

Functional Trivalent Chromium Plating: An Alternative to Hexavalent Chromium Plating

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We will discuss the work we are doing to develop a functional trivalent chromium plating process to replace hexavalent chromium plating. Hexavalent chromium plating has been used for many years to provide hard, durable coatings with excellent wear and corrosion resistance properties. However, hexavalent chromium baths have come under increasing scrutiny due to the toxic nature of the bath, effects on the environment, and workers' health. This is an update on our accomplishments to date to achieve properties comparable to existing hexavalent chromium plating. Continuing work on the bath chemistry, diffusion layer, hydrodynamics, and electrically mediated process parameters will also be discussed.

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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 shock absorber rods, hydraulic cylinders, 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 μm , 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/m^3 (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 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).

The chemistry of chromium provides a basis for understanding the toxicology. Chromium can exist in oxidation states ranging from II to VI. However, only Cr(III) and Cr(VI) are stable enough to actually be used. Cr(VI) is readily reduced to the more stable Cr(III) and in this process substances in contact with the Cr(VI) are oxidized. Cr(VI) compounds are very soluble compared to Cr(III) compounds. Therefore, in the environment Cr(VI) is much more likely, upon release into a stream or an aquifer, to dissolve and move with the flow. In fact, one method that has been used to stabilize Cr(VI) (make it less mobile) in the environment is to reduce it to Cr(III) (Taylor, 2001).

Cr(VI) is widely recognized as a human carcinogen. In a study recently published (Gibb, 2000), Cr(VI) was reported to cause increased incidences of lung cancer in a group of 2,357 workers at a chromate production plant. In the same study, the carcinogenic property of Cr(III) was also examined. The article reports “Cumulative hexavalent chromium exposure was associated with an increased lung cancer risk; cumulative trivalent exposure was not.” This

study “offers the best quantitative evidence to date of the relationship between Cr(VI) and lung cancer.” In previous studies, it was recognized that workers were exposed to a mixture of Cr(VI) and Cr(III), however, the relative contributions of each of the forms of chromium were not assessed. In the study cited above, the relative exposure levels were calculated and on the basis of their findings, the authors have indicated that exposure of workers to Cr(III) did not result in an increase in lung cancer.

Another report has been published in the scientific literature that also implicates Cr(VI) as a human carcinogen (EPA, 2000). This report states that the US Environmental Protection Agency has classified Cr(VI) as “a Group A known human carcinogen.” This same publication states “Cr(III) is much less toxic and is recognized as an essential element in the human diet.” EPA classifies Cr(III) as “a Group D carcinogen, not classifiable as to carcinogenicity in humans.” The acute and chronic effects of exposure to Cr(VI) and Cr(III) are described in detail in the EPA report cited in this paragraph.

In the case of the two forms of chromium, one can say that the chemistry and toxicology of each form is markedly different. Perhaps the most important facts to remember are that Cr(III) is rather insoluble and does not oxidize organic material. Cr(III) is poorly absorbed from the gastrointestinal tract and is not considered to be a carcinogen. Cr(VI) is very soluble, penetrates cell walls, and is a human carcinogen. Cr(VI) is very reactive and causes ulceration of the nasal septum and other tissues upon exposure as well as reproductive, gastrointestinal and dermal effects. However, Cr(III) is not without toxic effects and should be handled appropriately. To put this last statement in perspective, aluminum, for example, is not without toxic effects. Although aluminum is ubiquitous in our society today - cooking utensils are formed from aluminum, soda cans are formed from aluminum; but aluminum is, depending on the route of exposure and dose, potentially toxic (Occupational Safety and Health Guideline for Aluminum).

The use of Cr(III) in industrial and commercial processes is preferred over Cr(VI) on the basis of the comparison of the toxicities. Cr(III), like other metals (e.g. aluminum) must be handled appropriately since each of these metals is at some dose and via at least one route of exposure, capable of causing harm to the human (Taylor, 2001).

From an environmental perspective, plating from additive-free Cr(III) has several advantages relative to Cr(VI):

- 1) 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).
- 2) 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:

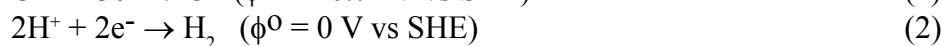
- 1) The Cr(III) plating bath is not sensitive to current interruptions (Shahin, 1992). Therefore, the innovative modulated reverse current approach used in this program is more suitable for Cr(III) plating than for Cr(VI) plating.
- 2) Drag in of chloride and sulfate from any previous nickel plating operations into the Cr(III) process is tolerated (Snyder, 1989). In contrast, chloride and sulfate drag-in upset the catalyst balance in a Cr(VI) 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 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 existing conventional DC Cr(III) plating is 2.5 μm (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.

