

Materials Characterization of a Non-Cyanide Silver Electrodeposit

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This paper presents results of a CRADA (Cooperative Research and Development Agreement) between Technic, Inc., and the Lawrence Livermore National Laboratory, directed at developing a non-cyanide plating solution for deposition of thick ($>125\ \mu\text{m}$) deposits. Results were quite successful with a succinimide-based formulation. Data are included on grain size (transmission electron microscopy), hardness, electrical resistivity, ductility, stress and wear.

Lawrence Livermore National Laboratory (LLNL) and Technic, Inc. entered into a CRADA (Cooperative Research and Development Agreement) in March 1995 with the goal of providing industry with an environmentally benign alternative to the currently used silver cyanide plating process. In September 1995, Eaton Corp. joined the CRADA partnership. The goals of the CRADA included:

- Development of a non-cyanide silver plating solution capable of depositing thick ($\sim 125\ \mu\text{m}$) deposits.
- Measurement of the properties of deposits produced in this solution for comparison with deposits produced in silver cyanide solutions.
- Demonstration that the new formulation could be scaled up for production installations.

Results from this work have been quite promising. The main objective of developing a non-cyanide solution capable of producing deposits as thick as $125\ \mu\text{m}$ was met early in the project. Property data, such as hardness and stress, were obtained and the structure of the deposit was analyzed via metallography and X-ray diffraction. These results were presented at the 17th AESF/EPA Pollution Prevention & Control Conference in February 1996.¹ The purpose of this paper is to provide an update on recent efforts at analyzing properties of deposits produced in the non-cyanide solution.

Experimental Details

The non-cyanide plating solution used for this project is Cy-Less L Silver, a proprietary product of Technic, Inc. This is a succinimide-based formulation covered by earlier patents.^{2,3} Recommended operating conditions are listed in Table 1. Deposits produced in a variety of cyanide silver solutions were also evaluated for comparison purposes. A non-proprietary formulation contained 40 g/L silver cyanide, 12 g/L potassium cyanide, 15 g/L sodium carbonate and was operated at 20°C . Proprietary formulations included: Technic Matte, Technic SilverE (antimony additive), Technic Silversene K (organic additive) and Technic

Table 1
Operating Conditions for Technic
Cy-Less L Silver Plating Solution

Silver content	15-30 g/L
Free succinimide	15-150 g/L
pH	7.5-9.0
Temperature	10-38 $^\circ\text{C}$
Specific gravity	1.05-1.20
Current density	0.2-2.0 A/dm ²
Anodes	Pure silver or inert
Anode-to-cathode ratio	1:1 to about 5:1
Anode efficiency	70-90%
Cathode efficiency	85-98%

Silver E-2 (colloidal selenium additive). Data were obtained on grain size (by transmission electron microscopy) hardness, electrical resistivity, ductility, stress and wear. Some proprietary gold deposits were included in the wear test part of the program.

Transmission Electron Microscopy

Transmission electron microscopy (TEM) was used to measure grain size and inspect structure. Grain size of the non-cyanide deposits was very small, ranging from 450 to 670 Å, with the smaller grain size obtained at the lowest current density (Table 2). By contrast, grain size of cyanide silver deposits containing no additives was around 40,000 Å. By using the defocusing contrast technique of Nakahara and Okinaka,⁴ voids trapped within the deposit were noted. These voids were small ($\sim 35\text{-}38\ \text{\AA}$ in diameter) and quite numerous ($\sim 2\text{ to }4 \times 10^{16}$ voids/cm³). Figures 1a and 1b show a non-cyanide deposit with and without defocusing contrast. The structure and voids were similar in appearance for all non-cyanide deposits. No voids were noted with non-brightened cyanide silver deposits.

The observation of many small voids has been reported for

Table 2
Grain Size Data From Transmission Electron Microscopy

Sample	Current density (A/dm ²)	Grain size Å	Voids/cm ³	Avg. void dia. Å
Non-CN*	0.32	450	2.04×10^{16}	36.6
Non-CN*	0.54	680	2.65×10^{16}	38.3
Non-CN*	1.07	670	2.64×10^{16}	35.2
Cyanide**	0.54	$>40,000$	None	—
Cyanide**	1.07	40,000	None	—

* See Table 1 for operating conditions.

** The cyanide plating solution contained 40 g/L silver cyanide, 12 g/L potassium cyanide, 15 g/L sodium carbonate and no brighteners.

