Pulse Plating of Hard Chromium From Trivalent Baths

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A trivalent chromium bath is relatively non-toxic compared with a hexavalent chromium bath. It is difficult, however, to obtain thick chromium electrodeposits from a trivalent chromium bath with direct-current plating. This paper describes a study using pulsed current to plate thick chromium electrodeposits for hard chromium applications from a trivalent chromium bath, using either ammonium formate or sodium hypophosphite as the complexing agent. It was found that the chromium plating rate using pulsed current was higher than that for direct current. Pulsed current improved the maximum coating thickness that could be obtained from the trivalent chromium baths. In addition, pulsed current decreased the internal stress of a trivalent chromium deposit by 25 to 75 percent. The internal stress decreased with decreasing current density, duty cycle and pulse frequency. When sodium hypophosphite was used as the complexing

agent in the trivalent bath, a significant quantity (15 to 30%) of phosphorus co-deposited on the chromium coating. The phosphorus content increased with decreasing duty cycle and with increasing pulse frequency. The microhardness of a trivalent chromium deposit obtained with pulsed current was in the range of 610 to 850 on Knoop's hardness scale. These values were comparable to that obtained with direct current. Increasing pulse frequency in the range of 10-1000 Hz increased the microhardness of the chromium deposit.

Hard chromium coatings, with a thickness ranging from 1.3 to 760 μ m¹ are used in the manufacturing, aerospace and other industries. Traditionally, hard chromium coatings are obtained from hexavalent chromic acid (Cr⁺⁶) baths, which are highly toxic and oxidative. Trivalent chromium ions are relatively non-toxic; its acceptable subchronic ingestion amount is 979 mg/day, as compared to the 1.75 mg/day for Cr⁺⁶ ions.²

Thick chromium coatings cannot be easily obtained from trivalent baths because of process limitations. Trivalent chromium baths are generally operated in the pH range of 1 to 3 and have a poor pH buffering capacity. Chromium electrodeposit thickness increases at the beginning of plating; however, the plating rate drops rapidly with increasing plating time, leading to a limiting deposit thickness. The reason is ascribed^{3,4} to two competing reactions at the cathode (*i.e.*, the

| Current Effic | eiency of Chr | omium Electrodep | osition | | | |
|--|---------------|------------------|--------------------|--|--|--|
| In an Ammonium Formate Bath with Different Pulse Waveforms | | | | | | |
| Average Current Density | Duty Cycle | Pulse Frequency | Current Efficiency | | | |
| A/m^2 | % | Hz | % | | | |
| 500 | | | 17.6 | | | |
| 1,000 | | | 9.6 | | | |
| 1,500 | 50 | 100 | 5.6 | | | |
| 2,000 | | | 3.1 | | | |
| 3,000 | | | 1.7 | | | |
| | 25 | | 7.6 | | | |
| | 50 | | 9.6 | | | |
| 1,000 | 75 | 100 | 8.2 | | | |
| | 90 | | 7.8 | | | |
| | 100 (DC) | | 6.2 | | | |
| | | 5 | 9.2 | | | |
| | | 100 | 9.6 | | | |
| 1,000 | 50 | | | | | |
| | | 1,000 | 9.9 | | | |

Table 1

chromium electrodeposition and hydrogen evolution reactions):

5,000

12.7

$$\begin{array}{ll} Cr^{+3} + 3e^{-} \rightarrow Cr & \varphi^{0} = -0.74 \text{ V vs. NHE} & (1) \\ 2H_{2}O + 2e^{-} \rightarrow H_{2}^{\uparrow} + 2)H^{-} & \varphi^{0} = -0.828 \text{ V vs. NHE} & (2) \end{array}$$

where ϕ^0 is the standard reduction potential at 25 °C. At the beginning of the plating process, hydrogen ions are reduced to hydrogen gas, and the pH of the solution at the cathode increases with the plating time. It was reported⁵ that the pH at the cathode rose to 8.4 and became stable after about 24 min of plating. The increase in pH induces precipitation of a chromium hydroxide film on the cathode surface,

$$Cr^{+3} + 3OH^{-} \rightarrow Cr(OH)_{3}(s)$$
 $K_{sn} = 10^{-29.8}$ (3)

which functions as a barrier and prevents further deposition of chromium on the cathode surface. Several studies⁶⁻⁹ have shown that hard chromium deposits of 50 to 150 μ m in thickness may be obtained from the trivalent baths at pH less than 1. These baths were prepared, however, by reducing chromic acid with alcohol-type reducing agent(s), rendering the process as environmentally hazardous as the hexavalent chromium baths.

