Electrochemical Effects in Electroplated Electronics Devices

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There are numerous substrate materials used in electronic devices that are electroplated with controlled thicknesses of nickel and gold. Baking, steam aging and solderability test requirements are prescribed in military[1] and federal[2] specifications. Poorly prepared substrates and inadequate plating and steam aging practices lead to the formation of corrosion products that degrade solderability performance. Electrochemical models, developed from basic electrochemical phenomenology, are proposed to explain the formation of corrosion products during plating and steam aging. The formation of such products can be prevented by taking corrective action in precleaning, etching, activation and plating operations.

Hybrid microcircuit packages are multi-component electronic devices used in high-tech military equipment. They also find application in medical devices for implantation in humans to alleviate many life-threatening illnesses. The devices are electroplated with limited thicknesses of nickel (1.25-8.75 µm) and gold (1.25-5.6 µm). In addition, there are post-plate baking and steam aging requirements, as specified in military specifications (see Appendix).[1]

Beginning with the assembly of electronic devices, it is necessary to satisfy the plater's requirements, in addition to those of the manufacturing engineer. Soils of carbonaceous nature can remain embedded at joints, which, even at the microscopic level, can cause poor adhesion between the substrate and the plated metal.

In the plating department, control of preplate solution concentrations, bath temperatures, immersion times and overall cleanliness are of extreme importance in achieving solderable electrodeposits. The use of surface-tension-controlling agents, particularly in nickel plating solutions, would be beneficial[3-5] but these are prohibited by the military specifications.[1] New materials have been developed, which, it is claimed,[6] do not co-deposit with the metal plate and do not affect deposit characteristics, such as stress. These materials enhance coverage of the substrate with the plated metal by lowering the surface tension of the plating solution. Unfortunately, the military standards lag in accepting these practices. The prohibition of these benign surface-tension-controlling agents[7] is a further challenge to the electroplater in balancing the bath chemistry.

Scope

Reliability of electronic components in service environments was discussed by Rickett and Payer.[8] The electrochemical reactions that occur *during the electroplating of electronic components* were not addressed by these authors, however. The electrochemical reaction mechanisms that prevail during precleaning and plating processes, and their effect on subsequent steam aging performance, are discussed below. The scope of this paper is accordingly two-fold:

1. Study of the effect on the quality of electrodeposits of (a) chemical attack on the substrate and (b) organic contamination, in nickel plating solutions.
2. Discuss the corrosion phenomena during (a) nickel plating, (b) steamaging and (c) at the center of a drop of stagnant water, in the form of electrochemical models.[9]

These electrochemical models form the basis for controlling and maintaining the precleaning and the plating solutions, so that electronic devices of highest quality can be produced.

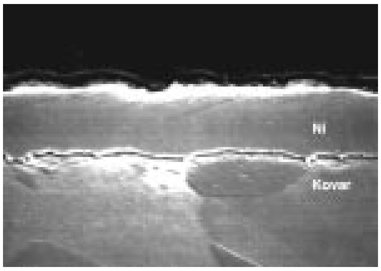

Fig. 1a—SEM cross section of nickel plated over a uniformly etched Kovar substrate. 2000X.

Effect of Chemical Attack on the Substrate in Precleaning

A controlled chemical reaction in a chemically balanced solution produces a smooth finish on a substrate. Figure 1a shows a cross section of Kovar (an alloy of Fe, Ni and Co) substrate that was uniformly etched in a balanced etching solution. This substrate surface was uniformly plated with nickel. An uncontrolled etching process, however, may leave grain boundaries in the Kovar substrate excessively attacked. This opens the possibility of incomplete substrate coverage and solution entrapment under the nickel deposit, as shown in Fig. 1b. Such entrapments can cause corrosion products during steam aging as depicted in Figs. 2a and 2b. Figure 2c shows an enlarged view of one such corrosion product.

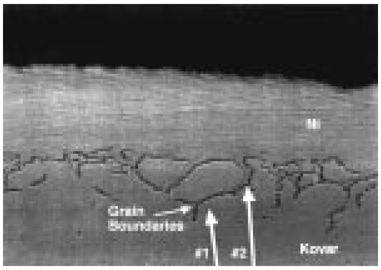

Fig. 1b—Optical cross section view of nickel plated over excessively etched Kovar substrate. 2500X.

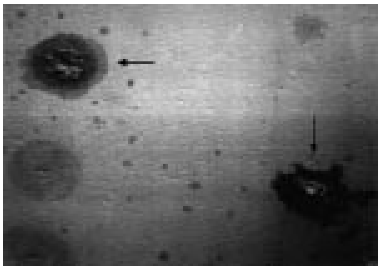

Fig. 2a—SEM photomicrograph of bleed-out (arrows) in Ni plate during post-plate baking and/or steam aging. 2000X.

