

INCO

NICKEL ELECTROFORMING

PROCESSES AND APPLICATIONS

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Origins and Progress

The specialized use of the nickel plating process for electroforming results in the manufacture of tools and products that are unique and often impossible to make economically by traditional methods of fabrication. These tools are indispensable for operations in the textile, communication, aerospace, building products, electronics, automotive, photo-copying and other industries.

Its origins are well-documented. Professor B.S. Jacobi of the Academy of Sciences, St. Petersburg, Russia, discovered electroforming during his investigations on galvanic cells. Jacobi used an engraved copper printing plate as the cathode in a copper sulfate solution and electrodeposited copper upon it. Although he had difficulty separating the electrodeposit from the engraved printing plate, where it could be separated, the deposit had accurately reproduced the details engraved on the original plate. Jacobi continued his work and officially described his results to the Academy of Sciences, October 4, 1838, in the following way: "In the experiment with an engraved plate covered by a very thin layer of vegetable oil, it was possible to produce another copper plate on which even the slightest imprints on the original plate were reproduced with the highest accuracy."

In 1842, Professor R. Boettger of Germany successfully electroformed articles of nickel using nickel ammonium sulfate solutions. During the latter half of the 19th century electroforming with iron was, also, investigated. The three metals - copper, nickel and iron - were, thus, electrodeposited and applied to the production of electroformed articles before 1870.

Following its discovery, electroforming was immediately applied to the reproduction of art objects, such as, bas-reliefs, sculptures and statues, and to the duplication of engraved plates for the printing of money because of its capability to reproduce minute surface detail with great fidelity.

Modern applications of electroforming are diverse and today nickel is used in a great variety of different electroforming applications. The reasons for its popularity include the fact that electrodeposited nickel can be strong, tough and resistant to corrosion, erosion and wear. Its mechanical properties can be varied at will between wide limits by changing plating conditions, by alloying with other elements, and by incorporating particles and fibers within the electrodeposited nickel matrix.

The technology of electroforming has steadily grown in importance and sophistication as indicated by current applications, which include:

?? textile printing screens;
?? components of rocket thrust chambers, nozzles and motor cases;
?? molds and dies for making automotive arm-rests and instrument panels;
?? stampers for making phonograph records,
?? video-discs and digital and audio compact discs;
?? mesh products for making porous battery electrodes,
?? filters and razor screens;
?? optical parts,
?? bellows, and
?? radar wave guides.

Nickel electroforming is truly a remarkable technology and its versatility ensures continued progress in the future.

This publication reviews the technology of nickel electroforming and provides basic process information as well as a summary of current applications. A bibliography is provided for readers who wish to pursue the subject in greater detail.

1. WHAT IS ELECTROFORMING?

Electroforming is the fabrication of simple and complicated components by means of electroplating. The basic fabrication steps are as follows:

- ?? a suitable mandrel is fabricated and prepared for electroplating;
- ?? the mandrel is placed in the appropriate electroplating solution and metal is deposited upon the mandrel by electrolysis;
- ?? when the required thickness of metal has been applied, the metal-covered mandrel is removed from the solution;
- ?? the mandrel is separated from the electrodeposited metal.

The electroform is a separate, free-standing entity composed entirely of electrodeposited metal. The standard definition adopted by ASTM Committee B8 is that "electroforming is the production or reproduction of articles by electrodeposition upon a mandrel or mold that is subsequently separated from the deposit". Electroforming is, thus, a metal fabrication process concerned with the production of articles, tools and components.

2. WHEN TO SPECIFY ELECTROFORMING

The question of when to specify electroforming as the method for producing a part is important. The answer will depend on the extent to which the designer or engineer can take advantage of the capabilities of the process. Consider the following capabilities:

- ?? The process can reproduce fine surface detail with great accuracy. An excellent example of this is in the production of electroformed nickel stampers (molds) for pressing compact audio and video discs. The accuracy of reproduction is within a fraction of a micrometer and this degree of accuracy makes possible the high quality stereophonic recordings available today.
- ?? An extension of this capability is in the duplication of complex surface finishes. Bright, semi-bright, matte, smooth, brushed, roughened surfaces and combinations of these can be reproduced without the need for machining or polishing individual components after fabrication. Wood-grains, leather patterns and other textures can be incorporated into molds and dies for plastics, zinc, and other materials - natural textures impossible to duplicate as faithfully as by electroforming.
- ?? The combination of modern photolithographic methods of generating patterns with the electroforming process makes it possible to reproduce flat parts with extreme precision and fineness of detail, including giving edges and walls of holes predetermined angles,

and is being extended to the forming of movable microdevices for medical, optical and mechanical applications.

- ?? Parts can be reproduced in quantity with a very high order of dimensional accuracy. The accuracy attainable will depend on the nature of the mandrel material and the accuracy with which it can be machined - usually within about 0.004 micrometers. Once the mandrel is prepared, all parts produced from it will be dimensionally accurate.
- ?? The mechanical and physical properties of the electroform can be closely controlled by selecting the composition of the electroplating solution and the conditions of deposition. Composites of various metals can be created; for example, radar wave guides of copper and nickel with inner linings of silver or gold have been fabricated by electroforming.
- ?? There is virtually no limit to the size of the object that can be electroformed. Nickel foil 4 micrometers thick is produced on a continuous basis, as well as textile printing screens up to 6 meters long.
- ?? Shapes can be made and reproduced that are not possible by any other method of fabrication; for example, seamless radar wave guides with two right-angle bends and with the interior made to close dimensional tolerances and with high surface finish. Seamless cylindrical belts, also, fall into this category.
- ?? Electroforming is applicable to the making of single pieces or large production runs. In the latter case, it is possible to start with one master and build up in several generations a number of successively negative and positive electroforms. As the number of positives produced increases, these are used to make more negatives, thus increasing the production rate until the desired capacity is reached, after which nothing but negatives are produced.
- ?? In the specific case of molds and dies for making plastics, zinc, and glass parts, electroforming can provide tooling with resistance to corrosion, erosion, and abrasion; with good heat conductivity and precise parting lines to minimize and eliminate flashing; and with high wear-resistance over long production runs.