Because the hydrogen evolution reaction is the main reason for the formation of the cathode film, one method to curb this problem is to use non-protonic solvents, such as



Fig. 1—Comparison of the thickness of trivalent chromium deposits from DC and pulse plating in an ammonium formate bath. Avg. current density 1,000 A/m²; pulse freq. 100 Hz, duty cycle 50%.



Fig. 2—SEM photomicrographs of chromium electrodeposits: (a) DC; (b) pulse plating in an ammonium formate bath. Time, 90 min; avg. current density 2,000 A/m²; pulse duty cycle 50%; pulse freq. 100 Hz.

gen and metal ion concentrations depends on the plating current density, pulse frequency and cathodic pulse duty cycle¹³⁻¹⁷. A recent study¹⁸ using a chloride-based trivalent chromium bath at pH 3 has shown that pulse plating increased both plating rate and the thickness of chromium deposit. In addition, pulse plating modifies the morphology of electrodeposit by enhancing the micro-throwing power and re-

molten salts. Bailey and Yoko¹⁰ used a molten LiF-NaF-CrF₃ electrolyte to deposit trivalent chromium ions onto stainless steel substrates. Varagas and Inman¹¹ deposited trivalent chromium from a molten LiCl-KCl bath. Generally, the current efficiency of chromium electrodeposition in the molten salts bath is nearly 100 percent; however, the adherence is poor and the microhardness of the chromium electrodeposit is low.12

The drawbacks of aqueous trivalent chromium baths may be overcome by the use of pulse plating. Pulsed current provides a better pH buffering capacity to the plating baths than direct current. This is because in pulse plating there are periodic currentoff times during which the pH and metal ion concentration at the cathode surface are able to recover by diffusion from the bulk electrolyte. The extent of recovery of hydro-



Fig. 3—SEM photomicrographs of trivalent chromium deposits after 3 hr of pulse plating; avg. current density 2,000 A/m², duty cycle 50%; pulse freq.: (a) 1 Hz; (b) 100 Hz; (c) 5,000 Hz; (d) DC plating at same current density.

ducing the internal stress and porosity of the deposit. Crackfree low-stress chromium deposits have been obtained with pulse current from hexavalent baths containing sulfate and fluosilicate as the catalyst.^{19, 20} These results (from the literature) indicate that it may be possible to use pulse plating to obtain thick chromium deposits from trivalent baths for hard chromium applications.

The objective of this study was to examine the effect of pulse plating on the properties of chromium deposits from trivalent baths. Particular emphasis was placed on plating thickness, internal stress, and microhardness of the chromium coating. A trivalent chromium bath containing either ammonium formate or sodium hypophosphite as the complexing agent^{21,22} was used for the investigation. The effect of pulse plating parameters, such as the average current density, duty cycle, and pulse frequency on the properties of chromium deposits were evaluated.

Experimental Procedure

A trivalent chromium plating bath¹⁸ was prepared according to the following composition: 0.4M $CrCl_3 \cdot 6H_2O$, 0.6M $HCOONH_4$, 0.2M NaOOCCH₃, 1.5M NH₄Cl, 0.5M KCl, 0.7M H₃BO₃, 0.1M NH₄Br and 0.2 g/L of dodecyl sodium sulfate. Because the main complexing agent in the solution was ammonium formate, we shall refer to this bath as the ammonium formate trivalent bath in this report. Another trivalent chromium bath²¹ employing sodium hypophosphite hydrate (NaH₂PO₂·H₂O) as the complexing agent was used in this study. This bath had the following composition: 0.4M $CrCl_3 \cdot 6H_2O$, 2.2M NaH₂PO₂·H₂O, 3.28M NH₄Cl, 0.2M H₃BO₃ and 0.1M NaF, and will be called the hypophosphite trivalent chromium bath in this paper. All of the chemicals used were of reagent grade, and deionized water was used for the preparation of the baths.

