Velour Electroplates of Copper & Nickel

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Using optical methods, it was determined that the nature of velour copper is mostly conditioned not by the crystallite sizes, but by the characteristics of their shapes. Nickel coatings plated onto a velour copper base are harder and have lower internal stresses in comparison with convenient nickel coatings.

There are two kinds of decorative copper and nickel electroplates: bright and velour. Velour coatings are those that produce the effect of colors. One of the most common and inexpensive ways to get velour nickel is an epitaxial growth on a velour copper electroplate.[1,2] Investigations of the nature of velour copper and nickel were initiated much later (about 1971) than those of bright coatings; therefore, the mechanism of formation of such coatings is not fully understood. It is obvious that the properties of such coatings are conditioned by peculiarities of the cathodic process, such as the accelerating effect of some additives, as well as increased penetration of sulfur compounds into the coating. The accelerating effect is still poorly studied. It has been noticed that these additives interact with Cu ions,[3-7] forming electrochemically active complexes or ox/red cycles,[7] covering only a part of the cathode surface.[8] It was thought important to investigate the influence of Cu velour coatings on the formation and physical/mechanical properties of a top Ni velour layer.

Experimental Procedure

Copper was plated from an electrolyte containing: $CuSO_4 \cdot 5H_2O$, 180 g/L, H_2SO_4, 120 g/L and additives inducing the velour effect: ethylene glycol, sodium 2-ethyl hexanol sulfate and NJA-1. Velour nickel was plated from an electrolyte containing: $NiSO_4 \cdot 7H_2O$, 180 g/L; NaCl, 50 g/L; H_3BO_3, 30 g/L and additives according to Bodnevas et al.[9] Temp = 50 °C. The sulfur content at two µm depth was determined using an X-ray electronic microanalyzer.

Optical properties of the coatings were investigated using a double-beam spectrometer by recording the dependence of reflected diffusion mirror light on the wavelength of the tested sample.

The study of overpotential induced by the additives was carried out using chronovoltammetric procedure at 20 °C. The sweep rate was 0.1 V/sec. The cathode potential was measured against a saturated silver chloride electrode, and the values were recalculated on the hydrogen scale.

The transition time (τ) was determined using Kuvan's procedure.[6] The velour effect was determined: (1) visually by comparison with the samples to be qualified as good velour coating - g, normal - n, and slight - s, and (2) by the ratio of the reflection coefficient R and wavelength (τ) in the infrared area.[10]

The leveling effect was measured by profilograph and the deposit hardness, expressed as Vickers, was determined with a microhardness tester and indentation measurement on the surface of a 10-µm thickness of the coating, using the following formula: $H = 1.854\ p/d^2$, where p = 20 g indenter weight and d = the length in µm of the diagonal of the indentation. Internal stresses were measured using the cathode bending method and the brightness by a glossmeter, assuming the light reflection from a silver mirror to be 100 percent. The sizes of cyystallites were determined from photographs obtained using an electron microscope (5000 to 10,000X).

Results & Discussion

The velour effect on copper electroplates has been evaluated by optical measurements of the mirror part of diffusion reflection in the infrared 2.5 to 25.0 µm wavelength (Fig. 1). At longer wavelength (τ = 4.5 µm), the reflection coefficient R rapidly transforms from diffusion part to mirror part. Using the change of the angle (R/τ), it is possible to calculate the size of copper crystallites and their identity. The more the crystallites are identical, the more abrupt is the transition from diffusion reflection to the mirror function and the angle is bigger and vice-versa. When smaller crystallites are present at the coated surface, the R transforms from the diffusion part to a mirror part at shorter wavelength (Fig. 1, Curve 1) and, with increase in the crystallite size (Fig. 1, Curve 2), the transition occurs at longer wavelengths. Comparing these curves with the standard lattice having 10-µm crystallite size, it becomes clear that the velour effect of copper coatings is mostly conditioned not by their size, as has been believed, but by the identity of the crystallites. Based on these experiments, it is possible to evaluate the crystallite sizes of a copper coating and their identity and, as a result, it is possible to choose the optimal technological conditions to form velour coatings.

By comparing electronic photographs and profilometric curves, it was established that simple crystallites are not present in the velour coatings, but those with peaks in the shape of steps forming laminar crystallite twins. In addition,

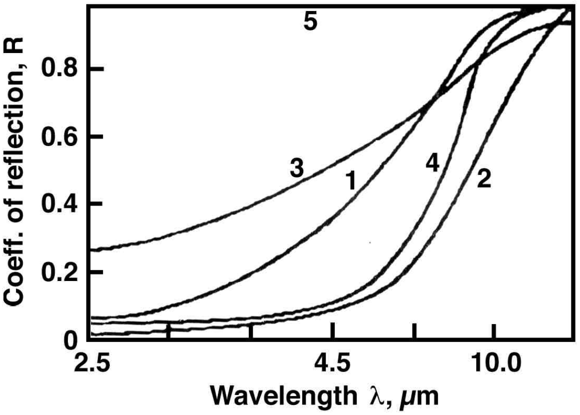

Fig. 1—Dependence of coefficient of reflection (R) on wavelength (τ) in the infrared range, 2.5 to 25 µm: (1) Velour copper coating with crystallite dimension of 10 µm; (2) Same, but crystallite dimension 16 µm; (3) Weak velour copper coating; (4) Aluminum coating—lattice crystallite constant of 10 µm; (5) Bright copper coating.