The engineer should, also, be familiar with the limitations of the electroforming process. The cost of an electroformed article may be relatively high if the same article can be mass-produced by a completely automated process. In the case of shapes, surface finishes, and fineness of detail that cannot be reproduced by any other means, cost becomes a secondary consideration. In the case of tooling, electroforming can be more versatile than and cost-competitive with pantographic machining, hobbing, chemical and electrochemical

machining, and other die-making techniques. The time to produce an individual piece by electroforming may be relatively long if wall thickness is great, but high-speed plating processes and the use of backing materials may overcome this. There are limitations in design; for example, sharp angles, corners, and very deep, narrow recesses may cause problems. It is difficult to achieve great or sudden changes in wall thickness by electroforming. Mandrels must be handled with care since defects caused by accidental damage will be reproduced in the electroform.

The engineer should, therefore, specify electroforming whenever:

- ?? The difficulty and hence, the cost of producing the object by mechanical means is unusually high;
- ?? Unusual mechanical and physical properties are required in the finished piece;
- ?? Extremely close dimensional tolerances must be held on internal dimensions and on surfaces of irregular contour;
- ?? Very fine reproduction of detail and complex combinations of surface finish are required; and
- ?? The part cannot be made by other available methods.

3. MANDREL TYPES AND MATERIALS

Mandrels may be classified as conductors or nonconductors of electricity, and each of these may be permanent, semi-permanent, or expendable (Table I). Whether or not a mandrel is a conductor will determine the procedures required to prepare it for electroforming.

Conductive mandrels are usually pure metals or alloys of metals and are prepared by the usual procedures, but may require application of a thin parting film to facilitate separation of the electroform from the mandrel (unless the mandrel is removed by melting or chemical dissolution).

Nonconductors must be made conductive by spraying the surface with a thin metallic film, usually silver. The thin film of silver, also, serves to facilitate separation of the electroform from the mandrel.

Whether or not a permanent or expendable mandrel should be used is largely dependent on the particular article that is to be electroformed. If no re-entrant shapes or angles are involved, it is possible to use permanent, rigid mandrels that can be separated from the finished electroform mechanically and re-used. If re-entrant angles and shapes are involved, it is necessary to use mandrel materials that can be removed by melting or by

chemical dissolution, or materials that are collapsible, such as polyvinyl chloride and other plastics.

The various types of mandrel materials each have their own advantages and disadvantages.

3.1 Permanent Conductive Mandrels

Austenitic stainless steel is an excellent material to use as a permanent, conductive mandrel. Although machining may be relatively difficult, it can be machined to close tolerance and given a high finish. Resistance to damage in use is good and being conductive, there is no need to metallize the surface before beginning the electroforming process. Austenitic grades of stainless steel readily form stable, passive films that prevent adhesion between electroform and mandrel.

Copper and brass are, also, used as permanent, conductive mandrels and are less costly than stainless steel. They are relatively easy to machine and are ideal when intricately engraved or textured surfaces are required. Separating the electroform from a copper or brass mandrel is easy provided the proper parting film is used (see below). Alternatively, copper and brass mandrels can be electroplated with thin deposits of nickel and/or chromium to facilitate parting and to prevent attack of the mandrel by the processing solutions.

Conventional steel can be used as a mandrel material; it is inexpensive and easily machined. It is usually necessary to nickel plate the entire mandrel and use a simple chemical treatment to ensure release from the mandrel (See Section 5).

Invar or Kovar are alloys that have low coefficients of thermal expansion and are relatively expensive. They are used in critical cases where dimensional accuracy is the chief concern. The electroform and mandrel are heated, and the greater thermal expansion of the electroform permits separation of the mandrel. They are resistant to damage in handling.

Pure nickel, although difficult to machine, may be used as a permanent mandrel. It requires simple treatment to ensure release from the mandrel.

3.2 Expendable Conductive Mandrels

Aluminum and its alloys may be used as expendable mandrel materials. They are easy to machine and can be given a high surface finish. They are relatively expensive, easily damaged and may not require metallization prior to electroforming. When used as

an expendable mandrel, aluminum and its alloys can be dissolved away from a nickel electroform in a 10 per cent solution of sodium or potassium hydroxide solution at room temperature.

Zinc-based alloys have similar characteristics and are used as expendable mandrels. The mandrel can be dissolved in a cold 10 per cent hydrochloric acid solution. Superplastic zinc alloys (zinc-aluminum-magnesium alloys) can be blow-molded into complex shapes at relatively low temperatures, 250°C. Bismuth can embrittle copper and nickel electroforms if it is not completely removed from the inside of the electroform, in which case the use of bismuth-free tin-zinc alloys are required.

3.3 Nonconductive Mandrel Materials

Waxes are useful because some can be readily cast and easily melted out of the finished electroform, but they have many disadvantages. They may be brittle, may have a poor surface finish, and are easily damaged. They are inexpensive, require metallization, and cannot be used to maintain high tolerances. Cheap grades of wax melt or soften when exposed to electroplating solutions operated at normal temperatures. There are only a few grades of wax, such as beeswax, that can be successfully silver-sprayed. Graphite-loaded wax which is conductive has been used successfully as an expendable mandrel.

Plastics materials can be used to fabricate permanent or semi-permanent mandrels, but being nonconductive, require the use of silver-spraying or other metallization techniques. In general, plastics are relatively cheaper and have inferior mechanical properties than metal mandrels, and cannot be made to close dimensional tolerances and with very high surface finish. Rigid plastic mandrels are often made from epoxy resins in the case of electroforms without re-entrant angles. For electroforms with re-entrant angles or shapes, collapsible plastics materials, such as polyvinyl chloride (PVC), are used. Special care is required in using these materials if an acceptable mandrel is to result.

Glass is very difficult to machine, is easily damaged, is relatively expensive, and requires metallization, but surface finish can be excellent and close tolerances can be maintained. It is, therefore, sometimes used as a mandrel material.

Wood, leather and fabrics can be used as mandrel materials when it is desired to reproduce their surface textures and patterns. These materials are porous, must be sealed, and then made conductive. It is often easier to duplicate the desired surface finish by casting with polyvinyl chloride and then electroforming onto the plastic replica of the surface.

Many solid materials can be used to fabricate mandrels for electroforming, but the following generalizations may help in selecting a suitable material:

- ?? Permanent mandrels are preferred for accuracy and for large production runs;
- ?? Expendable mandrels must be used whenever the part is so designed that a permanent mandrel cannot be withdrawn. Expendable mandrels of low-melting point alloys may be used for low-cost items not requiring close tolerances. Collapsible plastic mandrels have been used to fabricate parts with re-entrant shapes or angles.
- ?? It is important that the mandrel retain its dimensional stability in warm plating baths. Wax and most plastics expand when exposed to electroplating solutions operated at elevated temperatures. In such cases, it may be necessary to use acid copper, nickel sulfamate and other electroplating solutions that function at room temperature.

