Morphological and Hardness Properties of Bright and Leveled Silver Electrodeposit

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Relationships were established between the morphological and microhardness characteristics of silver electrodeposits. The silver deposits were produced from a low-cyanide silver-plating bath containing varied concentrations of appropriate leveling or brightening additives. Generally, an increase in the concentration of the additives was seen to decrease the grain sizes of the silver deposit. The broad trend was that bright deposits usually have fine grains, while the hardness of the deposits increases as the grain size decreases. There was no obvious correlation between the leveled silver deposits and the corresponding grain sizes or hardness values.

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Introduction

Traditionally, silver is widely used in industrial electroplating as a protective coating or an adornment for flatware, hollowware, jewellery, and art objects¹⁻ ³. Since the past half-century, engineering usage of silver electroplate has increased⁴⁻⁶. Some examples are for bearings, electrical and electronic circuit components, slip rings, wave-guides, and hot gas seals. The industrial applications of silver plating can be attributed to the unique properties of silver such as: high electrical conductivity and low-contact resistance, high thermal conductivity, chemical resistance, and lustrousness^{7,8}. Some of these properties are influenced by the morphological and hardness properties of silver deposit.

The modern industrial practice of the electrodeposition often requires plating solutions to produce deposits which are not only bright but which also level out surface irregularities that are present on the base metal. Silver plating baths that can produce bright deposits that do not necessarily have leveling ability are commonly available. It has been demonstrated that low 'free' cyanide silver plating bath produce leveling deposits which are also bright in appearance, when appropriate addition agents are added to the bath^{9,10}. The phenomenon of leveling may be simply defined as an electrodeposition process wherein more metal is deposited, per unit of time, in the recesses than on the high points of an irregular surface, the net result being a smoother surface⁹. There is great interest in understanding the phenomena by which many modern plating baths can simultaneously produce both bright and leveling deposits⁹⁻¹³. Efforts have been made to experimentally establish the characteristics of deposits to gain further understanding about the mechanism by which organic addition agents in plating solutions modify the deposition process as to produce leveling and/or brightened deposits¹⁴⁻²². These phenomena are important for industrial electroplating and often dictate bath formulation. The specific areas of major interest that are covered in this investigation involved the assessment of the grain size and hardness of a group of specimens plated with silver from low-cyanide electrolytes containing a variety of additives. This

investigation has been focused on providing a useful correlation between leveling, brightening, morphology and microhardness of silver deposits from the low-cyanide plating bath.

Experimental Work

Electroplating Solution

The test deposits were plated in low-cyanide silver plating bath containing organic addition-agents used in commercial electroplating. The organic addition agents that were employed in this study produced silver deposits, with various properties which include brightening and leveling. The results obtained and the conclusions drawn from this work are based on some 400 samples plated during the course of this investigation. The plating solutions were prepared from analytical grade reagents. The main composition of the cyanide bath that was used for this study is as follows:

33.5 gm/litre silver cyanide30 gm/litre potassium cyanide38 gm/litre potassium carbonatepH 11.2 - 11.7

The additives used for the different tests and their respective concentrations are as given in Table 1.

Electrodes

The anodes were strips of well annealed, rolled silver with purity greater than 99.97 percent and were usually of such sizes as to afford surface areas at least comparable in dimension to the cathode. Prior to electroplating, the anode strips were etched in 5 percent nitric acid and then washed in distilled water.

The cathodes were rectangular pieces of rolled copper sheet with 99.99 % purity (buffed by emery paper for certain leveling assessment) and of dimensions usually 1.5 cm by 2 cm. They were degreased with trichloroethylene, and then cleaned ultrasonically in a dilute solution of a commercial cleaner. The copper cathodes were subsequently etched by a dip into a dilute mixture of 10 and 12 percent sulfuric and nitric acids respectively.

Plating Procedure

The electroplating tasks were performed in agitated baths at room temperature and current densities, as outlined in Table 1. The plating cells were supported in a constant temperature water bath. The plating current was supplied from a DC power source with 60 amperes maximum current rating.

The plating current was pre-set by shorting out the cell. The cleaned cathode was connected to the circuit outside the plating bath. The current was then switched on so that electroplating proceeded at the instant of cathode immersion into the electrolyte.

The plating time was predetermined for each experiment to give the thickness of the deposit required, usually between 20 and 60 microns (depending on the test to be carried out after plating).

At the end of each electrodeposition, the current was switched off, the cathode was removed from the cell and thoroughly washed, first with distilled water, then methanol, and finally dried in hot air.

