Characterization of Chromium Deposits Obtained From Electrochemically Regenerated Electroplating Solutions

By N.V. Mandich, K. Mondal, J. Pattanayak & S.B. Lalvani

Two spent hard chromium plating solutions were regenerated using an industrially viable electroseparation method for removal of metal impurities. The spent and regenerated baths were used to obtain chromium electrodeposits that were compared with electrodeposits obtained from freshly made, impurity-free plating baths. The morphology of the electrodeposits was characterized by scanning electron microscopy (SEM). Comparative evaluation of the hardness and corrosion resistance clearly shows that the physical properties of the electrodeposits obtained from the regenerated baths are superior to the properties of the electrodeposits produced from the spent solutions. These properties are close to those obtained for the electrodeposits produced from a freshly prepared hard chromium plating solution.

Because of environmental and economic considerations, various methods are being tried for the purification and regeneration of heavily used or spent (unusable) hard and decorative chromium plating solutions. Regardless of the importance of knowing the physical properties of the electrodeposits produced from used vs. regenerated solutions, a literature search could not uncover any pertinent information.

Electrodialysis and ion exchange are at times used as possible methods for removing metallic impurities from spent chromium plating solutions. They are not always practical nor economical, however, for small and medium chromium plating installations. The main reasons are that the membranes used are susceptible to mechanical rupture and attack by the hot, concentrated chromic acid and fairly large amounts of effluents generated.¹⁻³ One long-neglected, although promising, practical, simple and economical method involves the application of d-c potential via ceramic membrane to remove metallic contaminants (impurities). This method is also known to practicing electrochemists and electroplaters as the "porous pot" (PP) technique.

Although originally used in the electroplating industry in the late 1800s, the lack of clear practical instructions and absence of any theoretical explanations suppressed its use for a long time. Lately, this method is gradually finding more acceptance in industry because of the simplicity of design and operation, compactness and low cost.

In previous papers,³⁻⁸ we have shown that when a spent, or heavily used or abused hard chromium plating solution containing metal impurities of iron, nickel, and copper is subjected to a d-c potential, the metal cations of Fe⁺², Ni⁺² and Cu⁺² electromigrate through a porous ceramic separator from the anode compartment to the cathode compartment. Because of their inherent negative charge, the dichromate and polychromate anions remain mostly confined to the anode compartment (bulk of the plating solution).⁹ Trivalent chromium ions simultaneously electromigrate back to the anolyte (bulk of the solution) where they undergo anodic reoxidation



Fig. 1—Experimental round porous pot. Electrode connections not shown. Illustration courtesy of Hard Chrome Plating Consultants, Inc.



Fig. 2—Industrial-size porous pot.

Table 1 Composition of Plating Solutions							
Solution	pН	Impurity	Spent Solutio mg/L	n %	Regene Solutio mg/L	rated n %	Removal %
Set 1 250 g/L CrO ₃ + 2.5 g/L H ₂ SO ₄	0.4	Iron Nickel Copper	11680 1964 9408	1.17 0.19 0.94	9000 1168 5720	0.90 0.11 0.57	23.0 40.5 39.2
Set 2 250 g/L CrO ₃ + 2.5 g/L HH ₂ SC	0.5 0 ₄	Iron Nickel Copper	2844 544 2356	0.28 0.05 0.23	2164 296 1308	0.21 0.02 0.13	23.9 45.6 44.5

and, consequently, hexavalent chromium is regenerated.3-7 In recent papers,⁵⁻⁸ we have shown that when hexavalent chromium, in the form of CrO₂, dissolved in water or actual plating solution, is used as a catholyte, the pH of the solution remains low and almost unchanged during the metal electromigration process. Evidently, it acts as a buffer. The metal impurities are therefore electrodeposited on the lead cathode and thus can be conveniently removed from the bulk of the electroplating solution. An additional advantage is that the Cr(VI) anions move across the ceramic membrane from the catholyte back to the plating solution (anolyte) and consequently no hexavalent chromium^{1,7} is left and thus lost inside of the "porous pot." The final benefit is continuous regeneration, by Cr(III) reoxidation on the outside anodes, of deleterious trivalent chromium that is always present in the bulk of the solution, to its hexavalent state.^{4,10} This important feature (reoxidation) and the influence of anode composition on reoxidation rate are beyond the scope of this paper, although comprehensive research is underway.¹¹

The focus of this research is to investigate and compare the physical characteristics (hardness) and electrochemical properties (corrosion resistance) of the electrodeposits produced from the new or regenerated vs. spent or heavily used, hard chromium plating solutions. In addition, the electrodeposit morphologies were characterized and compared by scanning electron microscopy (SEM).