4. MANDREL DESIGN AND FABRICATION

The ability to produce an electroform will, also, depend on the design of the mandrel. The electroforming operation can often be simplified by a few design changes, which do not impair the functioning of the piece. ASTM Standard B450, "Engineering Design of Electroformed Articles," contains useful information on this subject. Some of the design considerations include the following:

- ?? Exterior angles should be provided with as generous a radius as possible to avoid excessive buildup and treeing of the deposit during electroforming. Interior angles on the mandrel should be provided with a fillet radius of at least 0.05 cm per 5 cm (0.02 in per 2 in) of length of a side of the angle.
- ?? Wherever possible, permanent mandrels should be tapered at least 0.08 mm per meter (0.001 inch per foot) to facilitate removal from the mandrel. (Where this is not permissible, the mandrel may be made of a material with a high or low coefficient of thermal expansion so that separation can be effected by heating or cooling).
- ?? A fine surface finish on the mandrel, achieved by lapping or by electropolishing, will generally facilitate separation of mandrel and electroform. A finish of 0.05 micron (2 microinch) rms is frequently specified.
- ?? Flat bottom grooves, sharp angle indentations, blind holes, fins, v-shaped projections, v-bottom grooves, deep scoops, slots, concave recesses, rings and ribs can cause problems with metal distribution during electroforming, unless inside and outside angles and corners are rounded.

The method of fabrication of the mandrel will depend on the type selected, the material chosen and the object to be electroformed. Mandrels may be manufactured by casting,

machining, electroforming and other techniques. Permanent mandrels can be made by any of the conventional pattern-making processes.

5. PREPARATION OF MANDREL SURFACES

Non-conducting mandrels must be made impervious to water and other processing solutions, and, then, rendered conductive. Porous materials, for example, leather and plastic, may be impregnated with wax, shellac, lacquer or a synthetic resin formulation to make them impervious to water. A molten mixture containing 4 parts beeswax, 12 parts paraffin and 2 parts resin can be used for this purpose. The non-conducting mandrel is immersed in the wax mixture for at least 30 minutes until bubbling ceases, when it is removed and cooled. This will result in a considerable loss of detail and it may be preferable to use thin films of lacquer to seal porous, non-metallic mandrels.

Non-conducting materials may be rendered conductive in a number of ways. One common way is to apply a chemically reduced film of silver to the surface. Similar reduction processes are available which deposit nickel or copper. In general, these processes are carried out by spraying the reagent containing the metal of choice simultaneously with a specific reducing agent onto the surface of the mandrel using a double-nozzle spray gun. The chemicals react at the surface; the metal is reduced and is deposited on the mandrel surface. Chemical reduction processes are preferred because dimensional accuracy is not affected, the film has little adhesion, and parting is not difficult. If necessary, a silver film can be stripped from the nickel electroform with either nitric acid, warm sulfuric acid or a cyanide solution.

Other ways of making non-conducting materials conductive include:

- ?? using finely divided metal powders dispersed in binders ("bronzing");
- ?? applying finely divided graphite to wax, natural and synthetic rubbers that have an affinity for graphite; and
- ?? applying graphite with a binder.

A method growing in popularity is vapor deposition, which is most suitable for the relatively small mandrels used in the semiconductor industry, the optical disc industry and in the manufacture of holograms (see page 25). The mandrel must be made of a material that does not out-gas in the vacuum chamber. Conventional electroless processes are not generally used to metallize non-conductive mandrels because the good adhesion of the electroless deposit interferes with separation of the electroform from the mandrel.

With most metallic mandrels, a parting film on the surface helps in separating the electroform from the mandrel. After removing all traces of grease and oil by means of chlorinated hydrocarbon solvents, various metallic mandrels are given different treatments for this purpose.

Stainless steel, nickel, nickel- or chromium-plated steel are scrubbed with magnesium oxide, rinsed, and passivated by immersion in a 2% solution of sodium dichromate for 30 to 60 seconds at room temperature. The mandrel must then be rinsed to remove all traces of the dichromate solution.

Copper and brass mandrels that have been nickel and/or chromium-plated may be treated as described in the preceding paragraph. If not electroplated, the surface can be made passive by immersion in a solution containing 8 g/l sodium sulfide.

Aluminum alloys may require special treatments even when they are used as expendable mandrels to be separated by chemical dissolution. If the deposits are highly stressed, it may be necessary to use zincate or stannate treatments to achieve a degree of adhesion that will prevent lifting of the deposit from the mandrel. When low-stressed deposits (near zero) are being produced, treatment of the aluminum by degreasing, cathodic alkaline cleaning, and immersion in a 50% solution of nitric acid may be sufficient.

Zinc and its alloys may require no other preparation than conventional cleaning if used for expendable mandrels and are to be parted by chemical dissolution. In the case of nickel electroforming, it may be necessary to electroplate the zinc alloy with copper and treat it accordingly to prevent attack of the mandrel.

The fusible alloys employed to make expendable mandrels that can be melted away have a tendency to leave a residue of tin on the surface of the electroform. The mandrel can be plated with copper that is electropolished prior to electroforming to prevent this.

The processing of mandrels for electroforming is summarized in ASTM Standard B 431 (see bibliography) where details of some of the above preparation procedures are given.

6. NICKEL ELECTROFORMING PROCESSES

The nickel electroplating solutions commonly used for electroforming are the Watts, and conventional and concentrated nickel sulfamate solutions with and without addition agents.

Nickel fluoborate solutions are used, but their popularity appears to be declining. From a commercial perspective, the most important ones are those based on nickel sulfamate. The advantages of nickel electroforming from sulfamate solutions are the low internal stress of the deposits and the high rates of deposition that are possible, especially from

the concentrated solution (Ni-Speed). The formulations of these electroforming solutions are given in Table II.

6.1 Watts Solutions

The Watts bath contains nickel sulfate, nickel chloride and boric acid, and yields nickel deposits that are matte in appearance and that are stressed in tension. The solution is relatively inexpensive and is successfully used for electroforming.