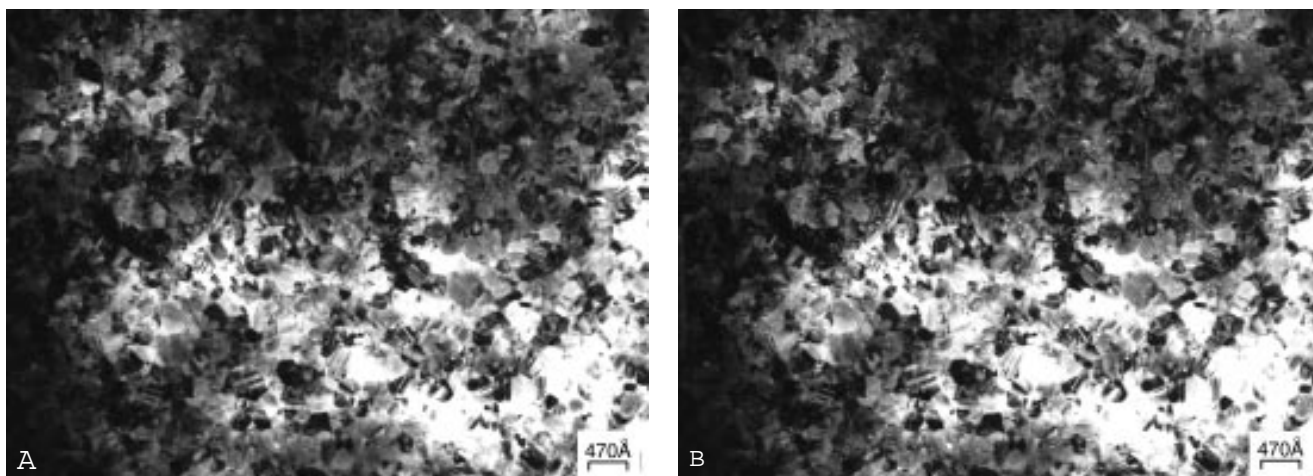


Fig. 1—TEM photos of non-cyanide silver plated at 0.32 A/dm²: (a) as deposited; (b) with defocusing contrast.

other deposits, including electrodeposited gold,⁴⁻⁹ evaporated gold,^{8,9} sputtered gold,^{8,9} electrodeposited nickel-phosphorus⁹ and electroless copper.^{4,9,10} As Nakahara has pointed out, voids are generally formed in thin films irrespective of the film preparation method (electrodeposition, evaporation or sputtering) as long as the deposition process involves a phase transformation from the vapor to the solid state.^{8,9} These voids can be extremely small (approximately 10 Å) and exhibit a density (about $1 \times 10^{17}/\text{cm}^3$).¹⁰ In the case of gold and electroless copper, outgassing data have shown that hydrogen is entrapped within the voids. Outgassing tests with our non-cyanide silver deposits revealed that hydrogen was entrapped in its pores.

Influence of voids on properties

The influence of small voids (less than 50 Å) on properties of thin films has not been well explored. Nakahara⁸ suggests that probable effects include a decrease in ductility, creep resistance, elastic modulus, adhesion, and corrosion resistance, and an increase in electrical resistivity and hydrogen embrittlement. Willcox and Cady⁷ noted an increase in hardness and stress in gold-0.4 percent nickel deposits that had a void density on the order of 10^{17} voids/cm³. As the result of the work reported in this paper, we report an increase in electrical resistivity, hardness, and stress, and improved wear resistance for non-cyanide deposits containing small voids.

Hardness

Joshi and Sanwald⁶ attributed a 54 kg/mm² hardness increase in gold deposits resulting from 10-Å voids with a density of $10^{17}/\text{cm}^3$. They calculated this hardness increase by using an equation developed for irradiated metals:¹¹

$$HV = 2C\mu b(Nd)^{1/2}$$

where HV is the hardness increase, C is a constant (~3), μ is the shear modulus, b is Burger's vector, N is the void density and d is the diameter of a typical void. Hardness of the non-cyanide deposits is around 135 kg/mm², compared to 55 kg/mm² for cyanide deposits from a solution with no additives. Use of the above equation for non-cyanide silver deposits (Burger's vector = 2.86×10^{-10} m and the shear modulus for silver = 2.64×10^4 MPa,¹² suggests that a 44 kg/mm² hardness increase can be attributed to the voids. This indicates that the small voids are responsible for about 50 percent of the hardness increase obtained with the non-cyanide deposits when compared with hardness of pure silver electrodeposits.

