

Palladium Plating

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Applications

Palladium, a precious group metal, has within the last decade emerged as a competitive metal finish for hard gold and, in some instances, soft gold. Palladium's attributes are its lower price and specific gravity relative to gold, and its comparable materials properties. Palladium and palladium alloys with nickel and silver have been primarily used for separable connectors and printed wiring board fingers. Recently, additional applications have been identified, including edge card connectors, switches, lead frames for plastic packaged ICs, solderable contacts, end terminations for multilayered ceramic capacitors, etch resist for PWBs, glass-to-metal sealed contacts, and battery cathodes.

In the late 1950s and '60s, wrought palladium and palladium-silver alloys were used as electronic contacts. The development of modern high-speed hard-gold plating chemistries resulted in a shift from wrought palladium to gold. However, the large increases and instabilities in the price of gold in the late 1970s resulted in a search for less expensive, reliable substitutes.

Palladium and its alloys of nickel and silver have been found to be satisfactory replacements in most applications.

Gold is recommended as a thin (1 to 5 $\mu\text{in.}$) cap to provide for better wearing properties, improved corrosion resistance and inhibition of "frictional polymers" formation. For high wear applications, *e.g.*, edge card connectors, Pd has been the preferred material due to its high hardness and excellent resistance to wear.

Processes

Palladium coatings can be applied by a variety of techniques, including pastes, vacuum deposition, electroless plating and electrodeposition. The majority of Pd used in the electronics industry is applied as a paste that is sintered on ceramic substrates used in multilayered ceramic capacitors. Electroplating of palladium and its alloys is the primary method used for electronic contacts. Barrel, vibratory, rack, step and repeat, and high-speed reel-to-reel plating techniques are commonly used to electroplate Pd. Pulse plating techniques have gained popularity in recent years.

Two major classes of palladium and palladium alloy plating solutions currently exist: Ammonia-based and organic amine-based. Typically, the ammonia-based chemistries use organic additives to impart lustre to the deposited films; The

organic amine-based chemistries are usually additive-free and produce bright to semi-bright deposits.

The ammonia-based solutions usually contain palladium as $\text{Pd}(\text{NH}_3)_4^{+2}$ complex where the anion can be Cl^- , Br^- , or SO_4^{2-} . The palladium concentration (metal content) can vary from 1 to 40 g/L depending on the application. Low-speed processes such as barrel or vibratory plating use the lower metal content, whereas high-speed processes use the highest concentrations. Conductivity and buffer capacity are achieved by additions of ammonium hydroxide and ammonium chloride, typically around 70-120 g/L. Phosphate ion is also used in this capacity, typically around 70-100 g/L. The typical pH range is 6.5 to 8.5, with operating temperatures from 30 to 65 °C. Organic additives are common in these ammonia-based chemistries. Surfactants, brighteners and stress reducers are typically used to obtain lustrous, low-stress deposits. In some cases crack-free, low-stress Pd deposits >1000 μm in thickness can be achieved. Palladium-nickel alloys can be deposited from ammonia-based solutions. Typically, the nickel ion is present as $[\text{Ni}(\text{NH}_3)_4 \cdot 2\text{H}_2\text{O}]^{+2}$. The nature of this ion is pH dependent and the number of ammonias can vary from two to six. Cl^- , Br^- or SO_4^{2-} are used as the anions. The nickel concentration (metal content) can vary from 1 to 25 g/L depending on the application and the specific alloy that is desired. For electronic applications, the Ni content (percent by weight) can vary from 10 to 40 percent. However, the most preferred alloy seems to be 20 wt. percent nickel. Conductivity and buffer capacity are achieved by additions of ammonium hydroxide and ammonium chloride, typically around 60-120 g/L. The typical pH range is 7.0 to 8.5, with operating temperatures of 30 to 65 °C. Organic additives are also used to obtain desired materials properties. Low stress, crack-free PdNi deposits >1000 μm in thickness can be achieved.

