400	25 700	20 100
Modulus of elasticity, psi $\times 10^6$	8.0	8.0	—
% Elongation, 2 in.	26	10	4.7
Hardness, Knoop no.	32	71	—

aluminum) and relatively hard, and exhibited a fine grain structure with an absence of ordered crystal orientation.

Deposits of nearly equal hardness and strength were produced in an NBS bath to which was added an EOS proprietary magnesium plating solution probably based on ethyl magnesium bromide in ethyl ether (ref. 60). Although no magnesium plated out with the aluminum, some strengthening effect was noted. The deposit had a yield of 17 600 psi, an ultimate tensile strength of 21 300, and a high modulus of 12.4×10^6 psi.

After initial laboratory research was carried out with small plating cells in a typical glove box arrangement, the mixed-ether process was scaled up to enable the electroforming of 12-in. aluminum mirrors and aluminum hollow-core solar panels 5 ft square (ref. 61). A separate electroforming facility was constructed away from the main laboratory buildings and provided with various safety features to protect against fire and explosion. The plating bath was prepared in a separate 200-gal, glass-lined steel tank and stored in a 600-gal underground tank. Electroforming was done in a phenolic-lined 316 stainless-steel plating tank with inside dimensions of 6×1.5 ft \times 6 in. high and 400-gal capacity. The electrolyte was cooled by circulation through a tubular heat exchanger. Various pumps for electrolyte and dry air or nitrogen were provided and controlled from a remote panel.

NASA established requirements for lightweight solar panels that would make possible the fabrication of large-area, 25 lb/kW solar arrays for space power applications. Previous developments by EOS (ref. 61) resulted in a 25-sq ft panel using an electroformed nickel hollow-core substrate supported in an aluminum double-box-beam frame with a weight-to-power ratio of 42 lb/kW. The development of a stronger electroformed aluminum in the mixed-ether bath noted above led to the successful fabrication of a solar panel based on an electroformed aluminum hollow-core substrate and a beryllium frame. A demonstration solar panel of this type was prepared, which weighed about 6 lb and had a calculated power output of 210 W, giving a weight-to-power ratio of 28.5 lb/kW. Calculations showed that the goal of 25 lb/kW could be achieved with minor design modifications and manufacturing controls.

The aluminum was plated on a copper mandrel. The anode and cathode were bolted together to form a unified structure during plating. Six hollow-core panels 5 ft square (three flat and three curved) were electroformed at current densities of 10 to 14

A/ft², 20° C bath temperature, and 6 gal/min circulation of electrolyte. After plating, the copper core was etched out with concentrated nitric acid, leaving a hollow-cored, very lightweight, but strong structure.

In fabricating solar cell arrays, the cell contacts and interconnects are generally silver-plated titanium. These contacts have tended to fail by peeling and loss of adhesion. JPL is studying alternative methods for contacts and interconnects on solar cells and has contracted with EOS for an investigation of their construction by aluminum electroforming (ref. 64). The work, which is continuing, is designed to use electroformed aluminum to hold the cell in place and make the necessary interconnection of the cells.

Another application of the aluminum electroforming process involved the production of six liners for lightweight pressure vessels for Lewis Research Center (LeRC). Aluminum was deposited on a copper mandrel about 12 in. in diam and 14 in. long. The plated mandrels were sent to Aerojet General Corp. for winding with glass fiber and impregnation with an epoxy resin. After wrapping, the copper mandrel was dissolved out with concentrated nitric acid at 60° C, leaving a light, strong tank for storing cryogenic fluids.

Under another contract with LaRC, Guidotti and Lui at EOS tested a great number of materials in an NBS-type aluminum-plating bath and investigated their effect on the mechanical properties of aluminum deposits (ref. 60). The electrolyte to which the additions were made was 3.73M AlCl₃ and 0.33M LiAlH₄ in diethyl ether. Eight of the materials having the greatest effect as compared with deposits made with no additions and in the mixed-ether bath are noted in table 11.

Larger hollow-core and flat-plate samples were electroformed in baths containing beryllium chloride, titanium acetylacetonate, and pyridine. The physical properties of these deposits equalled or exceeded those noted in table 11. The high strength and hardness of aluminum electroformed in the pyridine-containing bath suggests development of other applications in space hardware as well as industrial uses in areas where it is impossible to apply conventional forming techniques.

Other Developments

Applications of the NBS bath for plating aluminum on various substrates began to be reported shortly after Couch and Brenner published the results of their research in 1952 (ref. 32).

TABLE 11.—*Materials Having Greatest Effect as Compared with Deposits Made with No Additions and in the Mixed-Ether Bath*

Additive	Yield strength, psi	Ultimate tensile strength, psi	Percent elongation, 2 in.	Knoop hardness no.
None	9100	13 800	17	—
Anisole-ether bath	21 400	25 700	8-10	50-70
Beryllium chloride, 1.25M	—	16 000	0	54
Titanyl acetylacetonate, 0.04M	13 200	14 800	1-2.5	56
Carbanilide, 0.114M	15 100	16 600	1.5-5	45
Bis (2-butoxyethyl) ether, 17% by vol.	15 500	18 500	3-8	64
Benzonitrile, 0.175M	16 300	18 800	2-3.5	56
Ferrocene, 0.188M	17 100	21 300	10-11	70
4-amino-phenyl ether 0.09M	21 000	22 400	2-3.5	61
Pyridine, 0.124M	29 800	32 300	2.5-5	88

An investigation of the NBS process to clad uranium fuel elements for corrosion resistance was carried out by Beach and Faust at Battelle Memorial Institute during the period 1953 to 1955 (ref. 65). Aluminum deposits about 12 mils thick were electroplated directly on uranium and on uranium preplated with nickel, copper, or iron using procedures designed to give good adhesion. After conventional cleaning and activation, the substrate was dried with alcohol, treated with a solution of a fatty acid in ether (typically oleic acid), placed in the plating solution without current, and then plated (ref. 66). The plating bath contained 400 g/liter AlCl_3 and 6 g/liter LiH. Aluminum plated directly over uranium diffused into the substrate at 250° to 300° C, producing a poor bond and poor corrosion resistance. Aluminum deposited over uranium preplated with nickel or nickel-plus-copper resisted diffusion and provided maximum corrosion resistance. The plated aluminum cladding was equal in many respects to the more conventional brazed-on wrought aluminum cladding and avoided some of the difficulties in the brazing technique.

Alm and Binstock in 1958 also developed procedures for cladding nickel-plated uranium reactor cores with aluminum in the ether-hydride bath (ref. 67). The electrolyte was 3.5M in AlCl_3 and saturated with LiH. Pure aluminum anodes were used at an anode-to-cathode ratio of 1:1 to 50:1. Plating was carried out at 20° to 30° C using a periodic reverse cycle of 600 sec direct at

0.5 A/dm² and 60 sec reverse at 2 A/dm². Thicknesses up to 24 mils were deposited, but details of the deposit characteristics were not given. Adhesion to the nickel-plated uranium was accomplished by anodic treatment in the plating bath at 1.5 A/dm² for 5 minutes.

In 1959 Cooke and Kritzer plated aluminum on magnesium in an ether-hydride bath containing 600 g/liter AlCl₃ and 10 g/liter LiH (ref. 55). Current densities from 0.11 to 1.35 A/dm² at 20° C for 1 to 24 hr were used. Although a large number of chemical and/or mechanical cleaning and activating treatments were investigated, good adhesion was obtained only by using the Dow Chemical Co. proprietary pyrophosphate immersion zinc process followed by a copper flash. Poor adhesion of aluminum plated directly on magnesium was due to a reaction between the ether-hydride bath and magnesium.

More recently the NBS bath (3.5M AlCl₃ — 0.4M LiH) has been used to prepare high-strength aluminum composite tapes and sheets containing boron, SiC, beryllium, or steel filaments. Under NASA sponsorship, Alexander, Withers, and Abrams (refs. 68 and 69) at General Technology Corp. (GTC) developed techniques for electroforming aluminum around these filaments, either in a single layer or multiple layers. The electroformed multiple-layer boron-alumina composites had tensile strengths ranging from 30 000 to 62 000 psi and moduli of elasticity from 15 to 22 × 10⁶ psi. Much better physical properties were developed by stacking single-layer electroformed tapes in a die and hot-pressing to obtain a sheet material. A composite produced in this manner having 40% by volume of boron filaments had a typical tensile strength of 160 000 psi and a modulus of 28 × 10⁶ psi. These composite tapes and sheets are extremely useful engineering materials in applications requiring maximum strength-to-weight ratios and are being offered commercially by General Technology Corp.

All of the ether-hydride plating baths described previously pose fire and health hazards, even though they are used successfully in large installations. In a modified NBS bath developed by Beach, McGraw, and Faust at Battelle Memorial Institute (ref. 62), the volatility and flammability were considerably lowered by reducing the amount of ether or by replacing part of the ether with a quaternary ammonium salt such as 2-ethoxyethyl trimethylammonium chloride (ETMAC). Coherent deposits ranging in thickness from .003 to 5 mils were plated on steel and copper substrates at current densities from 0.5 to 15.5 A/dm². Deposits

from the ETMAC bath were harder than those plated in the NBS bath (70 to 100 Knoop hardness number vs 40 to 50) and probably stronger but less ductile. The research was sponsored by National Steel Corp., and The Battelle Development Corp. has been licensed to develop the processes and applications.

Applications

Like any other coating or metal forming process, aluminum plating and electroforming must meet both technical and economic requirements if it is to be useful to private industry. Government support of projects directed toward space-hardware requirements has provided much of the impetus for developments in aluminum electroplating. Now contractors who have been active in aluminum plating under NASA sponsorship are actively seeking commercial and industrial applications for the process. Any application must consider the relatively high cost of aluminum plating, estimated to be three to six times that of conventional plating in aqueous baths. Capital costs for a commercial operation are in the range of \$50 to \$100 000; thus, the process can compete only where the physical or chemical properties of aluminum warrant the increased cost.

The potential utilization of aluminum plating or electroforming lies in applications where light weight, corrosion resistance, high reflectivity, moderate strength, and high ductility or combinations of these are essential. Three general application areas have been identified.

Space hardware.—These include lightweight, high-strength, hollow-core structures for solar cells, solar concentrators, corner mirrors, aluminum-lined pressure vessels, and optics for telescopes and cameras.

Nuclear applications.—The property most useful in this area is corrosion resistance, primarily for cladding reactor fuel elements.

Commercial uses.—The aircraft industry has a continual need for lightweight structural members, which might be supplied by an electroformed hollow-core member; for instance, electroformed aircraft wings. Lightweight, glass-fiber-wound, aluminum-lined tanks for high-pressure fluids and gases, corrosion-resisting coatings on high-strength steel and titanium fasteners, and filaments of aluminum composite materials have potential applications in aircraft.

In the microelectronic industry, aluminum plating may be use-

ful for fabricating nonmagnetic components, for electroforming lightweight wave guides, and for applying corrosion-resisting coatings.

Other possible miscellaneous uses include anodized and colored coatings on steel, high-precision optical mirrors, anodic-type corrosion-resistant coatings on electric switch boxes and multi-metal brazed parts, the fabrication of aluminum heat exchangers, and high-temperature oxidation-resistant coatings in combination with nickel, iron, or chromium plating. Application of the ether-hydride process to plating continuous strip, sheet, or wire was demonstrated by Connor and Brenner in 1956 (ref. 36). This application does not appear economical at present, although it might be more justified for applying temperature-resistant, dif-fused Al-Ni coatings.

At least four companies have capabilities for aluminum plating and electroforming from the NBS or modified NBS electrolytes. Each of them is exploring the commercial markets for the process. Dr. S. Musikant of General Electric's Valley Forge Space Technology Center is directing company-sponsored work on the utilization of aluminum plating in industry. He is seeking applications in many of the areas noted above. In particular, he considers there is a potential for diffusion-bonded metal composites based on aluminum-plated wire; for coloring steel through anodizing and dyeing an aluminum coating; and for plating corrosion-resisting, nonembrittling coatings on alloys susceptible to stress corrosion cracking.

J. A. Carlson at EOS is also seeking markets for aluminum plating and electroforming. EOS now has capabilities for electroforming or plating structures as large as 5×5 ft in a 500-gal bath. It is exploring many potential applications but is particularly interested in markets for lightweight, high-strength, glass-fiber-wound, aluminum-lined pressure vessels up to 3 ft in diam and 10 ft long, which are used primarily for holding cryogenic fluids.

J. C. Withers, president of General Technology Corp. has reviewed a number of aluminum-plating jobs recently done by a modified NBS process. The company's facilities include various plating cells ranging in size from 1 to 1000 gal, which can accommodate parts in sizes up to 3×6 feet. Items that were processed include aircraft fasteners by barrel plating, hot-oven racks, special electric-switch boxes, parts to be dip-brazed, and special metal castings. Withers believes there will be a continuous and

increasing demand for aluminum plating, although the demand will be met in part by chemical-vapor-deposition methods.

K. Lui at TRW, Inc., is installing laboratory and commercial equipment for aluminum plating and electroforming in an ether-hydride bath. Investigations of aluminum alloy plating as well as commercial plating are to be undertaken.

BERYLLIUM PLATING

The low density (sp.gr.1.8), high melting point (1,280° C), high specific strength, and stiffness of beryllium make it a very attractive structural metal, particularly for aerospace applications. Conventional fabrication of beryllium involves the hot-pressing and sintering of beryllium powder into bars or blocks, from which a variety of machined-shaped parts can be made. These operations are very costly. Electroplating and electroforming therefore could be competitive for manufacture of beryllium articles.

A number of studies of the electrodeposition of beryllium from *nonaqueous solution* have been carried out. Wood and Brenner reviewed the literature as part of an extended experimental study of the plating of the nonaqueous group of metals from organic solutions (ref. 49). Coherent but stressed tubes containing up to 95% beryllium were electroformed in a bath containing dimethyl-beryllium and beryllium chloride etherate. Most of the baths gave brittle, black, or powdery deposits if any metal at all was plated out. A brittle, coherent 70% Be — 30% B alloy was deposited from an ether-beryllium borohydride bath, and Be-Al alloys were plated from mixed baths containing beryllium aluminum hydride and beryllium chloride.

As part of a contract with LaRC to develop technology required for electrodepositing high-strength aluminum alloys, EOS studied the plating of beryllium from ether solutions containing beryllium Grignard reagents (ref. 60).

A direct preparation method of heating beryllium metal, involving the use of an alkyl halide and a catalyst together in ethyl ether, produced too little beryllium Grignard to permit electroplating tests. Beryllium alkyls were indirectly prepared *in situ* by mixing beryllium chloride etherate with an ethereal solution of ethyl-magnesium-bromide (EMB). This produced a solution of dialkyl beryllium along with magnesium halides, from which only powdery Mg-Be alloy electrodeposits were obtained. A solution of ethyl lithium bromide (in benzene instead of EMB) with the

BeCl_2 etherate also produced a poor electrodeposit of beryllium.

Dilute alloys of beryllium in aluminum were obtained by either electrolysis of mixtures of BeCl_2 etherate with ethereal LiAlH_4 or with an NBS-type aluminum-plating solution (3.73M AlCl_3 , 0.33M LiAlH_4). The BeCl_2 — LiAlH_4 bath produced brittle, inferior alloy deposits compared with those produced by the BeCl_2 — NBS bath. The best alloy deposit was obtained at a BeCl_2 concentration of 1.25M. The deposit contained 0.04% Be with an average ultimate strength of 16 000 psi.

Attempts to electrodeposit beryllium from nonaqueous solvents have not resulted in deposits with acceptable physical properties; consequently, a practical beryllium-plating process remains to be developed.

MAGNESIUM PLATING

The formation of complex magnesium parts of low weight by electrodeposition would be a useful adjunct to more conventional manufacturing methods. Nonaqueous magnesium-plating baths have been investigated periodically for 50 years, but no practical processes have been developed. The early work on magnesium plating and investigations on the subject at NBS have been reviewed by Connor et al. (ref. 51). Magnesium plated from a solution of MgBr_2 in ether or tetrahydrofuran was dark, brittle, or powdery. White, metallic-looking deposits containing 70% to 90% Mg were obtained from borohydride and Grignard-type baths; the remainder was probably organic matter. The deposits did not make satisfactory coatings.

A 90% Mg—10% B alloy was electrodeposited from an ether solution of magnesium bromide and lithium borohydride, but the deposit could not be built up. A 7% Mg—93% Al alloy was plated from a bath containing magnesium bromide, aluminum bromide, and lithium aluminum hydride. Alloys of Mg with Zr, Ti, or Be were obtained from hydride or borohydride baths, but all of these were highly stressed, treed, or powdery.

Magnesium plating was investigated by EOS as part of its contract with LaRC on electroforming solar concentrators (ref. 59). The experiments were carried out with an EOS proprietary magnesium-plating bath based on a magnesium Grignard reagent. The improvement consisted of adding an alkyl halide periodically as plating proceeded. The slow addition of ethyl bromide was found to be most effective in retarding the formation of spongy and dendritic deposits. The highest current efficiency and best

deposit characteristics were attained by adding 0.03 mole of ethyl bromide per hour at a current density of 1.08 A/dm². Plating experiments were conducted for as long as 30 hr, and the appearance of the deposit was noted. Deposits up to 10 mils thick were made, but no quantitative data were given on their physical properties.

The plating of magnesium-aluminum alloys also was attempted using solutions of ethyl magnesium bromide ether containing various amounts of lithium aluminum hydride (ref. 60). All of the deposits from these baths were powdery, brittle, or highly stressed. A pure aluminum deposit with improved tensile strength and hardness was deposited from a mixed magnesium-aluminum hydride bath, as reported under aluminum plating. While none of this work resulted in a practical magnesium-plating method, these investigations showed sufficient promise to indicate that a viable process will eventually be developed.

Electroplating from Fused-Salt Baths

Fused-salt baths are expensive to operate, highly sensitive to atmospheric contamination, and corrosive to many container materials. They would probably never be seriously considered as commercial electroplating media, except for the fact that so many metals cannot be electrodeposited from aqueous solutions. The most important of such metals, from the point of view of potential applications, are Al, Ti and the refractory metals Zr, Hf, V, Nb, Ta, Mo, and W. In principle, it should be possible to plate-out these metals from fused-salt baths; however, there was a long period before coherent coatings were actually obtained. Experiment after experiment, from the time of Michael Faraday up to the very recent past, led to useless dendritic deposits. Finally, in 1964, the refractory metals were satisfactorily deposited from molten fluoride baths. Coherent aluminum electrodeposits have yet to be obtained from fused-salt baths, but bright deposits of Al-Mg alloy with interesting properties have been obtained from chloride melts. Iridium, which can be deposited (although with difficulty) by electrolysis of aqueous solutions, is more readily electroplated from molten cyanides.

Many of the unsuccessful attempts to electroplate from fused-salt media had one positive result. It was found that surface diffusion coatings could be formed fairly readily with compatible systems. "Titanided" iron and "beryllided" copper were among the first materials prepared by electrodifusion from fused-salt baths. Recently, a commercial molten-salt process, known as Metalliding, has excited considerable interest for modifying surface properties.

FUNDAMENTAL PRINCIPLES

Electrowinning of metals from molten-salt systems is common practice in industry, particularly for producing Al, Mg, and Na. The basic electrochemistry involved is straightforward and has been known since the time of Michael Faraday. However, in the commercially significant fused-salt electrowinning processes, the metals that separate out at the cathode are molten and immiscible

with the electrolyte at the operating temperatures. The cathode generally does not become electroplated. Such refractory metals as Ti, Zr, Hf, Nb, Ta, Mo, and W can be cathodically deposited quite easily by electrolysis of molten-salt systems; however, although the deposits are solid, they are not coherent but rather dendritic or powdery in nature.

In 1964, a major breakthrough in fused-salt electroplating was reported by Senderoff and Mellors of Union Carbide Corp. (refs. 70 and 71). The process they developed yields coherent deposits of Nb, Ta, Mo, and W, and it can be used to produce electroplated coatings, electroformed sheets, and objects of complex shape. It is not clear why the process succeeded, when previous attempts at producing coherent deposits from fused-salt systems had failed. The process, of course, does differ in detail from prior art, but it is difficult to pinpoint any single factor that accounts for the difference.

The conditions established by Senderoff and Mellors for electro-deposition of coherent coatings are best illustrated with reference to Nb deposits (ref. 72). The electrolyte contains 16% by weight of potassium fluoniobate (K_2NbF_7) in a eutectic mixture of alkali fluorides (KF-LiF-NaF; KF-NaF; or KF-LiF). The solution is kept in a sealed cell under an argon atmosphere, and is electrolyzed at a cathode-current density of 5 to 125 mA/cm² and an applied voltage between 0.1 and 0.25 volt. The anodes are Nb metal. One critical step in the process, which may be the key to its success, involves a preelectrolysis to reduce the average valence of Nb to the range 4.0 to 4.2. Niobium cannot be plated from a salt melt in which its average valence is as high as 4.6. The electrolyte composition is not critical; neither is the temperature, except that it must be above the liquidus of the electrolyte and not so high as to cause loss of coherence in the deposit. It has been postulated that poor coherence at high temperatures is due to excessive dissociation of fluoro-complexes (ref. 72). The current density is made high enough to minimize noble-metal contamination, but not so high that alkali metals begin to deposit. The exclusion of air and moisture from the atmosphere above the melt is exceedingly important.

The refractory elements, Ta, W, Zr, Hf, Mo, Cr, Ta, and V, can be plated coherently or electroformed in a manner very similar to that described above. The critical valence for ions in solution is +5 for Ta, +4.5 for W, +4 for Zr and Hf, and +3 for Mo, Cr, and V. It has been reported that "control of the valence is not excessively difficult" (ref. 72), but few practical

details have been described in the literature. A fundamental study of electrode reaction mechanisms indicates that an irreversible metal-producing step may be necessary for coherent deposition (ref. 72). Such irreversible steps have been identified for all the successful systems. On the other hand, Senderoff and Mellors were unable to deposit iron in a coherent form. The metal is deposited as dendrites in two reversible steps: $\text{Fe}^{+3} \rightarrow \text{Fe}^{+2}$ and $\text{Fe}^{+2} \rightarrow \text{Fe}^{\circ}$.

The Union Carbide fused-salt plating process produces true electroplates. The deposits formed are not alloyed with the substrate, and the rate of deposition is directly proportional to the current (Faraday's Law). In contrast, many fused-salt deposition processes reported in the literature produce diffusion coatings (refs. 73 to 75); that is, atoms from the plating bath diffuse into the cathode to form alloys or solid solutions. The rate of formation of diffusion alloys is proportional to the concentration gradient in the diffusion layer, and hence the rate decreases as the diffusion layer thickens. In true electroplating, the rate of formation of the deposit depends only on the current and is independent of solid-state diffusion rates.

The most recent and best published method for forming diffusion coatings electrolytically in fused-salt baths is the Metalliding process, developed by Cook (ref. 76). In Metalliding, a cathodic substrate is immersed in a molten fluoride bath, and the appropriate voltage is applied until the total current corresponds to the diffusion rate of atoms from the bath into the substrate at the operating temperature. Any further increase in current density results in the deposition of dendrites. The Metalliding process is self-limiting, in that diffusion rates decrease markedly as the alloy or intermetallic layer builds up.

SELECTED APPLICATIONS

Electroplating and Electroforming of Refractory Metals

The Union Carbide process for electrodeposition of refractory metals, discussed above, has been licensed to General Technology Corporation. GTC is exploiting the process for commercial applications under the trade name Metallating.* The major industrial interest at the present time seems to be in tantalum coatings and electroforms. Almost any electrically conducting material that can withstand the 700° to 850° C deposition temperatures can be successfully "tantaled." However, zirconium

*Registered trademark.

and other highly active metals that dissolve in the fused-salt bath generally have to be preflashed with nickel or copper prior to tantalum electrodeposition. Bond strengths of the coatings are excellent; deposits are fully dense and can be varied in thickness from 0.5 mil up to at least 0.25 inch. For most corrosion-resistant applications, 3- to 4-mil coatings are required.