The remaining hardness increase is attributed to the reduced grain size and codeposited impurities. The Hall-Petch¹³ equation relates the grain size, d, with the hardness, H, of a metal:

$$H = H_0 + K_H d^{-1/2}$$

The terms H_0 and K_H are experimental constants and are different for each metal. H_0 is the value characteristic of dislocation blocking and is related to the friction stress. K_H takes account of the penetrability of the boundaries to moving dislocations and is related to the number of available slip systems.¹⁴ The equation has been found applicable to several polycrystalline materials,¹⁵ electrodeposited gold,⁷ iron,¹⁶ nickel,^{17,18} chromium,^{19,20} and copper,¹⁴ hot hollow-cathode-deposited chromium,¹⁹ vacuum-deposited Ni-20Cr,²¹ and sputtered

Table 3
Impurities in Silver Deposits

Deposit	Current density A/dm ²	Carbon ppm	Hydrogen ppm	Oxygen ppm	Nitrogen ppm
Non-CN	0.32	1060	80	1660	300
Non-CN	0.54	820	82	1220	190
Non-CN	1.07	560	50	810	130
Cyanide	0.54	60	8	40	<10
Cyanide	1.07	40	7	120	<10

- Hydrogen, oxygen, and nitrogen were determined by gas fusion; carbon was determined by combustion in oxygen.
- See Table 1 for operating conditions.
- The cyanide plating solution contained 40 g/L silver cyanide, 12 g/L potassium cyanide, 15 g/L sodium carbonate and no brighteners.

Table 4
Electrical Resistivity

Material	Electrical resistivity microhm-cm
Bulk silver	1.8
Cyanide Deposits	
No brighteners (0.54 A/dm ²)	2.1
No brighteners (1.08 A/dm ²)	2.5
Technic matte	2.7
Silver E (antimony)	3.2
Silversene K (organic)	3.0
Silver E-2 (colloidal selenium)	4.0
Non-cyanide Deposits	
Cy-Less L (0.32 A/dm ²)	4.2
Cy-Less L (0.54 A/dm ²)	4.3
Cy-Less L (1.08 A/dm ²)	3.4
L-2* (1.08 A/dm ²)	4.7
L-2* (1.08 A/dm ² (Heated 60 min @ 93 °C)	3.5

- All solutions except the cyanide with no brighteners are proprietary products of Technic, Inc.
- * Modified version of the Cy-Less L solution.

gold²² and copper.²³ Hardness values of 55 kg/mm² for a grain size of 4 μ m compared with 135 kg/mm² for 600-Å grain size deposits suggest that a similar dependency is operative for silver deposits. Willcox and Cady⁷ observed an increase in microhardness from 80 KHN₅₀ to 230 KHN₅₀ for electrodeposited gold-0.4 percent nickel, where the grain size of the former was two orders of magnitude smaller than that for pure gold. Coincidentally, the grain size of our non-cyanide silver deposits is about two orders of magnitude smaller than that of pure electrodeposited silver.

Another contributor to the high hardness of the non-cyanide deposits are codeposited impurities. Ashiru²⁴ postulated that high silver hardnesses for bright deposits were the result of a large amount of additive incorporated in the deposits. Others have reported an increase in hardness with carbon content for gold,²⁵ nickel,²⁶ nickel-cobalt²⁷ and tin-lead electrodeposits.²⁸ The non-cyanide deposits have a high concentration of impurities, particularly carbon and oxygen, compared to those produced in the cyanide solution containing no additives (Table 3).

Electrical Resistivity

Electrical resistivity was measured per ASTM B193 and ASTM B114. Testing was done at 22 °C at a relative humidity of 42 percent. Specimens (free-standing 75- μ m-thick deposits) were mechanically cut to form a flat zigzag band three mm wide and up to 65 cm long. A four-electrode Thomson-Kelvin bridge was used with silver-plated electrodes. Each value in Table 4 is an average from six runs of the test. Experimental error does not exceed five percent. The data show that the cyanide deposits without additives have the lowest values of resistivity (2.1-2.7 microhm-cm). Cyanide deposits with antimony (~0.1%) were 3.2 microhm-cm, while cyanide deposits with selenium (ppm range) were 4.0 microhm-cm. The non-cyanide deposits ranged from 3.4 to 4.7 microhm-cm. Annealing of one of the non-cyanide deposits for 60 min at 93 °C reduced the resistivity from 4.7 to 3.5 microhm-cm. Others have noted a marked decrease in elec-

