



98 (9), 18-27 (December 2011)

Gold-Iron High Speed Electrolytes: An Effective Alternative to Cobalt and Nickel Hard Gold Electrolytes

by

Olaf Kurtz,1* Jürgen Barthelmes,1 Robert Rüther,1 Florence Lagorce-Broc,1 Michael Danker,1 David Brookes2 and Kevin Martin3 1Atotech Deutschland GmbH 2Atotech UK 3Atotech USA, Inc.

ABSTRACT

The following article highlights the introduction of a gold-iron hard gold electrolyte as an anti-allergic alternative to replace cobaltand nickel-containing hard gold deposits.

Keywords: hard gold, gold-iron, nickel replacements,

Introduction

A previous paper on gold-cobalt electrolytes has outlined the ever increasing demands of functional coatings that include improvements to atmospheric corrosion resistance, thermal and electrical conductivity, whilst maintaining low coefficients of friction with minimal wear¹ High purity gold coatings (without trace levels of alloying elements) cannot meet the strict hardness and wear requirements of the connector industry. Small introduced controlled amounts of a transition metal (usually cobalt or nickel and occasionally iron) may dramatically improve the hardness and wear resistance of the gold deposit. Processes used for these electronic applications are typically acidic to mildly acidic.²⁻¹⁰

Alloy gold coatings containing cobalt and nickel, when in contact with skin, may also become dermatologically problematic. The EU Commission for the Classification and Designation of Hazardous Substances has also issued a directive for cobalt and its salts with nitrate, sulfate, carbonate and acetate now re-classified as dangerous to the environment and very toxic to water organisms. In addition, cobalt chloride, nitrate, acetate, sulfate and carbonate are classified in Categories 2 (carcinogenic and reprotoxic) and 3 (risk of irreversible mutagenic damages).¹¹ Nickel and its salts had previously been re-classified in a new directive issued at the end of 2008 (Fig. 1).¹² The EU Commission's directive has consequences not only for the handling but also storing and permissible storage volume of these substances. This paper highlights that gold-iron processes are an effective and efficient alternative to the well-established cobalt and nickel processes.

Nickel and boron compounds	will be classified as			
Nickel sulfate Nickel chloride Nickel carbonate Nickel nitrate Nickel fluoride Nickel bromide Nickel hydroxide	Carcinogenic Category 1 Chromic toxicant Dangerous to the environment Many, also mutagenic and reprotoxic			
TetraboratesBoric acid	Toxic Reprotoxic Categories 1, 2			

Figure 1 - The EU Commission's re-classification of nickel and boron compounds.

Corresponding author: Dr. Olaf Kurtz Product Manager worldwide GMF - FEC/PMP Atotech Deutschland GmbH Erasmusstr. 20 10553 Berlin, Germany E-mail: olaf.kurtz@atotech.com





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Gold-iron electrolytes

The rapid growth of the printed circuit board industry of the 1950s had a significant effect on the development of hard-gold processes. The objective was to find alternatives to the alkaline pure gold processes, which at high temperatures attacked resist materials and bonding agents and provided deposits with limited abrasion resistance.¹³ Rinker and Johns were the first to develop a cyanide-based gold electrolyte utilizing nickel, cobalt or indium as alloying metals.¹⁴ At that time, iron (belonging to the same subgroup as nickel and cobalt), was not taken into consideration because of possible concerns that co-deposits would result in brittleness issues.¹⁵ However, later intensive studies of gold-iron deposit characteristics have allayed these concerns. It is only appropriate therefore, that iron together with cobalt and nickel can fulfill industry MIL and ASTM standards.^{16,17}

The following investigation involves a mildly acidic gold-iron high speed electrolyte.** Table 1 summarizes typical parameter ranges.

Table 1 - Working parame	eters of the gold-iron process
Working parameters	Range
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working parameters	Runge	
рН	4.2 - 4.7	
Temperature	60°C (Range = 40-65°C)	
Gold concentration	2.0 - 20 g/L	
Iron concentration	0.05 g/L	
CD Range	2.5 - 100 A/dm ²	

Morphology studies with focused ion beam (FIB)/ scanning electron microscope (SEM)

The deposit morphology was studied using a focused ion beam (FIB) in conjunction with a scanning electron microscope (SEM). All FIB/SEM samples consisted of a stainless steel substrate coated with an initial 5 μ m nickel (from a sulfamate electrolyte) followed by 5 μ m of gold. This FIB/SEM technique requires a high thickness due to gallium ions bombarding the test sample, creating the necessary fine micro-cuts perpendicular to the surface (Fig. 2).