Experimental Procedure

The batch glass reactor, representing laboratory size PP used for the regeneration of the spent plating solution is diagrammatically shown in Fig. 1. A detailed schematic of an actual, industrial size PP is depicted in Fig. 2. The outside compartment contains approximately 2000 mL of anolyte (i.e., the spent plating solution). The inside compartment, with a capacity of 750 mL, contains a porous, ceramic solid membrane (40% porosity and pore size approximately one μ m). Both the anode and cathode are constructed from technical grade lead grids. The inside compartment contains a solution of 250 g/L of technical-grade chromic acid. The regenerated plating solution was used to electroplate a chromium deposit in a 500-mL rectangular plating tank. Sulfuric acid was added to adjust the CrO₂/H₂SO₄ ratio to 100:1. The thermostatically controlled tank contains two square lead plates (25 cm²) as anodes, placed opposite each other. The 6 x 1 cm stainless steel (type 304) cathode, polished to No. 3 finish and thoroughly cleaned is placed in the center. The temperature of both compartments was kept in all experiments at 45 °C.

Table 2 Composition of Deposits

Sample	Iron	Nickel	Copper	Total Impurities
	%	%	%	%
Set 1				
a) Deposit from spent solution	0.48	0.12	0.23	0.83
b) Deposit from regenerated solution	0.12	0.05	0.07	0.24
Set 2				
a) Deposit from spent solution	0.13	0.04	0.07	0.24
b) Deposit from regenerated solution	0.10	0.04	0.07	0.21

Results & Discussion

Evaluation of Deposit Composition

Purification of the spent solution was carried out using the similar procedure and apparatus described in our previous paper.⁶ The used plating solution labeled "Set 1" was collected from the HBM Electrochemical and Engineering Company, Lansing, IL, and contained 250 g/L of 100:1 Sargent-type bath. The compositionally similar, but artificially contaminated solution labeled "Set 2" was prepared in the laboratory. The purification step involved the application of 14 A direct current (current density of 15.7 A/ft²) at 45 °C for a period of 24 hr. The data on removal of metal impurities are listed in Table 1.

The results indicated that up to 23 percent iron, 41 percent nickel and 39 percent copper removal can be obtained from the spent solution (Set 1) which is heavily contaminated. Also, up to 24 percent iron, 46 percent nickel and 45 percent copper removal was achieved from the synthetic spent solution (Set 2) used in this study. It must be noted that to obtain a broader set of results, the initial as well as the final impurity content of Set 1 solution must be greater than the corresponding impurity content of Set 2 solution.

Because Cr(III) is simultaneously generated inside the PP and regenerated at the outside anodes, measurements of Cr(III) concentration changes is rather complex and will be addressed in forthcoming papers.

Chromium Deposition

Electrodeposits were plated from 250 g/L CrO₂, 100:1, plating solutions listed in Table 1. Plating of both sides was carried out using a constant current (of about 0.28-0.35 A/ cm²) at 45 °C for one hr. The metal cathode used was 6 x 1 cm 304 SS plate, polished to No. 3 finish. The composition of the deposits was determined by dissolving them in 1:1 hydrochloric acid and analyzing the solution using inductively coupled plasma spectroscopy (ICP). The composition of the deposits is reported in Table 2. It can be seen from the table that the chromium deposits contain mostly chromium with small amounts of iron, nickel and copper. Set 2, with much lower initial concentration of impurities, behaved differently, with only iron concentration affected. The amount of impurities (Ni, Fe, and Cu) present in the deposits in Set 1 is proportional to the concentration of impurities present in the plating solution in approximately a 2:1 ratio for Fe and Ni and 4:1 for Cu. Upon regeneration of the contaminated plating solution, the level of impurities present in the electrodeposits is considerably reduced.