Promising commercial applications of tantalum coatings and electroforms, which are currently being explored, include: thermocouple wells, chemical processing hardware, heat exchangers, liquid-metal containment equipment, and nuclear reactor components. The superb corrosion resistance of tantalum, combined with its fairly high thermal conductivity, its ductility, workability, and weldability, make it an attractive metal for many applications. The use of plate rather than solid tantalum can reduce costs and provide parts with the surface properties of tantalum and the desirable bulk and mechanical properties of the substrate metal. In cases where all-tantalum hardware offers advantages over plate, the electroforming process can be a convenient means for fabricating intricately shaped parts.

The Linde Division of Union Carbide Corp. is investigating columbium-plated copper conduits for superconducting transmission lines. If the development is successful, it could be of major industrial importance in the years ahead.

Electroplating of Iridium

For very severe high-temperature applications in oxidizing environments above 1700° C, iridium-coated graphitic or refractory-metal hardware has shown a great deal of promise (ref. 77). Since the world's supply of Ir is fairly limited, applications can never be very widespread. On the other hand, there may be situations where no alternative solution is possible.

If Ir is to be used as a coating to protect a substrate against oxidation, the coating must be absolutely pin-hole free, since there is no mechanism of self-repair in service. Electrodeposition from fused-cyanide solutions has been explored as a means for applying coatings with the necessary integrity (refs. 77 to 79). Although the developments to date have met with limited success in the laboratory, many problems still remain to be solved before the process could be considered for commercial use.

The initial work on electrodeposition of Ir was concentrated on graphitic substrates (refs. 77 to 79). Rexer and Criscione of Union Carbide Corp. (ref. 80), under contract to NASA Headquarters, developed procedures for electrodepositing Ir on the

refractory metals W, Mo, and Nb. Exclusion of air and moisture from the plating bath was found to be extremely critical, and a gate valve had to be introduced so that the substrates could be placed into the fused-salt electrolyte without admitting air. Alumina crucibles were found to contaminate the salt bath, but ATJ graphite proved satisfactory. The fused salt is a mixture of 70 wt % sodium cyanide and 30 wt % potassium cyanide. Iridium anodes were used with refractory metal cathodes. Particular attention must be paid to surface preparation of the substrates to be plated. While coherent coatings have been produced, results are not as yet completely consistent.

Electroplating of Aluminum

Electrodeposition of aluminum surface coatings from Brenner ether baths was brought to a high degree of sophistication to satisfy NASA needs for the space program (see Chapter 3). Vapor deposition of aluminum on steel received a great deal of attention a few years ago, but the market now appears to be limited at best. Electrodeposition of aluminum from molten-salt baths may assume increasing importance in the future, as present developments become established.

The aluminum deposits formed by electrolysis of molten mixtures of aluminum chloride and sodium chloride are usually dendritic. Additions of small amounts of lead chloride or tin chloride to the salt bath improve the character of the deposits considerably, but not to the point of making them commercially attractive (ref. 81).

While attempts to electrodeposit pure aluminum coatings from fused-salt baths have been frustrating, the electrodeposition of Al-Mn alloys is both feasible and promising. Aluminum-manganese deposits, at least on steel, are bright and reflective as plated, and are at least as resistant to corrosion as pure aluminum (ref. 82). The fused-salt bath is made up of 80 wt % anhydrous aluminum chloride, 10 wt % sodium chloride, and 10 wt % potassium chloride. Anhydrous manganese chloride is added at concentrations of 0.4 % to 0.9%. At current densities above 50 A/ft², bright electrodeposits containing 16% to 45% Mn are formed on polished steel cathodes. As in most-fused salt processes, the baths must be kept meticulously clean.

The fused-salt process has an advantage over the Brenner bath in that the safety precautions are not as stringent; it also has an advantage over vapor deposition in that electrodeposited coatings are more adherent and easier to deposit on complex shapes.

The use of aluminum in molten-salt systems for secondary battery applications is promising in principle (ref. 83). The aluminum deposited on the cathode must adhere well, however. Dendritic growth would be detrimental to battery operation. In view of electrochemical measurements made by Del Duca of LeRC (ref. 83), it appears that aluminum could be used as the anode in a secondary battery when charged and discharged in alkali chloride-aluminum chloride molten salts at temperatures below 250° C. Dendritic growth seems to limit current densities to a maximum of 10 mA/cm² at the present time.

Control of Surface Properties

The use of molten-salt electrolysis to prepare diffusion-alloy coatings has been known for many years. Sibert and Steinberg reported in 1955 (ref. 73) on the formation of titanium diffusion coatings on iron during electrolysis of a mixed fluoride-chloride molten-salt solution. The coating consisted of four distinct layers—an iron-rich alloy adjacent to the substrate, a thin Fe-Ti intermetallic compound, an iron-rich β -Ti alloy, and finally, in the outer third of the deposit, a titanium-rich α -Ti phase. The deposit reached a thickness of 25 to 50 μ , after which titanium dendrites began to grow. Afinogenov, et al. (ref. 75), after an extensive study of the deposition of beryllium on copper, concluded that coherent coatings can be deposited from fused salts only if interdiffusion with the substrate is possible.

Serious commercial interest in diffusion alloys deposited from fused salts did not develop until after the Metalliding process was announced in 1962 (ref. 84). The major effort to date has been largely confined to boron diffusion coatings, which can give increased hardness and wear resistance to bearings, gears, tools, dies, wear plates, and seals. Boron from the anode diffused into the cathode under the influence of an applied emf produces very uniform alloy coatings, even in the vicinity of sharp corners.

The Metalliding process is applicable to the formation of many other diffusion-type coatings as well as borides. General Electric Co., for example, has electrodeposited silicide coatings on molybdenum that appear to be structurally superior to comparable coatings deposited by ordinary pack diffusion. Lewis Research Center is sponsoring several studies designed to assess the potential of electrolytically formed diffusion coatings for giving high-temperature oxidation resistance to alloys used in gas turbines.

Electroforming

Electroforming has been defined as the production or reproduction of articles by electrodeposition on a mandrel or mold that is subsequently separated from the deposit. Occasionally the mandrel may remain, in whole or in part, as an integral functional element of the electroform. Electroforming is an art, and its successful practice is largely dependent on the skill and experience of the operator. While detailed instructions for producing various electroformed objects are available, they do not guarantee the successful production of an article that has never before been manufactured by this process (ref. 85).

The discovery of electroforming is generally credited to a Russian scientist, B. S. Jacobi. In October 1838, he reported to the Academy of Sciences in St. Petersburg the reproduction in copper of a $3\frac{1}{2}$ -in. \times 5-ft engraver's plate by electrodeposition (ref. 86). He used a thin layer of vegetable oil as a parting medium; similar media are still used today to insure the release of the electroform from the mandrel, although silicone preparations or waxes are preferred. A copper sulfate plating solution was used by Jacobi, and a refined version of the same bath is in use today. Jacobi's technique, refined somewhat, was applied almost immediately to the production of electroformed stereotypes for printing of money and duplication or original production of artistic objects. Some of the early developments are noted in references 1 and 2. They foreshadowed the industrialization, the issuance of many patents, and new applications of electroforming during the latter half of the 19th and early years of the 20th centuries in Europe and the United States.

Electroforming is particularly suitable for the following applications:

1. Manufacture of intricate shapes not easily fabricated by other methods
2. Production of articles requiring close dimensional tolerance
3. Manufacture of large, thin-wall structures
4. Reproduction of fine-surface characteristics or detail
5. Formation of composite materials that cannot be made by other techniques

6. Synthesis of alloy compositions not possible by metallurgical methods.

The problems in electroforming are similar to those encountered in conventional electroplating, but the control of processing parameters is much more critical. Electroforms are generally relatively thick deposits of from 0.010 to 0.250 in., so better control of the plating bath and plating conditions over longer periods of time is needed than in processes in which thin deposits are laid down. Other factors requiring close attention are: design of the original part and the mandrel, anode placement and rack design to ensure uniform deposits, agitation, and filtration of the electrolyte.

If all of these factors are under control and the selling price is competitive, an electroformer may be successful and make a profit. Frequently, however, some of the factors entering into the cost of production are overlooked, underestimated because of competition, or optimistically ignored to get business. In the 1955 to 1965 period, interest in electroforming appeared to be quite high. The scope of activities in nickel electroforming in the United States and abroad was documented during a symposium organized by The International Nickel Co. in New York City in 1964 (ref. 87). The anticipated growth of the process—at least for manufacturing consumer items—has not materialized. Most of the applications today are for industrial uses, particularly in the aircraft industry. The consumer market failed to grow primarily because of the high cost of electroforming compared with such conventional operations as stamping, machining, and spinning.

The primary reason for the high cost of electroforming is the relatively slow buildup of metal by electrodeposition. According to Faraday's law, even at the highest practical current density (about 400 A/ft²), it requires about 3 min to deposit 0.001 in. of copper or nickel. Manufacture of an item 0.01 in. thick therefore requires about 30 min, compared with seconds for a die-formed article.

The major operations involved in electroforming typical structures are shown in figures 6, 7, and 8. The engineering design of electroformed articles, recommendations for solution composition and operating conditions, and the design, fabrication, preparation, and removal of mandrels are explained in detail in a series of ASTM publications (refs. 88 to 90). Other basic information on the process is available in ASTM Special Technical Publication No. 318 on electroforming, in plating and electroforming handbooks (refs. 91 to 94), and in literature from The Inter-

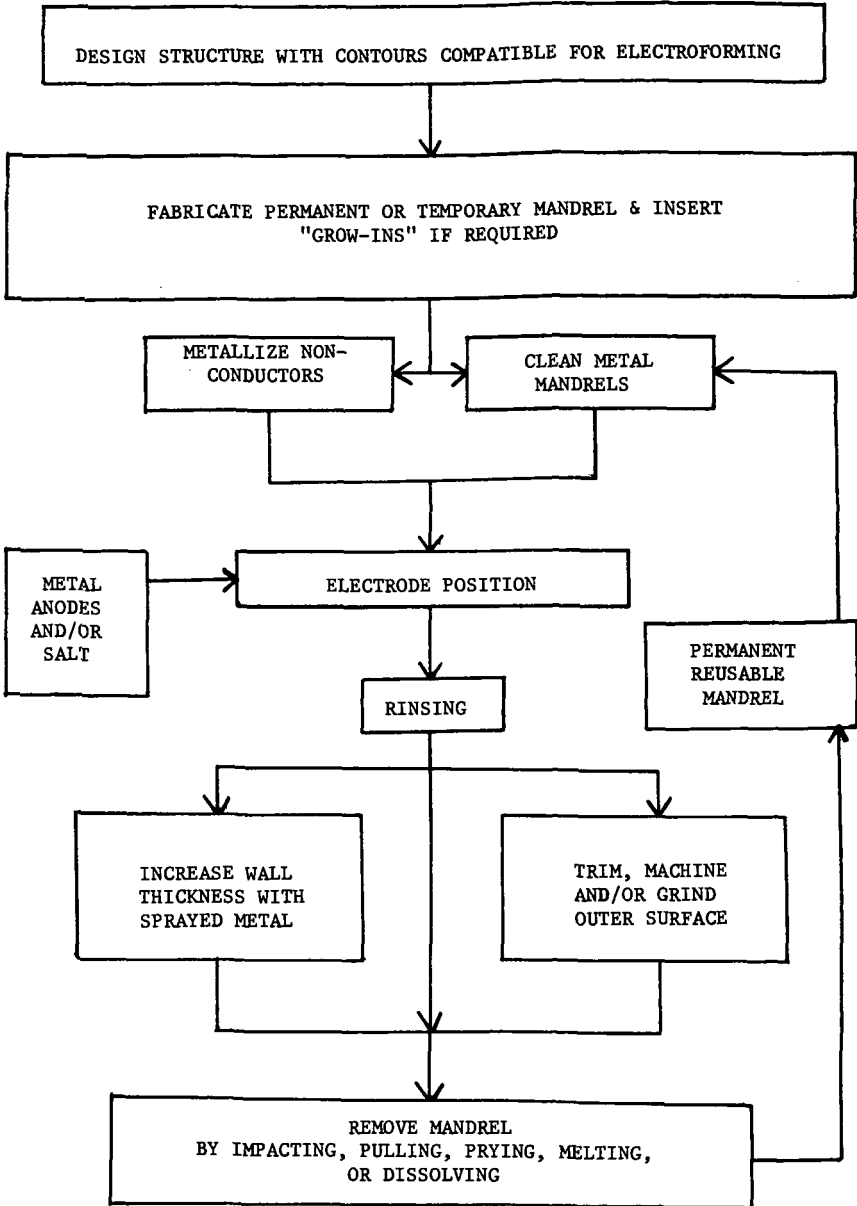
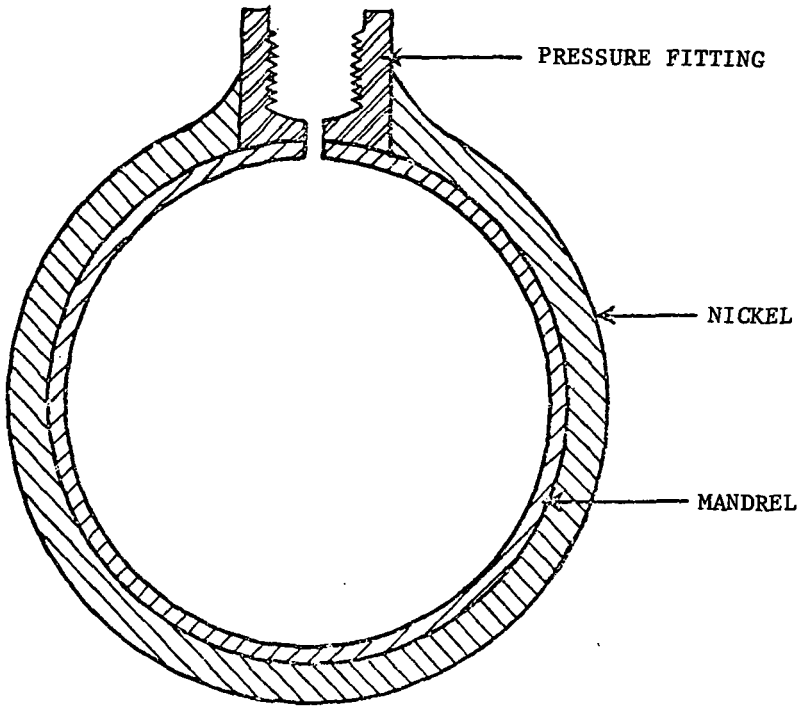
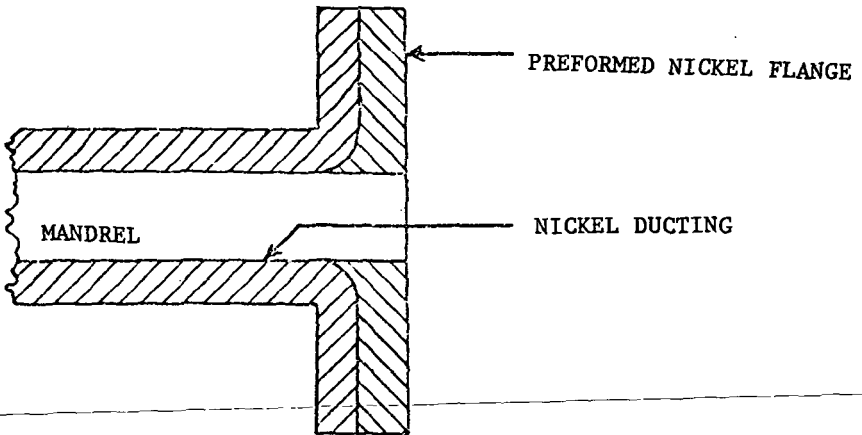


FIGURE 6.—Major operations for electroforming typical structures.

national Nickel Co., Inc. (ref. 95). Three surveys of electroforming—one by Safranek in 1964 (ref. 96), another by DeGroat in 1967 (ref. 97), and a third by O'Neill in 1970 (ref. 98)—have brought the art and advances in electroforming up to date. Some



SKETCH A. PRESSURE VESSEL



SKETCH B.

FIGURE 7.—Electroformed nickel structures with preformed inserts.

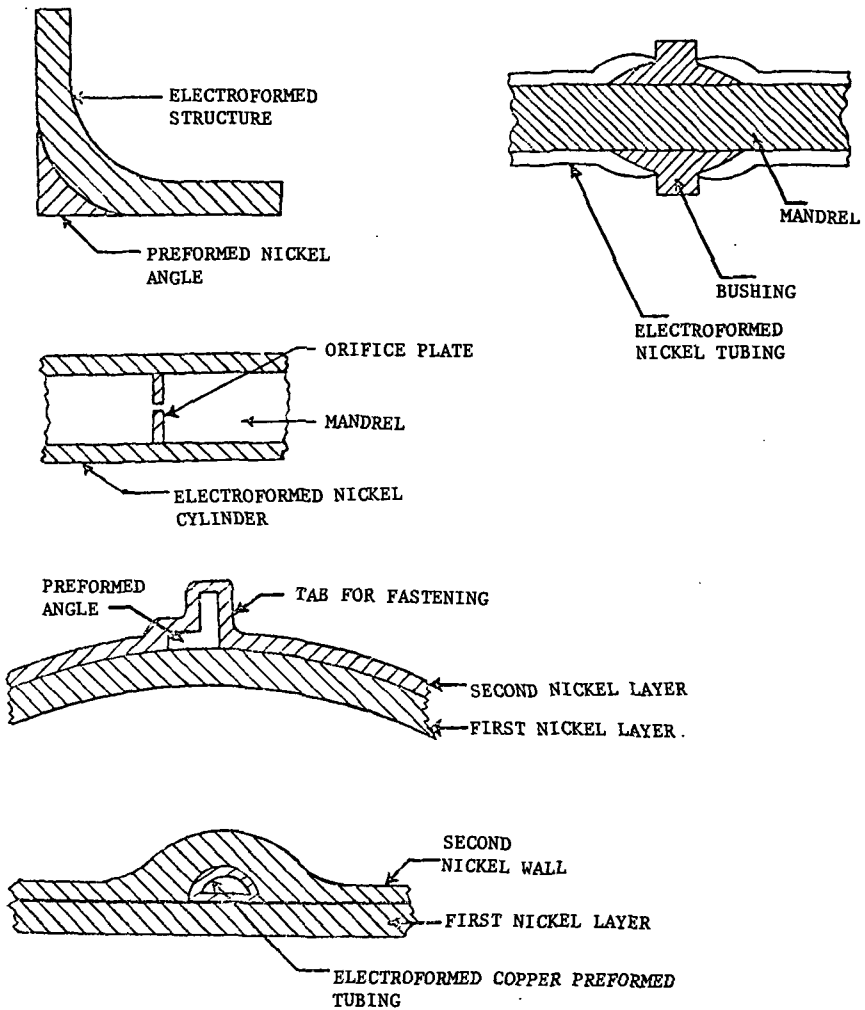


FIGURE 8.—Sections of electroformed structures with grown-in inserts.

of the more interesting and complex electroformed structures fabricated by NASA contractors, which represent an advance in the state of the art, are described in the sections below.

NICKEL ELECTROFORMING

More electroformed parts are made from nickel than from any other metal. Recent advances in quantifying the effects of bath composition and operating conditions on deposit characteristics make it possible to tailor these variables so that the properties desired in each part can be obtained. For instance, the hardness

of nickel electroforms may be varied from 130 to 250 DPH, tensile strength from 50 000 to 200 000 psi, elongation from less than 1% to 37%, and internal stress from compressive to zero to 25 000 psi tensile. The deposit characteristics needed for a particular application may be obtained by proper choice of the plating bath, addition agents, and plating conditions (ref. 99).

Three types of baths are in use for nickel electroforming—the Watts bath, the fluoborate bath, and the sulfamate bath. Each has its own characteristics, and the choice depends on the application. The sulfamate bath is preferred for most jobs, since it has the inherent advantage of producing hard, strong deposits with low internal stress, thereby minimizing the problems of cracking, blistering, and distortion of the electroform after its removal from the mandrel. Deposits from the Watts and fluoborate baths are more ductile and are preferred in electroforming foil thicknesses where low hardness and maximum flexibility are required. Bath composition, operating details, and deposit characteristics are given in several useful handbooks and special reports noted above (refs. 89 to 95).

Electroformed Nickel Mirrors and Reflectors

The production of curved metal mirrors or reflectors is an ideal application of electroforming. The curved shape, perfect finish, and thin cross section needed in precision mirrors or reflectors can be achieved most economically by the replication of a highly polished glass mandrel. The mandrel may be used either directly in the plating bath (after metallizing the surface) or, more commonly, as a master for casting low-cost, single- or multiple-use replica molds from epoxy resin. The replica is silvered, plated to the desired thickness, and removed to produce a precise metallic reflector.

The manufacturing of metallic reflectors is one of the earliest industrial applications of electroforming. A patent entitled "Process of Manufactured Head Light Reflectors" was assigned to D. Garrett (U.S. Pat. 282,879) in 1883. In 1896, a "Reflector Syndicate" plant in London manufactured reflectors by plating palladium and copper on a polished, silvered mold made of a mixture of sulfur and graphite (ref. 86, p. 76). The apparatus used was somewhat similar to modern production equipment, in that the mold was rotated horizontally in the plating bath over an anode set in the bottom of the tank. In this country, Bart Manufacturing Corp. produced over 35 000 reflectors per month

in 1924 and 1925, first on glass molds and later on metal molds. This company produced more than 6000 rhodium-surfaced, electroformed nickel anti-aircraft searchlight mirrors for the U.S. Army of World War II by 1943 (ref. 100). In the early 1960's, the same company experimentally electroformed 10-ft-diam thin nickel bulkheads for the Centaur space vehicle, thus demonstrating the feasibility of electroforming very large, thin, high-quality structural elements to a high degree of accuracy (ref. 101).

The electroforming method is also ideally suited to manufacturing solar concentrators or "space mirrors". Considerable development work in this area has been done by EOS (refs. 102 and 103 for JPL). Circular one-piece mirrors were electroformed in nickel baths using plastic, glass, or metal master mandrels. A nickel submaster was generally electroformed from the original master mandrel and used for production of the mirror. The glass or plastic masters were made conductive by applying a chemically reduced silver or copper deposit.

For nickel electroforming, EOS generally used the sulfamate nickel electrolyte and maintained close control over all operating and bath variables. Tensile strengths of 60 000 to 70 000 psi were common for most parts, and values as high as 280 000 psi were attained in special cases. In electroforming circular mirrors, uniform agitation over the whole surface was necessary to insure even quality. Rotation of the mirrors alone was not sufficient, since the surface speed near the rim is much greater than in the center. To overcome this, a combination of pumping and rotation was practiced. The selection of optimum rotating and pumping speeds and anode placement resulted in extremely uniform thickness and physical properties over the whole mirror. In later work, adequate uniform agitation was provided by pumping the filtered solution directly at the center of the mirror, and rotation was discontinued.

A 60-in.-diam, 0.008-in. thick nickel mirror was made on a silvered glass master. The supporting ring or torus around the rim of the mirror was electroformed separately in one piece. The mandrel employed was an aluminum tube, which was dissolved with hydrochloric acid after plating.