Electrically Mediated Plating

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



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 ($K_{sp} = 5.4 \times 10^{-31}$) 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 approach deals with overcoming this hydrogen evolution problem by utilizing electrically mediated plating.

The basis of electrically mediated plating is a charge modulated electric field, 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 t_{off} . The sum of the cathodic on-time, anodic on-time, 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).

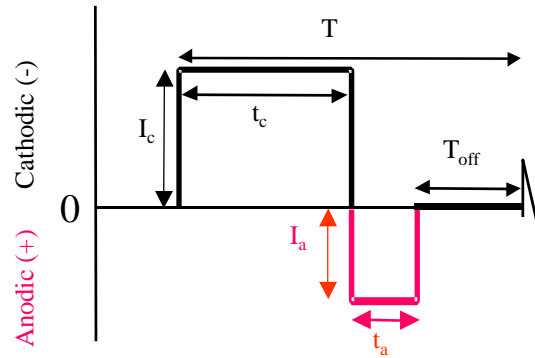


Figure 1: Schematic of an Electrically Mediated Waveform.

The current density during the cathodic on-time and anodic on-time is known as the cathodic peak modulation current density and anodic peak modulation current density, respectively. The average current density (i_{ave}) is the average cathodic current density ($D_c I_c$) minus the average anodic current density ($D_a I_a$).

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:

$$T = \frac{1}{f} \quad (3)$$

$$D_c = \frac{t_c}{T} \quad (4)$$

$$D_a = \frac{t_a}{T} \quad (5)$$

$$\frac{Q_c}{Q_a} = \frac{i_c t_c}{i_a t_a} \quad (6)$$

$$i_{ave} = i_c D_c - i_a D_a \quad (7)$$

$$T = t_c + t_a + t_{off} \quad (8)$$

Another condition is:

$$D_c + D_a \leq 1 \quad (9)$$

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 modulated 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:



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 high power consumption. In addition, hydrogen evolution during metal deposition leads to hydrogen embrittlement in the substrate or hydrogen bubble inclusion in the metal deposit. This adversely affects the electrodeposition 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 electrically mediated process parameters, one can alter the kinetics of both the metal deposition and hydrogen evolution reactions. While reaction kinetics can be modified using a process with a forward modulation only, hydrogen bubbles adsorbed on the electrode surface can be released during the off-time period. By adding an anodic modulation, one can 'tune' the anodic or reverse part of the waveform to consume the nascent hydrogen according to equation 10.

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 electrically mediated electrolysis as compared to DC electrolysis. To qualitatively illustrate how electrical mediation 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-steady-state 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:

$$i = nFD[dC/dx]_{x=0} = -nFD[(C_b - C_s)/\delta] \quad (11)$$

In steady state DC electrolysis, δ is a time-invariant quantity for given electrode geometry and hydrodynamics; this quantity is represented by δ_∞ . In electrically mediated electrolysis, however, δ varies from 0 at the beginning of a current modulation 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 $t = t_{\infty}$. The advantage of electrically mediated electrolysis 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/cm² for PRC electrolysis, while the corresponding values for DC electrolysis were less than 1 A/cm².

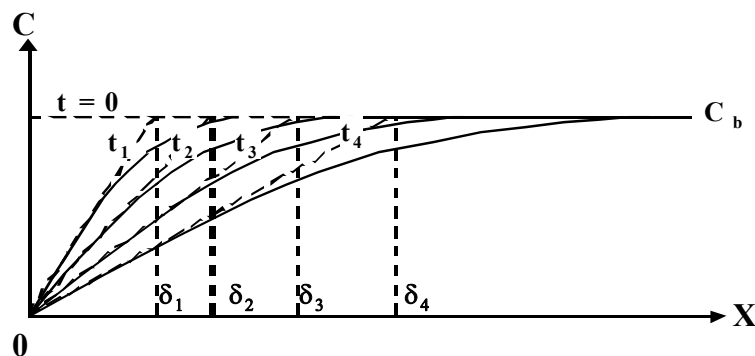


Figure 2: Mass Transfer in Charge Modulation by Diffusion.

Prior Work

In previously reported work we accomplished the following milestones:

- Plated from a trivalent chromium sulfate bath where the consumable was in the price range of chromic acid, (Renz, 2001).
- Simplified bath chemistry using an electrically mediated waveform, (Renz, 2001).
- Increased chromium plating thickness to 250 μm , (Renz, 2001).
- Maintained plating rate similar to hexavalent chromium, (Renz, 2001).
- Determined maximum diffusion layer thickness for plating from trivalent chromium sulfate bath, (Renz, 2002).
- Determined acceptable range for achieving bright plating, (Renz, 2002).
- Replated chromium on chromium, (Renz, 2002).
- Displayed superior corrosion resistance compared to laser coated surfaces. (Renz, 2003).
- Achieved a suitable chromium distribution for pump rotor wear tests at manufacturer (Renz, 2004).