The faradaic efficiency for electrodeposition was determined and is listed in Table 3. The cathode efficiency calculated for deposition from a freshly prepared hard chromium plating bath was found to be 23 percent, which is close to that reported in the literature for the given current density and temperature. Out of the two spent solutions, the spent Set 1 solution, which contains significantly more impurities than the synthetic spent Set 2 solution, has a lower faradaic efficiency for chromium electrodeposition (Table 3). The data suggest that upon purification, within experimental error, the faradaic efficiency for chromium electrodeposition is slightly decreased. This could be plausibly explained by the fact that in a contaminated solution, in addition to chromium electrodeposition, also iron, nickel, and copper electrodeposition can proceed as well. It is confirmed in the literature, that Cr/Fe and Cr/Cu alloys¹² and Cr/Ni alloys¹³ can be plated from a CrO₂-based solution. Because the Coulombic charge required for deposition of these bivalent impurities is three times lower than that needed for hexavalent chromium, the calculated efficiency is higher for the contaminated solutions in relation to the regenerated solutions. The other more plausible explanation is that Cr(III) will complex portions of Cr(VI) and lower the actual Cr(VI) concentration.¹⁴ It is well known that at lower concentrations, chromium baths always plate faster with all the other parameters being equal.

Determination of Mechanical Properties

Measurement of hardness is used to characterize the mechanical properties of the plated deposits. One of the major reasons for the widespread use of hard chromium plating is the high hardness that is indirectly related to its excellent wear properties. The commonly used device for measuring hardness is the Rockwell tester. Carefully prepared electrodeposits were used for this study. The data show that the sample prepared from spent Set 1 solution (the most contaminated), has the lowest hardness value of 57.1 Rockwell (scale C), while the chromium deposited from a freshly prepared solution has the highest hardness value of 77.5. Hardness was measured by indentation with a 150-kg load of Hull Cell panels plated with 25 µm of chromium (0.001 in.). Because of the small thicknesses of chromium, the values obtained cannot be taken as absolute, but rather as comparative (Table 4).

Table 3 Faradaic Efficiency for Chromium Electro	deposit	tion
	Cathode	Curr.

Solution	Efficiency (%)
Freshly prepared hard chromium plating solution (control)	23.0
Set 1 - Spent solution (obtained from industrial bath)	14.0
Set 1 - Regenerated solution	13.6
Set 2 - Spent solution (synthetic)	21.5
Set 2 - Regenerated solution	19.3

Table 4 Rockwell Hardness Measurements

Sample	Hardness Value (mean/median)
1. Control: Deposit from freshly prepared hard chromium solution.	77.5/77.0
2. Set 1	
a) Deposit from spent solution	57.1/58.0
b) Deposit from regenerated solution	69.6/69.0
3. Set 2	
a) Deposit from spent solution	68.2/68.0
b) Deposit from regenerated solution	77.5/78.0

When the spent Set 1 solution was purified and the deposit was produced, the hardness value of the deposit was found to be 69.6. This represents an increase of 22 percent. The deposit produced from the less contaminated solution (Set 2) had a hardness value of 68.2. Upon purification of the solution and subsequent deposition, the hardness value increased to 77.5, an increase of 14 percent. This same value was obtained for the deposit produced from the freshly produced hard chromium plating solution.

Corrosion Measurements

Electrochemical methods are routinely employed to measure the corrosion resistance of metals and alloys. The method used in this study was d-c potentiodynamic polarization. This method is in accordance with the American Society of Testing Materials (ASTM) procedure D-1242. The rate of corro-



Fig. 3—Chromium plate deposited from fresh solution. 1000X.

Fig. 4-(a) Chromium plate deposited from (a) spent Set 1 solution; (b) regenerated solution. 1000X.

sion of selected chromium coatings was determined in a sodium chloride solution (33 g/L in distilled water). The procedure involved creation of a current (*i.e.*, metal dissolution rate) vs. potential (*i.e.*, oxidizing power) plot. The active-passive regions of chromium corrosion were determined and the net anodic and cathodic currents were calculated from the experimental data. The potential at which the anodic and cathodic currents equal each other, E_{corr} and the corresponding corrosion current, I_{corr} , were measured.

The Tafel analysis method is used for calculation of corrosion characteristics. The corrosion rate in mils per year (MPY) is calculated using Faraday's law:

Corrosion Rate =
$$\frac{dW}{dt} = \frac{MI_{corr}}{nF}$$

where:

W = weight loss of specimen M = atomic weight n = valence of dissolution t = time F = Faraday constant

The corrosion characteristics of the deposits are reported in Table 5. The deposit produced from a freshly prepared hard chromium solution showed the lowest metal dissolution rate. The rate of dissolution is found proportional to the amount of impurities present in the plating solutions. For example, the deposit produced from the spent Set 1 solution that contains the highest level of metal impurities, is observed to have the highest corrosion (*i.e.* dissolution) rate. Once the contaminated solutions have been regenerated, the electrodeposits produced exhibit greatly lowered metal dissolution rates. These rates are of nearly the same order of magnitude as the corrosion rate observed for the deposit produced from the freshly produced hard chromium plating solution. Since the measured deposits are relatively thin (25 μ m) those corrosion values should be taken for comparative purposes only.