Table 5
Stress in Deposits

Condition	Stress (MPa)
Silver cyanide	10
Non-cyanide silver (as-deposited)	165
Non-cyanide silver (aged)*	97
Non-cyanide silver (heated at 38 °C for 1 hr)	77
Non-cyanide silver (heated at 38 °C for 2 hr)	55

- Measured using a version of the rigid strip technique. All deposits were 12.5 μ m thick and plated at 54 A/m².
- * Electrolytically aged, 1.8 A/L.

trical resistivity of silver deposits as a result of annealing.^{6,29,30}

The reasons for the higher values for the non-cyanide deposits include: 1) the small voids discussed above, 2) codeposited impurities and 3) finer grain size. Joshi and Sanwald⁶ attributed a decrease in electrical resistivity for gold deposits that contained up to 10¹⁷/cm³ voids to the voids being annealed out as a function of temperature. We noted a similar occurrence with our non-cyanide deposits because of an improvement (decrease in resistivity) was obtained as a result of heating. Another contribution is the total impurity content. With copper, Safraneck³¹ reported a direct correlation between total impurity content and resistivity for deposits produced in cyanide, fluoborate and pyrophosphate solutions. Figure 2 shows a similar correlation for the non-cyanide and cyanide silver deposits (with no additives). Of the impurities, oxygen (50-53 percent) and carbon (34-38 percent) are the prominent impurity constituents in the non-cyanide deposits, and this will be discussed in more detail later. Finally, with respect to grain size and its influence on resistivity, with acid copper sulfate deposits, Lamb *et al.*³² noted an increase in resistivity as grain size decreased. This same trend was noted with our silver deposits. For example, non-cyanide deposits with resistivities in the range of 3.4-4.2 microhm-cm had grain sizes of 0.067-0.045 μ m while the cyanide deposits with resistivities of 2.1-2.5 microhm-cm exhibited grain sizes around 4 μ m.

Of additional interest is the fact that the cyanide deposits with no additives exhibited higher values than reported by

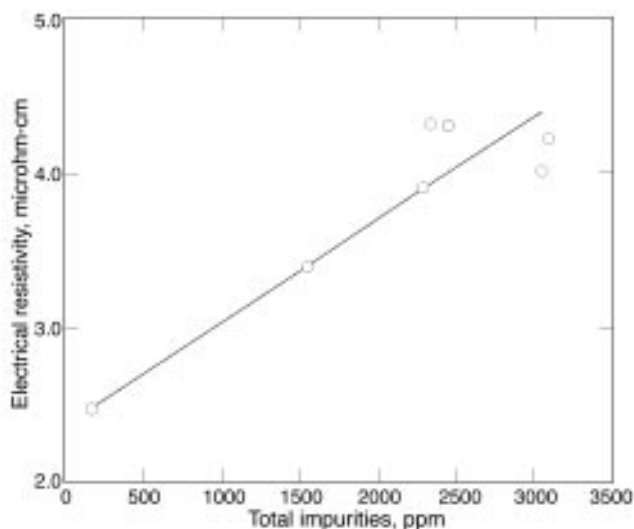


Fig. 2—Electrical resistivity of silver deposits as a function of impurity content.

others for cyanide containing solutions. For example, Balmer and Bailey³³ reported values of 1.69 to 1.85 microhm-cm for silver cyanide deposits used for electroformed wave guides. Although not mentioned, perhaps special care was taken to purify and maintain high cleanliness with these deposits because they were intended for wave guide applications. By contrast, no special care was taken with our silver cyanide plating solutions other than to circulate them through a carbon filtration unit for 24 hr prior to use.

Ductility

The zigzag strips used for electrical resistivity measurements provided a qualitative measure of ductility. In bending the 3-mm wide strips around a mandrel, ductility or lack thereof became quite evident, inasmuch as some were noticeably more brittle than others and would break. Figure 3 is a composite photograph showing some of the samples tested for resistivity. The cyanide deposits were clearly the most ductile and exhibited no sign of failure. Although only the cyanide deposits from the non-brightened solution are shown in Fig. 3, all cyanide deposits exhibited similar ductility. By contrast, all of the non-cyanide deposits exhibited

Table 6
Impurities in Deposits & Relative
Abundances (wt %) of Carbon, Hydrogen, Oxygen
& Nitrogen in Succinimide Compounds

Impurity	Non-cyanide Deposits*		
	0.32 A/m ²	0.54 A/m ²	1.07 A/m ²
Carbon	34.2	35.5	36.1
Hydrogen	7.5	3.6	3.2
Oxygen	53.6	52.8	52.3
Nitrogen	9.7	8.2	8.4

* Deposits plated at three different current densities were evaluated.