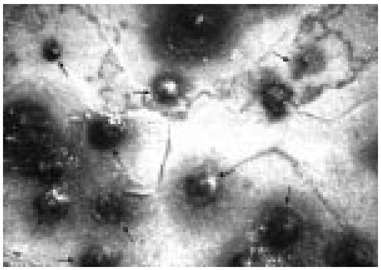

Fig. 2b—SEM photomicrograph of corrosion pits (arrows) developed in Ni plate during steam aging 2000X.

Effect of Organic Contamination in Nickel Plating Solutions

Sources of organic contamination in nickel plating solutions can be (a) external, resulting from carry-over of soils on poorly cleaned parts and surroundings, and (b) internal, because of introduction of inert products of carbonaceous materials. Organic contamination can cause skip plating (Figs. 3a and 3b) and cracked deposits (Fig. 3c). Other organic carbon-related defects can be poor adhesion, pitting, peeling and milky/hazy deposits.

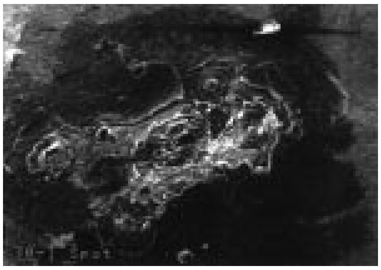

Fig. 2c—SEM photomicrograph of corrosion pit formed during steam aging. 5000X.

Fig. 3a—Dark area (arrows) where there is no Ni plate; an example of skip plating resulting from organic contamination either remaining over the substrate or present in Ni plating solution. 100X.

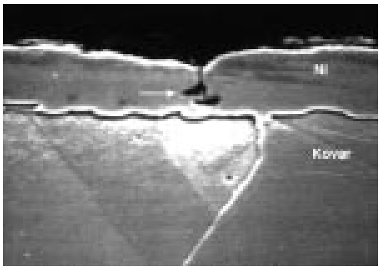

Fig. 3b—Optical photomicrograph of organic contamination (arrow) trapped in plated Ni. This area becomes a site for corrosion pit formation during steam aging. 1500X.

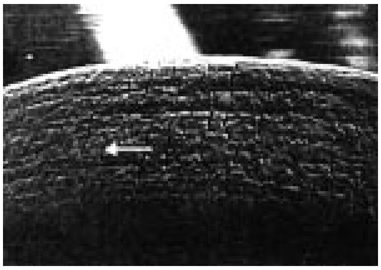

Fig. 3c—Cracks in Ni (arrow) in a Ni-plated lead terminal caused by bending. 100X.

Electrochemical Corrosion Phenomena

Electrochemical corrosion occurs in numerous ways and affects the quality of electrodeposits, such as preferential deposition of copper in substrate recesses and rusting during steam aging. These phenomena are explained in detail in the following paragraphs.

Dissimilar Metal Corrosion In Copper-Contaminated Nickel Solutions

Copper is known to plate out preferentially in recesses or low current density areas of ferrous substrates during nickel plating. Such copper deposits are non-adherent. Preferential deposition of copper on ferrous substrates in nickel solutions takes place as a result of differences in the electrochemical activity of Cu and Fe, shown as Model 1:

Model 1 - Dissimilar Metal Corrosion

Figure 4a shows iron (Fe) initially in touch with the copper-contaminated nickel sulfate or sulfamate plating solution. Figure 4b shows how a galvanic reaction starts. Iron gives up its reserve of two electrons to Cu^{+2} ions. Fe^{+2} ions enter the solution. Neutralized Cu atoms deposit at sites adjacent to the sites vacated by Fe atoms

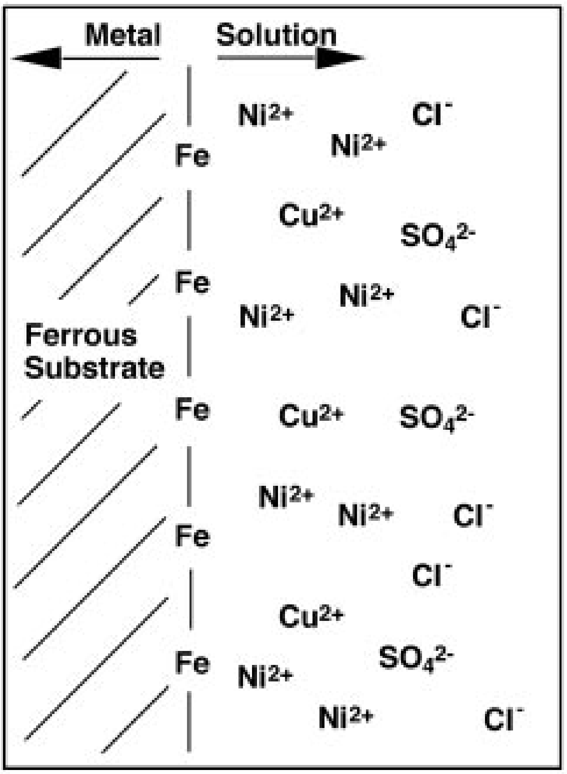

Fig. 4a—Iron in contact with plating solution containing Ni^{+2}, SO_4^{-2}, Cl^{-1}, and contaminant Cu^{+2} ions.