Another design developed at EOS was a rigid, hollow, one-piece mirror having a secondary electroformed backing skin joined to the reflective face skin at the edges, forming a one-piece monocoque-type structure. In this technique, the mirror was mounted at the center of the monocoque backing structure in contrast to the toroidally rigidized mirror in which support was

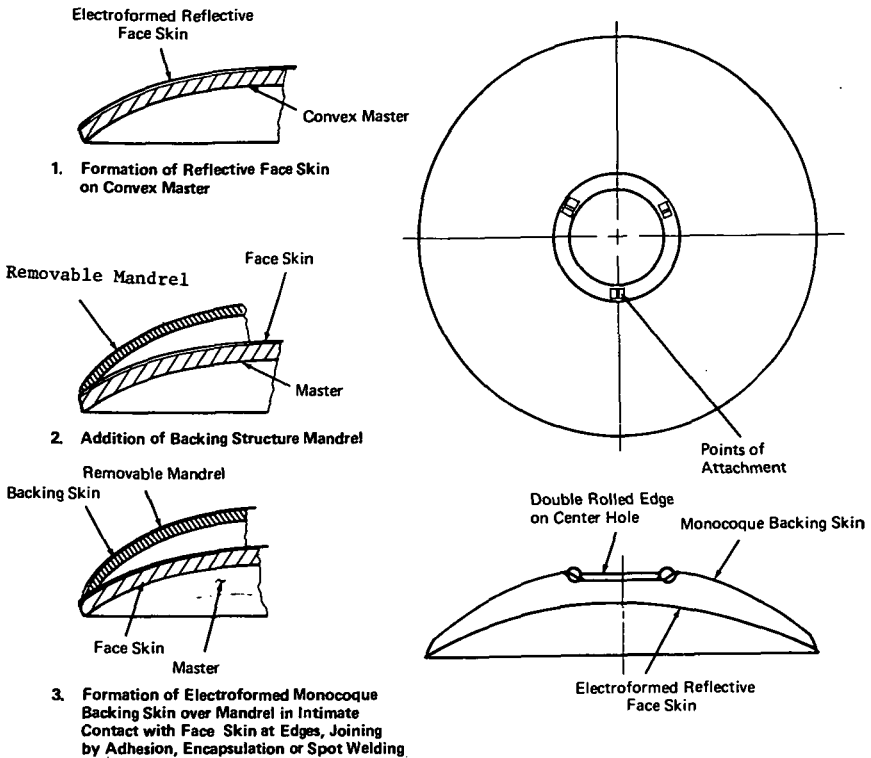


FIGURE 9.—Design of a monocoque rigidized one-piece concentrator.

provided at the rim. The scheme for electroforming this mirror is shown in figure 9. The reflective mirror skin was electroformed first, to 0.004 inch. (Mirrors with skins as thin as 0.0025 in. were fabricated, but some difficulty was encountered in removing them from the mandrel without distortion.) The low-melting alloy mandrel was removed with hot water and hot oil, leaving a hollow, one-piece, lightweight rigidized monocoque mirror.

The same technique was utilized in developing rigid monocoque petals for segmented mirrors. Petals were produced in varying skin thicknesses from 0.002 to 0.006 in. and specific weights from 0.19 to 0.45 lb per square foot. A double curvature around each lightening hole helped to rigidize the structure and increase its stability and strength.

Four other types of mirrors ranging from 12 to 46 in. in diam were electroformed by EOS for use in optical train assemblies at Manned Spacecraft Center (MSC) for an on-axis solar simulator (ref. 104). The mirrors were front-surfaced, nickel-electroformed replicas, epoxy-bonded to a support casting that contained

water cooling passages. Two types of mandrels were used, a 17-7-PH stainless steel master plated directly and an electroformed working mandrel made from a stainless steel master. Agitation was provided by rotating the mirrors in the tank and by solution pumping. Stress, solution concentration, and plating conditioning were closely controlled. Mirror surfaces were coated as a final step by vacuum deposition of $\text{Cr-SiO}_2\text{-Al-SiO}_2$.

Other large structures electroformed in nickel by EOS included a seamless, 51-in.-diam, spherical, thin-wall vessel for the storage of liquid hydrogen, and nickel sleeves designed to protect the leading edges of helicopter blades during landing and takeoff on rugged terrain (ref. 105).

The EOS studies carried out for NASA on the development of large, lightweight solar concentrators added considerable knowledge and refinement to the art of electroforming relative to operating parameters, stress determination and control, deposit characteristics, mandrel construction, and parting methods.

Electroforming Solar Panels

Prior to the development of the electroformed aluminum solar-cell panel noted in Chapter 3, EOS, under NASA sponsorship, manufactured a 25-ft² solar-cell panel comprising an electroformed nickel hollow-core substrate supported in an aluminum double-box-beam frame (ref. 106).

It was electroformed for 2.5 hr in a nickel sulfamate-nickel chloride-boric acid bath operated at a pH of 2 to 4, a temperature of 38° to 57° C, and an average current density of 20 A/ft.² A flat test panel electroformed just prior to the solar panel had the following physical properties:

1. Ultimate tensile strength, psi—150 000
2. Yield strength (0.2% offset), psi—109 000
3. Ultimate elongation (1-in. gage), %—11
4. Elastic modulus, psi— 25×10^6 .

The mandrel on which the panel was plated was fabricated from 6061-T6 Al sheet, 0.020 in. thick. Holes in the sheet were punched, drilled, and reamed to 13/16-in. diam on staggered 1-in. centers, leaving a final plating area of about 16%. After being formed to a biconvex shape, the mandrel was trimmed to size, cleaned, etched, and plated. A contour mask was used to insure uniform deposit thickness. After electroforming, the aluminum mandrel was etched out with 30% HCl. The completed, slightly curved nickel hollow-core substrate with a 3-mil skin weighed only 2.714

pounds. The addition of the aluminum supporting structure, solar cells, and electrical connections brought the total weight to 8.244 pounds. A weight-to-power ratio of 42 lb/kW was achieved, based on a power output of 10 W/ft² for a silicon solar cell 4 mils thick. The hardware and analytical data compiled demonstrated:

1. The stiffness-to-weight advantage inherent in a curved shell
2. The feasibility of fabricating large, foil-gage structures by electroforming
3. The lower total weight and lower thermal resistance obtained with the one-piece electroformed hollow-core structure as compared with adhesive-bonded structures.

This work led to the development of even lighter solar panels, using electroformed aluminum hollow-core structures, as noted in Chapter 3.

Similar nickel electroformed hollow-core structures were produced by EOS for unfurlable petals on a lightweight reflector designed to collect and concentrate solar energy in space. Nickel petals up to 22 $\frac{1}{4}$ ft long were electrodeposited for reflecting units that could be unfurled to a 45-ft diam and provide a total reflecting surface of about 2000 ft² (ref. 107). The wall thickness of the hollow structure was only 0.001 in., and the average weight of a panel in some cases was as low as 0.2 lb/ft². The development of these electroforming techniques provides a unique alternative to some of the assembly and bonding problems involved in conventional fabrication of lightweight, thin-gage, hollow, metallic structures.

Electroforming of Rocket Motor Injector and Composite Thrust Chambers

The effectiveness of electroforming in producing intricate parts with precisely located holes and internal channels is shown in the test models of the rocket-engine injectors for the Apollo Service Module reaction-control system. In conventional fabrication of rocket-engine injectors, subassemblies are welded, brazed, bolted, or press-fitted together; this type of construction led to high costs and unsatisfactory reliability. Methods of making one-piece injectors by electroforming were developed under contract by Camin Laboratory for MSFC and JPL (refs. 108 and 109).

The injectors were produced on a machined nickel master plate fitted with precise-diameter glass tubing, which created the orifices in the exact location and size desired. After about 0.120 in. of nickel was deposited, the unit was removed, and the surface was machined to establish the internal chamber connecting the

various injector holes. The glass tubes imbedded in the nickel were etched out with hydrofluoric acid, which did not attack the nickel electroform or mandrel. The original mandrel containing the glass tubes was then removed and a second mandrel without holes was fitted in place. Internal feed passages and manifolds were formed by filling the machined channels with conductive wax and continuing plating to a thickness of 0.25 inch. The units were then machined, holes for feed tubes were drilled into the manifold, the wax filler material was melted out, and the passages were cleaned with solvent. Photographs of the master mandrel with glass tubes, the electroformed shell, the complete injector, and sectional views revealing the internal passages are shown in figure 10. The complex nature of injectors that can be manufactured by this technique is illustrated in figure 11.

Other electroforming studies by Camin indicate the possibility of depositing injectors with orifices as small as 0.002 in., orifices with length-to-diameter ratios of 100, impinging sheet element injectors, and injectors containing variable-area feed passages for obtaining constant cross-flow velocity over each orifice.

This NASA-sponsored work demonstrated that the electroforming process can be used to fabricate complex parts with internal passages and orifices with reproducible hydraulic characteristics.

Electroformed Composite Structures

The interest in composite materials arises from the failure of conventional materials to meet design requirements for advanced space vehicle application. Two of the more promising methods of fabricating composite structures are (1) the electrodeposition of metals concurrent with filament winding, and (2) the hot pressure bonding of electrolytically deposited monolayer composite tapes. General Technology Corp. (GTC) carried out an extensive investigation of these techniques for LaRC (refs. 110 and 111).

The technique of electroforming composite metal-filament structures at GTC is illustrated in figure 12. The method depends on the electrodeposition of a matrix metal on a rotating mandrel on which a reinforcing filament composite can be fabricated at room temperature with accurate control over filament spacing and volume-percent loading. Since the electrodeposit grows around the filament, an intimate filament-matrix contact is established at the interface without alloying, resulting in a dense, strong composite structure.

Much of the early development work at GTC was done with

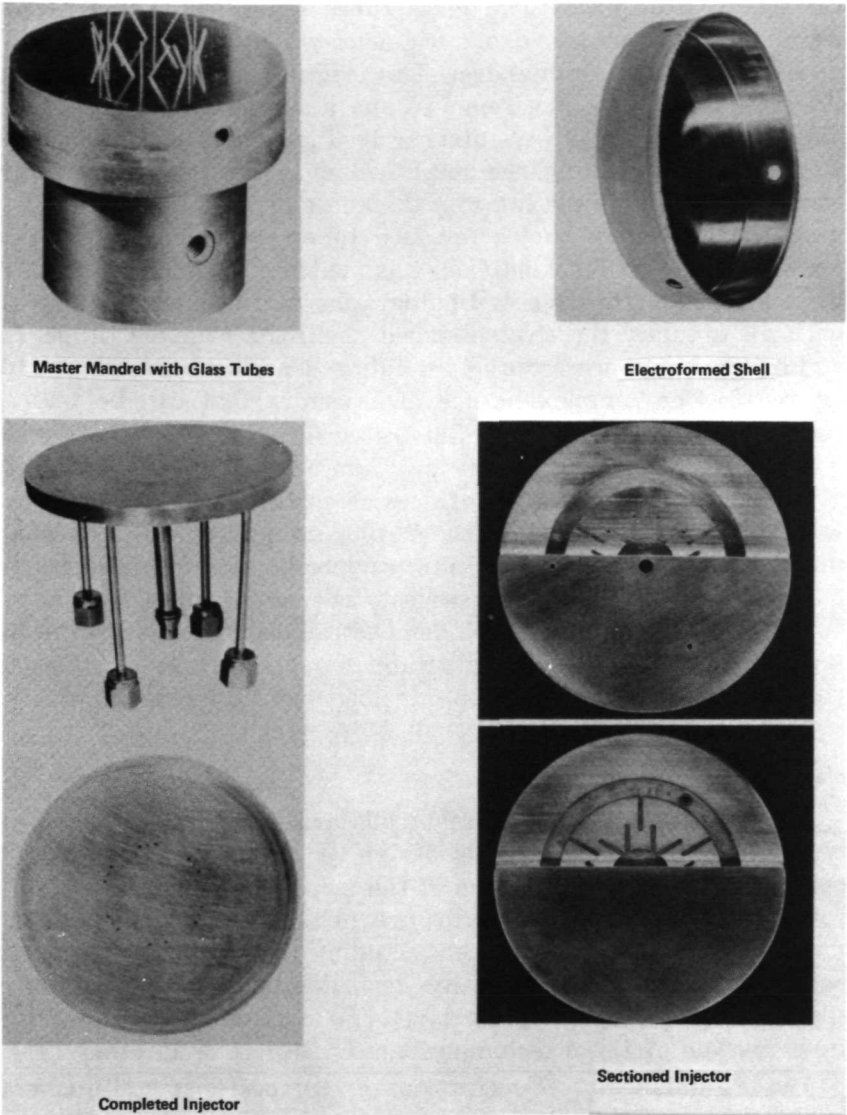


FIGURE 10.—Steps in manufacturing an injector.

electroformed nickel and tungsten wire as a convenient filament material to provide specimens for comparison of physical properties and to study variables in the process. The growth pattern characteristic of the process is shown in figure 13. It is obvious that the plating and filament-winding rate must be coordinated to produce sound, void-free structures. Figure 14 gives the location of potential void sites. Type-1 voids occur when growth from

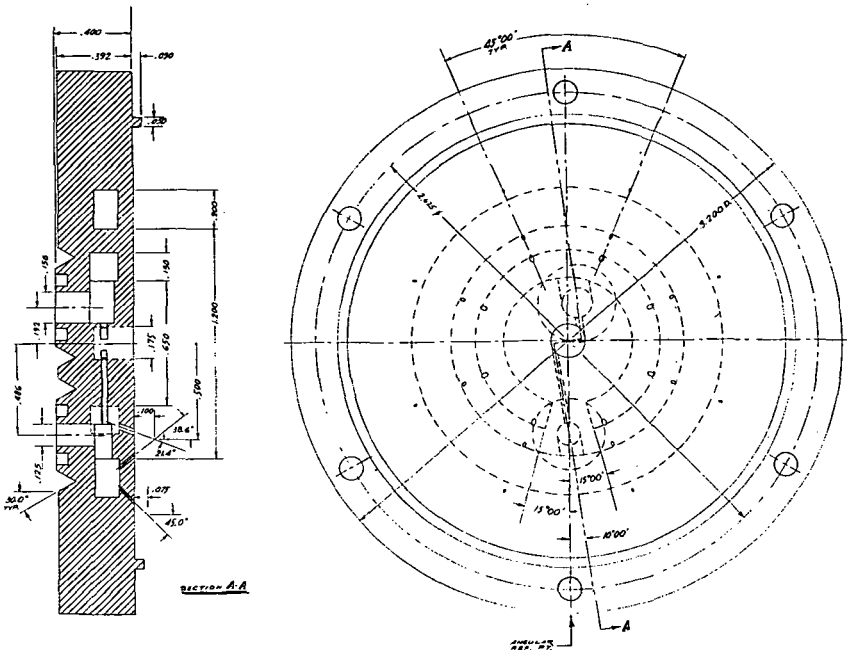


FIGURE 11.—Design of a II RCS injector.

two adjacent filaments intersect before the underlying deposit reaches the point of intersection; these defects can be avoided at wide filament spacing by pumping fresh plating solution over the mandrel and by using periodic-reverse plating. Type-2 voids are formed when the filament does not exactly fit the contour of the undercoat.

Tungsten filament-nickel composites with up to 52% by volume of filaments were prepared at GTC and tensile-tested; the results are shown in figure 15. The line on the graph gives the theoretical strength calculated from the law of mixtures. High-volume-percent loading tended to give values below the theoretical, while at lower loadings some samples were significantly stronger. Samples with tungsten-filament loading higher than 52% by volume showed excessive void entrapment and were unsuitable for testing.

Other research on nickel-boron and nickel-silicon carbide filament systems has indicated that electroforming is a better way to make sound fiber-reinforced composites than such metallurgical techniques as liquid metal infiltration, powder compaction, or extrusion (ref. 112).

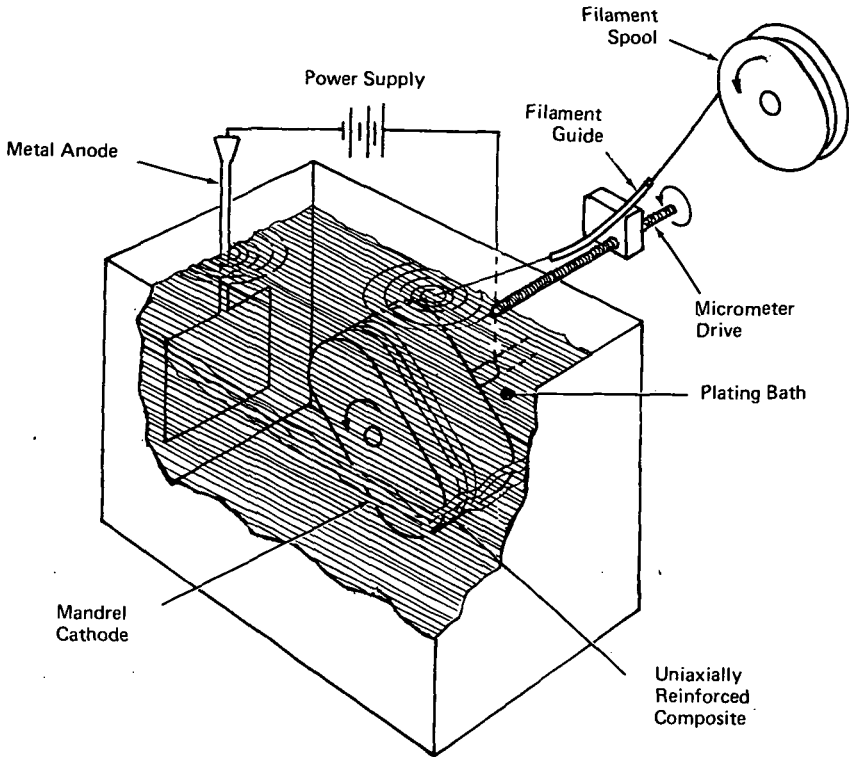


FIGURE 12.—The GTC electroforming process.

Electroforming Nickel Screens and Foils

Electroforming is being used in the manufacture of a wide variety of nickel screen products. The sizes range from small screens of 1000 mesh or finer for use in Vidicon TV cameras to large cylindrical 20 to 120-mesh screens for rotary-screen printing of fabrics. Thicknesses vary from less than 0.001 in. to 0.01 inch. Typically, the screens are electrodeposited on mandrels that have thin photoresists as the nonplating areas. The life expectancy of the resist material is relatively short, since it tends to peel off after a few cycles. Another problem is the tendency of the electrodeposit to creep over the thin resist and cause variations in hole size with variations in screen thickness. As part of a project carried out for LeRC on the development of improved battery plaques, Battelle Memorial Institute devised a method for electroforming thick nickel screens with controlled hole sizes (refs. 113 and 114). Commercial sintered porous-nickel-electrode plaques have large variations in pore size, which cause nonuniform dis-

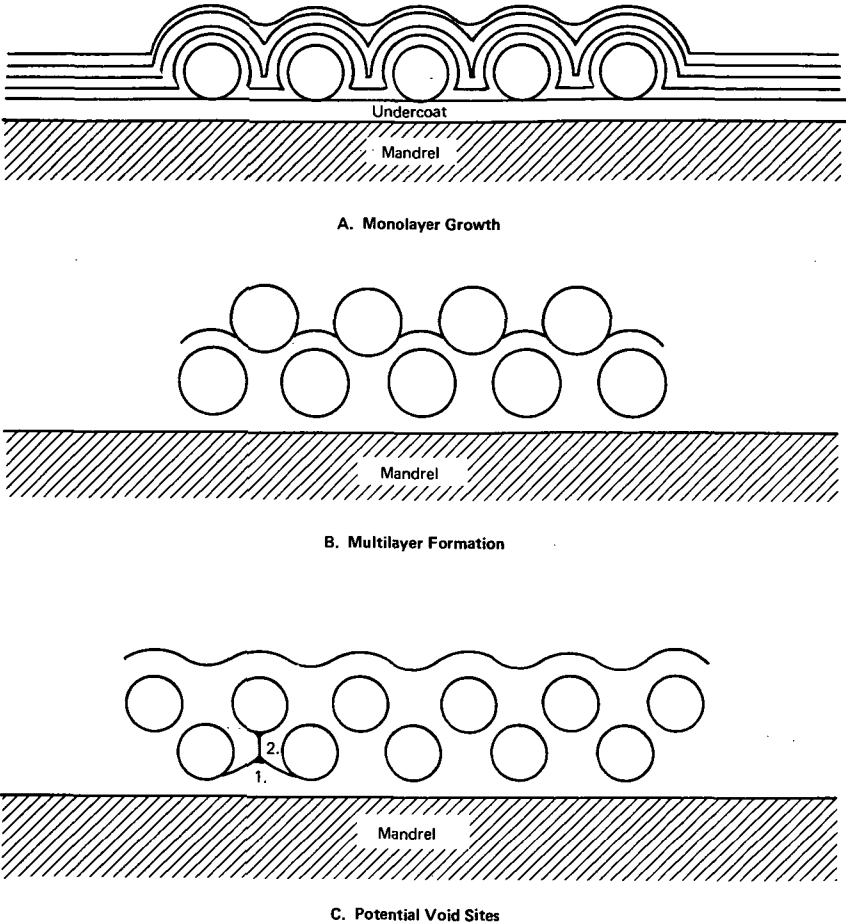


FIGURE 13—Schematic of electroformed composite formation.

tribution of active material impregnated in the pores. Better charge-discharge characteristics and cycle life can be expected with electrodes having uniform and controllable pores. No method was previously known for making such plaques with pores in the range of 0.00005 to 0.005 in. and up to 0.035 in. thick. One method developed by Battelle for making thick plaques was to cut and stack thin electroformed screens one on top of another in a die and diffusion-bond them in a hydrogen atmosphere furnace at 1090° C. The openings aligned sufficiently so that one could see through the stack. The pore volume was increased and weight decreased to some extent by careful etching with an iodine-alcohol reagent.

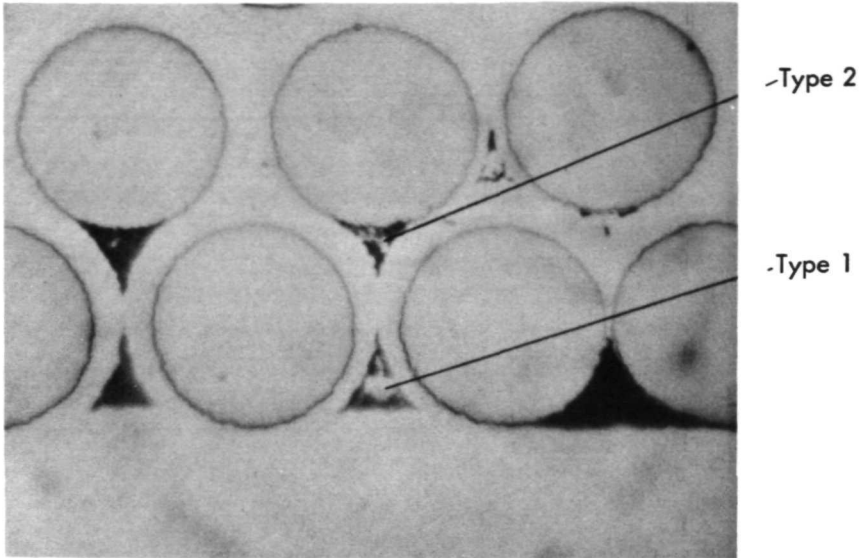


FIGURE 14.—Nickel-tungsten filament composites showing void formations.

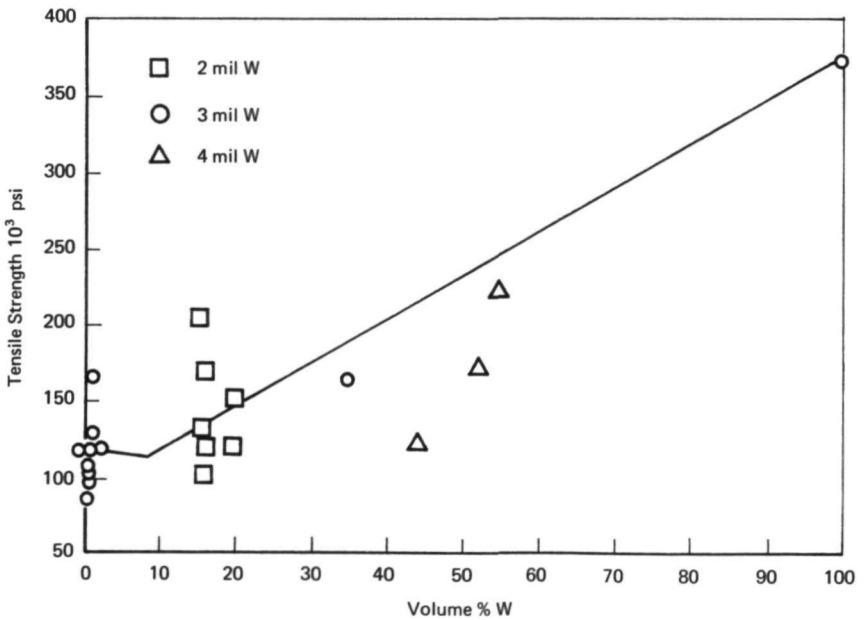


FIGURE 15.—Tensile strength vs volume percent filament for tungsten-wire-reinforced nickel composites.