Succinimide Compounds

Succinimide	Succinamic Acid	Succinic Acid	(Mono)Ammonium Succinate	(Di)Ammonium Succinate
48.5	41.0	40.7	35.6	31.6
5.1	6.0	5.1	6.7	7.9
32.3	41.0	54.2	47.4	42.1
14.1	12.0	0	10.4	18.4

some degree of brittleness. Of these, deposits plated using direct current appear less brittle than those deposited with pulsed current techniques. Also, for the direct current deposits, ductility improved as a function of current density (*e.g.*, the deposit plated at 1.08 A/dm² appeared noticeably less brittle than that plated at 0.32 A/dm²).

Voids in the deposits and hydrogen are potential causes of the lower ductility of the non-cyanide deposits. Pre-existing voids, along with hydrogen, are responsible for reduced ductility of electroless copper deposits.^{34,35} Chromate coatings on copper³⁶ and gold⁷ and nickel-phosphorus films prepared by electrodeposition³⁷ also contain a high density of voids that contribute significantly to brittleness in these films.

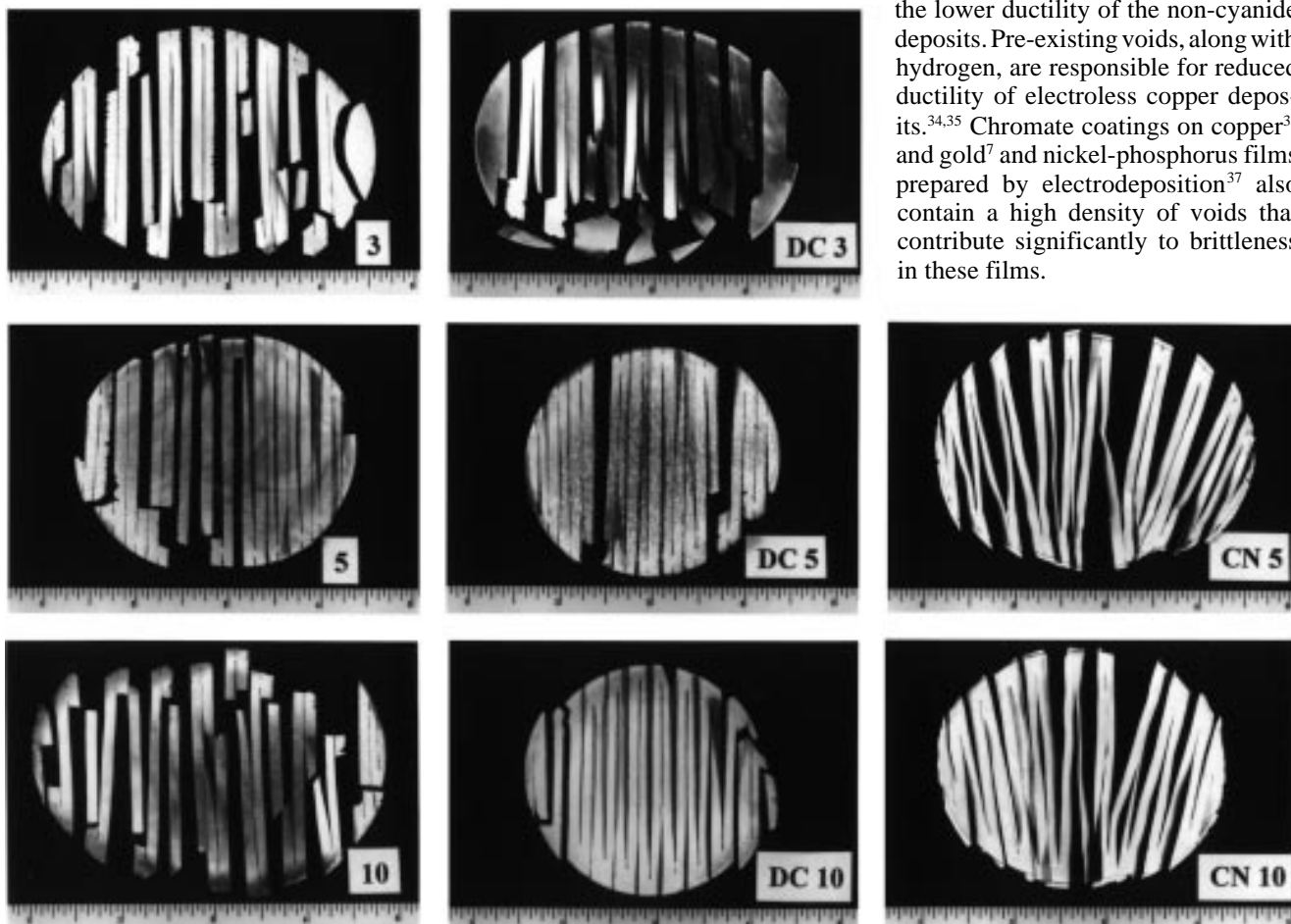


Fig. 3—Ductility of strips used for electrical resistivity measurements: photos 3, 5 and 10 show pulse current non-cyanide deposits plated at 0.32, 0.54 and 1.07 A/m²; photos DC 3, DC 5, and DC 10 show direct-current, non-cyanide deposits plated at 0.32, 0.54 and 1.07 A/m²; photos CN 5 and CN 10 show non-brightened cyanide deposits plated at 0.54 and 1.07 A/m².

Table 7
Falex ISC Pin-on-Disk Test Results for Non-Cyanide & Silver Cyanide Deposits*

	Non-cyanide	Non-cyanide	Cyanide E	Cyanide E-2	Silversene K	Silversene ST
Mass Loss(g)	0.0002	0.0002	0.0209	0.0105	0.0162	0.0161
Avg. scar width, disk (mm)	0.357	0.0363	0.337	0.334	0.315	0.415
Pin scar diameter (mm)	0.368	0.415	0.349	0.416	0.469	0.455
Disk Volume loss (mm ³)	0.0525	0.0592	0.0473	0.0461	0.0387	0.0884
Avg. friction co-efficient	0.76	0.84	0.6	0.7	0.76	0.76

*All solutions are proprietary products of Technic, Inc., Providence, R.I.

Stress

