Alternatives for Nickel In Electroplating Processes

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By Dr. Franz Simon

The potential of nickel as an allergen has caused some surface finishers to avoid its use. Nickel is typically used for its levelling ability to improve substrate quality, and as a diffusion layer. It is also a good alloying-element for gold-based alloy deposition.

This edited version of a presentation from the EAST session at SUR/FIN®'94—Indianapolis discusses the use of copper/tin and copper/tin/zinc electroplating as a replacement for nickel intermediate layer for decorative applications, and some technical applications.

A more costly alternative presented is a new, very ductile palladium.

Gold/nickel, and gold/nickel/indium processes are commonly used in gold alloy plating for decorative use. As substitutes, gold/iron systems with 0.3 weight percent (w/o), 1.4 w/o or 1.7 w/o are discussed. The higher-iron versions, with 1.4 and 1.7 weight percent Fe, can be excellent replacements for Au/Ni/In deposits in the color range 1N and 2N, according to ISO 8654 (DIN EN 28654).

Nickel is used extensively in electroplating processes for surface treatment. Typical applications are as intermediate layers, or as a partner for alloy depositions. The positive properties of nickel include its levelling power, and its brightening capacity. Because of these properties, polishing work can often be reduced by applying nickel intermediate layers, and it is comparatively inexpensive.

The negative properties of nickel are its allergenic character, and the carcinogeneity of specific nickel compounds. Nickel compounds in the form of dusts or aerosols, such as those used in the electroplating industry, can cause cancer.

The allergenic character of nickel has been of growing interest in recent years. Nickel allergies can be more serious than just minor skin irritations.

In the western hemisphere, 10 percent of all women and one percent of all men develop nickel allergies. The primary cause is ear-piercing, especially among girls in early childhood, so that pierced earrings can be worn.

When ears are pierced, a pole is usually placed in the opened channel to prevent it from healing. Nickel-containing materials are often used for keeping the pierced areas open. A sensitization against nickel occurs, and women who normally wear pierced earrings develop nickel allergies later. Most men develop the allergies as a result of their work (professional disease), although increasing numbers of men are piercing their ears.

Nickel allergy is developed in two steps—the sensitization phase (ear-piercing), and the acute phase (so-called allergy or disease). The later stage is caused when human skin comes in contact with nickel-containing material (costume jewelry).

People are surrounded by nickel-containing materials, in the form of metallurgically produced alloys that are present on many common items, such as cutlery, cooking pots, pans, prostheses, watchbands, eyeglasses, coins and containers. As an electroplated intermediate layer, or as an alloying material in electroplated deposits, nickel is present in various articles, such as watchbands, watchcases, costume jewelry, chains, eyeglass frames, buttons, writing utensils, scissors, etc.

Because nickel is classified as a serious allergen, it should only be used in applications where it is necessary and tolerable, such as in technical fields. In other consumer areas, especially in the decorative sector, nickel should be avoided or replaced.

Function of Nickel In Electroplating Processes & Electroplated Applications

One of the main reasons for using nickel is its capacity for levelling and brightening. Because of this, inferior substrate quality can be improved without costly polishing work. Nickel has been used to improve the quality of precious metal surfaces, such as silver and white gold. It has enhanced the surface quality of other common substrates in preparation for subsequent processes. Nickel also is used as a diffusion barrier against certain elements from the substrate, especially with copper-based alloys. If nickel were not used, the substrate material could diffuse into the final top layer—gold, for example—which would cause tarnishing and deterioration of quality. In the opposite direction, a nickel layer under gold prevents diffusion of gold into the substrate, and its eventual loss. This allows gold deposits to be used on inexpensive substrates.

Further, an intermediate layer of nickel is used for corrosion protection of base materials in severe environments. In practical use, such intermediate layers improve the corrosion properties of a substrate.

Nickel is used as an alloying element in electroplating processes. Nickel is alloyed with gold to increase hardness, reduce abrasive wear and improve brightness. Nickel is also an important color component for gold alloys. Until recently, many grayish or reddish-gray gold alloy deposits could only be produced at a reasonable price with nickel as an alloying ingredient.

Any potential alternative to nickel must match this performance, either as a multilayer or an alloy.