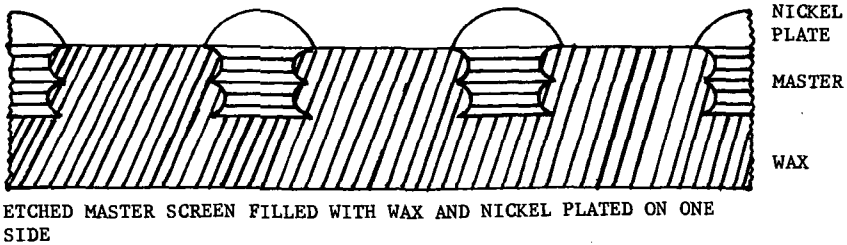
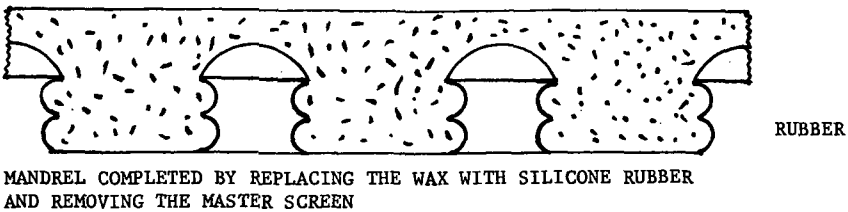
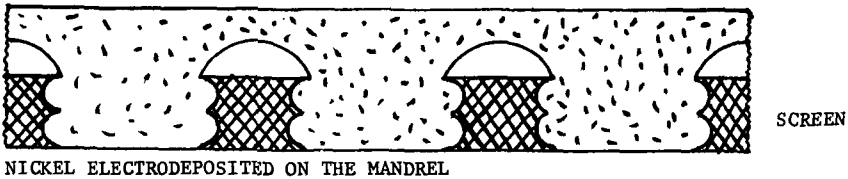
**A****B****C**

FIGURE 16.—Procedure for electroforming duplicate screens with controlled hole size.

A more practical approach was to electroform thicker screens directly on a mandrel with closely controlled hole sizes. The mandrel developed after several trials had a stainless steel sheet etched from both sides as the master screen. The plating mandrel was a silicone rubber negative of the master screen with a plated metal conductive layer at the bottom of the holes. The essential steps in making the plating mandrel were:

1. Fill the holes in the etched stainless steel master screen with wax

2. Coat one side with wax and clean off the reverse side
3. Plate nickel on the uncoated side
4. Remove wax and replace with a silicone rubber and also cover the plated nickel with rubber
5. Remove the stainless steel master screen
6. Electrodeposit nickel in holes left by removal of the master
7. Remove electroformed screen from the rubber mold, which then could be used to plate another screen.

The steps outlined above are shown in figure 16: "A" represents steps 1, 2, and 3; "B", steps 4 and 5; "C", step 6, represents the electroformed screen in place and ready to be removed from the mandrel. The hole size was controlled by the restricted section in the center of the hour-glass-shaped hole developed in the original etching of the stainless steel master screen from both sides. An important feature of this technique is that the deposit did not tend to creep across the surface of the silicone rubber projections and decrease the hole size, nor did a sharp or beaded edge grow at the top of the hole. This effect was attributed to the nonwetting of the silicone rubber by the plating solution. Other plastics found to be suitable were: RTV rubber, Teflon, nylon, polyethylene, and pure gum rubber. Materials wet by the plating solution and found to be unsuitable were: glass, plastisols, polyvinylchloride, and filled or pigmented plastics and rubbers. The technique for mandrel construction developed in this study can assist the electroformer in designing mandrels for producing parts that have holes of controlled size and need no edge machining.

Electroless Plating, Immersion Plating, and Mirroring

FUNDAMENTAL PRINCIPLES

The term "electroless plating" refers specifically to the deposition of metals by controlled autocatalytic chemical reduction. Since the deposit itself catalyzes the reduction process, the plating reaction is self-sustaining and relatively thick coatings may be built up. Immersion plating, in contrast, involves a displacement reaction, in which surface atoms of a metal of high electrochemical potential are replaced by atoms of lower potential relative to the solution in which the metal is immersed. Immersion plating is self-limiting: once the surface is completely covered by the deposit, further reaction is thermodynamically impossible. The zinc immersion process has already been mentioned in conjunction with plating on active-metal substrates (see Chapter 2).

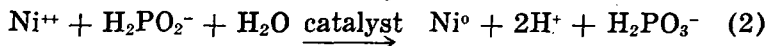
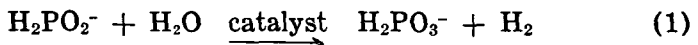
Mirroring involves metal deposition on surfaces simultaneously exposed to a metal-containing solution and a reducing solution. It differs from electroless plating in being nonselective. Mirrors will form spontaneously on any surface. Electroless deposits will form only on catalytic surfaces.

Electroless plating was discovered by accident in 1944 by Brenner and Riddell (ref. 115). They were trying to electroplate a nickel-tungsten alloy on the interior of tubes and thought that the addition of sodium hypophosphite to the plating bath might overcome an anodic oxidation problem. Whether they solved this problem is not recorded, but they did discover that the outside of the tubes become beautifully plated. This was unexpected, because only an inside anode had been used. Further investigation led to a patent on the process and introduced the technical community to the concept of electroless nickel plating (refs. 116, 117, and 118).

Electroless Nickel Plating

Fundamental Chemistry

The electroless nickel-plating process can be most simply described by the following two reactions:



Reaction (1) represents catalytic oxidation of hypophosphite ions in aqueous solution to orthophosphite ions with evolution of hydrogen gas. Reaction (2), which proceeds simultaneously, describes catalytic reduction of nickel cations to metallic nickel by hypophosphite anions in the presence of water. Both reactions are catalyzed by metallic nickel, which accounts for the possibility of building up fairly thick deposits. Hydrogen gas is evolved fairly vigorously throughout the plating operation.

The probable mechanism of electroless nickel plating has been reviewed by Gutzeit of General American Transportation Corp. (ref. 119). Gutzeit's review provides considerable insight into the effects of pH, hypophosphite concentration, temperature, and impurity concentration on plating efficiency. At least 34 patents were assigned to General American Transportation Corp. between 1953 and 1967 (ref. 120) covering various commercially significant aspects of electroless nickel deposition. Proprietary electroless nickel-plating baths and complete instructions for their use are available from several sources (ref. 2). The first and best known industrial electroless nickel-plating development is known as the Kanigen process.

Catalysts

The catalyst is essential to the process of electroless nickel deposition. Once plating has started, the deposition reaction becomes autocatalytic. In most cases of commercial interest, however, no nickel is present initially on the surface of the substrate. In general, any substrate metal of the first transition series—Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, and Pt—will catalyze the decomposition of an electroless plating bath. These metals are commonly known as dehydrogenation catalysts, and one of them must be present to initiate electroless nickel deposition. For metals that are more electropositive than nickel in the electroless plating bath, an initial nickel coating will form by displacement, as in immersion plating. For such metals as copper or manganese, which are neither catalysts in themselves nor higher in the electromotive series than nickel, one of the catalytic metals must be deposited before electroless plating is started, a process known as activation. Typically, activation of a part to be plated involves the deposition of a trace of nickel, either by electroplating for a few seconds or by touching the immersed parts with a more

positive metal. For metals such as Bi, Cd, Sn, Pb, and Mn, which poison dehydration catalysts, it is necessary to preplate with a thin deposit of copper and then to activate.

The fastest growing industrial application of electroless nickel plating is the metallization of plastics. None of the initiation methods discussed above can be applied to ordinary plastics. However, by immersing the plastic part in a warm dilute acid solution of palladium chloride (or a proprietary catalyst bath) and then reducing the adsorbed salt to metallic palladium, the surface of the plastic can be made suitably catalytic.

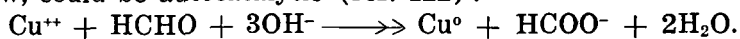
Deposit Characteristics

“Electroless nickel” deposits actually contain significant amounts of phosphorus, probably in the form of nickel phosphide, Ni_3P (ref. 121). Consequently, electroless nickel is harder than electroplated nickel, an advantage in many applications. It also provides better lubrication for parts in sliding contact.

If the surface of a part to be plated is uniformly catalytic, a uniform deposit of electroless nickel can be expected. Thus, for recessed areas, interior surfaces, and sharp corners and edges, it is much easier to build up films of constant thickness by the electroless process than by ordinary electroplating.

Electroless Copper Plating

Electroless copper plating is much less developed than electroless nickel plating. The reduction of cupric ion to metallic copper by formaldehyde in alkaline solution, as shown in the equation below, could be autocatalytic (ref. 122):



The proprietary baths are based on this process but contain various additives to improve plating speed, bath stability, and plating quality. It is instructive to compare, as in table 12, a typical copper mirroring formulation with a typical electroless copper bath. For mirroring, two solutions are made up, solution A serving as a source of cupric ions, and solution B containing the reducing agent. When the two solutions are rapidly mixed or simultaneously sprayed onto a substrate, copper plates out on all exposed surfaces. As the table shows, the electroless copper-plating bath is strikingly similar in composition to the mirroring formulation. It is scarcely surprising that the electroless copper bath decomposes fairly readily. The role of the surface catalyst in this process would be worth investigating in some detail.

TABLE 12.—*Comparison of a Mirroring Formulation with an Electroless Copper-Plating Bath Composition*

Mirroring		Electroless Plating	
Solution A:			
	<i>g/liter</i>		<i>g/liter</i>
Rochelle salt	170	Rochelle salt	140
Sodium hydroxide	50	Sodium hydroxide	40
Copper sulfate	35	Copper sulfate	29
Sodium carbonate	30	Sodium carbonate	25
Versene-T	20	Versene-T	17
		Formaldehyde (37%)	150
Solution B:		Plate at 21° C	
Formaldehyde	37 wt %		
Mix 5 parts of solution A with			
1 part of solution B at room			
temperature			

Electroless Deposition of Other Metals

The electroless nickel process, based on hypophosphite, can be readily extended to electroless deposition of cobalt and cobalt-nickel alloys (refs. 123 and 124). Electroless plating processes for iron and chromium, involving hypophosphite reduction of ferrous sulfate or a mixture of chromium halides respectively, have been patented (refs. 125 and 126), but their use is far from routine (ref. 127).

Several processes for the electroless deposition of gold have been reported, but Brenner suggests that the plating may actually be of the simple immersion type (ref. 127). The weight or thickness of a true electroless deposit should increase continually with time of exposure to the plating solution, and this does not seem to be the case with so-called electroless gold.

A true electroless process has been developed for palladium plating (ref. 128), based on catalytic hydrazine reduction of a palladium-amonia complex. A very large number of metals can be palladium-plated in this way—aluminum, chromium, cobalt, gold, iron, molybdenum, nickel, platinum, rhodium, silver, steel, tin, and tungsten. It is not clear that all of the metals are catalytic in themselves; many may simply have a higher electrochemical potential than palladium in the solution. Copper and copper alloys must be preactivated, usually with an immersion coating of gold. Unlike electroless nickel, the palladium deposits are more than 99.4% pure metal and are ductile even without heat treatment.

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APPLICATIONS OF ELECTROLESS PLATING

Plating on Plastics

The major growth area for electroless deposition processes is unquestionably the plating of plastics. All plastics can be plated, although the technical problems of assuring good coating adherence over long periods of service are significant.

The first large-scale commercial venture in metal-plated plastics was a notable failure. Delrin was successfully Cu-Ni-Cr plated and promoted for use in the automobile industry, one of the major potential markets. Much trouble was experienced with the product in service, and it was ultimately abandoned (ref. 129). The bad name thus acquired by the material is probably not justified, however. Electroless plating of plastics requires meticulous surface preparation, elaborate pretreatment, and controlled sensitization and activation. Because of the large number of fairly critical processing steps, which are not really well understood, difficulties are almost inevitable in the development of a commercial product. Nevertheless, none of the problems is insurmountable.

The failure of metal-plated Delrin in the marketplace did not hinder in any way the commercialization of plated acrylonitrile-butadiene-styrene (ABS) plastics. Platable grades of ABS have been developed specifically for applications requiring an electroless metal coating. The detailed procedures for fabricating commercial plated-plastic parts are for the most part proprietary to each manufacturer; the basic steps involved, however, are typically as follows (ref. 130):

1. Surface cleaning to remove grease and other contaminants that might adversely affect adhesion
2. Conditioning in an acid etching solution to improve the wettability of the plastic surface
3. Sensitization with a reducing agent such as stannous chloride
4. Activation, often with palladium chloride, to form a catalytic surface
5. Electroless copper deposition
6. Copper electroplating
7. Nickel electroplating
8. Chromium electroplating.

Plated ABS plastics have been used extensively in the automobile industry, replacing plated-zinc die castings in such applications as dashboard panels, door and window handles, grilles, door-lock buttons, cigarette lighters, and brake release handles.

The use of these materials in appliances and kitchenware, shower heads, lighting fixtures, and various accessories is growing rapidly.

Although plated ABS plastics have been commercially successful, they are by no means the only plastics that can be metallized by an electroless process. At GSFC, for example, high-bond-strength electroless copper coatings were very successfully applied to laminates of glass fiber and Teflon (ref. 130). The procedure was originally developed to meet the requirement for a copper-coated hyperboloid to be used in a radar experiment. It has since been used to provide rf shielding and electric conductors on Teflon parts. The plastic is cleaned with a nonchlorinated solvent and then etched with a proprietary Fluortech Safety Solvent to provide good wetting. An electroless copper plate can then be applied by any good proprietary method. The Shipley, method, for example, involves a three-step process—immersion in a catalyst bath, immersion in an accelerator bath, and immersion in the electroless copper bath. As a final step, ductile, leveling, bright, acid electrolytic copper is applied. Depending on the application, any desirable electroplate may be deposited subsequently. GSFC has also successfully plated copper over Styrofoam. Adhesion problems, however, might hinder commercial development.

Most industrial work in the plated plastics field has been concentrated on electroless copper preplates; however, other metals for which electroless processes are available can be deposited on plastics. The relative lack of ductility of electroless nickel, as compared with electroless copper, limits its use for many applications. Furthermore, nickel is not an ideal base for subsequent electroplating. The original Brenner-Riddell process for electroless nickel plating (ref. 116) required temperatures that are a little high for many plastics. Now, however, room-temperature processes are available (ref. 131).

Plated plastics have many potential uses. In consumer products, plating has been used primarily for decorative purposes. However, it has many functional advantages that will almost certainly lead to expanded industrial markets. In plumbing and marine applications, plated plastics are far more corrosion-resistant than electroplated metals. The plated plastic searchlight shown in figure 17A, for example, was designed for small boats and will retain its good appearance and operating capability for a long time. The impact resistance of plated plastics was an important factor contributing their wide acceptance for automobile grilles

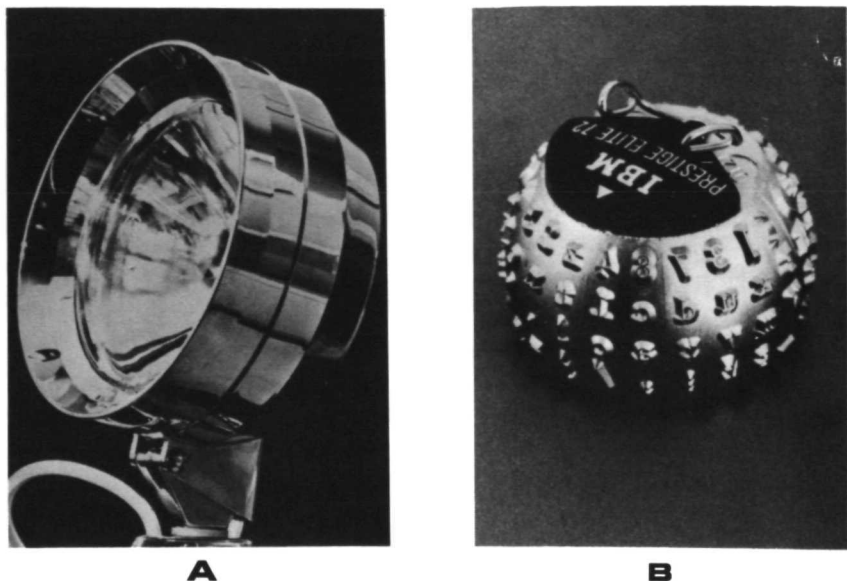


FIGURE 17.—Plated plastic products. A is a plated plastic searchlight; B is a typewriter printing mechanism.

as replacements for plated-zinc die castings. In this application there is a significant economic advantage as well.

The selectivity of electroless plating for catalytic surfaces can be of great advantage in preparing plastic circuit boards. Instead of laminating copper foil to the board and etching most of it away, selected parts can be covered by electroless copper and subsequently electroplated as desired. Electroless deposition is also excellent for through-hole plating.

The wear resistance of plated plastics can be highly advantageous in many applications. The typewriter printing mechanism shown in figure 17B is subject to continuous wear. Its plated surface gives long life to its sharp reproduction capability, and the lightweight plastic substrate facilitates high-speed operation. Electroless plating of plastics may also be a convenient means for soldering and joining plastic parts. As commercial plating processes are developed for a wider range of plastics, uses should increase rapidly.

Plating of Large Parts and Intricate Shapes

In the plating of intricate parts, the use of electroless methods can obviate the need for conforming anodes or current "thieves". NASA Marshall Space Flight Center, for example, used electroless deposition to nickel-plate the insides of wind tunnel nozzles 4 ft

in diameter. Both 4340 stainless steel and Neonite substrates were plated very satisfactorily. Although special tanks had to be built, the proprietary electroless nickel methods were found to be quite suitable. The Shipley process, according to some NASA scientists, has some advantage over the Sel-Rex process in terms of uniformity of the deposit and ease of replenishment of the bath.

The Kanigen process has been used with great success for electroless plating of metal mirror blanks for solar simulation (ref. 132). Electro-Coatings, Inc., plated a 118-in. collimating mirror for Jet Propulsion Laboratory. The base material of 356 cast aluminum was Kanigen-plated on the back (webbed) surface first, with the front surface masked off. Electroless nickel provided a uniform protective coating on the very irregular webbed surface. This would have been difficult to achieve by any other process. Furthermore, the electroless nickel facilitated the subsequent soldering of heating coils onto the back surface. After soldering, the front surface was first polished and then Kanigen-plated, with the back surface protected by a spun aluminum (non-catalytic) cap. The final surface finish was achieved by high polishing of the electroless coating and vacuum aluminization to maximize reflectance.

The smooth, hard, pore-free surface characteristic of electroless nickel makes it an excellent coating for metal optical equipment. It is thermally stable, adheres well to both aluminum and beryllium, and can be optically polished to a quarter of a wavelength. Coatings have been applied to blanks ranging in size from less than a square inch to 10 ft in diameter (ref. 132).

Improving the Solderability of Aluminum and Stainless Steels

Electroless nickel has been widely used in the space program to aid in the soldering of aluminum parts. It is similarly effective for stainless steel. Commercial electroless nickel processes, however, proved less than satisfactory for 7075 aluminum alloy and 303SE, 304, and 17-7PH stainless steels. General Electric Co., under a contract with GSFC, developed special cleaning methods and process control specifications that greatly improved the quality of electroless nickel coatings on these alloys and enhanced the solderability of the substrates (ref. 133).

Corrosion Protection

One of the primary functions of nickel coatings in general is to provide corrosion resistance to the substrates. The phosphorus

content of electroless nickel (ranging from 4% to 12%) appears to improve the already good corrosion resistance of the pure metal. Nonetheless, electroless methods are somewhat more expensive than conventional electroplating. Hence, in applications where the superior corrosion resistance of electroless nickel is not needed, the electroplate is normally used if possible.

For some instances, it is extremely difficult to apply a uniform nickel coating by simple electroplating; for example, the plating of threaded fasteners and recessed socket heads. North American Rockwell Corp., under contract with MSC, developed an electroless nickel/tin coating that was found particularly effective for protecting alloy steel fasteners from salt spray corrosion (ref. 134).

Electronics

The major use of electroless deposition in the electronics industry is for plating through holes in printed-circuit boards. Plated holes are often used to provide either a conducting path between the two sides of the board, or a wicking path for solder during component installation. Copper is the metal normally deposited. For this application, electroless plating is practically the only way to obtain uniform metallization of the nonconductive hole walls.

At GSFC, the Shipley proprietary electroless copper process has been found satisfactory for through-hole plating. The drilled boards are first cleaned in alkali, then vapor grit-blasted, ultrasonically cleaned, and acid-rinsed prior to the electroless deposition of copper. Once the holes have been made conductive, they may be electroplated to a wall thickness usually 1.5 to 2 mils.

Copper is the most widely used cladding material for printed-circuit boards. Aluminum is available for the purpose, but it is seldom used because the caustic solutions used to etch aluminum will attack most photoresists and screening inks. Schjeldahl Co., in connection with a contract with GSFC, found that electroless nickel provides a resist that is unaffected by caustic soda. In the Schjeldahl process, the aluminum is cleaned and then imprinted in the desired pattern with acid-resisting lacquer. The uncoated aluminum is then plated with electroless nickel by one of the proprietary methods. After the acid-resisting lacquer is dissolved or stripped from the surface, the pattern may be etched with caustic soda (ref. 135). Although extensive use of aluminum in printed circuitry is not anticipated, the metal does have attractive properties for special applications. The possibility of using elec-

troless-nickel resists solves at least one of the problems that may hitherto have limited industrial consideration of aluminum.

INNOVATIONS IN MIRRORING AND IMMERSION PLATING

Chemically Reduced Gold Coatings

Chemically reduced or mirrored films for commercial applications are generally produced by spraying. Typically, a double-nozzle spray is used; a metallic solution is fed to one nozzle and a reducing agent to the other, in proper proportion. Mixing generally occurs about six to eight inches from the nozzle heads, where the work to be coated is placed.

In the space program, a relatively new chemical reduction system for plating gold, known as the Lockspray-Gold* process, has been often used (ref. 136). Although the coating is applied in a relatively conventional manner, its use by the home hobbyist is probably precluded by the toxicity of the vapors. The coatings produced are better than 99.99% pure gold, with a copper content (the principal impurity) of less than 0.005%. Just about any substrate, with the exception of aluminum, beryllium, and magnesium, can be gold-plated directly. Adhesion can be a problem, however, particularly on the smooth surfaces required for obtaining specular coatings. Pretreatment with a stannous chloride sensitizer prior to gold spraying accelerates deposition of the first gold layer and helps adhesion somewhat. Plastics, unglazed ceramics, etched glass, alumina, beryllia, nickel, titanium, stainless steel, copper, and silver have all been quite successfully plated by this process. With aluminum, beryllium, and magnesium, a smut of fine particulate gold forms instead of an attractive, continuous film; however, if these metals are first anodized, even they can be satisfactorily plated.

By using dilute metal and reductant solutions, the process can be controlled to deposit transparent gold films. The first space "sunglasses," for example, were clear plastic visors coated with transparent Lockspray-Gold. The metal coating reflects the infrared, absorbs ultraviolet, and transmits the visible light.

Opaque Lockspray-Gold coatings were used on the interior surfaces of the NASA Gemini adapter sections to provide low emittance and thermal control. The sections were about 10 ft in diameter at the base and 8.5-ft-high. Specular gold coatings, which reflect 96% to 98% of incident radiant-heat energy, were applied

*Registered trade name.

to the heat shields for the Applications Technology Satellite rocket motor. Lockheed Aircraft Corp. has fabricated lightweight unfurlable antennas from gold-plated woven fiber glass and synthetic fabrics. Their performance in the space environment has been excellent.