The plating experiments were carried out in a ceramic cell (250 mL). The cathode was a piece of $0.02 \times 0.075 \times 0.0004$ m copper panel with an exposed surface area of 0.0008 m². The



Fig. 4—Internal stress of chromium electrodeposits from a trivalent ammonium formate bath as a function of avg. current density: time 30 min; pulse freq. 100 Hz; duty cycle 50%.

Table 2

Microhardness of Chromium Deposits from an Ammonium Formate Trivalent Bath & a Hexavalent Chromic Acid Bath

| | Average Current Density A/m ² | Duty Cycle % | Frequency Hz | Microhardness Knoop kgf/mm² |
|---------------|--|--------------------|-----------------|-----------------------------------|
| | | 100 (DC) | | 750 ± 60 |
| | | 75 | 100 | 710 ± 20 |
| | | | 5000 | 700 ± 20 |
| Trivalent | 2,000 | | | |
| chromium | | 50 | 1000 | 850 ± 10 |
| bath at 23 °C | | | 500 | 810 ± 140 |
| | | | 10 | 610 ± 40 |
| | | 100 (DC) | | 760 ± 20 |
| | 1,000 | | | |
| | | 50 | 100 | 740 ± 30 |
| | 1,000 | | | |
| Hexavalent | | 100 (DC) | | 950 ± 10 |
| chromium | 48 °C | | | |
| bath | 1,000 | | | |
| | | 100 (DC) | | 730 ± 10 |
| | 23 °C | | | |

anode was a piece of $0.05 \ge 0.05 \ge 0.0015$ m titanium panel. The copper cathode was degreased and electrocleaned in a dilute KOH solution before it was introduced into the cell. The pH of the solution was adjusted to 3 by adding KOH or HCl before experiments. The electrolyte was stirred by a magnetic stirrer, and the plating was carried out galvanostatically. Pulsed or direct current was supplied from a pulse power supply. The current waveform was monitored by a storage oscilloscope. All the experiments were carried out at the room temperature of 22 ± 1 °C.

The average Cr electrodeposit thickness over the cathode surface was determined by means of mass gain. The local Cr electrodeposit thickness was determined by the coulometric method. The surface morphology of Cr electrodeposit was examined under a scanning electronic microscope (SEM). The composition of the electrodeposit was analyzed by an energy dispersive spectroscope (EDS) attached to the SEM. The internal stress of the Cr electrodeposit was measured with the rigid-strip technique on a deposit-stress analyzer. The microhardness was measured on the cross section of the chromium electrodeposit, using a Knoop indenter with a 50-g load. The measured points were at 1/8, 1/4, 1/2, 3/4 and 7/8 of the thickness from the deposit surface, and an average hardness value was used.

Results & Discussion

Deposit Thickness & Current Efficiency

Figure 1 shows a comparison of Cr electrodeposit thickness for direct-current (DC) and pulsed-current (PC) plating in the ammonium formate bath without any surfactant. The Cr electrodeposits were obtained at a common average current density of 1,000 A/m². For pulsed-current plating, a pulse frequency of 100 Hz and a duty cycle of 50 percent were used. The results indicate that the plating rate of chromium with pulsed current was higher than that of direct current. The effect of average current density on the current efficiency of Cr electrodeposition was studied in the range of 300 A/m² to

 $3,000 \text{ A/m}^2$. No chromium deposits were obtained when the applied average current density was less than 300 A/m². Unlike hexavalent chromium plating, in which the current efficiency generally increased with increasing current density, the current efficiency of Cr electrodeposition dropped from 17.6 percent at 500 A/m² to 1.7 percent at 3,000 A/m² in this trivalent bath. Pulse plating experiments were also carried out at different duty cycles from 10 to 100 percent and at different pulse frequencies, ranging from 5 to 5000 Hz. Table 1 summarizes the average current efficiency of Cr electrodeposition with different pulsed current waveforms. The current efficiency of Cr electrodeposition first increased with increasing duty cycle, but dropped at high duty cycle. The highest current efficiency occurred approximately at 50percent duty cycle. By increasing pulse current frequency from 5 to 5000 Hz, the current efficiency of Cr electrodeposition increased from 9.2 percent to 12.7 percent.