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Contamination with copper in nickel solutions leads to localized corrosion and the creation of sites with severe pits and voids. Other contaminants in nickel solutions, such as alumina, calcium and silica create rough nickel deposits, while Cr has a tendency to inhibit the deposition of nickel in low-current-density areas because of its oxidizing nature. Zinc, cadmium and lead as contaminants cause dark deposits in low-current-density areas.[10]

Electrochemical Corrosion During Steam Aging

Electrochemical corrosion during steam aging is presented as corrosion with oxygen absorption in the form of Model 2:

Model 2 - Corrosion Resulting From Oxygen Absorption, A Model for the Rusting Of Ni/Au-plated Ferrous Substrates

Rusting, or the presence of brown stains and spots, is often observed after steam aging, largely in recessed areas where there is either minimal or no nickel plate, including bare racking and wiring spots. Diffusion of iron can take place through thinner layers of nickel during baking at elevated temperatures.

To appreciate the importance of taking preventive steps, a mechanism that produces the rusty spots and stains is proposed. Shown in Fig. 5a is a model for the rusting of a ferrous substrate during steam aging. Rusting initiates at sites where the nickel deposit is minimal or absent. Iron forms electrochemical cells with the electroplated nickel in the presence of oxygen and moisture.

Electrochemically, iron is anodic to nickel. An electrochemical cell is formed in the presence of oxygen, moisture and trace amounts of ionic contaminants. Four iron atoms are shown (Fig. 5a) to lose two sets of electrons each

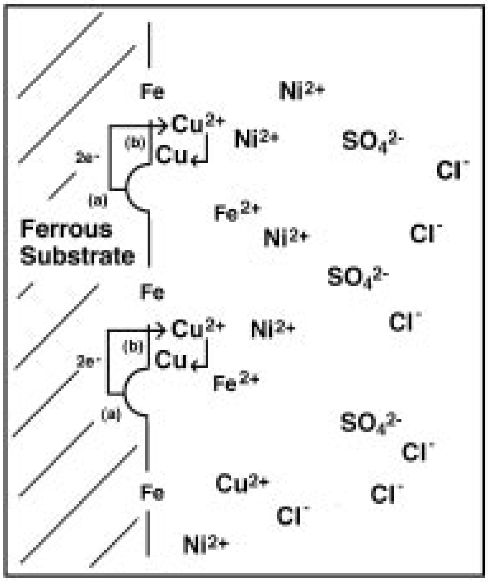

Fig. 4b—Iron ionizes (losing 2 electrons, site (a); a copper ion (Cu^{+2}) accepts 2 electrons and deposits at the adjacent site (b) in the substrate.

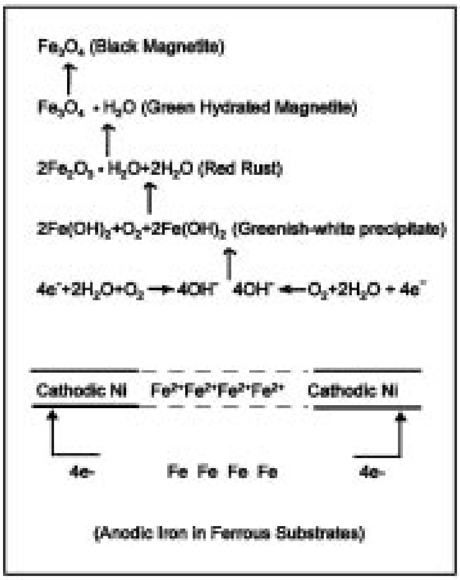

Fig. 5a—Corrosion caused by oxygen absorption—a model for the rusting of Ni- and Au-plated ferrous substrates during steam aging.

