Investigation of a Functional Trivalent Chromium Plating Process

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Hexavalent chromium plating has been used for many years to provide hard, durable coatings with excellent wear and corrosion resistance properties. Hexavalent chromium baths have come under increasing scrutiny, however, because of the toxic nature of the bath and the effects on the environment and workers' health. This project investigated a charge-modulated electric field process to overcome previous problems encountered in plating thick layers of trivalent chromium. This work identified a complex interaction between 1) the charge modulated electric field chrome plating process parameters, hydrodynamic conditions, and plating bath components. Lack of understanding of these complex interactions is most likely the hindrance to previous trivalent chromium developments. The project is being funded by the U.S. EPA.

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Introduction

Chromium coatings are widely used in a variety of industries. Plating operations are used to fabricate two types of chromium coatings, functional and decorative. Functional chromium coatings consist of a thick layer of chromium (typically 1.3 to 760 µm, Altmayer, 1995) to provide a surface with functional properties such as hardness, corrosion resistance, wear resistance, and low coefficient of friction. Applications of functional chromium coatings include strut and absorber rods, hydraulic cylinders. shock crankshafts and industrial rolls. Carbon steel, cast iron, stainless steel, copper, aluminum, and zinc are substrates commonly used with functional chromium. Decorative chromium coatings consist of a thin layer of chromium (typically 0.003 to 2.5 μ m, Altmayer, 1995) to provide a bright surface with wear and tarnish resistance when plated over a nickel layer. It is used for plating automotive trim/bumpers, bath fixtures and small appliances.

Hexavalent chromium (Cr(VI)) plating has been commercialized for many years. However, a Cr(VI) plating bath operates at an elevated temperature and produces a mist of chromic acid. Since worker exposure to (Cr(VI)) plating baths is regulated by OSHA, exhaust/scrubber systems must be installed for Cr(VI) plating operations and the exposure limit is 0.01 mg/m³ (Banker, 1995). The Clean Air Act, as well as local constraints, regulates the emission of chromium to the air and water. Since Cr(VI) plating produces hazardous air emissions, all of the Cr(VI) platers must control and monitor the bath surface tension and report the results to the EPA. In contrast, trivalent chromium (Cr(III)) platers are not required to monitor bath surface tension (Banker, 1995).

The USEPA has identified chromium as one of 17 "high-priority" toxic chemicals. The USEPA selected the high-priority chemicals based on their known health and environmental effects, production volume, and potential for exposure (Ember, 1991). Under former USEPA administrator William K. Reilly's Industrial Toxic Program, the high-priority toxic chemicals were targeted for 50% reduction by 1995 (Hanson, 1991). From an environmental perspective, plating from additive-free Cr(III) has several advantages relative to hexavalent chromium plating:

- Cr(III) is non-toxic, non-hazardous and is not an oxidizer. Therefore, meeting air quality regulations is easier and working conditions are greatly improved. The exposure limit for Cr(III) is an order of magnitude higher than Cr(VI).
- Disposal costs are significantly reduced for Cr(III) plating. Hydroxide sludge generation is reduced ten to twenty times because Cr(III) generally operates at a Cr(III) content of about 4-20 g/liter vs. 150-300 g/liter for a Cr(VI) bath.
- 3) Since there are no proprietary additives in the Cr(III) bath, the rinse water may be recycled.

In addition, Cr(III) has the following technical advantages:

- 1) The Cr(III) plating bath is not sensitive to current interruptions (Shahin, 1992). Therefore, the innovative modulated reverse current approach used in this program is more suitable for Cr(III) plating than for Cr(VI) plating.
- Drag in of chloride and sulfate from any previous nickel plating operations into the Cr(III) process is tolerated (Snyder, 1989). In contrast, chloride and sulfate drag-in upset the catalyst balance in a hexavalent chromium process.
- 3) Throwing power for Cr(III) plating, which is poor in a Cr(VI) bath, is good and similar to other metals such as copper (Snyder, 1989).

As described above, Cr(III) plating has numerous environmental, health, and technical advantages relative to Cr(VI) plating. Considerable research has been done to study Cr(III) plating, including the effects of the plating bath chemistry on plating thickness, brightness, hardness, and corrosion resistance (Scott, 1991; Constantin et al., 1991; Hwang, 1991) and the effect of current waveforms on chromium deposit structure, distribution, brightness, and hardness (Tu et al., 1990; Dash et al., 1991). By including proprietary organic additives, Cr(III) plating baths are commercially available (though not widely used) for decorative chromium coating applications. However, the additives are difficult to control because of their low concentration. Furthermore, the additives react and breakdown with time to form contaminants. Due to these contaminants, the used Cr(III) bath and rinse water cannot be replenished and recycled due to the "drag-in" and buildup of these contaminants. Finally, decorative Cr(III) plating still suffers from low current efficiency.