Experimental

We are continuing development to increase the hardness to the level of that achieved with hexavalent chromium deposits. Also, we are conducting wear tests to determine the relative wear difference between trivalent chromium and hexavalent chromium deposits. Our wear test consisted of a fixture, Figure 3, where one rod was rotated while the second rod was held stationary with a load. The rotating rod was mounted in a chuck. The stationary rod was mounted in a fixture free to swivel with a weight attached to provide a load. The bearing surface was lubricated during the test. The tests were run for 2 hours at 160 RPM with a 4.8 Kg load at the point of contact. Hardened and precision ground steel rods were tested against the chromium plated rods. These rods were also the source for the plated rods. The plated rods were not finished after plating.



Figure 3: Rotating Wear Test.

A trivalent chromium (Cr^{3+}) plated rod and a hexavalent chromium (Cr^{6+}) plated rod were tested against a hardened steel rod. The plated rods and the steel rods were all 12.7 mm (1/2") in diameter. Four tests were run. In the first test the Cr^{3+} plated rod was rotated against a stationary hardened steel rod. While a slight band was noticed around the Cr^{3+} rod with no magnification, it could not be seen when magnified and is in the center of the photo shown in Figure 4. The wear area of the hardened steel rod extends below the grind marks as shown in Figure 4. In the second test the rods were reversed. Some areas of the rotating steel rod had streaks of polish marks. Two bands are shown in Figure 5. The wear on the Cr^{3+} rod was less than that for the steel rod as was expected and shown in Figure 5. It consisted of slight polishing in the grind marks. In the third test a Cr^{6+} plated rod was rotated against a hardened steel rod. Some polished bands on the Cr^{6+} plated rod can be seen in Figure 6. The wear area of the steel rod, which extends beyond

the grind marks, similar to the one shown in Figure 4. In the fourth test the rotating steel rod contained polished areas similar to the steel rod in Figure 5, as shown in Figure 7. The wear area of the stationary Cr^{6+} plated rod had wear within the grind marks with a slightly larger footprint and slightly more polishing than the Cr^{3+} plated rod as shown in Figure 7.

Although the hardness of the chromium deposit was less for the Cr^{3+} rod than for the Cr^{6+} rod, 771 vs. 948 VHN/100, the wear on the Cr^{3+} deposit was equivalent or slightly less than that for the Cr^{6+} deposit. In addition, no wear in the form of polished areas could be found on the rotating Cr^{3+} rod compared to a slight polished band found on the rotating Cr^{6+} rod.

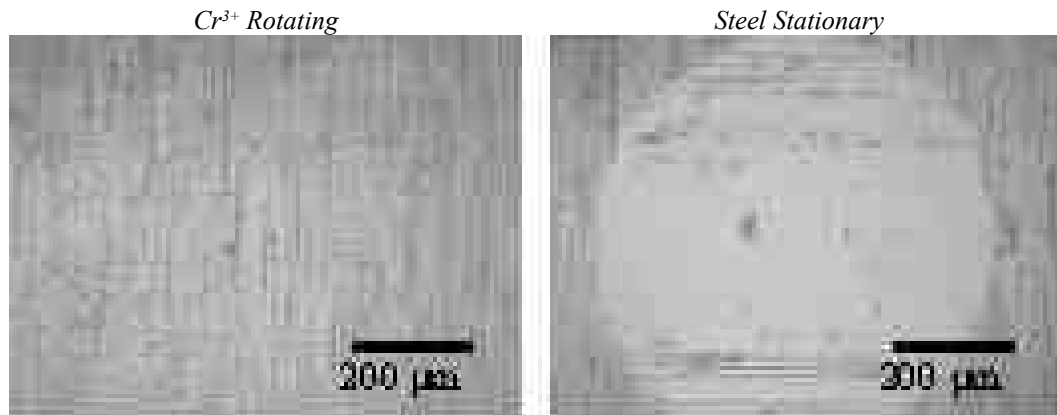


Figure 4: Rotating Wear Test.