Figure 2 - A high resolution FIB+FE-SEM (FEI Nova Nanolab 600) and a schematic illustration of the procedure.

The following FIB/SEM images (Fig. 3) illustrate sections measuring 10, 4 and 1 µm. A current density of 30 A/dm² was used during gold-iron deposition. These images highlight the very low nano-porosity of the gold-iron deposits.

^{**}Aurocor® HSF, Atotech Deutschland GmbH, Berlin Germany (Atotech USA, Rock Hill, SC).





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Figure 3 - Nickel/ gold deposits on stainless steel: CD = 30 A/dm²; 5 µm nickel sulfamate, 5 µm gold-iron (Detail 10 (left), 4 (upper right) and 1 (lower right) µm).

Quartz crystal microbalance study of metal deposition characteristics

Deposition rate and coating information of gold-iron electrodeposits at varying current density may be obtained by means of a quartz crystal microbalance (QCM).¹⁸⁻²⁰ The QCM is a very sensitive analytical method that permits the *in situ* detection of interfacial processes, *e.g.*, weight gain by surface electrodeposition. The measurement principle is based on the change in the natural frequency of a quartz resonator that can be excited to a resonant oscillation by AC voltage (piezoelectricity).

In 1959, Sauerbrey was the first, to develop a method for correlating changes in the oscillation frequency Δf and the mass deposited on it Δm :¹⁸

$$\Delta f = \frac{2f_o^2 \cdot \Delta m}{(\rho_a \mu_q)^{\frac{1}{2}} \cdot A} \tag{1}$$

The equation defines f_0 as the frequency of the quartz resonator, ρ_q and μ_q are the density and shear modulus of the quartz, respectively, *A* is the area and Δm the adsorbed mass of substance under investigation.

Inserting the Sauerbrey constant S_f allows Equation 1 to be simplified to:

$$\Delta f = -\frac{S_f \cdot \Delta m}{A} \tag{2}$$

The proportionality factor S_f is a material-specific parameter and is also referred to as the "integral coating weighing sensitivity." The QCM is a very surface sensitive technique and so the detection limit for mass deposition lies on the order of a few nanograms.

In this study the dimensions of the quartz crystal used were 0.3 mm thickness, 14 mm diameter and a surface area of 0.5 cm². Figure 4 shows the details of the electrode set-up. The electrolyte is pumped at constant flow onto the oscillating quartz crystal (WE) via an injection tube.





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Figure 4 - QCM electrode set-up.

From the frequency / time diagrams measured using the quartz crystal microbalance, it is possible to determine deposition rates and current efficiencies. Figure 5 provides typical experimental data with respect to change in current density and frequency as function of time. The time resolution is 1 sec and the frequency drift < 1 Hz to 300 kHz.



Table 2 shows the parameters used for sample preparation.

Parameters	Value
pН	4.6
Temperature	60°C
Gold concentration	8.0 g/L
Iron concentration	0.05 g/L
CD Range	Variable (1.0 - 70 A/dm ²)

Table 2 - Experimental	parameters	for the	gold-iron	process stud	y.
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Figure 6 shows the current efficiency and deposition rate data as function of the current density from the gold-iron QCM experiments. At 5.0 A/dm², the current efficiency is 71% and progressively falls at increasing current density to 23% at CD = 70





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A/dm². At 1, 5 and 10 A/dm², the deposition rate values were 0.4, 2.4 and 4.3 µm/min, respectively. At 70 A/dm² and 8.0 g/L gold, a deposition rate of 10.7 µm/min was achieved.



Figure 6 - Current efficiencies (L, thick bars) and deposition rates (R, thin bars) at varying current densities for 8.0 g/L gold.

Investigations of deposition rates at high flow rate

Deposition rate data was measured using a high-speed plating cell at a fixed flow rate of 2200 L/hr (Fig. 7).



Figure 7 - Photo of the MiniLab plating cell used for deposition rate investigations.

The effect of temperature on the deposition rate was investigated and resulted in an expected speed increase at higher values (Fig. 8). The highest achievable rate of 17.2 μ m/min was observed at CD = 70A/dm², T = 65°C for 8.0 g/L Au content.





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Figure 8 - Deposition rates of the gold-iron process at varying temperature and current density using the high-speed MiniLab test cell.

A further investigation shows that at increased gold concentration (from 8 to 16 g/L), greater deposition rates are achievable (Fig. 9). Above 30 A/dm², the differences become very noticeable. For example, at CD = 50 A/dm² and T = 60°C, the deposition rate at 8.0 and 16 g/L are 13.6 (Fig. 8) and 19.6 (Fig. 9) μ m/min, respectively.