Nickel sulfate is the main source of nickel ions in the Watts solution. Nickel chloride increases solution conductivity and has a beneficial effect on the uniformity of metal distribution at the cathode. Boric acid acts as a buffer to control pH at the cathode-solution interface. Anti-pitting agents (wetting agents) are essential for avoiding pitting due to the clinging of air and hydrogen bubbles.

With considerable care, the internal stress of the electroformed nickel can be controlled by means of organic addition agents. Typical stress reducers are saccharin, paratoluene sulfonamide, meta-benzene disulfonate, and 1-3-6 sodium naphthalene trisulfonate. All of these organic stress-reducing agents introduce sulfur into nickel deposits and this limits the temperature at which the electroform can be used in service. Nickel electrodeposits with small amounts of sulfur become embrittled when exposed to temperatures above 200°C. The exact temperature of embrittlement depends on the sulfur content, the time at the elevated temperature and other factors. Control of internal stress by means of organic addition agents requires an optimum level of the additive, regular replenishment as it is consumed, and frequent (or continuous) carbon treatment to control the concentration of decomposition products which form as a result of reduction of the additive at the cathode.

6.2 Conventional Nickel Sulfamate Solutions

A formulation for conventional nickel sulfamate solutions is included in Table II. In essence, these are analogous to Watts solutions in which the nickel sulfate is replaced with nickel sulfamate. The internal stress is lower than in the Watts solution, as indicated by the information at the bottom of the table. The zero stress level may be obtained by maintaining the solution in a high state of purity and by eliminating the nickel chloride. To assure efficient dissolution of nickel anode materials in the absence of chlorides, it is essential to use sulfur-activated nickel anode materials, such as S-Rounds electrolytic nickel or S-Nickel pellets. Even with extreme care, a zero stress level may be difficult to maintain without using small amounts of the organic addition agents referred to above. The additives function in nickel sulfamate, as well as in Watts, solutions.

A stable tensile stress can be maintained in conventional nickel sulfamate solutions by including nickel chloride in the formulation, by using an adequate anode area (1.5 to 2 times the area of the cathode), and by using a fully-active nickel anode material to maintain the potential on the anode basket as low as possible, thus avoiding oxidation of the sulfamate anion (described below). Under these conditions, the stress level normally is between 35 and 55 MPa (5000 to 8000 psi) tensile for a well-worked solution.

6.3 Anodic Oxidation of Sulfamate Anions

A phenomenon, which apparently only occurs in sulfamate solutions, is anodic oxidation of the anion to form species, which diffuse to the cathode where they are reduced. In some cases, this results in incorporation of sulfur, which acts to lower internal stress and brighten the deposit. This occurs, for example, at insoluble primary or auxiliary anodes, or at nickel anodes that are operating at high potentials.

At an insoluble platinum anode, a stress reducer forms which was identified as an azodisulfonate; it reacts at the cathode and introduces sulfur into the nickel deposit. The use of a small auxiliary platinum anode along with primary anodes to control stress by passing one to two per cent of the total current through the platinum is feasible and has been evaluated on a laboratory scale; although stress was controlled at a low value (compressive), the work confirmed that sulfur co-deposits and affects the ductility and other mechanical properties of the nickel, and its tendency to become embrittled when heated. The long-time effects of employing an insoluble auxiliary anode in this way have not been determined.

More than one sulfamate oxidation product may form. The one that forms depends on the anode potential. At an insoluble platinum anode, the electrode potential is high (1.2 volts vs. SCE), whereas in the concentrated solution (Ni-Speed) the electrode potential on the anode in the conditioning tank is controlled at a lower level, about 0.2 volts vs. SCE. The existence of several oxidation species in sulfamate solutions was confirmed by Chinese investigators in 1988. The Ni-Speed process discussed in the next section permits zero-stress plating at high rates while avoiding the co-deposition of sulfur.

6.4 Concentrated Nickel Sulfamate (Ni-Speed)

The concentrated nickel sulfamate process, Ni-Speed, was developed by Inco Europe Limited. It permits the deposition of nickel at high rates and at low stress levels in the deposit. It is particularly useful for electroforming where zero-stress conditions are required to produce perfectly flat electroforms and where thick deposits may be built up rapidly. Because low to zero-stress conditions can be achieved without organic addition

agents, there is no incorporation of sulfur and the deposits do not become embrittled when heated above 200°C.

The composition of the solution is given in Table II which lists the acceptable operating limits. The solution contains 600 g/l nickel sulfamate.

6.5 Nickel-Cobalt Alloy Plating

Nickel-cobalt alloys can be deposited from concentrated nickel sulfamate solutions with controlled internal stresses. The cobalt in solution can be maintained by the addition of cobalt sulfamate or by using electrolytic cobalt anodes connected to a separate power supply alongside the nickel anodes. The codeposition of cobalt increases the hardness and strength, and enhances the high temperature properties of the deposits. The cobalt content of the deposit rises with increasing amounts of cobalt in solution and declines as the current density increases. As the cobalt content of the solution is increased, the hardness of the deposit increases to a maximum value. The peak occurs at 35 per cent cobalt in the deposit which corresponds to about 6 g/l cobalt in solution. The internal stress of the deposit increases with current density and also with cobalt content of the solution.

It can be seen that there are a number of conditions under which nickel-cobalt can be deposited with zero stress and these are listed in Table IV.

Nickel-cobalt alloys can be deposited from conventional nickel sulfamate solutions and from nickel sulfate-based solutions, but the deposition of the alloys from the concentrated solution provides a means to control the internal stress without the use of organic addition agents.

6.6 Leveling Agents

The use of levelling agents, such as 2 butyne 1:4 diol, can improve metal distribution on the mandrel by suppressing the growth of nodules and by preventing the formation of a plane of weakness when electroforming into a corner. In general, levelling agents increase internal stress in the tensile direction. In the case of deposition of nickel or nickel-cobalt alloys from the concentrated solutions already discussed, it is possible to control the increase that results from the use of the levelling agent and achieve acceptable levels of internal stress. The initial concentration of butyne diol suggested for a concentrated solution with 1.25 g/L cobalt is about 20 mg/L with a replenishment rate of 0.5 mg/Ah at a current density of 3 A/dm². Although the breakdown products formed by organic addition agents generally increase internal stress, continuous filtration through carbon removes only the breakdown

products in the case of butyne diol and the stress can be closely controlled with this additive.