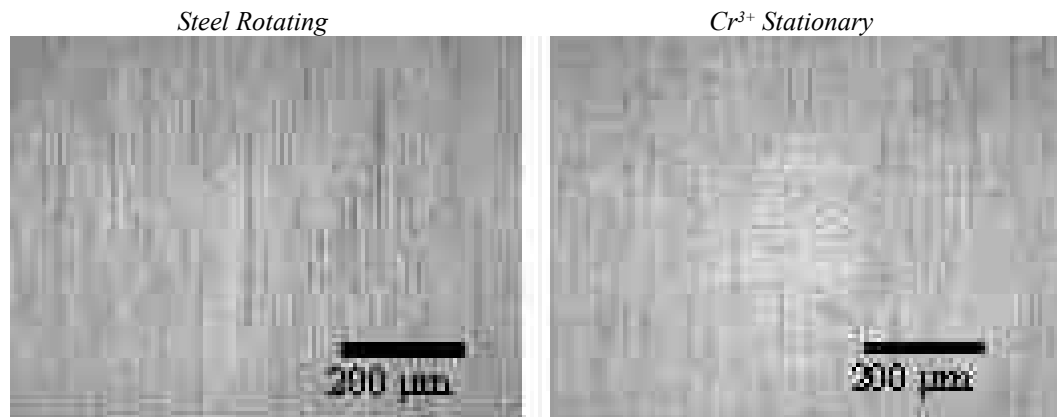


Figure 5: Rotating Wear Test.

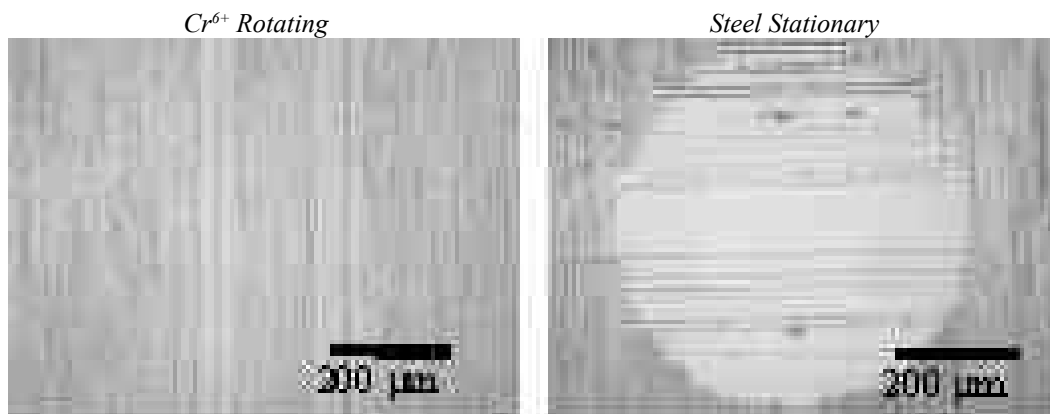


Figure 6: Rotating Wear Test.

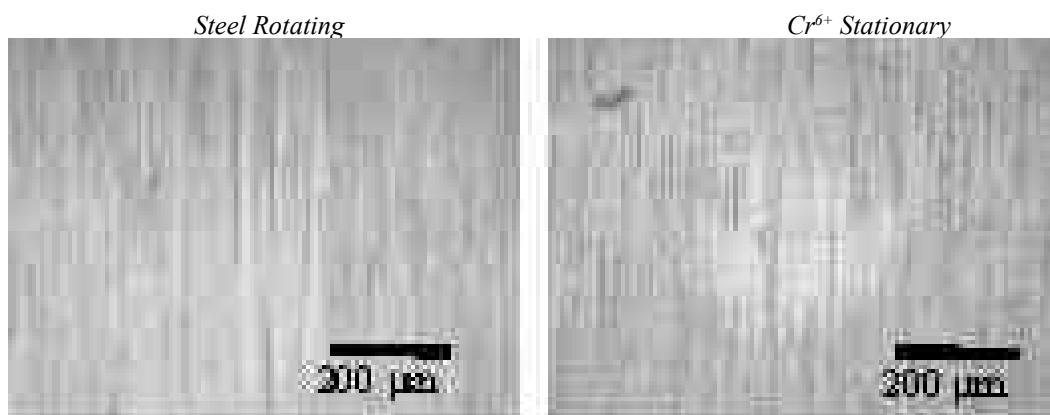


Figure 7: Rotating Wear Test.

Conclusions

In summary, we are continuing research and development to commercialize our trivalent chromium plating process. We have established the following:

- Plated from a trivalent chromium sulfate bath where the consumable was in the price range of chromic acid, (Renz, 2001).
- Simplified bath chemistry using an electrically mediated waveform, (Renz, 2001).
- Increased chromium plating thickness to 250 μm , (Renz, 2001).
- Maintained plating rate similar to hexavalent chromium, (Renz, 2001).
- Determined maximum diffusion layer thickness for plating from trivalent chromium sulfate bath, (Renz, 2002).
- Determined acceptable range for achieving bright plating, (Renz, 2002).

- Replated chromium on chromium, (Renz, 2002).
- Shown that the corrosion resistance of trivalent chromium deposits is superior to laser treated coatings.
- Constructed a pilot-line plating set-up to plate parts currently used in production to allow commercial evaluation (Renz, 2003).
- Achieved a suitable chromium distribution for pump wear tests at manufacturer (Renz, 2004).
- Achieved equal or slightly better wear resistance compared to a Cr^{6+} deposit against hardened steel.

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