Microstructural and Hardness Evaluation

The samples used for the cross-sectional microstructural evaluation consist of 50 microns thick silver electrodeposits plated on the copper cathode. Two small pieces about 1 cm² were cut from the middle of each piece, marked to indicate their orientation in the panel. They were subsequently plated heavily with copper backing to protect their edges during metallograhic preparation. The specimens were then mounted in bakelite in such a manner that one piece represented a vertical and the other a horizontal cross section of the silver deposit, with respect to the position of the panel in the plating solution. No appreciable difference in appearance of the two pieces was ever observed. The specimens were mechanically polished and then etched electrochemically in 5 percent potassium cyanide solution using 1.5 volt polarization for 15 seconds. Chemical etchants were tried, but they did not give satisfactory results. After electrolytic etching, the microstructure of the silver deposit from the samples was examined using a Scanning Electron Microscope (SEM). The morphological characteristics of the as-plated surface of the silver deposits were also examined in the SEM.

Hardness measurements were made on the electroplated silver specimens by the Leitz Miniload Hardness Tester. This was placed on a heavy wooden bench with a rubber mat to reduce vibrations. The unpolished surfaces of the deposits were first examined, but because the electrodeposit was thin compared to depth of the indent, the combined hardness of the specimen and the substrate resulted (i.e. 'anvil' effect). Therefore, subsequent measurements were made on the well-polished cross-sectioned samples.

It had been expected that a hardness profile of the deposit could best be obtained using a Knoop indenter but because of the softness of many of the deposits and consequently large indent size, a sideways 'anvil' effect was produced. Therefore, the measurements processed were those taken with the Vickers indenter, with a 25g load. The applied load produced pyramidal indents whose diagonals were always less than twice the distance to either edge of the cross-sectioned silver deposits.

The lengths of the two diagonals of the indents were measured using the instrument's eyepiece and averaged. From these average diagonal lengths, the hardness values were obtained by using tables provided by the manufacturer of the instrument, for the particular load and indenter. The hardness numbers were calculated from an average of six or seven readings on each specimen, and the individual readings were reproducible within a reasonable range. The limit for the poorest agreement was defined by values representing a deviation of ± 7 percent of the average value. In most cases, ± 2.5 percent deviation encompassed the range of the readings.

 Table 1

 Addition Agents, Sample Classification, and Plating Current Densities of Silver Deposits

Addition Agent	Sample #	Conc. (Molar)	CD (mA/cm ²)
NONE	NA	-	5.0
2-Butyne-1, 4-Diol	A1	4 x 10 ⁻⁵	5.0
	[A2]	10-3	5.0
	[A3]	5 x 10 ⁻³	5.5
Hexyl Alcohol	[B1]	6 x 10 ⁻³	4.5
	[B2]	10 ⁻²	6.0
Hexamine	[C1]	3 x 10 ⁻⁴	5.0
	[C2]	8 x 10 ⁻⁴	5.0
	C3	3 x 10 ⁻⁴	8.0
	C4	3 x 10 ⁻⁴	9.0
Propargyl Alcohol	D1	10 ⁻⁴	5.5
	[D2]	10 ⁻³	6.0
	[D3]	10 ⁻²	6.0
2,5-Dimethyl -	[E1]	10 ⁻³	6.0
2.5-Hexanediol	E2	10 ⁻²	6.0
Thallium Sulfate	[F1]	10 ⁻²	4.6
Thiosemicarbazide	G1	5 x 10 ⁻³	8.0
	G2	10-2	8.2
Diethyl Dithiocarbamate Sodium Salt	H1	5 x 10 ⁻³	7.0
	H2	10 ⁻²	7.0
Thiourea	[K1]	3 x 10 ⁻⁵	5.0
	K2	5 x 10 ⁻⁴	5.0
	K3	10 ⁻²	5.0
Thioacetamide	L1	10 ⁻⁵	4.1
	[L2]	10 ⁻⁴	4.0
	L3	10 ⁻³	4.2
Sodium Thiosulfate	[M1]	10 ⁻⁴	4.7
	M2	5 x 10 ⁻⁴	4.8
	M3	10 ⁻³	5.0
4:4 Tetramethyl Diaminothiobenzophenone	[N1]	5 x10 ⁻⁴	3.0
	[N2]	8 x 10 ⁻³	3.0
	N3	10 ⁻²	5.0
Diethyl Ammonium- Diethyl Dithiocarbamate	[P1]	7 x 10 ⁻⁶	5.0
	P2	10 ⁻³	4.5
	P3	10 ⁻²	4.5