If the Lockspray-Gold plating solutions are mixed together in a container, all accessible surfaces will be plated. While this method is more wasteful than spraying, it provides a good means for gold-plating tiny passages, the interior surfaces of long, narrow-bore tubes, and the exterior surfaces of microscopic particles.

Adherent Immersion Coatings for Magnesium-Lithium Alloys

In principle, the formation of an immersion coating depends only on the relative electrochemical potentials of atoms on the surface to be plated and atoms in the bath. In practice, the coating which forms is not necessarily adherent. The magnesium-lithium alloy, LA-141, is of considerable interest for airborne packaging, housing, and container applications because of its light weight and ductility. In many cases, structural components of the alloy should be plated with zinc or copper for grounding or rf sealing.

Attempts to copper-plate LA-141 directly have met with failure. Thermodynamic considerations indicate that a zinc-immersion deposit should form on the surface of the alloy, but when a standard bath is used, the deposit is powdery and nonadherent. IBM Corp., under contract to MSFC, found that a satisfactory zinc plate could be formed by a simple modification of the usual zinc-immersion process (ref. 137). Sodium carbonate, used in the standard bath, was replaced by sodium acetate to adjust the solution pH to 7.5 to 8.0. At a temperature of 74° to 85° C, a uniform, adherent blue-gray zinc-immersion coating was formed in a period of 2 to 20 min. For practical applications, it is often desirable to electroplate over the zinc with cyanide copper.

Electroplating from Gaseous Plasmas

The basic equipment required for electroplating is a tank filled with a suitable electrolyte and a low-voltage dc power supply. The part to be plated is immersed in the electrolyte and connected to the negative terminal of the power source, while a suitably selected anode is connected to the positive terminal. As current flows through the solution, metal ions plate out at the cathode, provided that the operating parameters have been properly chosen.

Aqueous ionic solutions have been historically the most important electrolytes for plating. Nonaqueous solutions and fused-salt baths have been explored as plating electrolytes for almost a hundred years but are only beginning to have commercial significance. Gaseous ionic solutions (almost a contradiction in terms) are in fact known and should be used increasingly as plating electrolytes.

If the space between the anode and the cathode were filled with a gas, such as air at room temperature and pressure, no current would flow. Electroplating could not occur, because no mechanism would exist for transporting ions from the anode across the air gap, and for discharging them at the cathode. On the other hand, if the space between the electrodes is filled with a low-pressure gas and a high dc voltage is applied, dielectric breakdown can occur; the gas then becomes electrically conducting, and ionic transport becomes possible. The ions formed in gaseous discharges are far more energetic than those transported by electrolysis of liquid solutions, and when they are discharged at the cathode they tend to adhere remarkably well. In fact, gaseous plating ions have been known to penetrate the cathode surface to a depth of several hundred angstroms, even under conditions of negligible coating-substrate solubility.

Electroplating in gaseous discharges was first reported by Mattox in 1964 (ref. 138) and is known in the literature as "ion plating." It must be carefully distinguished from "sputtering," which is not an electroplating process at all, although it is done in a similar type of apparatus. Ion plating has been investigated

extensively at LeRC by Buckley, Przybeszewski, and Spalvins for the deposition of high-quality, reliable, long-lived lubricating films. The commercial potential of the process for lubrication, corrosion protection of precision parts, plating on plastics, and manufacture of microelectronic components is being actively explored in a number of companies and independent laboratories. Fairly large-scale, practical industrial uses should emerge within the next few years.

A hybrid type of electroplating known as "electrodeless electrolysis" was investigated briefly by Brenner and Sligh under NASA sponsorship (ref. 139). In electrodeless electrolysis, the anode and cathode are surrounded by a low-pressure gas as in ion plating, but a plug of solid or liquid electrolyte separates the two electrodes. When a glow discharge is established by the application of a high voltage between the electrodes, current flows from one electrode through the surrounding gas into the solution, and through the gas to the other electrode. Electrolysis can occur, with metal dendrites appearing in the part of the electrolyte closest to the cathode. The process has not been used for electroplating, and if the dendritic growth proves to be the rule, it never will be; on the other hand, the practical potential of the process has not been explored at all. Changes that have been observed in the structure and conductivity of solid electrolytes subjected to electrodeless electrolysis appear to be unique. Whether they might also be useful is conjectural, but further study would almost certainly prove highly rewarding.

In most work with gaseous electrolytes, ionically conductive species are formed in a high-voltage gas discharge. Naiditch, under NASA sponsorship, studied electrodeposition from inherently conducting gaseous media (ref. 140). Solutions of silver nitrate in liquid ammonia, for example, when heated above the critical point of ammonia, form dense gaseous electrolytes from which silver can be electrodeposited in a fairly conventional manner. While the deposits formed in a few brief exploratory experiments were dendritic, the same was also true of fused-salt electrodeposits when they were first investigated. On the other hand, there are very satisfactory and far simpler competitive processes for silver plating. The investment that would be required for the commercialization of a process based on supercritical gases certainly could not be justified, unless the deposits formed were either of exceptional quality or unattainable by less costly means. Nonetheless, the entire field is in its infancy and very few methods have been investigated. Even the basic con-

ductivity data, which might be used for the preliminary selection of methods, is unavailable.

In summary, of the various gaseous electrodeposition processes discussed, only ion plating will be developed for commercial applications in the next 5 years. Any of the companies equipped to do sputtering can capitalize on a demand for ion-plated coatings, although very few are engaged in active marketing. The initiative will be supplied, as potential users begin to recognize the unique functional advantage of ion-plated films for a host of demanding applications. Electrodeless electrolysis and electrodeposition from inherently conductive gases are still of academic interest.

EXPERIMENTAL TECHNIQUES

Ion Plating

A schematic diagram of a simple ion-plating apparatus is shown in figure 18. As in conventional electroplating, a dc power supply maintains the workpiece cathodic and the source of plating atoms anodic. The "plating bath" is a glow discharge established in a low-pressure, inert gas between the two electrodes.

In actual operation and in the types of deposits produced, ion plating differs very considerably from conventional electroplating. The dc power supply for ordinary electroplating is customarily a battery or other low-voltage source. In ion plating, a very high potential (2 to 6 kV) is necessary to maintain the requisite dc gas discharge. Before the discharge is established, the plating chamber is evacuated to a pressure of less than 10^{-6} torr and purged several times with argon to remove residual gases. Next the chamber is filled with argon to a constant pressure of 20 to 35 microns. When a potential of 3 to 5 kV is applied across the electrodes, the argon ionizes and forms a pinkish-violet plasma (ref. 141). The Ar^+ ions impinge with high velocity on the cathode and have sufficient energy to knock (sputter) atoms from the surface of the workpiece, probably by a process of momentum transport (ref. 142). The sputtering process, which is continued for 10 to 30 min, serves to clean the surface to be plated. Finally, the anode containing the plating material is heated by a separate power source to a temperature high enough to cause vaporization, while the glow discharge is continued. Some of the thermally evaporated atoms are in turn ionized in the argon plasma and are accelerated towards the cathode, where plating can occur. Because the cathode is simultaneously plated and sputtered, the

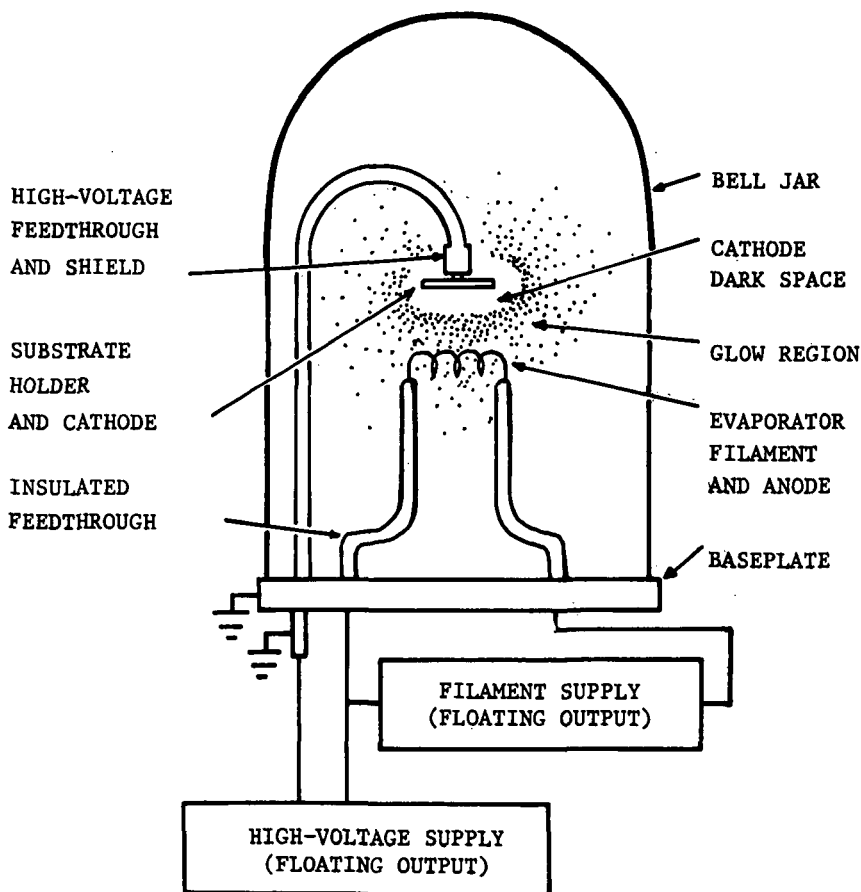


FIGURE 18.—Ion-plating apparatus.

rate at which plating atoms condense obviously must exceed the sputtering rate if a surface film is to be obtained.

In ion plating, the gas discharge functions quite differently from an aqueous electrolytic solution. The current-voltage characteristics of a discharge between two flat-plate electrodes in the pressure range of interest are shown in figure 19. Ion plating is carried out in the abnormal glow-discharge region, within which the current is adjusted until a glow completely covers the cathode. The appearance of the actual discharge during ion plating is shown in figure 20. The dark space is a region where ions are accelerated with maximum velocity toward the cathode.

Plating efficiency is highest when the dark space is as wide as possible. If the dark space is expanded to the plane of the anode, however, the discharge will be extinguished. The width of the

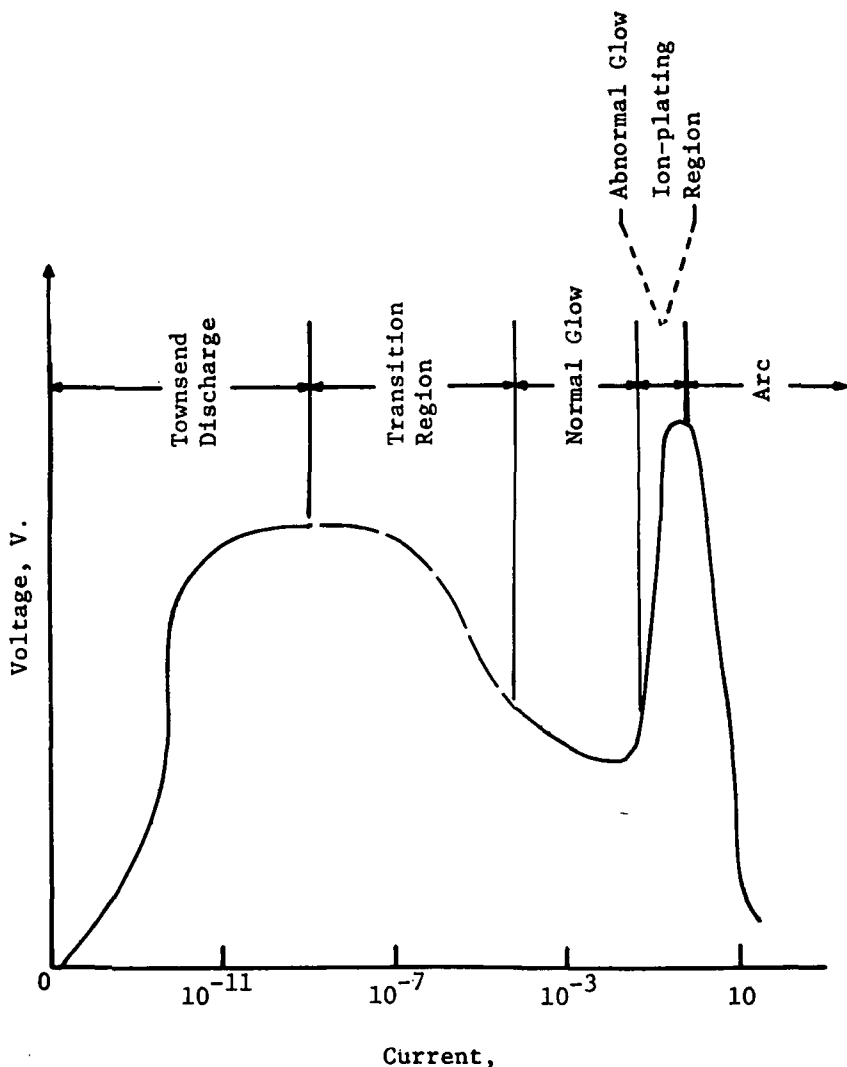


FIGURE 19.—Volt-ampere characteristics of gas discharge.

dark space varies inversely with the total pressure. Typical operating parameters are: argon pressure of from 25 to 30 microns; electrode space of from 4 to 6 in.; and current density of from 0.3 to 0.8 mA/cm². These parameters result in a cathode dark space several cm in width.

The particles deposited on the cathode during ion plating have an energy distribution ranging from the thermal energies characteristics of electroplating or vapor deposition (0.1 to 0.2 eV) up

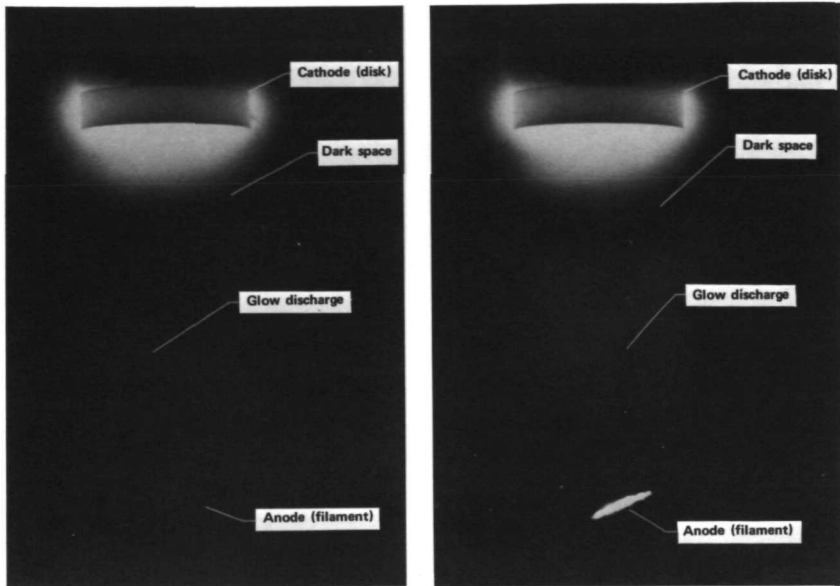


FIGURE 20.—Glow discharge during ion plating.

to several thousand volts acquired by acceleration in the dark space. The high-energy particles are responsible for some of the unique properties of ion-plated films.

Particle bombardment causes the cathodic substrate to be heated to about 200°C during ion plating, which can be a distinct limitation for some systems. According to Donald Buckley of LeRC, the temperature can be controlled to some extent by adjusting the voltage. Alternatively, the cathode may be imbedded in a shielded cold finger (ref. 143).

One advantage of ion plating over conventional electroplating or simple vacuum-vapor deposition is that complex configurations can be uniformly coated while the object is kept in a fixed position. Thus, back and front surfaces may be coated simultaneously, and the process is ideal for plating threaded bolts or the teeth of small gears (ref. 141). In conventional electroplating, specially designed current "thieves" or conforming anodes are required to get uniform coating of complex shapes. In simple vapor deposition, plating atoms travel only in straight lines.

Sputtering has been mentioned as a means of cleaning a surface prior to and during ion plating. Since the atoms sputtered or ejected from a cathodic source also can deposit onto nearby surfaces, sputtering represents another possible method of coating substrates. Actually, sputtering is a much older process than ion

plating and was used for depositing thin films as early as 1887 (ref. 142). However, intensive development of the sputtering process for controlled thin-film deposition did not begin until about 1955.

The simplest type of sputtering apparatus is shown schematically in figure 21. It is basically similar to the ion-plating apparatus, except that the source or material to be plated is made the cathode, while the workpiece is made the anode. A discharge is initiated between the two electrodes in an argon atmosphere at a pressure of 10^{-2} to 10^{-1} torr. The argon ions (Ar^+) formed in the discharge are accelerated toward the cathode source. The

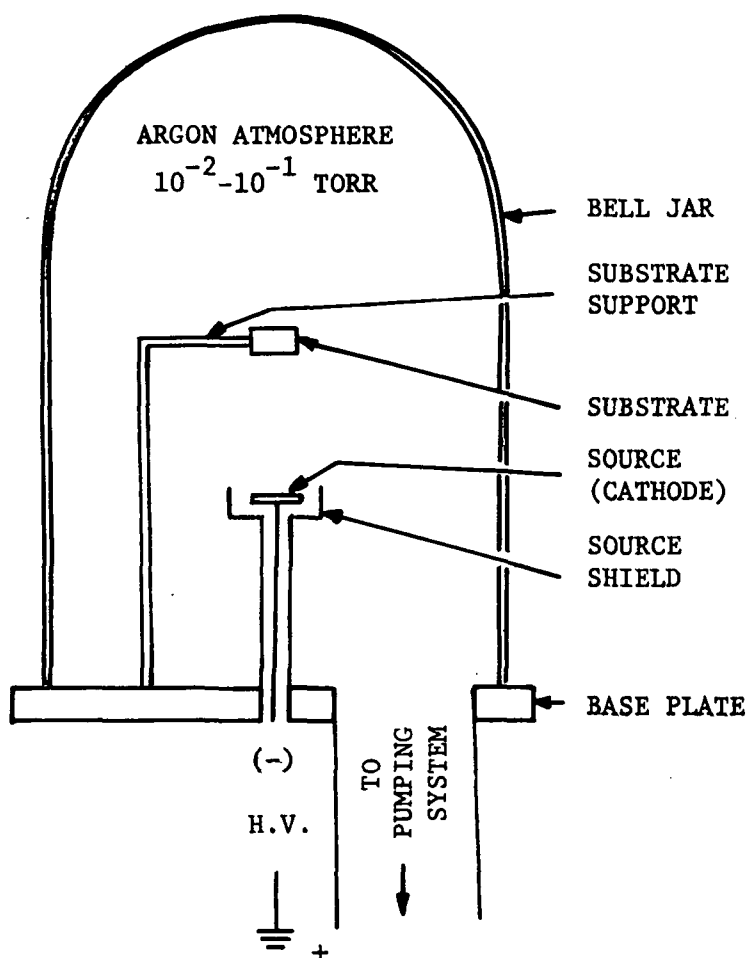


FIGURE 21.—Representative cathodic sputtering apparatus.

bombarding ions transfer sufficient momentum to the atoms of the target to cause them to leave the surface with energies many times higher than those of thermally evaporated atoms.

The rate of deposition of sputtered films is typically about 100 to 500 Å per minute. For maximum deposition efficiency, the substrate should be as close as possible to the cathode without disturbing the glow discharge. In practice, substrate and source should be separated by about twice the width of the dark space. There is some tendency for ion-current concentration near the edge of the cathode, causing higher rates of atom ejection in these areas; for uniform deposition, therefore, the cathode should be more extended than the substrate.

It should be clearly understood that sputtering is not an electrochemical plating process. Deposition of sputtered films on a substrate obviously does not require that the substrate be used as the anode. A separate anode could be used if more convenient, since the function of the anode is only to establish a gaseous discharge.

The sputtering technique, even in its simplest form, is quite versatile. It can be used to deposit oxides, nitrides, carbides, sulfides, and alloys as well as pure metals. The inclusion of reactive gases in the sputtering atmosphere can cause metallic atoms ejected from the cathode to be deposited on the substrate in the form of their respective compounds; i.e., inclusion of oxygen can result in oxides, nitrogen in nitrides, methane or carbon monoxide in carbides, and hydrogen sulfide in sulfides. By carefully controlling the relative rates of compound formation and sputtering, one can obtain a wide range of film composition. If a metallic alloy or a compound semiconductor is used as the cathode, the sputtered film will have the same composition as the source. This extremely useful characteristic of the sputtering process is not always attainable in simple vacuum vapor deposition of alloys at high temperatures.

In both sputtering and ion plating, there is an advantage to having the dark space, the region of high ion acceleration, as wide as possible. On the other hand, if the dark space expands—because of a decrease in ambient pressure, for example—to the point where it reaches the anode plane, the discharge will be extinguished. The triode system shown in figure 22 has been used at LeRC and elsewhere to sustain a discharge at very low pressures. The fundamental problem at low pressures is that the ionization by secondary electrons emitted from the cathode is insufficient. By introducing a hot filament (thermionic cathode) as shown, a flow of electrons will occur between the thermionic

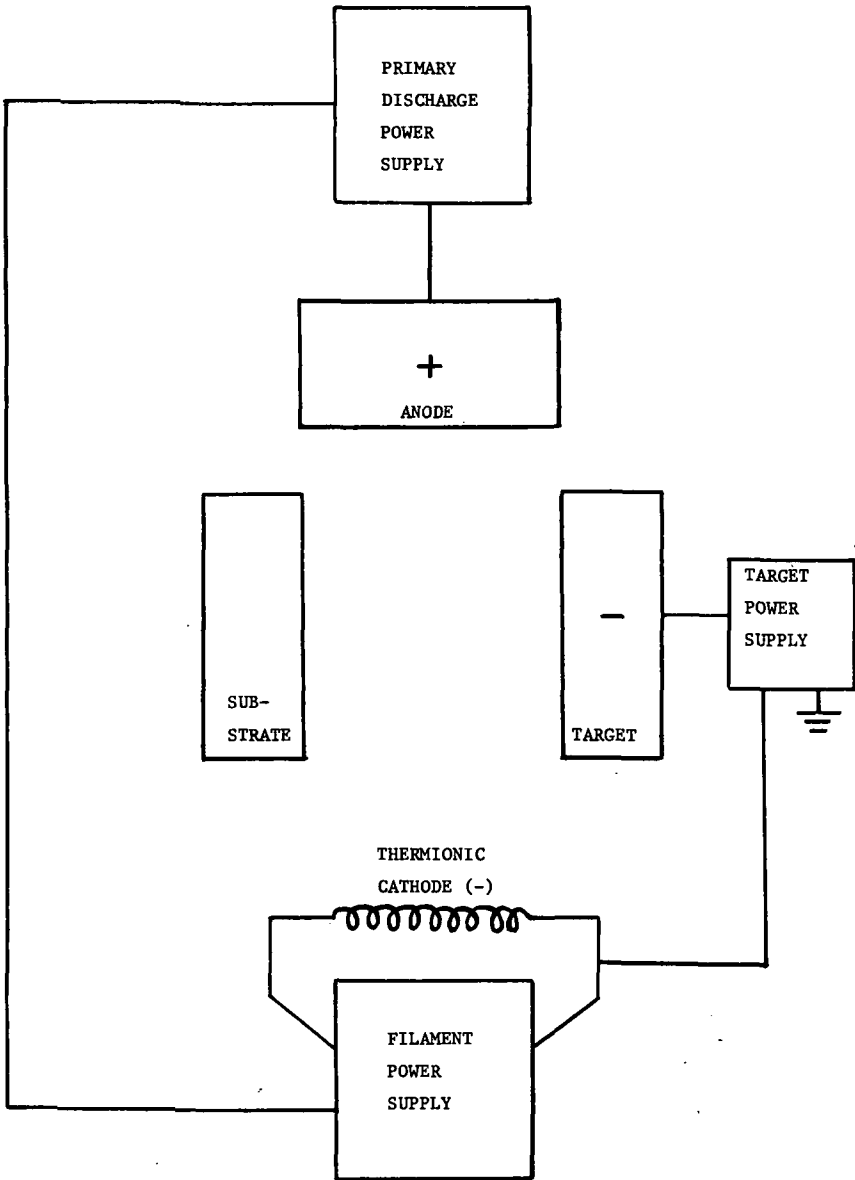


FIGURE 22.—Sputtering (triode) system.

cathode and an opposing anode, and a discharge can be established. When a negative potential above the sputtering threshold is applied to the target or source of plating atoms, sputtering occurs. The sputtered atoms then deposit on the specimen in the usual way. With reference to figure 22, the specimen is about 12.5

in. from the thermionic cathode, and target-to-specimen distance is about one inch. By sputtering at very low pressures, gaseous contamination of the coating and attendant porosity are minimized.