Stress was measured using a version of the rigid strip principle described in Ref. 38. With this technique, opposite sides of a two-legged strip are plated, and the resulting deposit causes the strip to spread apart. Deposit thickness for these tests was 12.5 μm . Data are summarized in Table 5. Stress for cyanide deposits was noticeably less than that for non-cyanide deposits. For example, cyanide deposits exhibited a tensile stress of 10 MPa compared to 165 MPa for non-cyanide deposits. Electrolytically aging the non-cyanide solution (1.9 A/L) reduced the stress to 97 MPa, and heat treating the deposits at 38 °C for two or three hr reduced the stress to 55 MPa.

Although various theories have been proposed to explain the origins of stress in electrodeposits, no overall theory that encompasses all situations has been formulated to date. Excellent review articles by Weil³⁹ suggest the following more prominent theories: Crystallite joining, incorporation of hydrogen, changes in foreign substances, excess energy and lattice defects. Based on data discussed earlier in this paper, three of the above can be linked to the stress in non-cyanide deposits—incorporation of hydrogen, lattice defects, and changes in foreign substances that accompany the impurities in the deposits, particularly the high amounts of carbon and oxygen. Still another factor is the small grain size. Others have noted a relationship between grain size and stress

for Ni⁴⁰ and Fe-Ni^{41,42} electrodeposits (*e.g.*, the smaller the grain size, the higher the level of stress generated). Clearly, this situation is a possible contributive factor with the non-cyanide deposits.

Codeposited Impurities

As mentioned above, oxygen and carbon are the major impurities in the deposited films. Observed impurities in the non-cyanide silver deposits at various current densities and also the relative abundances in several compounds related to or derived from succinimide are listed in Table 6. These data indicate that the relative atomic abundances are approximately constant with regard to current density, which suggests that the codeposited material may be a compound. Of the succinimide-related compounds, the closest material observed to the codeposited material is (mono) ammonium succinate.