to the cathodic nickel (Ni) on either side (see lower section of Fig. 5a). Nickel acts as a vehicle for the transport of those electrons to moisture which converts to hydroxyl ions (OH^-) in the presence of atmospheric oxygen. Accordingly,

$$4Fe = 4Fe^{+2} + 8e^-$$
$$8e^- + 4H_2O + 2O_2 = 8OH^-$$

The hydroxyl ions react with ferrous ions to form intermediate white-greenish ferrous hydroxide precipitate, which further reacts with more oxygen to form monohydrated ferric oxide. This is also known as red rust, which is seen in recessed or poorly plated areas of steam-aged components. These latter reaction mechanisms are shown as follows:

$$4Fe^{+2} + 8OH^- = 4Fe(OH)_2$$

(intermediate white-green precipitate)
$2Fe(OH)_2 + O_2 + 2Fe(OH)_2 = 2H_2O + 2Fe_2O_3 \cdot H_2O$ (red rust)

Ferrous hydroxide may also be converted into green hydrated magnetite, $Fe_3O_4 \cdot H_2O$, which, on losing its water molecule, becomes black magnetite, Fe_3O_4. White-greenish and black corrosion products are also often observed in addition to red rust.

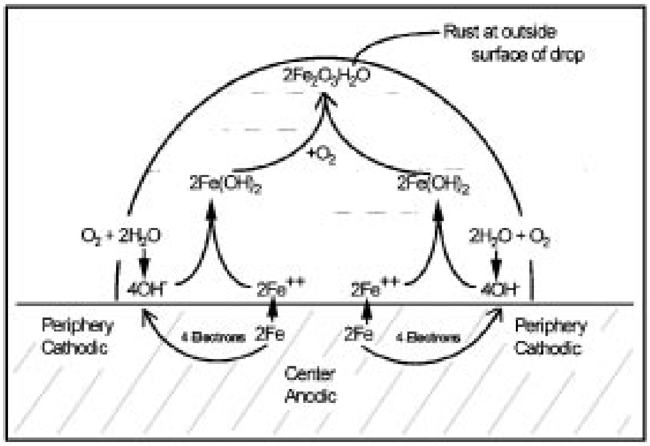

Fig. 5b—Corrosion caused by stagnant water between wet, flat, or cup-shaped ferrous substrates.

Electrochemical Corrosion From Trapped Stagnant Water

Corrosive liquids do not always pass or flow across the surfaces of the parts. Many electronic devices are such that they can hold condensed liquids in their recesses. Electrochemical corrosion resulting from trapped water is shown in the form of Model 3:

Model 3 - Corrosion Caused By Stagnant Water

A droplet of water is shown in Fig. 5b to be settled in a recessed area where nickel plating is missing or extremely thin. This droplet is surrounded by oxygen in the air. The iron under the water droplet becomes anodic and loses its electrons to the periphery of the water droplet, which becomes cathodic. Iron is converted into ferrous ions, which then react with water and oxygen, as explained earlier in Model 2 to form precipitates of ferrous and ferric hydroxides.

Conclusions

It may be concluded from the explanation above, that products of various colors and chemistries can form during plating and steam aging unless preplate cleaning, etching, activation and the plating operations are optimized. The electroplated metals become impermeable to oxygen and moisture penetration, and no bare spots, voids or contaminants remain on the plated surfaces.

Most common precleaning and plating related defects repeat themselves. Some defects are detected at post-plating inspection; others at the final inspection. Any defects that have made their way through these inspections end up being rejected by the customer.

Precleaning and plating practices are well established and can be custom tuned for specific products.[4,11-13] Attention to detail will ensure that components of acceptable quality will be produced.

Features described in texts on electrochemistry have been adapted to describe the electrochemical mechanisms that predominate in some plated hybrid electronic components. This is to provide a better understanding of the process for increased yield of the best products.

Editor's note: *This is an edited version of a paper presented at SUR/FIN® '95, Session I.*

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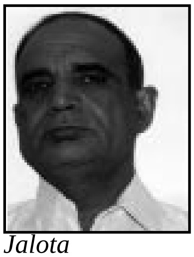
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Appendix

MIL Requirements for Hybrid Microcircuits
(MIL-H-38534B)

Package Body Materials	Lead Materials
Copper	Co-fired Metallization
Kovar	Kovar
Molybdenum	Nickel
Ceramics	Fe-Ni (59.0-41.0)
Cold-Rolled Steel	Fe-Ni (49.5-50.5)
	Copper (not for feed-through)
	Copper Core Fe-Ni Alloy

Plating Thickness

Strike Ni:	1.25 µm max.
Electro Ni:	1.25-8.75 µm
Electro Au:	1.25-5.60 µm

Post-plate Baking

Hours	Temperature
6 ±0.5	250 ±10 °C
22 ±1.0	200 ±8 °C
160 ±8.0	150 ±6 °C

Post-bake Steam Aging (MIL-STD-883D M.2003.7)

Hours	Temperature
8 ±1	92 ±4 °C

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