The sputtering of dielectrics presents special problems, because the charge of bombarding ions cannot be neutralized in a conventional system. If an rf voltage is applied to the surface of the dielectric, the space charge can be dissipated and sputtering can be sustained (ref. 144).

Electrodeless Electrolysis

In conventional electroplating, the conducting path between anode and cathode is a liquid electrolyte. In ion plating, the conducting path is a gaseous discharge. Brenner and Sligh, under NASA sponsorship, investigated the hybrid situation in which conduction occurs partially in the gas phase and partially in a liquid or solid electrolyte (ref. 139). Although the work has not yet been commercially applied, the results are nonetheless extremely interesting.

Electrolysis between a gas and a condensed phase is known in the literature as "electrodeless electrolysis." This name is a misnomer, since electrodes are used, even if they are not in contact with the condensed phase, and the electrolysis that occurs does not necessarily follow Faraday's law.

The simplest experiments of Brenner and Sligh in electrodeless electrolysis were carried out in the apparatus shown schematically in figure 23, and involved electrolytic decomposition of fused salts. The salt melt was contained in the bend of a fused silica U-tube and was separated into two portions by a porous diaphragm. An electrode was inserted into each arm of the U-tube in the space above the melt, and the system was evacuated to a pressure of 50 to 1000 microns. A glow discharge was established by application of 1000 to 3000 volts dc between the two electrodes. The current flow was of the order of 10 to 25 milliamperes. The glow discharge appeared in both arms of the U-tube.

With a silver chloride melt, silver dendrites were observed to form in the fused salt within the cathode compartment. The yield was roughly in accord with Faraday's law. Electrolysis of a cuprous chloride-potassium chloride melt, with copper powder added to the anode compartment to assure that all of the copper in solution was maintained in the univalent state, caused the formation of copper dendrites within the cathode compartment. The porous frit prevented any mass transport of metallic copper.

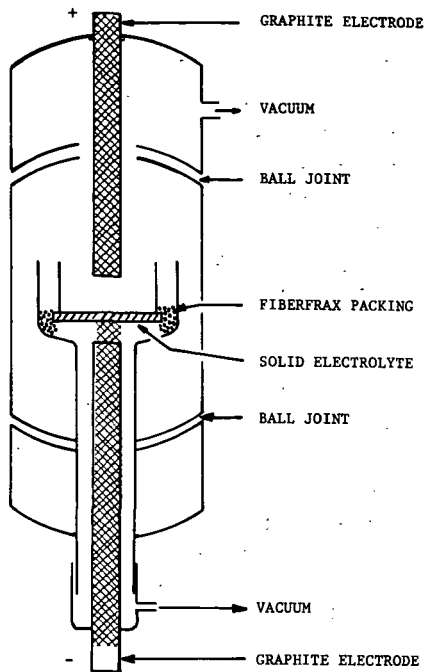
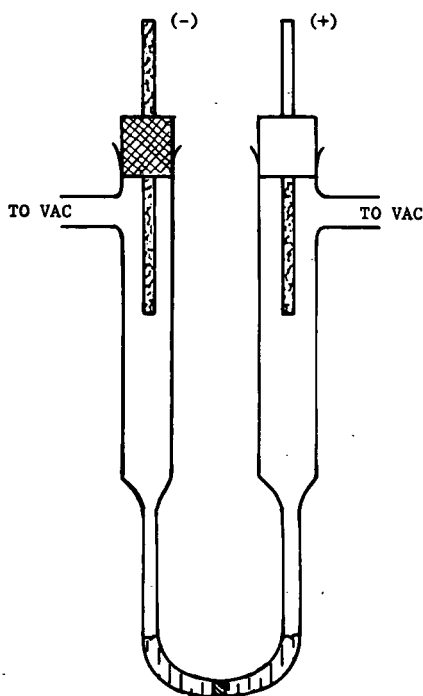


FIGURE 23.—U-tube for glow-discharge electrolysis of fused salts. FIGURE 24.—Apparatus for glow-discharge electrolysis of solid disk electrolytes.

Similar results were obtained with stannous chloride, cobalt chloride, and nickel chloride melts.

Brenner and Sligh also studied electrolysis of solid disk electrolytes in a plasma. The apparatus is shown schematically in figure 24. When the discharge is established between the two electrodes, current flows from one graphite electrode through the gas phase, thence through the solid electrolyte disk, and finally through the gas on the other side of the disk to the other graphite electrode. The Fiberfrax packing prevents the short circuiting of current flow between the edges of the disk and the middle of the funnel-shaped holder. Gas pressures were of the order of 0.1 to 1 torr. With a dc voltage of 1400 V between the electrodes, currents were of the order of 20 to 40 milliamperes. With many ceramics, the specimen had to be heated to become sufficiently conducting. When a solid silver chloride or silver iodide disk was used, silver dendrites grew on the cathodic side of the disk. With a single crystal disk of sodium chloride, an alkaline white film deposited on the walls of the cathode chamber, probably the product from

reaction of vaporized metallic sodium with ambient gases. Color changes, as yet unexplained, were observed in barium titanate disks, and the disks became more conducting. Electrolysis of glass disks produced dramatic changes in appearances, different on the anode and cathode side, which have not been elucidated.

The pioneering work of Brenner and Sligh in electrodeless electrolysis calls attention to a relatively unexplored means for bringing about chemical changes electrolytically. Some of the many unanswered questions that might be studied to assess fully the practical potential of the method include the following: What is the nature of the gas discharge, and do changes in its characteristics affect electrodeposition? What is the influence of cell geometry (electrode spacing, electrode-sample spacing, electrode size, etc.) on the electrolysis reactions? What are the electrode reactions? What changes are brought about in the solid during glow-discharge electrolysis of disks? How can the structure of the deposited metals be altered? It is too early to judge the kinds of applications that might emerge from such research, but the field does seem well worth investigating.

Electrodeposition from Dense Gaseous Electrolytes

A gaseous electrodeposition process, which is still very much in the research stage, was investigated by Naiditch under NASA sponsorship (ref. 140). Naiditch was able to electrodeposit metallic silver from dense gaseous solutions of silver nitrate in ammonia. A 0.036N AgNO_3 solution in liquid ammonia was prepared at -78°C , and heated into the dense gaseous state above the critical point of ammonia (132.9°C , 112 atm). Electrodeposition was accomplished between two platinum electrodes at a current density of 1.6 mA/cm^2 and a voltage of 0.5 V. Crystalline deposits of silver precipitated out on the cathode; however, there was a tendency for crystalline needles or dendrites to grow from sharp corners. For electroplating, dendrites are, of course, very undesirable, but the possibilities for whisker growth or the growth of special crystalline forms could be of some interest. Perhaps of greater importance is that the general field of classical electroplating from inherently conducting gaseous media has hardly been touched.

APPLICATIONS OF ION PLATING AND SPUTTERING

The equipment used in ion plating and sputtering is basically quite similar. Ion plating, however, is an electrochemical process,

while sputtering is not; consequently, the character of the deposits, the kind of parts that can be plated in a one-step process, and the type of film that can be deposited differ significantly between the two processes.

The characteristic differences of the deposits formed by sputtering and ion plating are closely related to the energies of the depositing atoms. In sputtering, particle energies are far greater than thermal energies and can be as high as 100 eV. In ion plating, the depositing metal ions may have energies up to thousands of volts, and hence can be physically driven below the surface of the substrate. Typical penetration depths range from 50 to 150 Å/keV. Thus, ion plating enables the formation of a graded interface, even when the substrate and coating are mutually insoluble. Such an interface generally promotes adherence. In ion plating, the sputtering of the part to be plated, which precedes and accompanies the plating process, effectively removes surface contaminants that often prevent the formation of a strong interfacial bond. In sputtering, it is not the substrate but the plating source which is bombarded with ions. Still, some substrate surface cleaning may be produced by the relatively high-energy bombarding atoms (ref. 143). Ion plating can be used to coat complex configurations in a single-step process with a stationary workpiece. Sputtering is strictly a line-of-sight process.

At present, ion plating is limited to the deposition of metals. Sputtering is far more versatile and has been used to deposit alloys, compounds, semiconductors, and insulators. Moreover, it has been developed much further than ion plating. However, since a company equipped to do sputtering can do ion plating equally well, specific applications of the two processes are considered together in this discussion. In some cases in which sputtering has been used quite satisfactorily, ion plating could produce a superior product. In other cases, only one of the processes may be applicable.

Lubricating Films

Significant advances in the state of the art of ion plating and sputtering have been made by Donald Buckley, John Przybyszewski and Talivaldis Spalvins at LeRC. The group has been concerned primarily with the deposition of solid-film lubricants for high-vacuum space applications. The techniques they have developed, however, are applicable to a far wider range of general coating problems.

The solid-film lubricants most commonly used today are gold and molybdenum disulfide. Gold films are normally electrodeposited and have not been free from problems in space applications (cf. Chapter 2). Molybdenum disulfide is usually mixed with binders and applied as a slurry, a method which is particularly unreliable and poorly reproducible. As a result, variable failures of bearings and bearing components have come to be expected. However, for space applications, lubricants must have reproducible endurance characteristics, often over a 5-year period.

Lewis Research Center is exploring new techniques for the application of film lubricants, with particular emphasis on ion plating for deposition of metals, and dc and rf sputtering for deposition of compound films. Film friction characteristics and endurance life are measured in ultrahigh-vacuum friction experiments. Typically, the solid lubricant is applied to a 2-in.-diam flat disk and is tracked constantly with a hemispheric rider until the lubricant fails. The friction coefficient is monitored continuously with a strain-gauge assembly that restrains the rider. Friction tests are generally conducted at speeds of 20 to 40 ft/min with loads of 250 and 500 g in a vacuum of 10^{-11} torr. The friction test is quite standard, but the vacuum system is unique to NASA.

Buckley and his associates comprise one of the very few groups in the country investigating the practical potential of ion plating for deposition of metallic films. The very attractive properties that have been discovered make it almost certain that the demand for such coatings will grow substantially over the next few years. Comparing ion-plated gold films and electroplated gold films as lubricants on a stainless-steel bearing gauge, Buckley found the ion-plated film to be far superior, especially in vacuum. The heat of sliding friction tends to cause blistering of the electroplated films, while the ion-plated films remain very tenacious. Furthermore, there are no pin-hole problems with ion plating.

The burial of coating atoms below the surface of the substrate during ion plating can be particularly advantageous. In microscopic cross-section, the interface between the ion plate and the substrate can be so diffuse that it is impossible to determine where the coating ends and where the substrate begins. This type of interface is highly desirable where exceptionally strong bonds are required. In friction experiments, failure of a diffuse ion-plated solid-lubricant film, when it occurs, is gradual. With electroplated films, where diffusion into the substrate is minimal, a very sharp failure is observed as soon as the rider breaks through the lubricant.

By controlling the voltage during ion plating, it is actually possible to produce either a sharp or a diffuse interface; the Lewis group has demonstrated this with nickel coatings on tungsten. The highly diffuse interface is unique to the ion-plating method. In tensile tests, ion-plated coatings flow with the substrate, and show no tendency to chip or peel.

Comparing ion-plated gold films on Ni-10Cr with vapor-deposited or sputtered films, Spalvins and Buckley found that the ion-plated films had both the lowest friction coefficient and the longest endurance life (ref. 145).

NASA has interested Hohman Plating and Manufacturing Co. (Dayton, Ohio) in doing ion plating on a service basis. Hohman does specialized metal finishing of many kinds, and has available most of the vacuum equipment needed for ion plating. The company built an 18-inch bell jar system for commercial ion plating essentially according to NASA plans. No large scale applications have emerged, but Hohman has ion-plated prototype parts for many specific applications. The greatest interest appears to be in lubricating films; this may reflect only the lack of property data for other applications. Hohman at present has support from a consortium of companies to investigate the broad commercial potential of the ion-plating process. Although the specific findings of the program are confidential, the future looks quite promising. Hohman can now ion-plate pieces up to 8 in. long and 4½ in. in diameter. The power source is sufficiently large to handle parts 20 in. in diam and 30 in. long, but a new vacuum system would be required.

The sputtering of solid-film lubricants has been investigated intensively. Sputtering is not limited, as is ion plating, to the deposition of metals, but can be used to deposit compounds or even organic polymers. The best known solid-film lubricant is molybdenum disulfide (MoS_2), which is a semiconductor; it can readily be sputtered in a triode dc apparatus, such as that shown in figure 22. A simple diode apparatus also could be used, but film quality is improved by the lower operating pressure of the triode system. Experiments by Spalvins on sputtered MoS_2 films deposited on nickel, nichrome, and niobium disks showed an average friction coefficient of 0.05 and an endurance life of over a million cycles (ref. 146). Actual friction traces of a niobium hemispherical rider sliding on coated and uncoated niobium disks are shown in figure 25. The endurance of three MoS_2 films—two deposited by commercial processes and one by sputtering—is shown in figure 26. The data demonstrate the superior properties of the

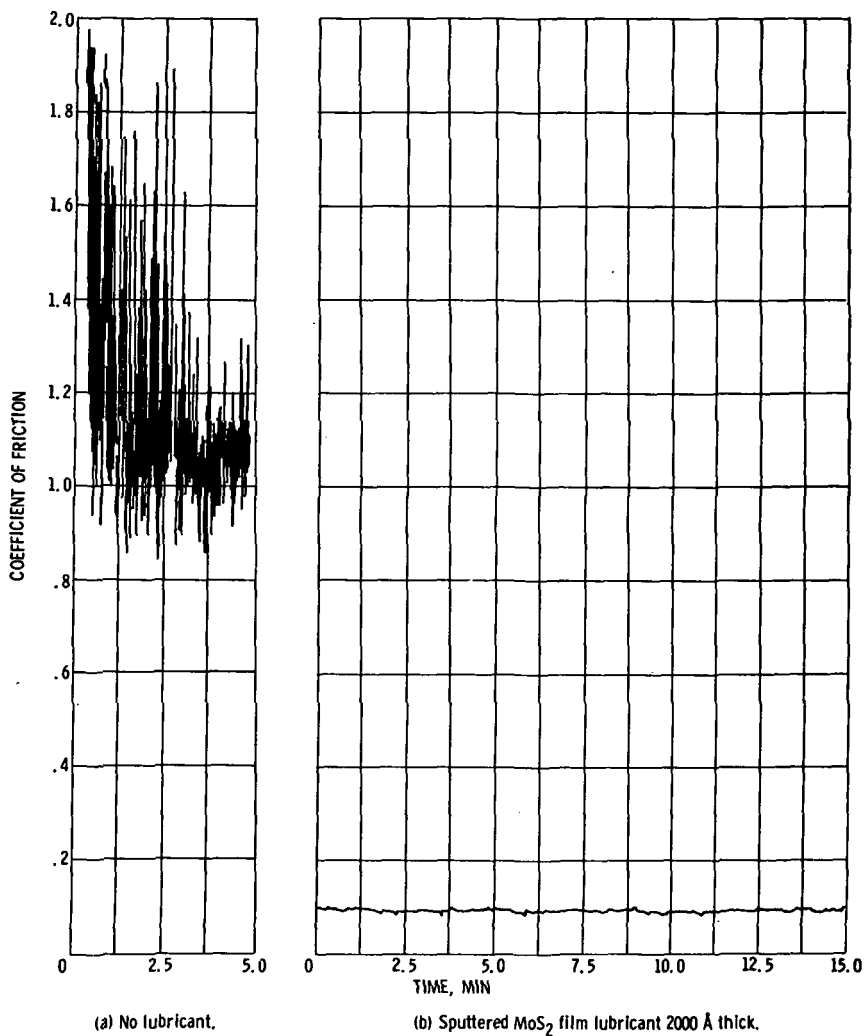


FIGURE 25.—Actual friction traces of niobium sliding on niobium with and without a sputtered MoS₂ film (Pressure, 10^{-11} torr; load, 250 g; speed, 5 ft/min).

sputtered film in vacuum. Furthermore, the superior results were obtained with thinner than normal films. The sputtered film is noncrystalline, is about 200 Å thick, and has a particle size of less than 30 Å. The amorphous nature of the deposit may be because, in both sputtering and ion plating, a continuous film forms immediately without nucleation (ref. 145). That is, there is no tendency for initial condensation at selected surface sites, which occurs in vapor deposition.

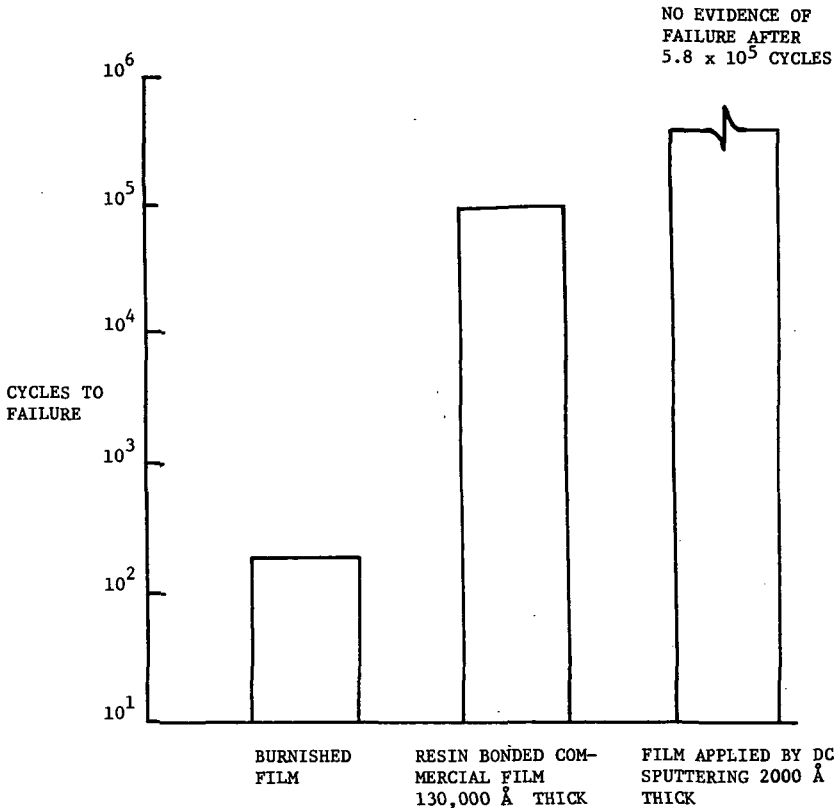


FIGURE 26.—Endurance lives of MoS_2 films applied by various techniques.

The remarkable results obtained at LeRC with sputtered MoS_2 films prompted Varian to develop the process further for use on rotating parts in its own vacuum systems. Varian has offered to sputter-coat parts with solid-film lubricants on a service basis (ref. 147). The company had done sputtering commercially for many years, and has experimented with MoS_2 films before, but the NASA work pointed up the practical potential.

Spalvins has sputtered films of tungsten disulfide and gold as well as MoS_2 and has found that the coefficient of friction is at least as low as that of films deposited by other techniques, while the durability and adherence are far better (ref. 146). For gold, ion plating might have some advantages over sputtering; for the sulfides, ion plating is inapplicable, at least at present.

Dielectrics cannot be sputtered with a simple dc triode or diode apparatus, but they can be sputtered by using an rf-diode mode with a superimposed dc bias voltage. The rf-sputtering method was used by Spalvins to deposit both polytetrafluorethylene

(PTFE) insulating films and MoS₂ semiconductor films as lubricants (ref. 144). A remarkable phenomenon was observed during rf sputtering of MoS₂. At a particular specimen-to-source distance, with the specimen completely immersed in the plasma sheath, the coating deposited on all sides fairly uniformly. Ball bearing components, for example, were completely coated, including the ball pockets of the cages. The sputtering of PTFE was quite successful, although the films had a yellow appearance. The lightest color and the composition closest to the original source were obtained at the lowest power inputs. The films adhered surprisingly well to glass and metal surfaces. Polyimides have been sputtered successfully also.

The lubrication of slip rings is particularly difficult because, ideally, two almost opposing requirements should be met: (1) excellent electrical contact across the sliding interfaces, and (2) separation of the sliding surfaces by a low-shear-strength lubricant film. It might be expected that very thin MoS₂ films, which could be applied to slip-ring surfaces by sputtering, could provide the necessary lubrication without degrading the electrical properties. Przybyszewski and Spalvins applied such films by dc triode sputtering to copper, silver, and beryllium disk specimens and to copper disk specimens ion-plated with gold, rhodium, or palladium (ref. 148). Continuous, adherent, low-friction films were obtained on all specimens except OFHC copper. Unfortunately, contact resistances were quite high (>1 ohm) for all systems except silver in contact with MoS₂-coated Ag (0.015 ohm). Contact-resistance peaks were also quite high.

Recently the Lewis researchers have been exploring new ideas for lubricating slip rings. Gallium was found to be an excellent lubricating material for the application, giving particularly low noise on copper or copper-beryllium alloys. It has been applied both by ion plating and by brush plating; the ion plate is more adherent but has a higher contact noise. Gallium has an exceptionally low vapor pressure for such a low-melting-point material, and no contamination of nearby surfaces was observed in a vacuum of 10⁻¹¹ to 10⁻¹² torr over two years of continuous operation.

Plating on Surfaces with Various Configurations

The ion-plating method is almost unique in its ability to plate complex shapes uniformly in a single operation with a minimum of special design. In figure 27, the evaporation and plating characteristics of vacuum evaporation or sputtering are compared with

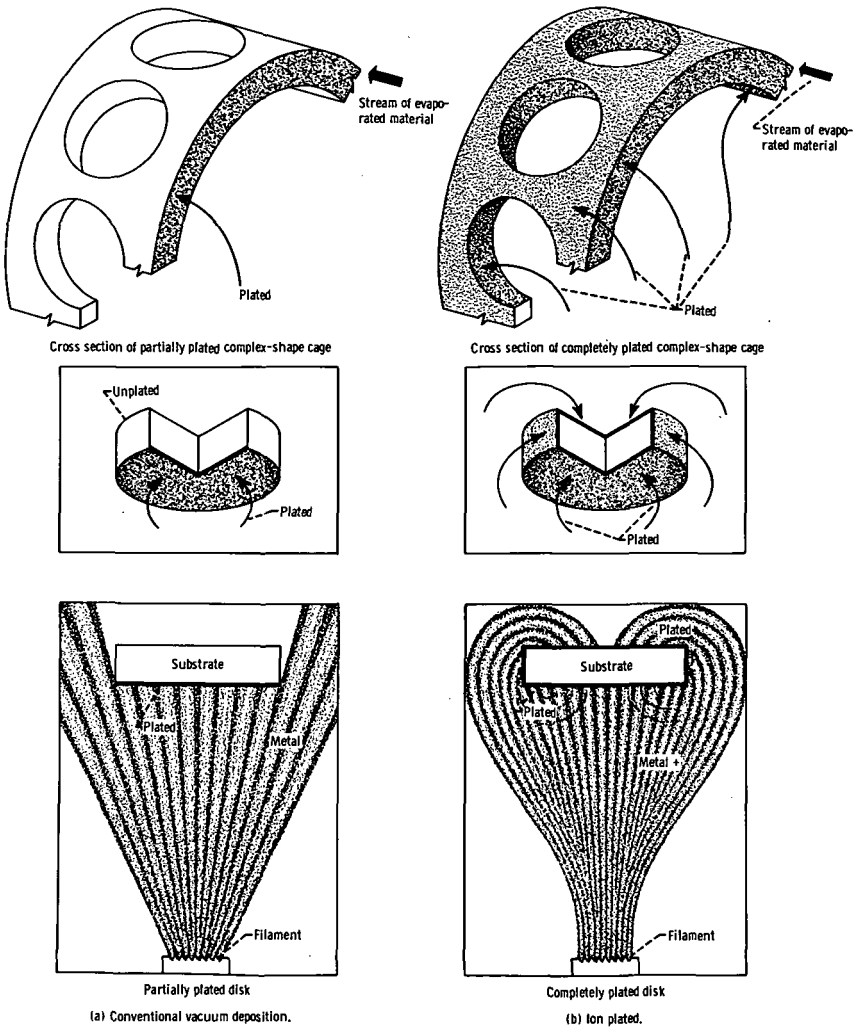


FIGURE 27.—Comparison of conventional vacuum-deposition with ion-plating techniques.

those of ion plating. In sputtering, as in simple vacuum evaporation, plating atoms travel in straight lines, and only those parts of the substrate in a direct line with the source become plated. In ion plating, the plating ions travel in complex paths and can reach all parts of a substrate, no matter what its shape.