Replacing Nickel Intermediate Layers With Bronze or Palladium

Applications of Bronzes As Substitutes For Nickel Intermediate Layers

There are many potential alternatives to nickel as intermediate layers, such as bronzes, palladium or cobalt. Like nickel, however, cobalt is under examination as an allergen or carcinogen. For intermediate layers, bronzes can replace nickel. There are processes available for white or yellow bronze deposits. White bronzes are hard and tarnish-resistant, whereas

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yellow bronzes are hard, but of inferior corrosion resistance when compared to white bronzes.

The bronze systems under investigation are alkaline or cyanide based, using copper cyanide and stannate. Complexing agents, buffers, brighteners and levelers were used to develop proprietary processes to achieve reproducible, reliable results. Nowadays, processes are available to deposit white or yellow layers for decorative and technical applications. Modifications for rack and barrel plating are available.

White bronzes are very corrosion resistant in the salt spray test (DIN SS 50021), the Kesternich test (DIN 50017), artificial sweat, or the thioacetamide test. Because of their high copper content, yellow bronzes based on copper/tin, or copper/tin/zinc, are not as corrosion-resistant. Yellow bronzes, however, have a levelling power and a brightening effect that can improve the surface quality significantly. A combination of yellow bronze, with a top layer of white bronze, can be used to replace bright nickel of the same layer thickness.

At 400–550 VHN, the hardness of bronzes is significantly higher than that of electroplated bright nickel (300 VHN).

The diffusion properties of white bronzes were examined in temperature/time tests. When the temperature does not exceed 80 °C, the constituents of the bronze do not diffuse into the top layer of gold, which can cause tarnishing or deterioration of quality. At temperatures above 165 °C, a significant diffusion takes place, leading to the conclusion that for decorative applications, where such temperatures are not applied, bronzes are a sufficient diffusion protection layer for a final top layer of precious metal, such as gold. For technical applications, however, where higher temperatures might occur, or severe tests are applied, bronzes should not be used to replace nickel or palladium.

As to the levelling capability and brightness-forming properties of bronzes, 10 microns of a combination of yellow and white bronze is equivalent to the same thickness of bright nickel. Bronzes exhibit a better throwing power than nickel, resulting in a more even thickness distribution.

The advantages of bronze make its use possible in many applications, not just where skin compatibility is required to avoid allergies. It can also be used where superior solderability, hardness, corrosion resistance, brightening properties, thickness distribution, wear resistance, or diamagnetic properties are needed. Bronzes can be used for costume jewelry, buttons, haberdashery, buckles, trouser clips, zip strippers and parts for high-frequency technology (diamagnetic, not paramagnetic properties).

Bronze alloys also kill bacteria very quickly, just as copper, and have better bactericide properties than silver. In tests with *staphylococcus aureus, staphylococcus epidermidis* and *enterococcus*, bacteria were strongly diminished after a short period of exposure to bronze. Bronze can be applied on plated door handles and bathroom fittings, especially in places such as hospitals. Bronze is superior to copper or silver for this application, because it does not tarnish.

Palladium as a Substitute For Nickel Intermediate Layers

Palladium can be substituted for nickel as an intermediate layer to avoid nickel allergy effects. It is also being considered as a replacement for gold, because it costs less.

Recently, there have arisen some concerns about palladium allergy. According to available information, a palladium allergy does not seem to exist. There may be some skin irritation associated with its use in the dental field, but it has not been proven that a real allergy exists. The skin irritations that have been reported are not comparable to a real allergy, such as that caused by nickel. They have only been traced to the oral area. These findings still allow palladium to be used for applications such as costume jewelry and utensils for daily use.

There is a relatively new plating process that yields very ductile deposits, which are crack-free and bendable around a diameter of 20 mm. CASS corrosion testing yields good results, even after 70 hr of exposure. This new system is based on palladium chloride as a palladium salt and specifically developed proprietary additives. The deposits are 99.9 percent pure, bright and brilliant. The maximum available thickness is 10 microns with a hardness of 250 VHN. Such layers are already being used as an underlayer for gold in decorative applications, such as eyeglass frames, watches and jewelry. As a diffusion barrier under a final gold top layer, 0.3–0.7 microns of palladium seem to be sufficient.

The electrolyte contains a palladium content of 8–12 g/L at room temperature, at a pH of 8.9. At 1.0 A/dm², a deposition rate of 0.3 microns per min is achieved. Rack and barrel applications are possible with the new system. To avoid contamination of electrolyte, a gold st palladium strike, is recommended the main palladium layer is dep The sensitivity of all palladium ba silver, copper, zinc, or cyanide co nation should be kept in mind to a long process life.