Currently, functional chromium plating from a Cr(III) bath is not commercially available because of the difficulty to plate thick chromium coatings with the appropriate properties. In addition, the low current efficiency and low plating rate of Cr(III) baths lead to unfavorable economics. Due to the rapid drop in current efficiency, the practical limit for Cr(III) plating is 2.5 μ m (Tu et al., 1993). The plating thickness increases quickly at the beginning of the electroplating process. As plating continues, the deposition rate diminishes and becomes negligible.

Charge Modulated Electric Field Plating

During Cr(III) plating, chromium is deposited and hydrogen is evolved at the cathode, as described in the following reactions:

$Cr^{3+} + 3e^- \rightarrow Cr (\phi^0 = -0.74 \text{ V vs SHE})$	(1)
$2\mathrm{H}^+ + 2\mathrm{e}^- \rightarrow \mathrm{H}_2 \ (\phi^{\mathrm{O}} = 0 \ \mathrm{V} \ \mathrm{vs} \ \mathrm{SHE})$	(2)

The current efficiency for chromium plating from a Cr(III) bath is usually below 20%; therefore, about 80% of the current is used for the hydrogen evolution reaction. As a result, the pH near the cathode surface increases dramatically and chromic hydroxide (K_{sp} =5.4 x 10⁻³¹) precipitates in the high pH layer at the cathode. The sedimentation of chromic hydroxide covers the cathode surface and its thickness increases as the plating time and pH increase. This promotes an increase of cathode polarization, a further decrease of chromium plating efficiency (i.e. increase in hydrogen evolution reaction), and the increase of impurities in the plating film. All these factors retard the normal growth of crystals in the plating film, leading to the prevention of further plating of chromium. The evolution of hydrogen continues as the only reaction. The precipitation of chromic hydroxide at the cathode also results in surface cracks and reduces the hardness and brightness of the chromium coating. Faraday's intellectual property deals with overcoming this hydrogen evolution problem by utilizing Charge Modulation.

A schematic of a rectangular Charge Modulated Electric Field waveform is shown in Figure 1. It essentially consists of a cathodic (forward) current modulation followed by an anodic (reverse) current modulation and a relaxation period. The cathodic peak current is I_c and the cathodic on-time is t_c. The anodic peak current is I_a and the anodic on-time is t_a . The relaxation time is toff. The sum of the cathodic on-time, anodic ontime, and relaxation time is the period of the modulation (T = $t_c + t_a + t_{off}$) and the inverse of the period of the modulation is the frequency of the modulation. The ratio of the cathodic on-time to the period (t_c/T) is the cathodic duty cycle (D_c) , and the ratio of the anodic on-time to the period (t_a/T) is the anodic duty cycle (D_a) .



Figure 1: Schematic of a Charge Modulated Electric Field Waveform.

The current density during the cathodic on-time and anodic on-time is known as the <u>cathodic peak</u>

modulation current density and anodic peak modulation current density, respectively. The average current density (i_{ave}) is the average cathodic current density (D_cI_c) minus the average anodic current density (D_aI_a) .

Once the average current density (i_{ave}) , modulation frequency (f), cathodic duty cycle (D_c) , anodic duty cycle (D_a) , and the cathodic to anodic charge ratio (Q_c/Q_a) are given, the cathodic and anodic on-time and relaxation time $(t_c, t_a, and t_o)$ and cathodic and anodic peak current density $(i_c and i_a)$ are determined from the following equations:

$$T = \frac{1}{f} \tag{3}$$

$$D_c = \frac{1}{T} \tag{4}$$

$$D_a = \frac{t_a}{T} \tag{5}$$

$$\frac{Q_c}{Q_a} = \frac{i_c t_c}{i_a t_a} \tag{6}$$

$$i_{ave} = i_c D_c - i_a D_a \tag{7}$$

$$T = t_c + t_a + t_{off} \tag{8}$$

Another condition is:

$$D_c + D_a \le 1 \qquad \qquad 9)$$

It should be noted that the cathodic on-time, anodic on-time, relaxation time, and the cathodic and anodic peak modulated current densities are additional parameters available to control the electroplating process compared to conventionally used DC plating. In DC plating, the cathodic current is turned on and held for the duration of the plating process.