6.7 Metal Matrix Composites and Other Innovations

Electroplating processes that result in the incorporation of particles uniformly dispersed throughout an electrodeposited metal matrix have been investigated in connection with electroforming. By careful selection of the particle to be occluded, it is possible to obtain nickel electroforms with unique mechanical and physical properties. Oxides, nitrides, carbides and borides have been incorporated in nickel and nickel alloy deposits to produce high-temperature, oxidation-resistant materials. The codeposition of mica with nickel results in a deposit with a low coefficient of friction. The incorporation of fibers in metal matrices by means of electrodeposition is also possible and is receiving renewed attention at this time.

Electroless nickel processes have, until recently, been considered unsuitable for forming applications because of the lack of ductility of the deposits. Bellows have, however, reportedly been successfully formed electrolessly.

The possibility of creating articles with unusual properties through the incorporation of metallic and non-metallic particles and fibers, either electrolytically or electrolessly, exists and may extend the utility of electroforming even further.

7. PROPERTIES OF ELECTROFORMED NICKEL

The mechanical properties of electroformed nickel are influenced by the operating variables - pH, temperature, and cathode current density. The constituents of the solution, if their concentrations are not kept within specified limits, and relatively small amounts of metallic impurities can, also, affect mechanical properties. The properties are interrelated and steps taken to increase the hardness of the deposit usually increase its strength and lower its ductility. The refinement of crystal structure, for example by the use of organic addition agents, is accompanied by increased hardness and tensile strength, and reduced ductility. Typical properties of deposits from various additive-free baths are included in Table II.

The influence of operating variables on some of the properties of nickel deposited from Watts and conventional nickel sulfamate solutions is shown qualitatively in Figure 6. Deposits from these types of nickel baths are affected differently by the same variables. For example, in the Watts solution tensile strength is relatively independent of plating solution temperature, pH and cathode current density; it increases with increasing nickel and chloride in solution. In the sulfamate solution, tensile strength decreases with

increasing temperature to 50°C, increases with increasing pH, and decreases with increasing cathode current density; it decreases slightly with increasing nickel and chloride in solution. The operating variables, as well as the specific constituents, affect the properties of electroformed nickel.

In addition, the mechanical properties, especially the per cent elongation or ductility, are affected by the thickness of the electroformed nickel used in determining the properties. The ductility increases with increasing nickel thickness up to about 250 micrometers after which it becomes relatively constant. This was shown in the classic work by Zentner, Brenner and Jennings (1952) for deposits from Watts solutions and is also true for nickel deposits from sulfamate solutions. Mechanical testing should be done at the thickness of interest even though it may be more convenient to test thick deposits.

The properties of nickel electroformed from sulfamate solutions can be affected by uncontrolled anode behavior, which results in the oxidation of the sulfamate anion. The oxidation products can lower the internal stress and increase the sulfur content of the deposits. The extent to which these changes in internal stress and sulfur content affect the ultimate tensile strength and per cent elongation of sulfamate nickel electrodeposits has been studied (Chart, 1977). Nickel sulfamate deposits with tensile internal stress were obtained from conventional solutions; the stress was stable at 50MPa. (The solution contained 70 g/l of nickel metal as the sulfamate, 0.1 g/l of chloride added as nickel chloride hexahydrate, and 35 g/l boric acid. The pH was 4.0, temperature 60°C, and cathode current density 540 A/m²; the bath was operated with air agitation.)

After the tensively stressed deposits were prepared over a range of thicknesses, similar compressively stressed deposits were prepared by including a platinum foil anode in the circuit and passing 1 to 2 per cent of the total current through the auxiliary anode; the current density on the auxiliary anode was 2.7 A/m². This procedure gave deposits with an internal stress that was 71 MPa in compression.

The ultimate tensile strength varies with nickel thickness but becomes stable above 250 micrometers. The strength of the compressively stressed deposits is greater than that of the tensively stressed deposits. Annealing at 371°C for 2 hours lowers the tensile strength of the compressively stressed and tensively stressed deposits to approximately equal values. Annealing at the higher temperature lowers the tensile strength even further, but the decrease is significantly greater in the case of the compressively stressed deposits.

The ductility shows greater variation with thickness than does the ultimate tensile strength. The ductility is greater for the tensively stressed deposits than for the compressive ones in the as-plated condition. Annealing at 371°C increases the ductility of both types of deposits. Annealing at 760°C increases the ductility of the tensively stressed

deposits, but lowers the ductility of the compressively stressed ones to values below the as-plated ones. The measurements of ultimate tensile strength and per cent elongation (ductility) were made by standard uniaxial tension testing. The deposits were also analyzed chemically. The tensively stressed deposits contained less than 1 part per million sulfur, whereas the compressive deposits contained about 40 parts per million sulfur. Metallographic and electron microprobe analyses conducted after annealing showed brittle failure in compressive deposits heated at 760°C, as well as high sulfur (380 to 500 ppm) contents in grain boundaries.

The work established that the oxidation products formed at an insoluble platinum anode in sulfamate solutions lower internal stress and result in the codeposition of sulfur. The codeposition of small amounts of sulfur affects the mechanical properties of electroformed nickel especially at high temperatures. It is important to control the anode behavior to achieve consistent results in electroforming from sulfamate solutions.

8.CONTROL OF ELECTROFORMING PROCESSES

Successful electroforming requires careful control of the purity of the electrolyte and of the operating variables, such as pH, current density, temperature and agitation. In this respect, control is similar to that of decorative nickel electroplating. Control is more difficult and perhaps, more critical in the case of electroforming because processing may take hours or days to complete. The common problems encountered in electroforming include controlling metal distribution, internal stress, roughness and nodular formation. Addition agents may help overcome some of these problems, but their concentrations must be closely controlled.

8.1 Metal Distribution

The variation of the thickness of the metal deposited at various points on the surface of a mandrel is related to current distribution. Recessed areas will receive less current; areas that project from the surface will receive higher current. The current density and the rate of metal deposition will be lower in recessed areas than at areas, which project from the surface. The result is that metal distribution will be non-uniform in many cases. The deposit will be relatively thin in recessed areas and relatively thick on projections.

Some electroplating solutions are less sensitive than others to variations in current density. The capability of a plating solution to deposit uniformly thick deposits despite variations in current density on the surface of an electroform is measured by its throwing power. Throwing power is the relationship between metal distribution and the variables: conductivity, polarization, current efficiency, and geometry. Studies of the throwing power of nickel plating solutions suggest that throwing power can be improved by reducing current

density, by increasing the distance between anode and cathode, and by increasing the pH, temperature, and metal content of the bath. All-chloride nickel plating solutions (which are not used for electroforming because of the high internal stress of the deposits) have better throwing power than Watts solutions. Sulfamate solutions are better than Watts solutions but not as good as the all-chloride solutions.