Surface Morphology

The surface morphology of Cr electrodeposits was not significantly changed by pulsed current. As a typical example, the SEM photomicrographs of chromium electrodeposits obtained from direct-current and pulsed-current plating are shown in Figs. 2a and 2b, respectively. The samples were plated for 90 min at the same average current density of 2,000 A/m^2 . For Fig. 2b, the duty cycle of the pulsed current was 50 percent and the pulse frequency was 100 Hz. Both deposits have a nodular structure with a nodule size of 0.5 to 8 μ m in diameter. The nodular size increased with plating time as well as with the average current density.

Figures 3a to 3c are the SEM photomicrographs of trivalent chromium electrodeposits after 180 min of plating at pulse frequencies of 1, 100, and 5,000 Hz, respectively. The applied average current density was 2,000 A/m² and the duty cycle of the pulse current was 50 percent. The nodular size increased with increasing pulse frequency. Figure 3d is the SEM photomicrograph of a Cr electrodeposit after 180 min of



density 1,000 A/m²; pulse freq. 100 Hz.



Fig. 6—Internal stress vs. pulse frequency for Fig. 5-Internal stress of chromium deposits obtrivalent chromium deposits from an ammonium tained from a trivalent ammonium formate bath as formate bath: Time 30 min; avg. current density a function of duty cycle: Time 30 min; avg. current 1,000 A/m²; duty cycle 50%.



plating with direct current at 2,000 A/m². Compared to the case of pulsed-current plating, the average nodular size obtained with DC was larger. The EDS spectra in the photomicrographs revealed that a small amount of carbon (less than 2 % wt) was included in the deposit. Because no carbon electrode was used in the plating cell, the carbon was probably from decomposition of the organic complexing agents (NH₄COOH and NaOOCCH₂) at the cathode. It was also found that the chromium electrodeposit obtained at a low average current density was brighter than that obtained at a high average current density.

Internal Stress

Figure 4 shows the effect of varying average plating current density on the internal stress of Cr electrodeposits. In the case of pulsed-current plating (solid line in the figure), the samples were prepared with 30 min of plating at a duty cycle of 50 percent and a pulse frequency of 100 Hz. The internal stress was compressive in nature, and increased linearly with increasing average current density, from 20 MPa at 1,000 A/m² to 76 MPa at 3,000 A/m². At a low current density of 500 A/ m^2 , the internal stress increased to 65 MPa. The internal stress of Cr electrodeposits obtained from direct-current plating was also plotted as a function of average current density in Fig. 4 (dashed line in the figure). The results indicate that, pulsed current reduced the internal stress of chromium electrodeposits by two to four times in the current density range of 1000-3000 A/m². Figures 5 and 6 show the internal stress of Cr electrodeposits as a function of the duty cycle and pulse frequency, respectively. The results indicate that the internal stress increased linearly with the duty cycle and with the logarithm of pulse current frequency. The Cr electrodeposit obtained with direct-current plating (corresponds to 100% duty cycle in Fig. 5) had the highest the internal stress of 83 MPa. The yield strength of pure Cr is 250 MPa,²³ and the measured internal stress of Cr electrodeposit fell in the elastic regime of the stress-strain curve.

DC and (b) pulse plating from a trivalent hypophosphite bath: Time 60 min; avg. current density 1,000 A/m²; duty cycle 25%; pulse freq. 100 Hz.