The superior bendability and cor properties of the new system were onstrated in a comparison with de placed from three different system posits using the new palladium-ch based solution were compared w acid palladium-sulphate-based so and a slightly alkaline palladiur based electrolyte. Results showe the palladium-chloride, with newly oped additives, is superior, showi crack formation, and no corrosion CASS test, even after 70 hr of expo

It has been well established that dium functions as well as nickel diffusion barrier.

Many questions remain unansw about the possibility of replacing with bronzes and palladium, but observations of basic tendencies c made. Bronzes and palladium are parable to nickel with regard to hard color, corrosion protection, soldera further platability, and wear resist. Bronzes, especially the combinati yellow and white, are comparable to with regard to levelling and bright properties. Bronzes and nickel are rior to palladium in this regard, bec palladium usually has no significan elling and brightening power.

For diffusion properties, palladiu equal to nickel. The use of bronze diffusion barrier is primarily limite decorative applications. Bronzes ca used for some technical application not in the broad range over which n can be applied. In regard to duc bright nickel is the most brittle when pared to bronzes and palladium. Y bronze can be ductile, whereas w bronze is brittle. Palladium from the system shows a very high ductility.

Palladium is, by far, the most ex sive. For most applications, bronze the logical replacement and a cost e tive alternative to nickel. Palladiu important in some applications, e cially in the eyeglass frame industry used less as a replacement for a ni underlayer than it is as a corrosion-re tant noble metal intermediate layer, der final gold plating.

Nickel-free Gold Processes

Nickel-containing gold alloy deposi use today contain between 0.05–4 we percent of nickel in the deposit. These alloys are used for technical and decorative applications. The alloys include gold/nickel (or gold/nickel/indium), or systems for gilding based on gold/copper/silver/nickel, gold/copper/cadmium/nickel, and gold/copper/nickel. Because most of these alloys are used in decorative applications, nickel as an alloying element must be avoided. Limiting conditions, such as color match, and deposit properties, such as wear, tarnish and corrosion resistance, should be observed.

Nickel-free gold-depositing processes have been available for many years, including:

- Gold/indium
- Gold/tin
- Gold/silver
- Gold/copper/silver
- Gold/palladium
- Gold/copper/palladium
- Gold/cobalt

These deposits sometimes have a different color, or different deposit properties, so they cannot generally be used as identical replacements for nickel-containing deposits.

Gold/iron systems, where iron is the replacing component for nickel, can be substituted for gold/nickel/indium deposits that are widely used in decorative applications on costume jewelry, bathroom fittings, etc. Gold/nickel/indium solutions and deposits are used extensively, because of the wide range of color shades that are possible, including 1N and 2N colors according to standard DIN EN 28654. Wear resistance, corrosion resistance and tarnish resistance are excellent with these systems. The wear resistance of gold/nickel/indium is superior to gold/nickel and gold/cobalt deposits. So, any substitute must be compared with the standard set by gold/nickel/indium plating systems.

Gold/iron

Successful substitution was accomplished with the development of new gold/iron systems designed to deposit 1.4 and 1.7 percent iron, respectively, in the gold lattice. The deposit is, therefore, in the range of 23.5 carats, with a hardness of 220 VHN. Tarnish resistance is good, and the colors achieved are 1N and 2N, respectively. The operating ranges of current density, pH, and temperature are extraordinarily large, resulting in the same color over the whole range of parameters.

Because 1.4 and 1.7 percent are much higher iron concentrations than what is encountered in more conventional gold-iron alloys (typically 0.3 weight percent maximum), the question arises: Is the iron codeposited homogeneously or heterogeneously?

Magnetic susceptibility measurements on conventional gold/iron layers, with 0.3 percent weight of iron, showed that the ferromagnetic part of the susceptibility is nearly negligible, and the paramagnetic amount is low, corresponding to the low amount of iron. The low codeposited amount of iron is, therefore, diluted in the gold lattice homogeneously. With deposits containing high iron amounts of 1.4–1.7 weight percent, the values for both the ferromagnetic and paramagnetic components are significant. Knowing the ferromagnetic value of the susceptibility, one can calculate the proportion of mass of magnetizable iron for each system, which works out to 13 and 14 ppm of iron, respectively. This means that only one-thousandth of the total codeposited iron is present in a heterogeneous stage.