* Specimens in square brackets are leveled

Table 2Grain size distribution, ranges from I to V(Group 1 being the coarsest while Group V is the finest)

Group No.	Average Grains Diameter	Specimen Nos.	
Ι	Bigger than 7µ	NA, A1, [A2], [C1], [C2]	
П	4 to бµ	[A3], [B1], [B2], C3, C4, [F1]	
ш	3µ	D1, L1, [L2], [M1]	
IV	1.5µ	[E1], G1, H1, [K1], M2	
V	Less than 1µ	[D2], [D3], E2, G2, H2, K2, K3, L3, M3	

Results and Discussion

Morphology

Most of the etched cross-section specimens gave columnar, fibrous, or banded microstructures that did not allow the use of a single linear dimension to define the respective grain sizes. The cross-sectional microstructure of the silver deposits from the cyanide bath containing no addition agent (sample NA) is columnar (Figure 1). The corresponding surface morphology of the as-plated sample NA is shown in Figure 2.



Figure 1 - Columnar structure observed in etched cross-section of silver deposit from the cyanide bath in the absence of additive (specimen NA).



Figure 2 - Surface morphology of the asplated silver deposit from the cyanide bath in the absence of additive (specimen NA).



Figure 3 - Surface morphology of the as-plated silver deposit from the cyanide bath in the presence of variety of additives.

- (a.) [Cl], typical of grain size Group I.
- (b.) C3, typical of grain size Group II.
- (c.) D1, typical of grain size Group III.
- (d.) [El], typical of grain size Group IV.
- 5 **K3, typical of grain size Group V.**

Examination of the as-plated samples revealed microstructures, which by simple measurements and visual observation could be classified into fivegrain size groups. In all the micrographs examined, each member of a group was distinctly different from the members of other groups in size.

It was found that five groups were adequate to encompass all the specimens studied in this investigation, and there was no problem in deciding in which group to place any specimen. A classification of all specimens is given in Table 2. In addition, the micrographs of typical specimens from each group are shown in Figure 3. The specimens displayed were [C1], C3, D1, [E1], and K3. It is important to note that Figures 2 and 3a are specimens NA and [C1] respectively, they both belong to Group 1, and it can be seen that they have comparable grain sizes.

The relationship between grain size and brightness is illustrated in Figure 4, the panels can be identified by Table 1, and the samples that are labelled in square brackets are leveled. It is quite obvious that there is a general trend indicating that the grain size decreases with increasing brightness, apart from the hexamine specimens. There is, however, a scatter because the members of a given brightness class span two or more grain-size groups, and a given grain-size group may span progressively from one, two, or three brightness classes. However, group III encompasses only single brightness class i.e. semi-bright deposits that consist of collections of both leveled and unleveled deposits. As seen in Figure 4, eleven out of the seventeen fully bright deposits belong to grain-size group V, indicating that fine grained deposits are usually bright.

Hexamine specimens (C3 and C4) with big grain sizes gave fully bright deposits. This suggests that although bright deposits are usually fine grained, this condition is neither necessary nor sufficient for brightness. a sub-micron scale observation of the surface topography of all panels at much higher magnifications (> x 10,000) revealed a more general relationship for brightness. On the basis of shallow length and distribution of the grains, all bright specimens have surface microstructures which were much flatter and smoother than the dull specimens on the sub-micron scale. All the bright panels also have grains that showed no deep grain boundaries or protrusions, which extended more than 0.4 (m from the surface plane.

The deposition of bright silver deposits can be described as another form of leveling on the submicron scale, where the scratches to be leveled are of the order of the wavelength of light. This is supported by the fact that the brighteners in Group 6, e.g. thioacetamide are capable of exhibiting weak leveling effects on small scratches, when their concentrations are very low^{9,23}. The leveled deposits so produced were observed to have coarser grains than the brightened deposits at higher concentrations e.g. [L2] and L3 deposits.

Typical bright silver deposits that are fine grained and with no leveling effects are shown in Figures 5, 6, and 7; all these micrographs reveal the peaks and valleys induced by the scratches of the roughened substrates. A leveled deposit with coarser grain size, group III, can be seen in Figure 8. An unleveled deposit with grain size that is equivalent to Group III is shown in Figure 9, the substrate's scratches were revealed. The initial and final stages of leveling action by impacted by propargyl alcohol capable is illustrated in Figure 10. The deposit is fine grained and simultaneous leveled and brightened. These observations point to the fact that there is no well-defined relationship between grain size and leveling power. Also, as seen in Figure 4, samples of leveled deposit may be found amongst all the grain size groups. Thus, leveled deposits may be coarse (Figure 8) or fine grained (Figure 10b). However, in most cases, leveling agents have grain size inhibiting effects, but this was in most cases less pronounced than the brighteners.

