The Voltammetric Determination of Sulfuric Acid In a Chromium Plating Bath

By L.W. Ullrich

A precipitous negative current infection that depended on the sulfuric acid concentration was observed in current-voltage curves generated in chromic acid baths. The infections were more abrupt than those calculated for shifts in the ratio of chromic to sulfuric acids. Cylindrical copper cathodes and an anode to cathode ratio of 3.2 to 1 appeared optimum for a voltammetric procedure potentially useful for production control.

o provide close analytical control of the sulfuric acid concentration in a chromium bath used in a small shop and avoid the 24-hr delay for gravi-T metric determinations, a search for another procedure was started. A specific ion electrode for sulfate was discouraged by the manufacturer because of the harsh chromic acid environment. Ion chromatography seemed inappropriate for the busy platers who would have to use it. A voltammetric method described in some early reports¹² looked promising but insufficient detail was supplied to permit its immediate use. This paper describes an investigation of the method,

According to one reference the current-voltage curve generated by slowly increasing the current density on a brass cathode placed between two lead anodes would show a current inflection at a current density that depended on the ratio of chromic to sulfuric acids. However, no details were given on the size or spacing of the electrodes or the rate of current increase (ramp rate) or current wave form.

After preliminary trials in a 1135-L production tank produced encouraging results, a controlled study of process variables was undertaken in a 6-L glass vessel.

Experimental Conditions

The experimental system and initial conditions are given in Fig. 1 and Table 1, respectively. Nine different sets of curves were generated while current was plotted as a function of applied voltage. Four different sizes of rectangular and three different sizes of cylindrical cathodes were probed initially. Table 2 lists the sizes of the copper coupons and tubes used for this study.

Voltammetric curves were generated manually after setting the potentiometer to nullify the galvanic current induced by the lead-copper couple. When equilibrium was achieved, the current was raised in 0.1 A increments. Usually less than a minute was needed for observing and recording each change in potential. After each curve was plotted, the chromium (or deposit of undetermined composition) was stripped in hydrochloride acid, dipped in nitric-sulfuric acid solution³ and rinsed with distilled water.

Lead anodes were not allowed to remain in the chromic acid bath for more than an hour without an applied current. When removed, they were hung on a rack without rinsing, but electrolyzed after reimmersion using a dummy cathode to reform the desirable black-brown anode film.

Table 1 Initial Experiment Conditions

Anode and area	Chemical lead, 613 cm ²
Anode to cathode distance	3.8 cm (1.5 in.)
Anode to anode distance	12 cm (4.6 in.)
Cathode	Copper sheet and cylinders
	(Table 2)
Cr0, concentration	250 g/L
HSO concentration	2,5 g/L
Cr [*] concentration	0.1 g/L
Temperature	25 ±0.2° C (77 ±0.36° F)

Table 2 Copper Cathodes

	Area		Anode:cathode
No.	cm²	in²	area
Flat 1	97	15	6,31
Flat 2	194		3.2:1
Flat 3	310	48	2.0:1
Flat 4	503	78	1.2:1
Cylinder 1	97	15	6.3:1
Cylinder 2	194	30	3.2:1
Cylinder 3	290	45	2.1:1
•		1	



Fig. I—Schematic diagram of a laboratory plating system.

Results

Discernible current inflections were reproduced but the sharpest inflections were obtained with cylindrical cathodes and an anode: cathode area ratio of 3.2:1. A submerged length of 37 cm (14.5 in.) for a copper cylinder with a diameter of 4 cm (1.6 in.) was preferred when the anode to cathode distance was 3.8 cm ((1.5 in.) and the anode to anode distance was 11.7 cm (4.6 in.). These spacings were rigidly held by using gages cut from fiberglass reinforced epoxy sheeting. Chemical lead anodes with a face area of 613 cm' (95 in.') were used for all experiments.

With the cell geometry described above, fresh solutions were prepared with 250 g/L of chromic acid and different concentrations of sulfuric acid. Current inflections were noted but the curves were complex. After a sharp drop in the current, more than 0.5 V had to be applied to restore the current to its previous value. Thereafter, the current increased more rapidly with increasing voltage than it had initially. The positive current inflection was assumed to be the positive current inflection described in Ref. 1.

The positive inflections were not as well defined as the negative inflections. Figure 2 illustrates the negative inflection observed with a solution containing 2.0 g/L of sulfuric acid. A similar curve was later found in a paper published recently! However, the drop in current in this curve was not as precipitous. perhaps the difference was a function of the ramp rate.

The letter "B" in Fig. 2 designates the breakaway current, which can be considered analogous to the end point of a titration. Figure 3 is a plot of the breakaway current values obtained with different concentrations of sulfuric acid in the 250 g/L chromic acid solution. The crossed dots are the calculated regression line points⁵, which closely fit the actual data points. This fit was substantiated by calculating the Pearson correlation coefficient which was equal to

0.987. (A perfect correlation with a positive slope has a value of 1.00.)