Figure 9 - Deposition rate vs. current density at 16 g/L gold, T = 60°C.

Contact resistance measurement

A detailed study on the effect of thermal aging on measured contact resistance was carried out. Testing was carried out with the contact resistance measuring device in accordance with the EN IEC 512 Standard²¹ (Measuring parameters: *I* = 10 mA, *U* = 20 mV, *F* = 5 cN). For each test sample, the mean from 30 individual measurements was taken. Gold thicknesses of 0.3 and 0.8 μ m were used over a 1.5- μ m nickel underlayer. Contact resistance measurements of "as-plated" deposits produced constant values of 2.5 – 3.0 m Ω over a current density range of 10 – 50 A/dm² (Fig. 10). Little influence noted at varying thickness. Even after artificial aging (16 hr at 260°C), constant contact resistance values below 5.0 m Ω were observed (Fig. 11). At increased temperature (300°C for 5 min) little change to contact resistance was observed (Fig. 12). Hence, over a wide 10 to 50A/dm² current density range, the Au/ Fe deposits provide consistently low contact resistance values, irrespective of aging conditions and thickness.





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Figure 10 - Stable contact resistance over a 10 to 50 A/dm² current density range for 0.3 and 0.8 µm Au/ Fe deposits.



Figure 11 - Contact resistance vs. current density after heat treatment (260°C / 16 hr) measured at 0.3 and 0.8 µm thickness.



Figure 12 - Contact resistance vs. current density after heat treatment (300°C / 5 min) measured at 0.3 and 0.8 µm thickness.





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Iron codeposition investigations

The weight percentage of alloying metal was measured using atomic absorption spectroscopy (AAS). Analyses show that the wt% of co-deposited iron decreases at increasing current density. Under optimum conditions, 0.28 wt% Fe was found to occur at $CD = 10 \text{ A/dm}^2$ decreasing to 0.14 wt% at $CD = 70 \text{ A/dm}^2$ (Fig. 13).



Figure 13 - Iron co-deposition vs. current density at 8.0 g/L Au, pH 4.6, T = 60°C.

Hardness evaluation of gold deposits

To measure hardness by the Martens' procedure, test samples were prepared comprised of 5 μ m each of bright nickel followed by the gold electrodeposit. Marten's hardness (HM) is defined as maximum bearing stress F_{max} divided by the contact area A_{s} :²²

$$HM = \frac{F_{max}}{A_s} \tag{3}$$

Martens' hardness values incorporate both plastic and elastic deformation forces and are applicable for all metals. This procedure is universally accepted and defined in both Berkovich and Vickers methods.²³ The Fisherscope H100C (Fig. 14) was used for the measurements. Hardness measurements at varying current densities were carried out using optimum process conditions to determine the effect of iron incorporation on micro-hardness. Figure 15 confirms a similar trend to wt% Fe co-deposition at varying current densities, peaking at low current density.



Figure 14 - Fisherscope H100C used to determine Marten's micro-hardness of gold electrodeposits.





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Summary

The investigations carried out outline the performance of the gold-iron process over a wide range of parameters (including gold content and flow rate) using both quartz microbalance technique and high-speed plating cells. The Au/ Fe process provides an effective and efficient alternative to the traditional gold-cobalt or gold-nickel systems and electrodeposits satisfy the internationally accepted MIL Spec G45-204, type II/ grade C specification.

FIB/SEM deposit examinations highlight low porosity and contact resistance measurements suggest excellent stability even after accelerated aging / heat treatment (to 300°C / 5 min).

Deposition rate studies using both quartz microbalance at varying electrolyte flow rate and also the MiniLab high-speed test cell demonstrate exceptionally high values over a wide current density range. Wt% iron co-deposition trends were found to be comparable to the Au/ Co system, *i.e.*, decreasing with increasing current density. The highest Marten's hardness value of 1844 was measured at 10A/dm² for a 0.28 wt% Fe co-deposit.

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About the lead author



Dr. Olaf Kurtz obtained his Ph.D. in Physical Chemistry, investigating the growth of rhodium on rhenium [0001] and graphite surfaces by means of ultrahigh vacuum test methods (with Profs. Christmann/Ertl, Nobel Prize winners in Chemistry 2007). He has been working with Atotech since 2000, assuming various positions such as R&D and product manager for microstructure technology developments. He is currently the worldwide product manager for Atotech's Functional Electronic Coatings (FEC) business unit.