the velour effect depends also on the crystallite shape. The velour effect is most prominent when the steps and total crystallite area ratio is in the range of 3.5 to 4.0.[11]

Formation of such copper crystallites can be conditioned by the distribution of sulfur on the cathode surface, which depends on the degree of adsorption on different crystallite shapes of compounds containing sulfur. It has been determined that up to ~0.06 percent of sulfur is accumulated on the cathode during velour copper coating, this being almost twice as much as usual coatings.

In addition, there are more sulfur compounds at the cathode bulges than in hollows, and this sulfur relationship is very much dependent on the current density, which is in the range of 1.2 to 2.6 A/dm². It has been determined that sulfur-containing compounds used in electrolytes to electroplate copper cover up to 40 percent of the cathode surface.[8]

Active and passive cathode areas were calculated using the Matsuda model and some other methods.[12-15] It has been found that passive areas in the formation of copper velour coatings are three times as large as active areas[3,8,15] and are about 21-26 µm in diameter.

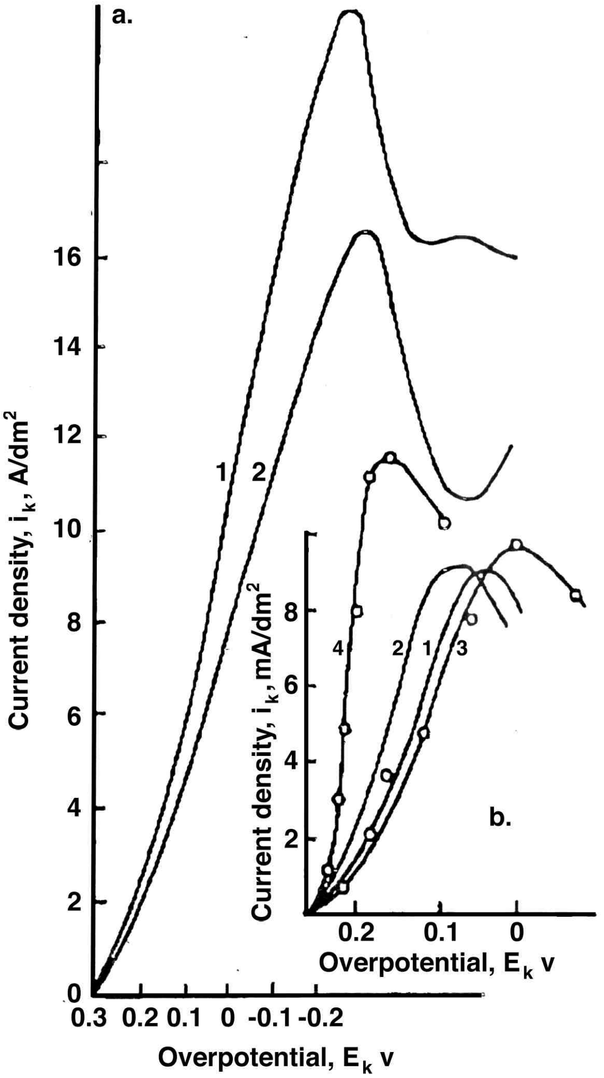

Fig. 2—Current density/overpotential curves:
(a) 1. Without additives; 2. 0.5 mL/L ethylene glycol, 0.06 mL/L NJA-1, 0.03 g/L NaCl.
(b) 1. 7.5 g/L $CuSO_4 \cdot 5H_2O$, 42.2 g/L H_2SO_4; 2. 7.5 g/L $CuSO_4 \cdot 5H_2O$, 42.2 g/L H_2SO_4 and 0.8 mmol 2- sodium ethylenehexanol sulfate; 3. Theoretical curve calculated for two-step process, where $\alpha n_\alpha = 0.53$, $D = 6.1 \times 10^{-6}$ cm/sec and $K_s = 1.9 \times 10^{-4}$ cm/sec; electrolyte as in Curve 1; 4. Theoretical curve calculated for one-step process, where $K_s = 7 \times 10^{-7}$ cm/sec; electrolyte as in Curve 1.