Increase in concentration of the electroplating additives was seen in most cases to decrease the grain size of the deposit, e.g. panels [L2] and L3; also panels [M1], M2 and M3 (Tables 1 and 2).

Increase in current density has the effect of decreasing grain size and in some cases also inducing brightness in the sample.



Figure 4 - Relationship between grain size and brightness of the silver cyanide electrodeposit. Results are also in correlation with leveling. (Specimens in square brackets are leveled).



Figure 5 - SEM micrograph of silver deposit plated on grooved cathodes at room temperature and with agitation from the cyanide bath containing 5x10⁻⁴M Diethyl ammonium-diethyl dithiocarbamate, 6 mA/cm². Specimen is nonleveled, fine grained, and bright.



Figure 6 - SEM micrograph of silver deposit plated on grooved cathodes at room temperature and with agitation from the cyanide bath containing 8x10⁻²M Thiosemicarbazide, 8mA/ cm². Specimen is non-leveled, fine grained, and bright.



Figure 7 - SEM micrograph of silver deposit plated on grooved cathodes at room temperature and with agitation from the cyanide bath containing 7x10⁻⁴M Sodium thiosulfate, 5 mA/ cm². Specimen is non-leveled, fine grained, and bright.



←10µ→

Figure 8 - SEM Micrograph of silver deposit plated from cyanide bath containing 10⁻⁴M thioacetamide, 4 mA/cm², on grooved cathodes at room temperature and with agitation. The deposit is leveled and semi-bright.



 $\leftarrow 10\mu \rightarrow$

Figure 9 - SEM Micrograph of silver deposit plated from cyanide bath containing 10⁻⁵M thioacetamide, 4 mA/cm², on grooved cathodes at room temperature and with agitation. The deposit is non-leveled and dull.



Figure 10 - SEM micrograph illustrating the leveling process of bright, fine grain, silver deposit from the cyanide bath containing 5x10⁻³ M propargyl alcohol at 5.5 mA/cm², room temperature and with agitation (a) after 5 minutes of plating and (b) after 20 minutes of plating.

Microhardness

The hardness results covered a range from 60 to 190 VHN. These in fact are the characteristic hardness values expected from silver electrodeposits in most typical applications^{7,8,18}. Figure 11 compares the Vickers hardness values with brightness for all specimens, there is a general correlation, and Figures 4 and 11 are, to a certain extent, quite similar. Figure 12 was prepared to examine more closely this similarity. It is clearly shown that the microhardness increases as the grain size decreases. This is expected as a standard metallurgical behavior. But in the silver plated specimens where the variety of co-deposition possibilities arising from the use of numerous addition agents might be expected to affect the hardness, it does appear somewhat encouraging that there is such a definite trend.

It was also noticed from Figures 11 and 12 that, no dull or coarse grained (Group I) deposits have a hardness value greater than 100 VHN. There also seems to be a justification on the basis of Figure 11, for the frequent assertions that bright deposits are more likely to be harder than dull deposits.

The hardness values were plotted against concentration of the organic materials in the solution (Figure 13). The diagram shows that the hardness increases as the concentration of addition agent is increased. A study of the effect of current density on hardness - for a given concentration of additive in the plating bath - did not show any convincing trend. But in a few cases, the increase in current density yielded harder deposits provided the grain size was also reduced with the current density increase. Hardness has no correlation with leveling. A close look at Figure 11 and 12 will show that leveled deposits occupy positions at 25 VHN intervals from 50 VHN to 175 VHN. Thus leveled deposit may be "hard" or "soft"; depending on additive and operating conditions.

Conclusions

There does exist a broad trend which indicates that a decreases in the grain size of silver deposit leads to increase in brightness and increase in hardness features. There is no obvious correlation between the leveled silver deposits and their grain sizes or hardness.



Figure 11 - Relationship between hardness and brightness properties of leveled and unleveled silver electrodeposits.



Figure 12 - Relationship between microhardness and grain sizes of silver electrodeposits.



Figure 13 - Effect of the concentration of additives on microhardness of electrodeposited silver from cyanide bath at constant current densities

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