Spalvins et al. ion-plated gold on various complex substrates with remarkable results (ref. 141). Disk specimens were coated on front, back, and sides with 1500 Å of gold. Interference microscope measurements of film thickness at random points on the

disk were all in the 1300 to 1500 Å range. Results of ion-plating ball bearing components with a thin film of gold are illustrated in figure 28; even the ball pockets were plated fairly uniformly, despite the fact that the cage was not rotated or moved. Two complex stainless steel surfaces which were ion-plated satisfactorily are shown in figure 29. In all cases, adhesion, measured by the adhesive tape test, was excellent. When aluminum surfaces are ion-plated with gold, a dark purple film, probably AuAl_2 , is formed initially, and the characteristic gold-colored surface develops as plating proceeds. This behavior is to be expected when the plating material and substrate can form stable intermetallic compounds.

The excellent adherence, uniformity, and freedom from porosity—even in thin films—that are characteristic of ion plating, together with its ability to coat complex shapes, makes it an ideal method for coating precision parts. Although electroplating requires far less capital investment, it is not ordinarily precise enough for many aircraft parts and precision instruments. An ion-plated surface will duplicate the substrate; for example, if the substrate has a mirror or matte finish, the plated coating will have the same characteristics.

Corrosion Protection

The widely advertised platinum-edged and chromium-edged razor blades are sputter-coated. Their superior performance is ascribed to improved corrosion resistance. In the commercial razor-blade process (according to Donald Buckley of LeRC) batches of 75 000 blades are strung on a skewer, placed in a vacuum chamber, and sputtered simultaneously.

Sputtering and ion plating, where applicable, are ideal methods for deposition of corrosion-resistant films when close dimensional tolerances are critical. Thin films deposited by these techniques can exhibit desirable properties that could be obtained only with thicker films if another deposition technique were used. In the razor-blade application, the coatings are so thin that the edge does not have to be rehedged after plating. In spite of the thinness of the deposit, the coatings are pinhole-free and extremely adherent.

Corrosion is so universal and of such economic significance that the potential applications for sputtered and ion-plated protective films are many. Cost effectiveness can be a major factor in using the processes, however, since the technology of ion plating and

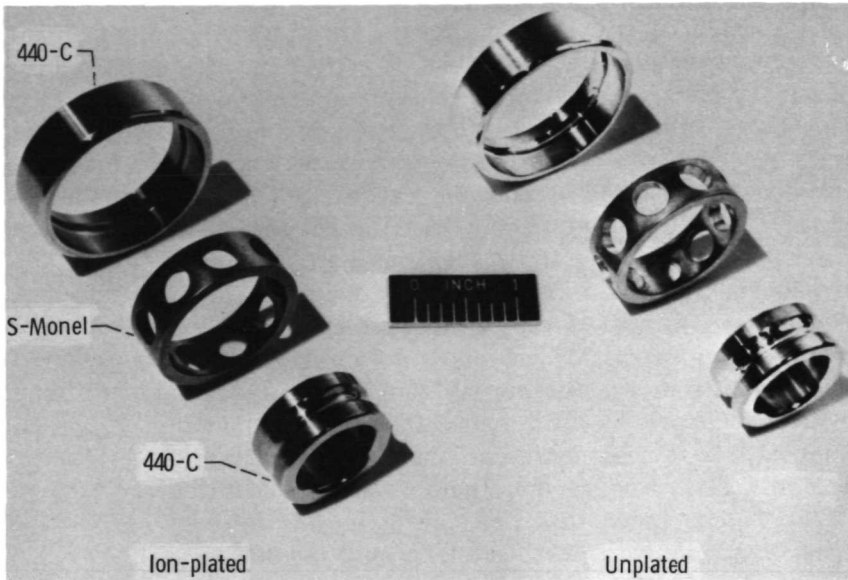


FIGURE 28.—Gold-ion-plated and unplated bearing assembly.

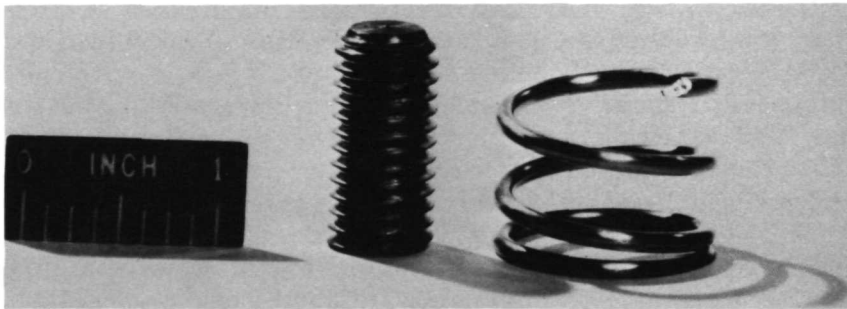


FIGURE 29.—Ion-plated complex surfaces of stainless steel.

sputtering is complicated and the necessary capital equipment is expensive. Furthermore, the processes are not readily adaptable to mass production. Nonetheless, the film properties attainable are unique, and the competitive advantages of the processes should not be overlooked.

Microelectronics

Sputtering has been used in the microelectronics industry for years. In fact, a continuous sputtering machine, as opposed to the batch-type bell-jar systems discussed so far, has been in operation at Western Electric's Allentown plant since 1964 (ref. 142).

Erpenbach of JPL used ion plating in an unconventional form to deposit crystalline carbon films on copper substrates to reduce secondary electron emission in electronic components (ref. 149). The copper substrate was made the cathode and an insulated base plate served as the anode. A dc voltage of 5 kV was impressed between the electrodes, and the cathode glow was adjusted to about 2 mA/cm² and evenly distributed across the substrate. After sputter-cleaning of the substrate with argon, either methane or propane gas was admitted to the apparatus; in three minutes, the copper was coated with a thin, adherent film of carbon. The nature of the deposition process is not entirely clear. An observed color change in the discharge from blue to bluish purple may indicate the presence of hydrogen, formed undoubtedly by decomposition of the hydrocarbons. Neither the carbon-bearing decomposition products nor their states of ionization are known. It can be concluded that ion plating in the presence of reactive gases may yield some rather unexpected results.

Sealing and Joining

There has been much interest recently in infrared detector windows for airborne and space applications. Typical window materials with suitable optical and structural properties are difficult to seal in place. John Tarpley of Goddard Space Flight Center has been exploring a sputtering process for metallization of Irtran-4 windows. By sputter-cleaning the window with Ar⁺ ions and then sputtering, the sequence, a thin flash of titanium and 2.5 to 3 μ of copper, Tarpley has deposited an adherent coating on Irtran-4 that enables the windows to be brazed or soldered in a conventional way. The intermediate titanium layer promotes adherence; copper does not adhere well when sputtered directly onto Irtran-4 surfaces.

Alloy Deposition

Ion plating, as generally practiced, is not suitable for the deposition of alloys. Very recently, however, Talivaldis Spalvins of LeRC dropped binary alloy powders onto anodic boats maintained so hot that both alloy components vaporized instantaneously into the glow discharge. Two Pb-Sn compositions and an 85 Cu-15 Au alloy have been ion-plated by this method. Alternatively, well controlled multiple-source anodes might result in deposits of alloy films.

Sputtering, in contrast, is one of the best methods available for

alloy plating, since the sputtered film will generally have exactly the same composition as the source (ref. 142). Even a variable alloy composition can be obtained by sputtering if an asymmetric cathode source is used. Christopher Gross of LaRC has synthesized W-Pd alloys, 5 to 12 μ thick, by co-sputtering from a 4 in. \times 4 in. palladium source with a 1 in. \times 4 in. tungsten mask deposited off center. Although the properties of the deposited alloys were similar to those of arc-melted materials, the co-sputtered deposits were single-phase throughout the alloy range, while the arc-melted material became two-phase on cooling. The sputtered film is quite stable, with no observed transformation to two phases at temperatures up to 1100° C. A special advantage of co-sputtering, in contrast to co-vacuum vapor deposition, is the very small dependence of the deposition rate on temperature. In addition to preparing W-Pd alloys, Gross has prepared alloys of Mo and Hf with many of the platinum-group metals. The materials have good potential for high-temperature strain gauge applications.

Plating on Plastics

Since the substrate need not be at anode potential in a sputtering process, plastics can be sputter-coated. The basic limitation stems from the high energy of the plating atoms, which degrades into heat when the atoms collide with the substrate. The resultant temperature rise can melt many plastics. Furthermore, some substrates, such as Formvar, are damaged by bombardment with high-energy particles.

In ion plating, as in conventional electroplating, the substrate serves as a cathode; hence, it would not appear possible to ion-plate insulating materials of any kind. Donald Buckley and his associates at LeRC, however, have very successfully ion-plated polyimides, PTFE, and alumina with platinum. They accomplished the seemingly impossible by enclosing the insulating substrates within a cathodic metal cage, and found that the plating ions did reach the workpieces inside. In ion plating, the particle energies are higher than in sputtering; as a result, the substrate surface temperatures rise to about 200° C during the process, which is a distinct limitation for plastics. Some control of the temperature is possible by external cooling and adjustment of the voltage.

Joseph Judd of LaRC is applying metallic coatings to transparent elastomers by a process that is neither sputtering nor ion plating but does employ electric fields. His apparatus is shown schematically in figure 30. The elastomer to be plated is held against the metallic electrodes, and the plating metal is vaporized

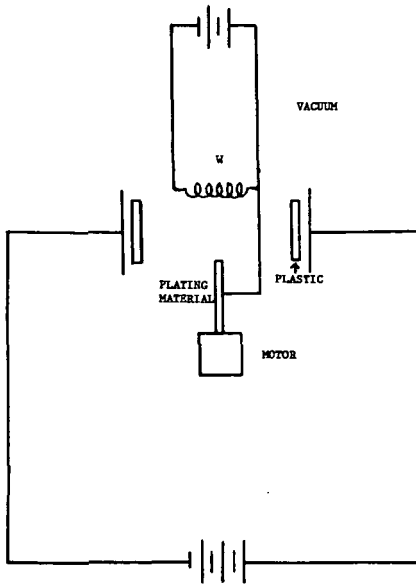


FIGURE 30.—Metal plating of elastomers.

by intermittent arcing to a heated-tungsten spiral. The plastic surfaces are cleaned by argon sputtering prior to plating.

Coatings of gold, silver, aluminum, indium, and copper less than 1000 Å thick have been applied successfully to silicone and urethane polymers. Some difficulty has been experienced in plating Fluorel polymers. In elongation tests on the plated systems, microfractures normal to the direction of pull are observed at about 7% to 8% elongation. Indium plates remain ductile over the largest degree of elongation. Electrical conductivity is maintained in the plated systems up to 50% elongation despite the microcracks, although the value of the conductivity, of course, changes. The primary application within the space program is to screen out direct sunlight in flexible windows.

Industrial Potential

The capital investment required for commercial sputtering or ion-plating equipment is variously estimated at \$180 000 for a typical production unit, and up to \$1 000 000 for a fully equipped production sputtering shop (ref. 150 and 151). Since fixturing of parts, pumpdown, and recycling to atmospheric pressure can be quite time-consuming, unit costs can be appreciably reduced if a large number of parts are coated in one pumping operation. Sputtering is used commercially in tantalum thin-film integrated-circuit technology (ref. 142), in the coating of razor blades (ref.

151), and in the production of decorative metallic coatings on metals, glasses, and ceramics (ref. 150).

Several companies do sputter-coating on a service basis; among them are Varian Vacuum Division, Palo Alto, California; Electrotec, Garland, Texas; and Hohman Plating and Manufacturing Co., Dayton, Ohio. Hohman provides ion-plating services as well, and the other companies probably would do such work if there were a demand. It is a simple matter to adapt sputtering equipment for ion plating.

Ion plating will almost certainly add a higher cost to the finished product than sputtering or conventional electroplating. On the other hand, no other method produces coatings with quite as good adherence (ref. 152). Thus, for coating high-precision parts, ion plating could be the most economic choice in the long run. For example, Fafnir Bearing Company (Bristol, Conn.) supplies rotating X-ray tubes lubricated with silver. The company's experience indicates that deposition of the silver by ion plating would greatly improve the quality of the final product, and initial experiments with ion-plated silver on tool-steel substrates support this contention. Fafnir does not now have ion-plating or sputtering equipment and experienced some difficulty in getting prototype parts plated commercially. Since ion plating is far from a routine process at the present time, quotations for doing the work were quite high. However, as experience is gained in both laboratory and industrial ion plating, development costs for novel applications should drop.

The Sandia Corporation has several industrial applications of ion plating under active investigation. The IMAC division of Varian (San Mateo, California) ion-plates mirrors for high-intensity arc lamps; the tight adhesion of the ion-plated coating to the substrate prevents blistering and coating-substrate separation from thermal shock. Western Electric (Allentown, Pa.) has found ion plating to be an excellent process for electroding of ferrites. Ion plating of beryllium with silver permits the use of brazing techniques which would otherwise be difficult with beryllium. McDonnell-Douglas (St. Louis) is ion-plating aluminum onto high-strength steels to prevent hydrogen embrittlement. Oak Ridge applies gold to tungsten by ion plating and then builds up the thickness by electroplating. Since gold is completely insoluble in tungsten, electroplating alone will not result in a desirable diffusion-type interface; ion plating drives the gold atoms into the tungsten substrate in spite of the lack of solid solubility, and therein is its advantage.

Anodized Films and Conversion Coatings

STATE OF THE ART

Anodized Films

Most of the discussion in preceding chapters has dealt with the electrodeposition of metallic films on cathodic workpieces. In this chapter, film formation on anodic workpieces will be considered. Active metals (such as Al, Ti, Ta, Be, and Mg) are always covered by a thin natural oxide skin. If an active-metal workpiece is made the anode of an aqueous electrolytic cell and the natural oxide is insoluble in the bath, oxide growth may occur because of the outward migration of metal ions or inward migration of oxygen ions under the influence of an applied current. In general, the anode attracts negative ions in solution and serves as a sink for electrons. Thus, typical anode reactions include the reduction of metal atoms to metal ions and the reduction of anions such as O^- , Cl^- , and F^- to neutral atoms or molecules. Anodic film growth involves the deposition of an adherent, insoluble product on the anode surface by reaction between species formed at or attracted to the anode.

The most significant type of anodization in practice is the deposition of anodic oxide films in aqueous solutions. Frequently, the term "anodization" in the trade literature refers solely to electrodeposition of oxide films on aluminum and aluminum alloys. Although aluminum anodization is certainly the most important commercial anodization process, applications requiring oxide-anodized beryllium, titanium, and tantalum are increasing. In the space program, anodic fluoride films on magnesium are found useful for providing a clean surface that will accept painting or protective resin sealing.

In general, anodic films are used for corrosion inhibition, electrical insulation, thermal control, sealing and joining, wear and abrasion resistance, and often for providing a beautiful surface finish. A number of notable innovations in anodic film deposition methods and some promising new applications have

grown out of the space program in recent years. Emphasis on quality control in aluminum anodization, the development of reliable techniques for beryllium anodization, and the introduction of sophisticated methods for repair of anodized films in situ, for example, may have broad implications for future commercial developments. The use of hard anodized aluminum as a printed-circuit-board material seems highly promising, particularly for high-power, low-frequency printed circuits. The finding that thick, porous anodic coatings are a good base for subsequent electroplating of active metals could extend the scope of applications for both aluminum and titanium alloys.

Conversion Coatings

Conversion coatings are generally films of oxide, phosphate, or chromate that are deposited by chemical reaction between a metal substrate and an aqueous electrolytic solution. Typical solutions contain an attacking agent, an inhibiting agent, and a film-forming agent. The proprietary Alodine or Iridite coatings, which are chromate conversion coatings, are used fairly commonly to protect aluminum and aluminum alloy surfaces. For some applications, conversion coatings are competitive with anodized films. Although the exact compositions of the chromate conversion coating baths have not been reported, they certainly contain hexavalent chromium compounds in an acid solution. The composition of the protective film formed on aluminum is also unknown, but insoluble compounds of chromium and aluminum are certainly deposited. The chromate films are quite soft when freshly deposited, but they develop high abrasion resistance within a day after rinsing and drying. While chromate films are not nearly as durable or wear resistant as anodized films, they are much less costly to apply. They adhere tightly to the substrate and will "self-heal" to some extent if damaged; this phenomenon has been ascribed to the transport of soluble chromates into damaged areas from the adjacent film.

The protective properties of Alodine or Iridite conversion coatings are seriously degraded at temperatures above 54° C. In spacecraft, this presents serious problems for welding and bakeout.

It has proved very difficult to obtain satisfactory conversion coatings on 2219 aluminum. Alcoa, under contract to Marshall Space Flight Center, investigated the problem in considerable detail. Close control of process parameters can greatly improve performance in a 168-hour salt spray test. Particular attention must be paid to mechanical finish. The standard Iridite 14-2 plat-

ing bath can be made more effective for 2219 alloys if lower than normal solution pH and higher than normal concentrations are employed (ref. 153).

A proprietary conversion coating known as Titanium Hard Coat has been developed for titanium alloys (ref. 25). The nature of the coating is unknown, but it has excellent wear and corrosion resistance.

TECHNIQUES OF ANODIZATION

Aluminum

Three basic types of anodizing processes have been used for aluminum in the space program. These are classified in Military Specification MIL-A-8625C as follows:

1. Type I—chromic acid anodizing
2. Type II—15% sulfuric acid anodizing
3. Type III—hard anodizing.

General operating procedures for all three types of anodizing are described in reference 2.

Type I Anodization

Type I films, which require no post-anodization sealing, can often be applied more economically than Type II films. The cost savings can be quite significant, particularly for large-scale operations. Type I coatings are also frequently preferred if there is a possibility of solution entrapment in joints, recesses, and weldments, because the chromic acid process leaves no corrosive residue. Type I anodizing has been reported unsuitable for aluminum alloys containing more than 5% copper (ref. 2), but Max Sharpe of Marshall Space Flight Center states that it forms good films on the higher copper alloys except under certain heat treatment conditions. Although the optimum chromic acid concentration for Type I anodization baths has been reported as 5 to 10% (ref. 2), Mr. Sharpe's group has obtained best results at higher concentrations.

Type II Anodization

The Type II process is the most common method for anodization. The porous nature of Type II anodized films prior to sealing is used to particular advantage in the production of colored surface finishes on aluminum and its alloys. The porous aluminum oxide absorbs dyes well, and subsequent sealing helps to prevent color loss in service. Anodized and colored aluminum is being used extensively in giftware, home appliances, and architectural ap-

plications. The final surface finish can be quite beautiful. In the space program, the use of anodized aluminum foil dyed in various colors can eliminate the need for painting. Although dyed anodized films are reasonably color-fast, they have a tendency to bleach under adverse environmental conditions, such as direct sunlight. The problem is particularly acute for spacecraft, but it is also significant for exterior architectural structures.

Dyeing of sulfuric-acid-anodized aluminum is basically simple. After anodization, the workpiece is immersed in a water solution of an appropriate dye at a temperature of 66° C for several minutes. The work is then sealed against further staining by immersion in water at 93° C, which converts the Al_2O_3 film formed in anodization to the hydrate, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. The resultant increase in volume closes the pores in the coating and hence improves corrosion resistance. Various procedures are used to prevent leaking of the dye before the pores are completely closed (ref. 2).

Normal Type II anodic coatings do not withstand the space environment particularly well, because of both outgassing, and the tendency of the dyes to fade. Scientists at MSFC found that these problems could be minimized by close control of the anodizing, dyeing, and sealing parameters. The addition of Unichrome-110 to the sealing bath eliminated the smutty deposit that often forms in this step.

Type III Anodization

In the Type III process, a sulfuric acid electrolyte is used, but the bath is maintained at -4° to 10° C rather than 16° to 26° C, the temperature used in Type II anodization. Because the rate of solution of the coating in the electrolyte is much slower at the lower temperature, the resulting film is hard and dense. To minimize processing time, current densities are typically higher for Type III than for Type II anodization. Voltages are also higher. The thickness of Type II coatings is in the range 0.1 to 1.0 mil for most applications, while Type III coatings are commonly in the 1 to 2-mil range. A sealing step is not necessary following hard anodization, since the oxide deposit is nonporous as formed. Lapping of a hard-anodized surface results in an exceedingly smooth, hard finish resembling polished stone.

The usefulness of hard-anodized coatings could be greatly extended, according to C. Jackson and M. Sharpe of MSFC, if the degree of crystallinity of the anodized deposit could be more closely controlled. Film crystallinity is increased at higher sulfuric acid concentration, lower bath temperature, and higher current

density; on the other hand, lower concentrations, higher temperatures, and lower current densities promote porous Type II coatings rather than the hard, dense, amorphous Type II coatings that are desired.

Beryllium

Beryllium, due to its high stiffness-to-weight ratio and low density, is an attractive material for aerospace and other structural applications where light weight is important. However, the toxicity of beryllium compounds, particularly in finely divided form, presents special handling problems. Flaky or powdery corrosion products formed on the metal are also potentially hazardous. One approach to improving the corrosion resistance of beryllium is to deposit adherent anodized oxide films.

Anodization methods applicable to beryllium are in a far more primitive state of development than those of aluminum. Solutions of 0.1N nitric or sulfuric acid do not provide a suitable anodization medium, possibly because of film dissolution. Crystalline anodic films have been applied in the laboratory from solutions of chromium oxide (CrO_3) in nitric acid (ref. 154). Amorphous films have been deposited from ammoniated ethylene glycol (ref. 155).

At Marshall Space Flight Center, a chromic acid anodizing procedure has been under development by the Materials Engineering Laboratory, which could form the basis for a practical production process. At present, however, considerable operator skill and experience in the anodization art is required to achieve the kind of coating uniformity and adherence that will impart corrosion protection. The NASA process produces an adherent, jet-black beryllium oxide film on polished and lapped surfaces, and a dull, dark film on rough machined surfaces. Process control is exceedingly critical.

Although details of the chromic acid anodizing process have not been firmly established, the current state of the art is of interest. Prior to anodization, beryllium parts must be carefully cleaned and deoxidized. The cleaning procedure involves: (1) ultrasonic cleaning in xylene for 30 min, (2) vapor degreasing in Freon #113 for 10 min, and (3) rinsing in Ridolene #53 at 65° C for 15 to 20 seconds. These steps are repeated until a water-break-free surface has been obtained. Parts are deoxidized immediately after cleaning in a solution of 20% chromic acid in de-ionized water. The final step involves rinsing in de-ionized water, first at room temperature and then at 66 to 93° C. Parts

are dried with filtered dry air; they must not be touched, and should be anodized within two hours.

Anodization is carried out in a solution of 10 wt % chromic oxide in de-ionized or distilled water. Temperature must be closely controlled at $18 \pm 1^\circ \text{C}$. Parts are anodized at a current density of 1 A/in.² for 30 to 40 minutes. (Longer times may be needed for some applications.) To achieve uniform current distribution, conforming cathodes, suitably shaped by trial and error, are often necessary, particularly for proper anodizing of blind holes, bores, and deep cavities. High current densities, high solution temperatures, or excessively long times will cause undesirable black surface powders. It is important that the beryllium substrate material be free from impurities; carbide inclusions, for example, are very detrimental to the corrosion resistance of the anodic film.