The ammonia-based chemistries can be problematic, and are subject to base metal contamination (e.g., Cu etching), ammonia gas evolution, and fluctuations in pH resulting from ammonia loss. However, these factors can be controlled by operating at the lower end of the pH and temperature range, thereby minimizing the activity of the ammonia species. A typical problem with Pd and Pd alloys is plating close to or above the limiting current. This can result in burnt deposits or in the incorporation of hydrogen, which can lead to high internal stresses and the formation of cracks.

The second major class of palladium solutions uses proprietary organic amines instead of ammonia to complex the palladium. The palladium concentration (metal content) varies from 1 to 40 g/L depending on the application. Conductivity and buffering are achieved by the presence of phosphate ions (70-120 g/L), or similar conducting salts. The typical pH range is 9 to 12, with operating temperatures of 40 to 65 °C. Organic additives may be used, but typically these solutions are additive-free. Solution control is generally easier to maintain with the non-ammonia-based chemistries. Copper contamination does not seem to be a major problem and can be controlled. Because of the high pH, passivation of nickel-plated substrates can be a problem. In addition to making certain that the nickel remains wet prior to plating, lower-pH palladium strike chemistries, based on the organic amine chemistries, can also be used.

A minor class of palladium electroplating solutions operates at low pH, generally in the range of 0 to 3.0. Based on PdCl_2 , these solutions use concentrated hydrochloric acid. The resulting solutions are so corrosive that non-precious metal substrates are easily dissolved. Additions of AgCl can

produce a palladium-silver alloy solution. Recently, sulfonic acid-based solutions for palladium-silver alloy plating have been reported.

Post-plating

For electronic applications, palladium and palladium alloy deposits are typically over-plated with a thin (1 to 5 μm .) gold cap. Both hard and soft gold have been used. At thicknesses above 5 μm ., the soft gold cap is susceptible to adhesive wear. Therefore, the use of hard gold is recommended. In the presence of organic vapors and micro-motion (fretting) of mating surfaces, palladium vs. palladium tends to catalyze the formation of frictional polymers, just as Rh, Pt, and Ru tend to do. However, this occurs only under very specific conditions of high frequency micro-motion, with low contact loads (<50 g, typically 10 g) and in ambients high in organic vapors.

Many electronics suppliers require the application of lubricants to gold and gold-flashed palladium contacts to improve wear and corrosion resistance.

Health Impact

Palladium and its complexes are generally much less toxic than platinum and its salts. Palladium salts are also much less hazardous than cyanide salts used in gold plating. Recent toxicological studies, which included contact (dermal) sensitivity, eye irritation, acute oral toxicity and others, have demonstrated that cyanide solutions are much more toxic than palladium. However, when using ammonia-based solutions, adequate ventilation and protective equipment is required because of the volatility of ammonia and its associated toxicity. The organic amine-based solutions require protective equipment (eye protection, gloves, rubber apron) due to the high alkalinity of these solutions.

Environmental Status

Palladium can be removed from waste solutions and rinse waters by electrolysis or by the use of a strong cation exchange resin. Following removal of the palladium, the typical solution formulations employed can usually be neutralized and disposed of in the appropriate manner.

Trends

Gold-flashed palladium and gold-flashed palladium alloys are now being used in a variety of applications where hard gold and in some cases soft gold were formerly used. Palladium's attributes are its relatively low price and specific gravity (~12 g/cc for Pd and 17.3 g/cc for hard Au) and its comparable, and in some cases, superior materials properties. For example, because palladium is harder than hard gold, it appears to be superior to gold in wear resistance and has been the preferred contact finish in the emerging edge card connector markets. Palladium is also being used on lead frames for plastic packaged integrated circuits where it simplifies the processing of ICs and improves the reliability by improving the hermeticity of the package. Glass-to-metal sealed contacts are another area of interest where large cost savings are realized due to process simplification. Palladium is also being used as a cathode for batteries, where it has increased the reliability and longevity of this product.

The late 1970s and early '80s saw palladium alloys emerge as low-cost alternatives to gold. In the late '80s, there was a fundamental change in the perception of palladium, not only as a lower cost alternative to gold, but as an alternative that provides technological advantages. P&SF