The electroformer will usually select a nickel process based on the mechanical and physical properties specified, rather than throwing power. Metal distribution is then improved by proper racking, and by the use of thieves, shields, and/or conforming or auxiliary anodes. The use of these processing aids makes it possible to control metal distribution and obtain relatively uniform deposits. Although these techniques are optimized by trial and error, simulation of the electroforming operation combined with the determination of cathode potential profiles can facilitate the design and placement of shields and auxiliary anodes. Computer software is available to help improve metal distribution at the cathode.

8.2 Internal Stress

The control of internal stress is extremely important in electroforming. Internal stress refers to forces created within an electrodeposit as a result of the electrocrystallization process and/or the codeposition of impurities such as hydrogen, sulfur and other elements. The forces are either tensile (contractile) or compressive (expansive) in nature; rarely are electrodeposits free of some degree of internal stress. Excessive tensile or compressive stress can cause the following problems: 1) distortion of the electroform when it is separated from the mandrel; 2) difficulty of separating the electroform from the mandrel; 3) curling, peeling or separation of the electroform prematurely from the mandrel; and 4) buckling and blistering of the deposit which is usually indicative of high compressive stress.

Internal stress is influenced by the nature and composition of the nickel plating solution (see Table V). The all-chloride solution produces deposits with the highest internal stresses. Nickel sulfamate solutions without chlorides produce deposits with the lowest internal stresses. As discussed, organic additives can be used to control internal stress of electrodeposited nickel, but since these additives invariably introduce sulfur they must be used with caution and due consideration. Sulfur codeposited with nickel increases its hardness and strength, and reduces ductility. Sulfur affects the high temperature properties adversely, and nickel deposits with sulfur cannot be heated above 200°C without becoming embrittled. The codeposition of small amounts of manganese has been shown to prevent embrittlement of sulfur-containing nickel electrodeposits and allows heating above that temperature. The concentrated nickel sulfamate process discussed above can be operated at high current densities to yield deposits with very low or zero internal stresses,

the techniques being shown to be effective with nickel as well as nickel-cobalt alloy electroforming.

Internal stress is controlled by specifying the electrolyte and maintaining its purity, and by using organic addition agents. Control of current density and the other operating variables is also important.

8.3 Roughness

Any condition, which would tend to cause roughness in decorative plating will have a much more serious effect on electroforming operations. Nodules, nuggets and trees will form. These become high current density areas, and the larger they get, the faster they grow and the more they rob surrounding areas of deposit. As a consequence, the filtration rates used in electroforming are very high in an effort to prevent roughness; the rates may amount to passing the entire solution through a filter one or more times an hour.

The sources of roughness include airborne dirt. It is good electroforming practice to keep the plating area clean by vacuum cleaning and to supply the plating room with filtered air keeping the room under an inch or so of pressure. These precautions are especially necessary when the plating tank has an exhaust system, which draws air across the bath.

Electroformed stampers for making compact discs are made in clean rooms under exacting conditions of cleanliness. Anode particles may also cause roughness and are controlled by means of anode bags and diaphragms; higher filtration rates and cathode agitation may be beneficial. The crystallization of bath chemicals on anode bags, tank walls and super-structures which may form at low temperatures or because of inadequate solution agitation may cause roughness problems when these particles fall or are brushed into the solution. The crystallized salts tend to dissolve slowly and may become attached to the cathode. Accumulated salts should be removed carefully or washed away when the bath is not in use. Deionized water should be used to make up the plating and rinsing solutions to avoid the formation of particles from precipitation of hard water constituents.

8.4 Treeing

Treeing at edges and corners may be troublesome and is minimized by the use of shields or by the choice of electrolyte; for example, high-chloride solutions are better than Watts baths in this respect. Certain addition agents, such as the levelling agents discussed above, suppress the treeing tendency. Another approach applicable in many cases is to extend the mandrel beyond the dimensions actually desired, so that the treeing occurs on a part of the electroform that can be machined away. If nickel electroforming is interrupted to

remove trees and nodules by machining, the machined nickel surface must be activated to insure good nickel-to-nickel adhesion. Methods of preparing nickel surfaces for deposition with nickel have been standardized (ASTM Standard B 343).

8.5 Other Control Techniques

Agitation of every kind, singly or in combination should be employed whenever possible to control burning and pitting at high current density sites. Solution agitation, either air or mechanical, may induce roughness, however, unless the solution is kept clean by using a high filtration rate. Cathode rotation, when applicable, is an effective means of solution agitation. In addition, cathode rotation can ensure uniformity of deposit thickness from point to point around the circumference. (Inequalities along the axis of rotation have to be overcome by other means). When rotation is used, brushes or other commutating devices must be provided to conduct current to the cathode. Care must be taken that these devices are designed so that no lubricating grease or metal particles resulting from the wear of bearing surfaces fall into the plating solution.

9. POST-ELECTROFORMING OPERATIONS

The operations that are performed after electroforming is completed are machining and final finishing of the electroform; parting or separation of the electroform from the mandrel, and backing the electroform.

9.1 Machining and Finishing

Necessary machining or other mechanical finishing operations are usually performed before the electroform is separated from the mandrel to avoid deformation. The machining and grinding of electrodeposited nickel may be difficult. Directions for machining and grinding of nickel and other electrodeposits have been published (Carr 1956).

9.2 Parting

Electroforms are removed from permanent mandrels mechanically by the use of one or a combination of several of the following techniques:

- ?? Impact, by a sudden pull or hammer blow.
- ?? Gradual force, applied by a hydraulic ram to push, or a jack-screw or wheel-puller to pull the pieces apart.

- ?? Cooling, for example with a mixture of dry ice and acetone. This works best if the mandrel has a lower coefficient of expansion than the nickel. On withdrawal from the cold bath, the electroform will expand faster than the mandrel permitting separation.
- ?? Heating, with a torch or hot water or oil bath, either to melt or soften a parting compound or to take advantage of a difference in coefficients of expansion between mandrel and electroform.
- ?? Prying, with a sharp tool may be used with care to separate relatively flat pieces, such as phonograph record stampers or engraving plates.