Morphological Properties

A SEM micrograph of electrodeposit obtained under magnification of 1000X, from a freshly prepared hard chromium

Table 5				
Corrosion Characteristics of Electrodeposits				
Sample	E _{corr} , mV	I_corr, mA/cm ²	Dissolution rate, mpy*	
1. Deposit produced from freshly prepared hard chromium solution (control)	-100	0.27	0.04	
2. Set 1				
a) Deposit from spent solution	-945	1707	265	
b) Deposit from regenerated solution	-50	0.63	0.10	
3. Set 2				
a) Deposit from spent solution	-265	316	49.04	
b) Deposit from regenerated solution	-100	0.63	0.10	
* Mil per year				

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plating solution is shown in Fig. 3, where some microcracks typical of chromium electrodeposits are visible. The observed morphology is relatively uniform and appears to form a continuous chromium layer. Figures 4a and 5a are SEM micrographs of the electrodeposits produced from the spent Set 1 and Set 2 solutions. Figures 4b and 5b are the SEM micrographs produced from regenerated Set 1 and Set 2 solutions respectively. In comparison with the SEM micrographs obtained for the hard chromium electrodeposits (Fig. 3), micrographs of the deposits from the contaminated Set 1 and Set 2 solutions appear to have grain boundaries that are almost in contact with one another and the deposits seem to be "burnt." When the Set 1 and Set 2 solutions were regenerated by electropurification, the micrographs of the obtained deposits appear to display characteristics (Figs. 4b and 5b) that are very similar to those of deposits produced from a freshly prepared hard chromium plating solution (Fig. 3), on the same substrate and under the same plating conditions.

Conclusions

Although experienced chromium platers knew empirically or intuitively that the absence of metallic impurities would improve hardness and corrosion properties, the results presented in this paper clearly quantify the improvement. These results should keep concerned platers aware that although a

> chromium plating solution is tolerant of heavy use and abuse, some of the important, but less apparent properties, can be drastically affected.

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References

 R.P. Rentz et al., Proc. AESF SUR/ FIN 99, Session V (1999).
G.C. Cushnie & W. Anderson, 10th AESF/EPA Conf. on Environmental Control, Orlando, FL (1989).



 $Fig. \ 5-(a) \ Chromium plate \ deposited \ from \ (a) \ spent \ Set \ 2 \ solution; \ (b) \ regenerated \ solution. \ 1000 X.$

- 3. U.S. Army Corps of Engineers, *Evaluation of Electrodialysis for Chromic Acid Recovery and Purification at Corpus Christi Army Depot* (AD-A242677, Sept. 1991).
- 4. N.V. Mandich, *AESF Chromium Colloquium*, Orlando, FL (1994).
- J. Pattanayak, N.V. Mandich, K. Mondal, T. Wiltowski & S.B. Lalvani *Environ. Technol.*, 20, 317 (1999).
- J. Pattanayak, K. Mondal, N.V. Mandich, T. Wiltowski & S.B. Laivani, *Metal Fin.*, accepted for publication.
- S.B. Lalvani, J. Pattanayak, K. Mondal, N.V. Mandich & T. Wiltowski, J. Electrochem. Soc., submitted for publication.
- N.V. Mandich, J.R. Selman & C.C. Lee, *Plat. and Surf. Fin.*, 84, 82 (Dec. 1997).
- 9. N.V. Mandich, Plat. and Surf. Fin., 84, 97 (June 1997).
- 10. N.V. Mandich, Metal Fin., 97(6), 100 (1999).
- 11. K. Mondal, N.V. Mandich & S.L. Lalvani, J. Appl. *Electrochem.*, submitted for publication.
- 12. C. Casper, J. Res. Nat'l. Bur. Stand., 14, 643 (1935).
- 13. M.F. Quaely, *Plating*, **40**, 982 (1953).
- 14. N.V. Mandich, Metal Fin., 97(8), 42 (1999).

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