For chromium plating from a Cr(III) bath, we use a cathodic modulation with either a long duty cycle or a large modulated current to deposit chromium, followed by an anodic modulation with either a short duty cycle or a small pulse current to convert the nascent hydrogen gas formed during the cathodic cycle to H^+ , and a relaxation period to allow the Cr(III) ions to diffuse to the cathode surface and be available for subsequent deposition. During the cathodic portion of the modulation, chromium is deposited and hydrogen is evolved, analogous to conventional chromium plating. During the anodic portion of the modulation, we can selectively consume the nascent hydrogen according to the following reaction:

$$\mathrm{H}_2 \to 2 \mathrm{H}^+ + 2\mathrm{e}^- \tag{10}$$

In this manner, a low pH is maintained and chromic hydroxide precipitation is avoided. By properly adjusting the anodic and cathodic peak currents, the anodic and cathodic duty cycles, and the frequency, nascent hydrogen can be consumed. In addition, we can constrain the above parameters so that the net plating rate for our Cr(III) process is equivalent to that currently used in the Cr(VI) process.

Elimination of Hydrogen

The evolution of hydrogen during a metal deposition process results in a low current efficiency and a high power consumption. In hydrogen evolution addition. during metal deposition leads to hydrogen embrittlement in the substrate or hydrogen bubble inclusion in the metal deposit. This adversely affects the electrodeposit in terms of 1) low corrosion resistance, 2) poor adhesion to the substrate, 3) high internal stress, and 4) excess porosity. By properly adjusting the charge modulated parameters, one can alter the kinetics of both the metal deposition and hydrogen evolution reactions. While reaction kinetics can be modified using a charge modulated electric field (no reverse cycle) waveform, hydrogen bubbles adsorbed on the electrode surface can be released during the off-time period. By using charge modulation, one can 'tune' the anodic or reverse part of the waveform to consume the nascent hydrogen according to the following reaction:

 $\mathrm{H}_2 \rightarrow 2 \mathrm{H}^+ + 2\mathrm{e}^- \tag{11}$

In this manner, a low pH is maintained and chromic hydroxide precipitation is avoided.

Furthermore, hydrogen is not permitted to diffuse into the substrate or be incorporated in the deposit. Finally, by compensating for the anodic current with an increased cathodic current, the overall electrodeposition rate is maintained and the net current efficiency is improved.

Mass Transfer

Unlike DC electrolysis, the mass transfer characteristics of charge modulation are a time dependent process. Charge modulation causes concentration fluctuations near the electrode surface and reduces the effective Nernst diffusion layer thickness. Consequently, very high instantaneous limiting current densities can be obtained with charge modulation as compared to DC electrolysis. To qualitatively illustrate how charge modulation enhances the instantaneous mass transfer rate, consider the case of a single rectangular cathodic current modulation. Before the current is turned on, the concentration of the diffusing ion is equal to the bulk concentration, C_b. After the current is turned on, the concentration near the cathode drops and a diffusion layer builds up. Using the non-steadystate Fick's law of diffusion, this concentration profile as a function of the distance from the electrode surface, X, is depicted in Figure 2. The corresponding thickness of the Nernst diffusion layer, δ , is also shown in Figure 2 for various time periods. The mass transfer limited current density is related to the concentration gradient at the electrode surface and to the thickness of the Nernst diffusion layer by:

$$i = nFD[dC/dx]_{x=0} = - nFD[(C_b-C_s)/\delta]$$
(12)

In steady state DC electrolysis, δ is a timeinvariant quantity for given electrode geometry and hydrodynamics; this quantity is represented by δ_{∞} . In charge modulation, however, δ varies from 0 at the beginning of the charge modulation process to a value of δ_{∞} when the steady state Nernst diffusion layer is fully established. The corresponding diffusion current density would then be equal to an infinite value at t = 0 and decreases to a steady state value of the DC limiting current density at t = t_∞. The advantage of charge modulation is that the current can be interrupted (e.g., at t = t_a) before δ

has a chance to reach the steady-state value. This allows the reacting ions to diffuse back to the electrode surface and replenish the surface concentration to its original value before the next current modulation. In this way, one obtains a diffusion controlled modulated current density greater than the steady state limiting current density. This diffusion controlled modulated current density can be made very large if one employs a current modulation of very short duration followed by very long relaxation time to permit the surface concentration to recover to the bulk value. Modeling work by Chin (1983) has indicated that limiting current densities obtained under the pulse reverse current (PRC) conditions of low duty cycle and high frequency, can be two to three orders of magnitude greater than the DC limiting current density. Vilambi and Chin (1988) confirmed the earlier modeling work with experimental studies for a copper sulfate bath for selected pulse periods and duty cycles in PRC electrolysis. They reported peak current densities as high as several hundred A/cm^2 for PRC electrolysis, while the corresponding values for DC electrolysis were less than 1 A/cm^2 .