Expendable mandrels are melted or dissolved out as follows:

- ?? Zinc alloys are dissolved with hydrochloric acid.
- ?? Aluminum alloys are dissolved in strong, hot sodium hydroxide solutions.
- ?? Low-melting alloys are melted and shaken out. The alloy may be collected and used over. If "tinning" occurs, a nickel electroform may be cleaned with strong nitric acid.
- ?? Plastics of the thermoplastic kind may be softened by heat so that the bulk of the mandrel may be withdrawn, after which the electroform is cleaned with a suitable solvent. An alternative is to dissolve the entire mandrel with a solvent.

The separation of mandrel and electroform should be considered at an early stage since the separation can be simplified by certain design changes. A fine surface finish facilitates parting. Gripping devices may be incorporated on the mandrel and a knock-off block may be provided so force can be applied for separating the mandrel and the electroform. A taper can be specified when feasible.

9.3 Backing the Electroform

It is often necessary to back the electroform with some other material which is then finished to specified dimensions to fit into a bolster or onto a printing press. This is true, for example, in the case of molds, dies, printing plates and tools in general.

The most important backing methods include the following: 1) casting with low-melting temperature alloys; 2) spraying with various materials; 3) electroplating with other metals; 4) use of thermosetting resins; and 5) spark-eroded steel back-ups and electrochemical machining techniques that sink conforming cavities in the back-up material.

10. ELECTROFORMING APPLICATIONS

The utility of electroforming technology is evident in its diverse applications. When nickel electroforming is applied to best advantage, it results in tools, components and products that are unique.

10.1 Tools, Molds and Dies

The largest category of electroformed products is tools. Included in this category are molds and dies, press tools, foundry patterns, diamond cutting bands and abrasive wheels.

Molds and dies for producing leather grained textures and lustrous finishes on the surfaces of plastics and other molded materials are well developed. Electroformed molds are used in making auto arm rests, taillight reflectors and molded dashboards and instrument panels. They have also been used to make ballpoint pen bodies, plastic caps, switch plates, chocolate and rubber products, ice cream and ice pops, plastic dolls and plastic fresnel lenses.

Applications where the ability to reproduce extremely fine detail is critical include phonograph, video disc and compact disc stampers, and embossing plates and printing plates for stamps and currency.

In addition to pre-recorded video and compact discs, nickel electroforming is being used to make polycarbonate discs onto which users can record information for permanent data storage. The polycarbonate discs have a micro-textured surface with controlled reflectivity.

When data is recorded by means of a laser and special equipment, the reflectivity is increased at points on the surface. The permutations in reflectivity are read back with a suitable laser to regenerate the original information (Watson, 1990).

The stampers to reproduce holographic images are made by nickel electroforming because very fine lines, which vary in depth and width, must be reproduced faithfully to achieve the holographic effect. These rainbow-colored images appear on credit cards, corporate annual reports, magazine covers and currency to guard against counterfeiting. The largest hologram that has been reproduced on a large scale was the one on the cover of the December 1988 issue of National Geographic, which was created to commemorate the 100th anniversary of the magazine. The front cover displays a three-dimensional view of the world, which virtually explodes before one's eyes, in keeping with the theme of the issue, "Can Man Save This Fragile Earth?" The embossing dies were made from nickel sulfamate solutions by Electroformed Nickel Inc., Corona, California, and the covers were reproduced by American Bank Note Company, Suffern, N.Y. This relatively new application is expected to continue growing.

A notable trend in recent years is the increase in the size of the products being made from electroformed nickel molds. Electronics Metal Finishing (EMF), Colorado Springs, CO, has specialized in producing large electroformed nickel molds for more than twenty-five years and has one of the largest plating tanks in the world devoted exclusively to electroforming, 6750 cubic feet containing 45,000 gallons of nickel sulfamate solution. Some of the items electroformed by EMF are abrasion strips for the leading edges and tips of helicopter blades; electroformed molds for making plastic composite housings for airborne radar; pressing plates for embossing paneling and siding for the construction industry; molds for rotational and vacuum molding of automotive interior parts; molds for making canoes by rotational molding; and molds for producing automotive hard-tops. A singular achievement was the production of electroformed tooling for the molding of graphite-epoxy wing skins for jet aircraft which required the use of mandrels 32 feet long by 12 feet wide (Logsdon, 1990).

10.2 Mesh Products

Electroformed nickel mesh products comprise a large number of current applications. Chief among these are textile printing screens which are used to produce multicolored patterns on textiles, wallpaper and carpeting. The most popular printing screens are seamless electroformed cylinders of nickel consisting of mesh with many fine, precise holes. The designs are created on the screen mesh by photoresist techniques, which block some of the openings and leave others free. The screens are mounted on rotary textile printing machines on color feed tubes, which are inside and concentric with the larger screens. Color is forced through the open areas of the mesh by means of a magnetic roll held against the inside of the screen. Each screen feeds one color; machines with up to twelve different screens have been used to create intricate and detailed designs.

A relatively new development involves the continuous electroforming of porous substrates for fabricating battery electrodes. One approach involves the deposition of nickel onto woven plastic fiber mesh, which is prepared by established plating on plastics technology; the plastic mandrel is removed after plating by heating. Although all the details have not been disclosed, a porous mesh which can be impregnated with active nickel hydroxide results and is being used in the fabrication of nickel-cadmium batteries. Other variations of this approach are being investigated.

Other mesh products which have been made by electroforming include filters and sieves, and electric razor screens.

10.3 Other Products

Besides tools and mesh products, a number of other unique products are made. Nickel foil 4 to 50 micrometers in thickness is electroformed continuously on rotating drums using concentrated nickel sulfamate solution. Space mirrors and a variety of optical parts are commonly made by electroforming. Seamless bellows, which are sensitive to changes in atmospheric pressure, are made in many sizes and shapes for aerospace and other applications. Radar wave guides are one of the oldest uses of the technology. Seamless nickel belts for use in copiers and in cigarette machines are now well established applications. Components of rocket thrust chambers, nozzles and motor cases have been successfully electroformed.

What this review of applications indicates is that important segments of industry... aerospace, automotive, textile printing, copying machines, consumer products, batteries...utilize electroforming as a method of fabrication to yield a diverse list of unique products.

11. INCO NICKEL ANODE MATERIALS

The anode materials conceived and introduced by Inco include active nickel anode materials with unique shapes, which are ideal for use in titanium anode baskets. The active ones are particularly useful for electroforming.