Physical/Chemical Properties of Normal (no additives) & Velour Copper & Nickel Electroplates

H—hardness, kg/mm²; V—internal stress, kg/cm²; B—brightness, %; D—crystallite size, µm; i_k—current density, A/dm²; E—velour effect

Copper Coating

NS	i_k	H	V	B	D	E
1	2	90	290	4	4	—
2*	2	127	120	3	7	g
3	4	100	396	6	3	—
4*	4	120	180	3	4	g
5*	2	116	170	4	4	s

Nickel Coating

NS	i_k	H	V	B	D	E
1	2	218	348	1.0	5	—
2*	2	320	315	3.0		3
3	4	248	570	1.5	5	—
4*	4	325	473	3.5	7	g
5*	2	298	320	2.0	8	s

*velour coatings

Another indication of the dimensions of the active surface of the cathode area under the influence of the additives is the increase of the overpotential of 20 mV in the low-current-density area (1-2 A/dm²) before the diffusion potential appears (Fig. 2a, Curves 1 and 2).

Theoretical polarization curves (Fig. 2b, curves 3 and 4) were calculated from chronovoltammetric curves by the equation below,[11] assuming that the process is irreversible and consists of two steps and one step accordingly:

$$i_k = nFAc\sqrt{DB\pi}\ x\ (bt),\ \text{where}$$

N = the quantity of electrons involved in the reaction
A = cathode surface area
c = Cu^{+2} concentration
D = Diffusion Coefficient
B = αn_α, $\nu F/RT$, where α is the transfer coefficient and n_α is the quantity of electrons in the limiting reaction
$\pi^{1/2}\ x\ (bt)$ = potential function
ν = sweep rate

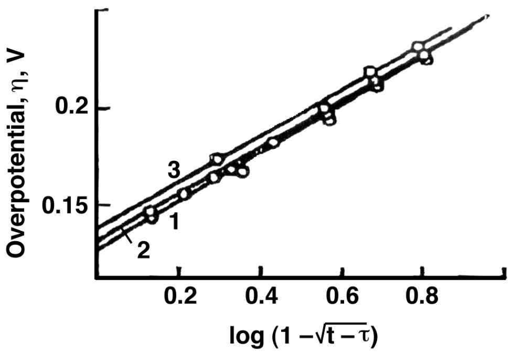

Fig. 3—Dependence $\eta = \log [1-(t/\tau)]$ on additive e conc. in the electrolyte: 1. Basic electrolyte; 2. Basic plus 0.01 M e; 3. Basic plus 0.1 M e. Current density (i_k) = 4.9 mA/cm².

The standard rate constant (K_s) was determined using the following equation:[16]

$$i_k = nFcK_s \exp[-\frac{\alpha n_\alpha F (E-E_0)}{RT}], \text{ where}$$

E_0 = the standard potential

The theoretical curve coincides satisfactorily with the experimental curve (Fig. 2, Curves 1 and 3).

When 2-ethyl sulfate sodium salt (additive e) was added, the experimental curve(Fig. 2b, Curve 2) was in the range of more positive potential because of possible formation of complexes on the cathode surfaces.[17]

The additive e doesn't change the nature of the process, which is still two steps because the theoretical curve for the one-step process $Cu^{+2} + 2e^- \rightarrow Cu^0$ (Fig. 2b, Curves 2 and 4) is totally different.

To determine the overpotential, the equation $\eta = \log (t-\tau)$ was used. When the curves were extrapolated to $\tau = 0$, the overpotential was 120 mV higher in the presence of additive e (Fig. 3).

To get more identical copper-plated crystallites, copper was deposited through metal lattices where the wire thickness of the walls was 0.2 to 0.4 mm, the cell diameter was 5 to 10 µm and the distance from the cathode 0.5 to 2.0 mm. The velour effect of copper coatings in this case was 20 percent higher.

As is known, electroplating may proceed until some thickness continues the structure of the substrate (*i.e.*, epitaxially grow). Velour nickel was plated over velour copper, and the influence of the copper layer on the physical and mechanical properties of the velour nickel was studied.

As seen from the table, velour copper and nickel coatings compared with conventional coatings are harder, the crystallites are larger, but the internal stresses are lower.

Findings

1. It has been determined that up to 0.06 percent of sulfur is included velour copper electroplates in amounts twice that of usual coatings. The content of sulfur found at the bulges exceeded that in the hollows by 1.2 to 2.6 times.
2. The passive area of velour copper was determined to be 21 to 26 µm in diameter, and this value is three times higher than for an active surface. It has been determined using optical methods that the velour effect of copper electroplates is mostly conditioned not by crystallite sizes but by their identity. Crystallites having the shape of steps are predominant in velour coatings and they develop laminar twins. It is supposed that such a formation of crystallites is conditioned by a different quantity of absorbed additives in various places on crystallites.
3. The velour effect of copper coatings increases up to 20 percent when depositing copper from a solution with additives through a metal lattice.
4. Nickel coatings deposited onto velour copper acquire a velour effect, the intensity of which depends on the velour effect of the basis metal. Both copper and nickel velour coatings are harder, less stressed and with larger crystallite compared with conventional coatings.

Editor's note: *Manuscript received, December 1997.*

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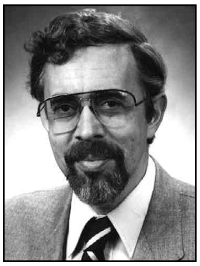

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