Microhardness

The results of microhardness measurements of Cr electrodeposits obtained from the ammonium formate bath are summarized in Table 2. The microhardness of chromium deposits from this bath ranged from 610 to 850 kgf/mm² on the Knoop hardness scale. These values were comparable to 730 kgf/ mm² for a hexavalent chromium deposit obtained at room temperature of 23 °C and were 15 to 35 percent lower than the hardness value of 950 kgf/mm² of a hexavalent chromium deposit obtained at 48 °C. In trivalent chromium plating, the microhardness of chromium electrodeposits obtained with pulsed current was about the same as that obtained with direct current. As pulse frequency increased from 10 Hz to 1000 Hz, the microhardness of chromium electrodeposits increased from 610 to 850 kgf/mm².

Cr-PAlloy Deposit

Pulse plating experiments were also carried out in a hypophosphite-based trivalent chromium bath. It was found that the plating rate of pulsed current was higher than that of direct current. The Cr electrodeposit plated from this bath was generally brighter than that from the ammonium formate trivalent bath. Figures 7a and 7b are the SEM photomicrographs of Cr electrodeposits obtained with direct-current and pulsed-current plating, respectively. The EDS spectra in the photomicrographs show that significant quantities of phosphorus were codeposited with chromium. The phosphorus content in the deposit was plotted against the duty cycle in Fig. 8. All the samples in the figure were plated for 60 min in the hypophosphite bath at an average current density of 1,000 A/m^2 and a pulse frequency of 100 Hz. The phosphorus content decreased from 30 percent at a 5-percent duty cycle





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Fig. 8—Phosphorus content in chromium electrodeposits from a trivalent hypophosphite bath as a function of duty cycle: Time 60 min; avg. current density 1,000 A/m²; pulse freq. 100 Hz.

Fig. 9—Internal stress of Cr-P deposits from a trivalent hypophosphite bath as a function of average current density: Time 30 min; pulse freq. 100 Hz; duty cycle 50%.

Fig. 10—Internal stress of Cr-P deposits from a trivalent hypophosphite bath as a function of pulse duty cycle: time 30 min; avg. current density 2,000 A/m²; pulse freq. 100 Hz.

to 18 percent at a 100-percent duty cycle (DC). Similar results were observed by Deneve and Lalvani²⁴ from another hypophosphite-based trivalent chromium bath. It was also found in the current investigation that the phosphorus content increased with increasing pulse frequency. Figure 9 shows the effect of average current density on the internal stress of Cr-P deposits. For both DC and PC plating, the internal stress increased with increasing average current density. For the same plating conditions, the internal stress of Cr-P electrode-posits obtained with DC was 1.5 to 2.5 times higher than that with pulsed current. Figure 10 shows the internal stress of chromium vs. duty cycle. The internal stress increased linearly as the duty cycle increased, and the chromium electrodeposit obtained from direct current plating (100% duty cycle) had the highest internal stress.

Findings

An experimental study was made to examine the feasibility of using pulsed current to deposit hard chromium from an ammonium formate and a hypophosphite trivalent chromium bath. The effect of pulse parameters, such as the average cathodic current density, pulse duty cycle, and pulse frequency, on the properties of chromium deposit was studied.

- 1. The chromium-plating rate with pulsed current was higher than that with direct current. Pulsed current improved the maximum coating thickness that could be obtained from the trivalent chromium bath.
- 2. The cathode current efficiency of trivalent chromium plating increased with increasing pulse frequency and with decreasing average current density. In the ammonium formate bath, a maximum current efficiency was obtained at a pulse duty cycle of 50 percent.
- 3. Pulsed current decreased the internal stress of chromium deposits by 25 to 75 percent, depending upon the plating current density and pulse conditions. The internal stress decreased with decreasing current density, duty cycle, and pulse frequency.
- 4. A significant quantity (15 to 30%) of phosphorus was

included in the chromium deposit from the hypophosphite bath. The phosphorus content in the deposit increased with decreasing pulse duty cycle and with increasing pulse frequency.

- 5. The chromium deposits exhibited a nodular microstructure. The nodule size with pulse plating was smaller than that with direct-current plating.
- 6. The microhardness of trivalent chromium deposits obtained with pulsed current was in the range of 610 to 850 on the Knoop hardness scale. The value was comparable to that obtained with direct current. An increase in pulse frequency in the range of 10 to 1000 Hz increased the microhardness of chromium deposit from the ammonium formate bath.

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