Figure 2: Mass Transfer in Charge Modulation by Diffusion.

Experimental

A trivalent chromium bath was used in all of the experiments. It consisted of chromium chloride as the consumable source of chromium, various carriers, and a wetting agent. It was adjusted to a pH of 2.5 and electrolyzed for one hour using a nickel plated rod.

Hydrodynamic Impingement

A 3-liter cell was used for these experiments. The cathode was a ϕ 9.5 mm ground and hardened steel rod placed between two graphite anodes 12 cm apart. A pump was used to provide flow (9.6 L/min) to three distinct piping arrangements (flow to one side, flow to two sides, and flow to the bottom).

Taguchi Array

After the above test were run, a Taguchi array was designed to vary the charge modulated frequency (10, 50, 100 Hz), current density (20, 50, 100 A/dm^2), and rotation speed (500,1000, 1500 rpm). A DC test was also run.

Results and Discussion

In prior work, Faraday achieved 1) an improved plating rate, 2) equivalent hardness, and 3) an improved current efficiency as illustrated in Table 1. Additionally, our work has correlated thickness as a function of electrolysis time as illustrated in Figure 3. These successes, however, have not yet been validated in a job shop production environment.

Faraday's Cr ⁺³ Process	Table 1: Data C	omparison of a Current Cr ⁺⁶ Process and
		Faraday's Cr ⁺³ Process

	Current Cr ⁺⁶ Process	Faraday Cr ⁺³ Process
Plating Rate	0.76-1.27	1.44
µm/min		
Hardness	842	844
(Vickers)		
Current	24%	35%
Efficiency		



Figure 3: Chromium Plating Thickness vs. Plating Time

Hydrodynamic Impingement

Each of these configurations yielded areas of chromium plating. However, there were also areas that either had too high of a flow rate and yielded no plating or areas that had too low of a flow rate and yielded a burned deposit. Impingement from one side produced a chromium plate except in the area of highest impingement as shown in Figure 4. Impingement from two sides, keeping the total flow the same as above, produced two smaller areas with no plate, but the thickness was still not consistent as shown in Figure 5. Impingement from the bottom produced an erratic pattern as shown in Figure 6.



Figure 4: Impingement from One Side



Figure 5: Impingement from Two Sides



Figure 6: Impingement from the Bottom

Taguchi Array

Table 2 shows the results of the Taguchi array for rods 15-24. The rods are shown in Figure 7. The main criteria for acceptable plating are a shiny surface and a reasonable plating rate. The plating times were adjusted to use the same ampminutes on all of the rods. Rod 15 was determined to be the best based on the above criteria, with a shiny surface, and a plating rate of 0.89 μ m/min. Although Rod 19 had a higher plating rate (2.59

 μ m/min), the appearance of the deposit was not acceptable.

Conclusions

In summary, the advantages of utilizing charge modulation in Cr(III) plating include:

- increasing the chromium plating thickness in Cr(III) plating by converting hydrogen gas to H⁺, decreasing the pH near the cathode and eliminating the precipitation of chromic hydroxide;
- increasing the purity, hardness, and brightness of the plating film by eliminating chromic hydroxide precipitation;
- reducing hydrogen embrittlement by consuming nascent hydrogen during the anodic period;
- therefore, increasing the corrosion resistance of the plating film.

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Rod No.	15	16	17	18	19	20	21	22	23	24
Cr thickness (µm)										
Тор	20	0	0	5	35	1.5	2.5	2	1.5	2.5
Middle	15	0	0	0	35	1	0	1	1	2
Bottom	25	0	0	7	0	2	3	2.5	2	3.5
Average Cr thickness (µm)	20	0	0	4	23.3	1.5	1.8	1.8	1.5	2.7
Plating Time (min)	22.5	9	4.5	22.5	9	4.5	22.5	9	4.5	22.5
Plating Rate (µm/min)	0.89	0	0	0.18	2.59	0.33	0.08	0.20	0.33	0.12
Appearance (where plated)	shiny	dark	dark	shiny	dull	shiny	shiny	shiny	shiny	shiny

Table 5: Plating Results of Rods 15-24



Figure 7: Appearance of Rods 15-24

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