The active nickel anode materials include S-ROUNDS electrolytic nickel and S Nickel pellets. These products owe their activity to the small, controlled amount of sulfur incorporated during production. Activity refers to the anode potential, which these materials assume when they are dissolved anodically in various nickel plating solutions. The sulfur-activated nickel anode materials marketed by Inco are the most active materials available. That is, they dissolve at the lowest electrode potentials for a specified current density.

The tendency for passivation associated with commercially pure nickel is absent in the case of the sulfur-activated products. As a result, products like S-ROUNDS electronic nickel and S Nickel pellets dissolve smoothly without the formation of metallic residues in all nickel plating solutions irrespective of the chloride content. The low dissolution potentials save electrical power; the savings in power costs are significant. The uniformity of dissolution results in improved settling characteristics in the baskets. In addition to contributing to uniform current distribution, improved settling of the load in the basket protects the titanium from electrochemical attack. The nonmetallic residue that forms is insoluble nickel sulfide, which displaces copper impurities from solution. Nickel plating solutions operated with S-ROUNDS or S Nickel pellets always have unusually low copper present as an impurity for this reason.

The shapes of S-Rounds and of S Nickel pellets ---button-shaped in the case of S-Rounds and spherical in the case of the pellets--- are also advantages. By eliminating sharp, pointed corners, settling of the load in the baskets is facilitated. The spherical shape has added advantages in that it facilitates the loading of odd-shaped baskets and baskets placed in other than the vertical position because the pellets tend to roll and flow. In fact, the flowability of pellets lends itself to the semi- or complete automation of the basket-loading operation. These products have relatively high packing densities, which minimize basket maintenance and contribute to power savings. An added benefit is that they can be handled safely.

As mentioned, sulfur-activated nickel anode materials are preferred for electroforming from nickel sulfamate solutions because they prevent the uncontrolled formation of sulfamate oxidation products, which affect internal stress, appearance, mechanical properties and composition of the deposits. In addition, active nickel anode materials make it possible to operate nickel electroplating processes with little or no chloride ions in solution. This is an alternate means of reducing internal stress during electroforming since chloride ions are known to increase stress.

The sulfur-free, non-activated products supplied by Inco are also used in electroforming and plating when chloride ions are present in solution. These include R-Rounds electrolytic nickel, screened Nickel Pellets for Plating, Nickel Flats (available only in Europe), and electrolytic nickel one-by-one inch squares. The unique shapes of R-Rounds, Nickel Pellets, and Nickel Flats make these products ideal for filling titanium anode baskets safely. The absence of sharp corners contributes to uniform settling of the load in baskets, which leads to the same advantages already described. All these products form small amounts of metallic residues, which are easily retained in anode bags. Being sulfur-free, these products dissolve non-uniformly and at higher anode potentials than do the sulfur-activated products. The sulfur-free, non-activated forms of nickel are popular for electroplating in general, but there is a decided preference for S-Rounds electrolytic nickel and S Nickel pellets for electroforming.

Inco nickel anode materials for electroforming and electroplating are shown in the accompanying photographs.

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Table I - TYPES OF MANDREL MATERIALS

TYPES	TYPICAL MATERIALS
CONDUCTORS	
Expendable	Low-melting point alloys; e.g., bismuth-free 92% tin and 8% zinc. Aluminum alloys Zinc alloys
Permanent	Nickel Austenitic Stainless Invar, Kovar Copper and brass Nickel-plated Steel
NON-CONDUCTORS	
Expendable	Wax Glass
Permanent(or Semi-Permanent)	Rigid and collapsible plastics; e.g., epoxy resins and polyvinyl chloride. Wood

**Table II - NICKEL ELECTROFORMING SOLUTIONS
AND TYPICAL PROPERTIES OF THE DEPOSITS**

	Electrolyte Composition, g/L		
	Watts Nickel	Conventional Sulfamate	Concentrated Sulfamate
NiSO ₄ ·6H ₂ O	225 to 300		
Ni(SO ₃ NH ₂) ₂ ·4H ₂ O		315 to 450	500 to 650
NiCl ₂ ·6H ₂ O	37 to 53	0 to 22	5 to 15
H ₃ BO ₃	30 to 45	30 to 45	30 to 45
Operating Conditions			
Temperature, °C	44 to 66	32 to 60	Normally 60 or 70
Agitation	Air or mechanical	Air or mechanical	Air or Mechanical
Cathode Current Density, A/dm ²	3 to 11	0.5 to 32	Up to 90
Anodes	Nickel	nickel	Nickel
PH	3.0 to 4.2	3.5 to 4.5	3.5 to 4.5
Mechanical Properties			
Tensile Strength, MPa	345 to 485	415 to 620	400 to 600
Elongation, %	15 to 25	10 to 25	10 to 25
Vickers Hardness, 100 gram load	130 to 200	170 to 230	150 to 250
Internal Stress, MPa	125 to 185 (tensile)	0 to 55 (tensile)	Zero stress can be obtained At various combinations of current density and temperature. See text.

Table III - RELATIONSHIP BETWEEN TEMPERATURE, CURRENT DENSITY AND PLATING RATE FOR DEPOSIT ZERO STRESS CONDITION IN CONCENTRATED NICKEL SULFAMATE SOLUTIONS

Temperature, °C	35	40	45	50	55	60	65	70
Current density A/dm ²	1.1	2.7	4.3	8.1	13.5	17.8	21.6	32
A/ft ²	10	25	40	75	125	165	200	300
Plating Rate micrometers/hour	12	31	50	94	156	206	250	375
Mils/hour	0.5	1.2	2	3.7	6.2	8.2	10	15

Table IV - PLATING CONDITIONS AT 60°C FOR ZERO STRESS DEPOSITS IN COBALT-CONTAINING CONCENTRATED NICKEL SULFAMATE SOLUTIONS

Cobalt Concentration in Solution, g/L	Current Density, A/dm ²
0.75	10
1.0	7.5
1.25	5.1
1.5	3.0

**Table V - TYPICAL VALUES OF INTERNAL STRESS FOR NICKEL
ELECTROFORMING SOLUTIONS**

Electroforming Solution	Internal Stress, MPa
Watts	110 to 210
Watts with hydrogen peroxide	275 or higher
All-Chloride	205 to 310
Fluoborate	100 to 175
Fluoborate with hydrogen peroxide	100 to 175
Sulfamate, no chloride	0 to 55
Sulfamate, with chloride	55 to 85
All-Sulfate	110 to 140