Wear

Two types of wear tests (Taber and pin-on-disk) were used for evaluating deposits. Coating thickness for all tests was 25 μm and substrate material was copper. Coatings included in the tests were non-cyanide silver, unbrightened silver cyanide, proprietary silver cyanides and some proprietary Ni- and Co-hardened golds. The Taber tests were performed in accordance with ASTM D4060, using CS-17 wheels with

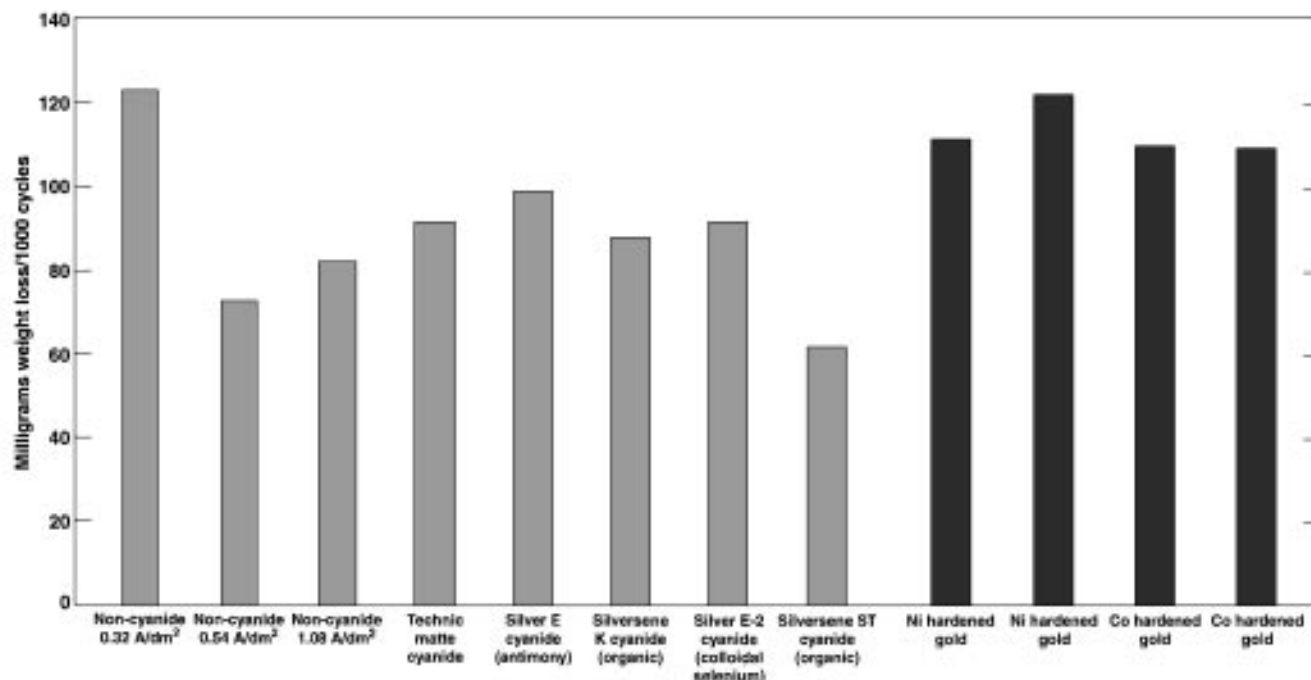


Fig. 4—Taber wear test results.

100-g loading at 70 rpm for 1000 cycles. Results of the Taber tests are included in Fig. 4. Aside from the non-cyanide deposit plated at 0.32 A/dm², all silver deposits performed better than the gold deposits. Non-cyanide deposits plated at 0.54 A/dm² and 1.08 A/dm² were among those exhibiting the least wear.

The pin-on-disk tests were performed in accordance with ASTM G99. The pin was a ball-type with a diameter of 1.27 cm, constructed of 52100 steel. Pin load was 300 g. Testing was done at a humidity level of 18 percent and temperature of 23 °C. No lubricant was used, linear speed was 15.5 cm/sec and test duration was 1 hr. Results of these tests, included in Table 7, show that the non-cyanide deposits exhibited less mass loss than any of the cyanide silver deposits. In addition, although not obvious from Table 7, the friction coefficients of the non-cyanide deposits were less erratic than those of the cyanide deposits.

Summary

A non-cyanide silver plating solution has been developed that is capable of producing sound, thick (>125 µm) deposits. Transmission electron microscopy was used to show that the deposit is extremely fine grained (~10 Å) with a high void density (about 10¹⁷/cm³). The deposit has a higher electrical resistivity than cyanide silver deposits, higher stress, and improved wear resistance.

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