X-ray emission spectroscopy showed a homogeneous distribution of iron and gold in the layer. There are no indications of heterogeneous agglomerations of iron. The Roentgen contrast pictures show a uniform greyish appearance. If iron had been deposited heterogeneously, there would be lighter colored spots visible, indicating an element of lower ordinal number, as compared to gold.

The determination of the lattice constant of the gold/iron lattice did not lead to conclusive results. There was only one lattice constant found for deposits with 1.4 and 1.7, or 0.3 weight percent of iron, by diffractometry diagrams. Thus, elementary iron could not be determined. It should be considered, however, that X-ray reflection peaks for gold and iron, to some extent, overlap at the same angles; therefore, this method does not lead to conclusive results. More credence was given to actual corrosion and wear test results, because these properties are important for practical use.

Deposits with 1.7 and 1.4, and 0.3 weight percent of iron, were compared to gold/nickel/indium deposits with 2.3 and 0.8 weight percent of nickel. The tests included salt spray, ammonia vapor; nitric acid vapor, thioacetamide, and artificial sweat. Results showed that gold/iron deposits with different amounts of codeposited iron were at least equal to gold/nickel/indium layers in every case. In the ammonia vapor test, gold/iron deposits were even superior to gold/nickel/indium layers. In all cases, there was no attack and no tarnishing in the thioacetamide and artificial sweat test.

Considering wear characteristics, gold/nickel/indium exhibits a wear rate of about 2.5–4 mg/(cm^2 x 100 strokes) in the Ericksen test. The wear rate of gold/iron deposits is in the same range—between 4 and 4.5 mg/(cm^2 x 100 strokes). Compared to conventional gold/nickel and gold/cobalt deposits, they exhibit a slightly higher wear rate. It can be concluded that gold/iron deposits exhibit the same range of order of wear properties.

Gilding Baths

Gilding baths are plated as top layers on decorative pieces to assure a uniform color over the whole piece, independently of areas with high or low current densities.

Conventional color gilding solutions contain nickel as a hardening agent and/or an alloying element. An interesting range of color shades can be achieved by adding nickel. Conventional gilding baths contain about 1 g/L of gold and 1–2 g/L of of potassium cyanide. Alloying metals are silver, copper, cadmium, nickel, and iron, or combinations thereof. With these alloying elements, about 50 different color shades can be produced, with a caratage equal to, or higher than, 20 carats. The maximum thickness of the deposit is limited to 0.2 µm. The tarnish resistance and quality of color are very good. Newly developed systems use iron for the same function as nickel.

In the color range of 0N, 1N, 2N, 3N, 4N, and pure gold color, new systems that are totally nickel-free are available. The compromises with regard to color are negligible. Caratages achieved with the new systems are very high (20.8–23.8 carats). The alloys deposited are based on gold/silver/copper, or gold/silver/copper/cadmium.

Some Concluding Thoughts

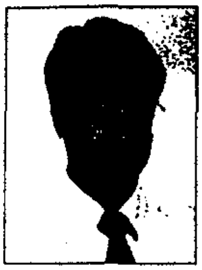
Nickel can be replaced in electroplating processes used for the deposition of intermediate layers and final gold alloy layers.

Bronzes or palladium can be used with good results for intermediate layers. Bronzes are cost-competitive with nickel, and palladium can be used at the upper end of the cost range. There have been new systems developed to plate white and yellow bronze, and a very ductile palladium.

Iron can be used to replace nickel in gold alloy deposits. Iron is physiologically nonallergenic. New plating solutions, using iron as an alloying element, have been developed, with deposit properties that are at least as good as gold/nickel or gold/nickel/indium systems.

Nickel provides many color shades that are desired by the industry. More development will be necessary to replace nickel further. If nickel is to be totally avoided, the range of color shades is limited, and this will require more flexibility from the applier of color golds to provide the colors desired by customers. ❑

About the Author



Dr. Franz Simon is manager of technical applications for plating precious and nonprecious metals at Degussa Electroplating, Demetron GmbH, Postfach 1240, D 73502 Schwäbish Gmünd, Germany. Employed by the firm since 1976, he holds a PhD in chemistry from the University of Frankfurt.