Titanium

Anodic films are formed quite readily on titanium in almost any electrolyte. A review of titanium anodization has been prepared by Battelle Memorial Institute under contract to MSFC (ref. 25). The dependence of the properties of anodic films on the deposition technique is not as sharply defined for titanium as for aluminum. Nevertheless, variations in anodic-deposition parameters can produce films of very different characteristics; some are hard, thin, and crystalline, while others are soft and thick. In the very early stages of anodization, highly colored films have been observed.

In commercial applications, titanium is anodized primarily to improve the corrosion resistance of the metal in acid media. As with aluminum, however, anodization can be used to vary surface emittance and to provide a degree of thermal control, particularly in spacecraft. In addition, anodic films can be decorative and protect against the staining and discoloration of titanium parts during handling. Anodic films formed in $\text{NaNH}_4\text{HPO}_4$ solutions have been used to protect titanium surfaces from hot-salt stress corrosion (ref. 25).

An analog of Type II anodization for aluminum has been reported for Ti-5Al-2.5Sn alloy (ref. 25). Samples were anodized in a 20 wt % solution of sulfuric acid at 20°C for 20 min with lead cathodes. Sodium hydroxide anodizing was performed in a 5 wt % solution at 95°C and 50 A/ft² for 20 min with mild steel cathodes. The thickness of the films varied with anodizing time. Because the deposits were porous, they were sealed in boiling water.

Highly colored films can be formed by brief anodizing in sulfuric acid. These films change from yellow to purple as anodization time is increased.

REMOVAL AND REPAIR OF ANODIZED FILMS

Simple Film Stripping

Once an anodized finish has been applied to a properly cleaned metallic substrate, the film tends to be very adherent, stable, and highly resistant to liquid penetration. Consequently, the film is quite difficult to remove except by sanding, which tends to damage the substrate. A convenient method for stripping an anodized finish from aluminum without damage to the underlying metal was developed by North American Rockwell Corporation in the course of a contract with the NASA Manned Spacecraft Center (ref. 156). A felt template, cut to size, is placed over the part to be stripped. The felt is slowly saturated by applying a solution of nitric acid (10 to 12 wt %), chromic acid (1 to 2 wt %), and hydrofluoric acid (0.4 to 0.6 wt %) through a plastic squeeze bottle to prevent dripping. The saturated cloth is allowed to remain in contact with the surface until the anodic oxide appears to have been completely removed (about 3½ min). The stripped part is then promptly rinsed with water to remove all of the acid solution. This simple technique can be used to remove the oxide from a fairly well defined area.

Rapid Brush Anodizing

Most oxides are brittle at ordinary temperatures, and anodic oxide films, particularly when thick, can be gouged easily. Convenient techniques for *in-situ* repair of anodized structures after assembly can effect large cost savings. The repair technique most commonly used in industry is brush anodizing. The damaged part is connected to the positive pole of a zero to 50-volt dc power supply. Usually, a carbon cathode, wrapped with an absorbent material and saturated with a suitable electrolyte, is moved across the damaged area at a selected voltage until the anodic coating is repaired.

North American Rockwell Corp. found that repair time could be reduced to 2 to 3 min, instead of the more usual 20 to 30 min, by using specially designed V-shaped cathode applicators. The cathodes are made of stainless steel, faced with 10 mils of platinum, in contact with acid-saturated polyurethane. While the

polyurethane resists wetting at first, it saturates very nicely if the electrolytic solution is pushed through the pores and wet with the fingers. The method was found particularly convenient for repairing aluminum-tube ends in spacecraft.

Electrolyte Concentration in Brush Anodizing

Grumman Aircraft was faced with repairing anodic coatings on aluminum to restore its original thermal control properties, particularly its emittance (ref. 157). For repair of Type I coatings, chromic acid electrolytes were tried in concentrations of 8, 10, and 20%, but the coating was too thin. Additions of 4 to 8% sulfuric acid to a 10% chromic acid solution provided both thicker coatings and higher emittance values. A Selectron, Ltd., proprietary electrolyte also proved suitable. The Grumman findings reveal that repair is a different problem from depositing the original film. Type I anodic coatings are applied in 5 to 10% chromic acid baths, and sulfuric acid additions are below 0.1% (ref. 2).

Satisfactory repair of Type II coatings on aluminum required sulfuric acid concentrations greater than 50% in the Grumman work, in contrast to concentrations of about 15% needed to deposit the original oxide (ref. 158).

Brush Anodizing of Large Parts

A very sophisticated portable brush or spray anodizing machine was developed and built by Reynolds Metals Company under contract to Marshall Space Flight Center. The instrument can be operated on vertical, horizontal, or overhead surfaces and has proved particularly useful for *in-situ* Type II anodizing of seams and welded joints (ref. 158). The sulfuric acid electrolyte (26 to 30 wt % concentration) is pumped continuously from a storage reservoir through hoses to a moving anodizing head and back to the reservoir. The head is held against the aluminum to be anodized and is designed to flush the acid across the surface at about 300 ft/min. Typical current densities are close to 100 A/ft². Half-mil anodic coatings are formed at a rate of about 15 in./min.

Unfortunately, a repaired anodized area cannot readily be sealed by normal immersion or steam techniques. Treatment of the anodic films with Alodine, however, gives chemical-conversion-type sealing (see below), which provides adequate protection to parts in a standard 240-hour ASTM salt-spray test. In the present context, Alodine is used for sealing Type II anodic coat-

ings; an Alodine chromate conversion coating alone will withstand the salt-spray test, as discussed in the next section.

APPLICATIONS

Anodized films and conversion coatings are generally used in industry for corrosion resistance or decorative finishes. Experience gained in the space program has provided new insights into the potential of these traditional applications and has identified a number of novel uses as well.

Corrosion Protection

Galvanic Corrosion

When two dissimilar metals are used in contact, problems can arise from galvanic corrosion. To prevent this, the use of corrosion-resistant stainless steel (CRES) or titanium fasteners for aluminum housings is common. If the aluminum is protected by a dense, tightly adherent coating that electrically insulates it from the fastener, galvanic corrosion is prevented; but if anodized or Alodized coatings break down for any reason, metal-to-metal contact may be established with very deleterious results.

North American Rockwell Corp., under contract with MSFC, investigated the corrosion behavior of 347CRES and 6Al-4V-90Ti alloys in intimate contact with Alodized and Types I and II anodized aluminum-alloy panels (ref. 159). The alloy couples were subjected to the standard ASTM salt-spray test for the specified 240 hours in the case of anodized aluminum, and 168 hours in the case of Alodized aluminum, or until failure, if that occurred sooner. Type II anodized coatings unquestionably provided the best corrosion protection. The anodic oxide film is an electrical insulator and quite impervious to the salt spray. The thicker Type II coatings offered somewhat better resistance to salt spray than the thinner Type I coatings. Alodized chromate conversion films provide good corrosion protection but are also relatively good conductors of electricity; hence, with the Alodized film acting as an electrolyte, galvanic corrosion can occur. If either anodized or Alodized films break down, the extent of galvanic corrosion varies with the electrochemical potential of aluminum relative to the dissimilar alloy.

North American Rockwell also found that chromate conversion coatings will not withstand a 168-hour salt spray test. However, the company worked with suppliers of coatings (two Iridite and one Alodine), and found that coating performance could be

greatly improved by meticulous process control. The most important factor seems to be deoxidation of the surface prior to coating.

Restoration of Corrosion Resistance after Welding

Chromate conversion coatings of the Iridite and Alodine types are applied to the Saturn V tank-skin sections after fabrication to protect the 2219-T87 aluminum alloy against atmospheric corrosion during subsequent processing. In joining operations, the conversion coatings are seriously damaged by heat up to six inches from the weld area. Corrosion resistance, which is then lost, can be restored only by mechanically removing the damaged coating and manually applying a conversion-coating solution that is two to three times more concentrated than the normal bath. A spray touch-up treatment with a conventional solution helps to improve the protection of aged or abraded coatings (ref. 160).

Corrosion Protection of Magnesium Alloys

Magnesium alloys, because of their low density and high stiffness-to-weight ratio, are quite attractive for many airborne structures. Unfortunately, magnesium alloys are also highly sensitive to corrosion and must be kept absolutely free of moisture. The trapping of moisture beneath paint films is particularly insidious. The key to providing an adequate protective finish on a magnesium alloy is scrupulous surface cleaning.

Conventional cleaning procedures are entirely inadequate for magnesium parts. The major problem is that cathodic surface impurities cannot be completely removed in normal cleaning baths. The IBM Space Guidance Center, in the development of a protective finish for the Saturn V guidance system, found that fluoride anodizing could provide a surface with the proper degree of cleanliness (ref. 161).

After ordinary cleaning, conventional wrought magnesium alloys are anodized in 40% ammonium bifluoride solution at voltages increasing up to 120 volts. Cathodic impurities are dissolved in the early stages of anodization, and the current drops as an insoluble magnesium fluoride film forms on the alloy surface. The cleaning procedure can be considered complete when the current density falls below 5 A/ft². Magnesium alloy La141A, which contains 14% lithium, must be handled somewhat differently; after standard degreasing, this alloy is heat-treated for one hour at 220 to 225° C to cause lithium to migrate to the

surface, rinsed in cold water to remove lithium nitrides and oxides, caustic-cleaned, and then fluoride-anodized for 45 to 60 min after the current density has dropped below 5 A/ft².

Fluoride anodizing causes the formation of a MgF₂ surface film, which is abrasion-resistant and offers some degree of corrosion protection in itself. However, for the wrought alloys, the film is only a few microns thick, and it is better to use the anodizing solely for cleaning. The fluoride film is then stripped by immersion in a 50% chromic acid bath at 88° C or above for 3 or 4 min. A chromate conversion coating, which is self-healing, is then applied prior to further processing. The magnesium fluoride film on La141A builds up to a thickness of 0.2 to 1.0 mil and is used for protection as well as for cleaning. During anodizing the lithium content of LA141A causes the formation of soluble lithium fluoride as well as magnesium fluoride. Leaching of the lithium fluoride makes the coating somewhat porous; consequently, it is an excellent base for paint or surface-sealing resins.

Final finishing of the chromate- or fluoride-coated parts involves the application of an organic surface-sealing resin and sometimes an overcoat of paint.

Thermal Control

In spacecraft, anodic oxide coatings on aluminum serve not only to impart corrosion resistance but also to provide some degree of thermal control. A fairly versatile method for preparing opaque anodic oxide films with high reflectance and high infrared emittance on aluminum was developed by Lockheed Missiles and Space Company under contract to MSFC (ref. 162). In this process, stable inorganic dispersants are stirred into the anodizing bath and become incorporated into the anodic deposit. The color, opacity, reflectivity, and emittance characteristics of anodic films can be varied by the use of different dispersants.

The anodizing bath used in the Lockheed process is an aqueous solution of sodium aluminate (2.5 g/100 ml) rather than a conventional sulfuric or chromic acid bath. A finely divided dispersant is added at a rate of about 5 g/100 ml. Anodization is done at 25° C in a well-stirred bath with an initial current density of 40 mA/cm². As the voltage increases, current density must be reduced. Anodization times are of the order of 5 to 10 min. In the absence of a dispersant, the reflectivity of the anodic oxide film is 65%; occlusion of ZnO into the film raises the reflectance to about 79%, and occlusion of particulate TiO₂ further increases

it to about 93%. The use of colored pigments may provide interesting decorative finishes. The anodized film need not be sealed or otherwise treated after deposition.

Anodized aluminum was used very effectively for thermal control in the Laser Ranging Retroreflector (LRRR) package, which Armstrong and Aldrin left on the Moon as part of the Apollo 12 mission. The LRRR package (fig. 31) contains an array of 100 retroreflectors and is used in conjunction with an Earth-based laser telescope to measure Earth-to-Moon distances with an accuracy of 6 in. For good optical performance, the retroreflectors had to be mounted so that they would be almost isothermal. The retroreflector prisms were held in cylindrical cavities machined into an aluminum panel. The prisms were held in place by retainer rings. An analysis of the thermal-control requirements indicated that the cavity walls should have low emittance and that the retainer rings should have high emittance. Ordinary machined 6061 aluminum surfaces have measured emittances of 0.021 to 0.024, which proved quite satisfactory for the application. The retainer rings were fabricated from 1100-series aluminum and sulfuric acid-anodized to a thickness of about 0.3 mil. The total hemispherical emittance of the unsealed anodized surfaces was found to be 0.75 and was stable to uv radiation and proton bombardment. For space applications, sealing must be avoided, since the hydrated surface film degrades upon exposure to high-energy radiation.

The Jet Propulsion Laboratory specifications for coating aluminum alloys to produce surfaces of high thermal emittance and low solar reflectance call for black-dyed, sealed Type II anodization. It was found that Ciba's Oxanol fast black GL-2 dye is particularly stable and resistant to outgassing. The dyed films are sealed first in nickel acetate, and finally in boiling water (ref. 163).

Fabrication of Printed Circuit Boards

The Boeing Company, under contract to Marshall Space Flight Center, investigated the use of hard-anodized aluminum (Type III) as a printed circuit board material (ref. 164). This is a completely unconventional application having considerable commercial potential in the growing electronics industry. The hard anodized film provides excellent dielectric insulation, while the aluminum substrate permits rapid heat dissipation. In high-power, low-frequency printed circuits, the heat generated can

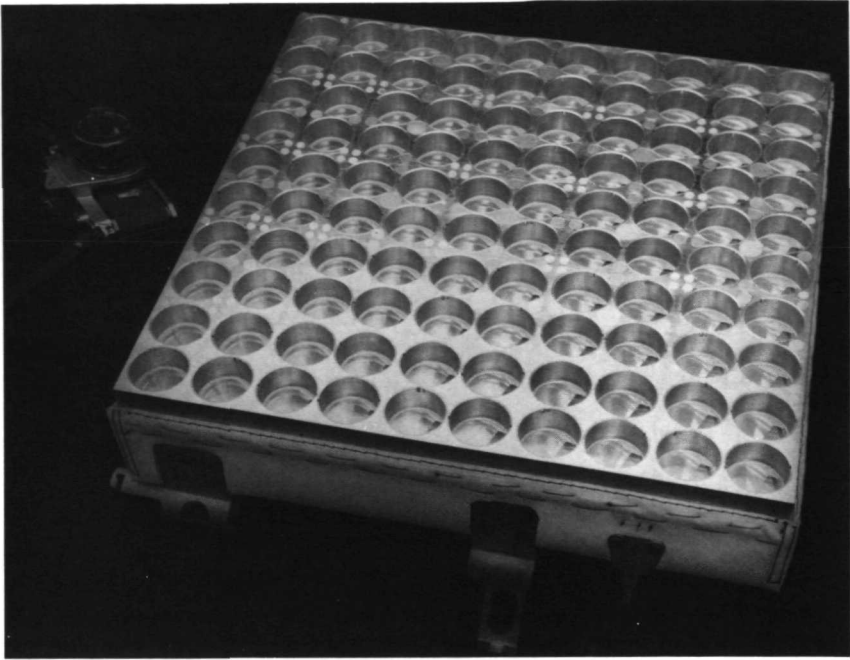


FIGURE 31.—Laser-ranging retroreflector holder.

be as high as 100 W/in^3 . Common organic circuit board materials have poor thermal conductivity and cannot dissipate heat fast enough to maintain satisfactory operating conditions for the mounted components.

Boeing hard-anodized 50-mil plates of several aluminum alloys for 45 min at -4°C in a bath containing 15% sulfuric acid, 3% oxalic acid, and 3% ammonium tartrate, by weight. Carbon dioxide gas was bubbled through the bath to provide both cooling and vigorous stirring. Copper foil was bonded to the hard-coated plates with a commercial adhesive, and printed circuit boards were prepared in the usual way. Although there would be some technical problems in developing the laboratory process for commercial use, the feasibility of producing hard-coated aluminum-core printed-circuit boards has certainly been demonstrated.

Laps

Lapping is used to produce smooth, accurate surfaces. Lapping plates are commonly made from fairly soft, porous materials that are charged or rolled with appropriate abrasives. Such laps are generally short-lived, because loss of precise contours occurs. Furthermore, the articles being lapped often become galled or

scratched during the smoothing operation. Bonding of the abrasive to the lapping plate, to hold the abrasive grits in place, gives improved performance, but the durability of commonly used bonding agents is quite poor. William Abernathy of Marshall Space Flight Center found that a hard anodic coating can function as an excellent bonding agent for abrasive grit. Thus, fine laps can be made from aluminum that is charged with such abrasives as diamond and then hard-anodized (refs. 165 and 166). The combination of a hard surface and a firmly held abrasive allows greater pressures, higher cutting speeds, and cooler operation, and essentially eliminates galling and scoring problems. The lightweight aluminum substrate is also more convenient to handle than more conventional materials such as cast iron.

Pretreatment of Active Metals for Electroplating

The thin, tightly adherent oxide films that form naturally in air on aluminum, beryllium, and titanium alloys prevent proper adhesion of electroplated coatings. Thick, porous anodic coatings, however, provide a very suitable base for subsequent electroplating.

Southwest Research Institute (ref. 167), under a NASA contract, showed that phosphoric acid-anodized aluminum could be readily copper-plated and subsequently soldered. After the aluminum alloy surfaces were cleaned in 5% hydrofluoric acid for 3 to 5 min, samples were anodized in 30 volume % phosphoric acid at 72 to 76° F with stainless steel cathodes. Current densities were of the order of 10 A/ft² at voltages of 60 to 90 volts, and optimum anodizing times were of the order of 6 min. After anodizing, thorough (but not prolonged) rinsing is essential. The oxide film must not be allowed to dry and hence lose all electrical conductivity prior to plating. The anodized panels, with the current at a density of 50 A/ft², were immersed in a copper sulfate-sulfuric acid bath for plating. The high current density was maintained for 2 min to promote rapid coverage of the otherwise soluble anodic oxide with copper. A current density of 10 A/ft² was then used for the remaining 3 min of the plating cycle. The plated alloys were readily solderable, withstood a 30-min baking cycle at 177° C without flaking, and were as ductile in bend as the uncoated materials. Semibright nickel was similarly deposited over the anodic films, also with excellent results. One great advantage of the anodizing-pretreatment over the more usual zincate immersion treatment (see Chapter 1) is that the final copper plate can be heated without peeling or blistering.

The NASA-developed Ti-6Al-4V alloy has aroused considerable commercial interest. In the space program, it was necessary to protect the alloy from attack by liquid oxygen. Marshall Space Flight Center found that adherent, protective electroplates of copper and nickel could be deposited over an intermediate anodic oxide formed in hydrofluoric and acetic acids (ref. 168). A solution of glacial acetic acid and hydrofluoric acid at 49° C was used for anodizing. Voltage was applied to parts prior to immersion in the bath. An anodizing voltage of 10V was applied for 20 to 40 min with a current density of 20 A/ft². The anodized samples had to be transferred to a rinse tank within 30 sec and kept moist to assure subsequent satisfactory plating. An adherent copper plate was deposited from a fluoborate solution. Nickel plating was preceded by a strike in a Wood's bath or all-chloride bath. The final nickel coating was applied from a nickel sulfamate solution. Coating adhesion was excellent.

Bonding

The process known as "anodic bonding" is beginning to attract a fair amount of attention, particularly for glass-to-metal and glass-to-semiconductor seals. In spite of the name, the electrochemistry of the process is not entirely clear; anodization may

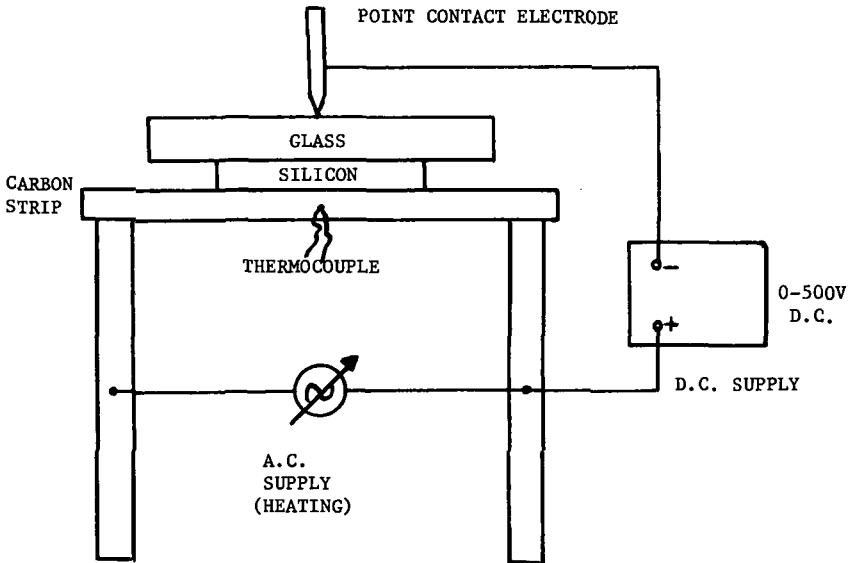


FIGURE 32.—Apparatus for anodic bonding.

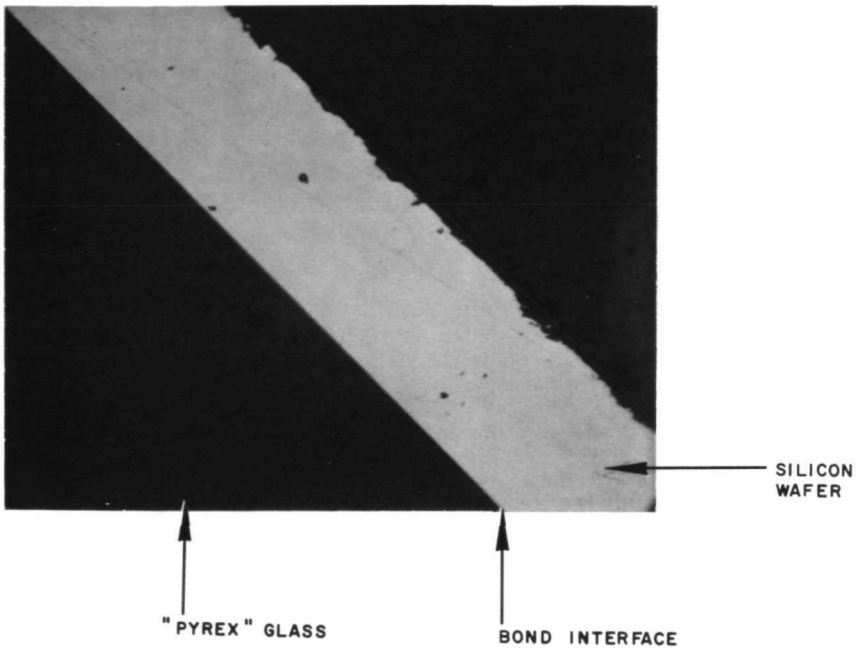


FIGURE 33.—Anodic bond of silicon to glass (500° C, 400 V dc).

not be involved. The bond is made by applying a dc voltage between the glass and metal (or semiconductor) at moderately elevated temperature, with the metal (or semiconductor) anodic and the glass cathodic. A simple apparatus used by Motorola, under contract to Jet Propulsion Laboratory, for bonding glass to silicon is shown in figure 32 (ref. 169). The parts to be bonded are heated to within 200 to 300° C below the softening point of the glass by means of a carbon strip ac resistive heater. A dc voltage of 400 to 500 V is applied between the carbon anode in contact with the silicon and a point-contact cathode in contact with the glass. Current flow is of the order of 1 to 4 mA. As the bond forms, white-light interference fringes are observed, which disappear when intimate contact is made. A photomicrograph of a silicon-to-Pyrex bond is shown in figure 33. The bond is strong, uniform, and void-free. The basic patent (U.S. Patent 3,397,278) on the process is held by Mallory Corporation.

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