During the next set of experiments, the chromic acid concentration was varied while the sulfuric acid concentrations also were changed. The current-voltage curve generated by each combination had the same characteristic shape as that in Fig. 2. There was a sudden negative current inflection and a subsequent need for a higher voltage to restore the current to the value observed before the drop. The breakaway current again was directly related to the sulfuric acid concentration. able 3 shows the increased values of the breakaway current with increasing concentrations of sulfuric acid. However, there were only small changes in the breakaway current when the chromic acid concentrations differed.

Regression lines for Table 3 data were similar to that in Fig. 3. The slopes of the lines and the Pearson correlation coefficients calculated for each chromic acid concentration are given in Table 4.

Figure 4 shows the breakaway currents replotted as a function of the ratio of chromic to sulfuric acids for the bath containing 250g/L of chromic acid. Table 5 gives the slopes

	Breakaway	Table 3 Current	Inflections	
H_2SO_4		Breakawa	y current, A	
cone.,	245 g/L	250 g/L	255 g/L	265 g/L
g/L	CrO₃	CrO ₃	CrO₃	CrO ₃
2.00	2.3	1.9	2.0	2.0
2.31	2.6	2.4	2.4	2.4
2.62	3.0	2.8	2.9	2.9
2.93	3.4	3.5	3.5	3.3
3.24	4.0	4.1	4.0	3.9



Fig. 2—Current-voltage curve for a solution containing 250 g/L chromic acid and 2.5 g/L sulfuric acid.



Fig. 3—Breakaway data points and regression line for a solution containing 250 g/L chromic acid and 2.0 to 3.25 g/L sulfuric acid.

Т

of the lines and the Pearson correlation coefficients for the breakaway values for all chromic acid solutions. Although the correlation coefficients do not differ greatly from those in Table 4, the Table 4 coefficients are higher. Thus Table 4 data provide strong evidence that the sharp, negative current inflection observed with increasing voltage is a function of the sulfuric acid concentration and only indirectly related to the ratio of the chromic to sulfuric acid concentration.

Discussion

The above procedure for determining the sulfuric acid concentration was adopted for a production bath where the concentrations of impurities and chromic acid can vary considerably. Although some information was collected, insufficient data have been assembled to evaluate practical aspects.

Although previous reports indicated that the ratio of chromic to sulfuric acids in a chromium plating bath could be determined by a voltammetric procedure, the precipitous negative current inflection that depended on the sulfuric acid concentration was unexpected. The sharpness and reproducibility of the inflection seem precise and accurate enough for analytical applications. However, the influence of the waveform and impurities such as trivalent chromium, iron and chloride ions have not yet been determined. Although a relatively slow ramp rate seems useful, instrumentation for further study would be desirable.

Table 4				
Line	Slopes	and	Pearson	Coefficients

CrO₃ conc., g/L	Regression line slope	Pearson correlation coefficient
245	0.73	0.989
250	0.57	0.987
255	0.61	0.996
265	0.66	0.996



Fig. 4—Breakaway data points and regression line based on the ratio of chromic acid to sulfuric acid; the chromic acid concentration was 250 g/L.

		Tab	le 5		
Line	Slope	s and Pe	earson	Coeff	icients
	Based	on CrÔ	3:H2SC)4 Ratio	05

Chromic Acid g/L	Ratio of CrO₃to H₂S0₄	Regression Line Slope	Pearson correction Coefficient
245	122.5 106.1 93.5 83.6 75.6	-26.8	"0.%67
250	125.0 106.2 95.4 85.3 77.2	-21.4	-0.973
255	127.5 110.4 97.3 87.0 78.7	-23.4	-0.960
265	132.5 114.7 101.1 90.4 81.8	-26.4	-0.980

References

- 1. K.E. Langford, *Analysis of Electroplating and* Related *Solutions,* Robert Draper Ltd., Middlesex, England, 1962; p. 338
- F.A. Lowenheim, *Modern E/ectrop/sting*, Second Edition, John Wiley "and Son, Inc., New York, 1963; p. 95.
- 3. N. Hall, *Metal Finishing Guidebook-Directory,* Metals and Plastics Publications, Inc., Hackensack, NJ, 1981; p. 175.
- 4. K. Nishimura et al., Metal Finishing, p. 45 (Mar. 1987).
- 5. Snedecor and Cochran, *Statistical Methods*, Sixth Edition, State University Press, Ames, IA, 1976; p. 147.
- A. Naiman, R. Rosenfield and G. Zirkel, Understanding Statistics, Second Edition, McGraw-Hill Book Company, New York, NY, 1977; p. 208.



About the Author

L. William Ullrich is a chemist in the research laboratory of the Hospital for Special Surgery, New Y ork, NY, where he belongs to a group investigating the deposition of calcium and phosphorus to form bone. The principles of this research show similarities to the electrodeposition of metals. Mr. Ullrich holds a BSc in chemistry from Rutgers University and is currently pursuing a graduate degree.