Hard Chromium Plating From Trivalent Chromium Solution

G. Hong, K.S. Siow, G. Zhiqiang & A.K. Hsieh

A new trivalent chromium process has been developed that allows a sustained deposition reaction at a high rate for more than 20 hours and provides a deposit with a thickness of 450 microns and hardnesses of up to 1200 Vickers. The effects of chromium concentration, a number of carboxylic acids, a group of buffers, temperature and solution pH on deposition rate, deposit thickness and the ability to plate continuously have been investigated. We propose that normal growth of the trivalent chromium deposit would gradually diminish to either an unacceptably low rate or a complete termination as a result of increasing pH, followed by the formation and precipitation of a series of Cr(III) hydroxides on the cathode surface. The key to the success of this plating process lies in the use of carboxylic acids as complexing agents to promote the chromium deposition reaction, and a group of buffers—including boric acid, aluminum salt and another carboxylic acid—to keep the solution pH sufficiently stable within a certain range, hereby preventing the precipitation of chromium hydroxides on the cathode surface. Ion exchange membranes must be used to separate the anode from the cathode compartment and to prevent oxidation of solution constituents at the anode. They also maintain the stability of the solution constituents and sustain a high rate of deposition over a prolonged period. The hardness of the deposit can be greatly increased after heat treatment in a suitable temperature range.

Introduction

Conventional hard chromium plating technology using hexavalent chromium has been used for more than 100 years and still remains dominant in the chromium plating industry. Because of serious health and environmental problems, strenuous attempts have been made over the last 50 years to obtain a commercially viable trivalent chromium [Cr(III)] plating bath as a replacement for the conventional hexavalent [Cr(VI)] bath.[1-7] However, no viable commercial trivalent hard chromium plating process has been successful.[8-9] The chromium deposition process only proceeds for a short time. After about a half an hour of electrolysis, the deposit becomes black with an eventual loss of metallic appearance and finally peels off. All of these trivalent chromium processes yield only a few microns of chromium deposit suitable for decorative usage. Some publications have described thick chromium deposits produced from Cr(III) solutions using various Cr(III) electrolytes[10-15] and plating methods.[16-18] However, a number of factors have limited the industrialization of these plating processes.

The great difference between the Cr(III) and Cr(VI) deposition process is attributed to the chemistry and electrochemistry of the Cr(III) and Cr(VI) solutions.[19-20] Chromic acid has a much higher solubility in aqueous solution and a very low solution pH. However, it also exhibits a high positive deposition potential from the Cr(VI) state to chromium metal, which effectively prevents the precipitation of Cr(III) hydroxides. At the same time , chromic acid maintains a constant deposition rate over a prolonged period. On the other hand, Cr(III) and its complexes are kinetically inert, have a lower solubility in aqueous solution and a very negative deposition potential. Hydrogen evolution accompanies chromium deposition. There is also a higher pH environment, especially in the vicinity of cathode surface. This leads to the precipitation of Cr(III) and its complexes. Therefore, several problems arise when depositing thick chromium plating from a trivalent solution.

The first problem is how to promote and maintain the activity of the chemical and electrochemical kinetics of Cr(III) and its complexes for a continuous deposition process. The normal growth of a trivalent chromium deposit is greatly restrained by the inertness of hexa-aqua Cr(III) and its complexes.[19-21] The second is how to prevent the rise in solution pH, particularly at the cathode surface, and therefore prevent the formation and precipitation of Cr(III) hydroxides.[22-23] Finally, the third is how to maintain the stability of the constituents of the Cr(III) electrolytes and prevent the oxidation of Cr(III) and its complexing agents. This could have a deleterious influence on the chromium deposition reaction over a prolonged period. All of these problems can be attributed to the characteristics of the Cr(III) complexing agents, buffers and the process control of the chromium deposition.

In our work, a combination of two carboxylic acids, carboxylic acid (I) and (II), was selected and used as a Cr(III) ligand in the solution. Carboxylic acids (I), (II) and (III) are selected from the following groups:

- Monocarboxylic acid: $CH_3 \cdot (CH_2)_{n-1} \cdot COOH$, such as formic acid, acetic acid, propinoic acid and butyric acid.
- Dicarboxylic acid: $COOH \cdot (CH_2)_{n-1} \cdot COOH$, such as oxalic acid, malonic acid, succinic acid, glutaric acid and adipic acid.
- Hydroxyl substituted carboxylic acids: glycolic acid, lactic acid, malic acid, tartaric acid and citric acid.
- Amino substituted carboxylic acid: glycine, alanine, aspartic acid, iminodiacetic acid, glutamic acid, nitrilotriacetic acid and ethylenediaminetetraacetic acid.

Table 1
Composition of the Cr(III) Solution

Component	Amount
Chromium(III) salt	0.6 - 1.0M
Carboxylic acid (I)	0.3 - 0.5M
Carboxylic acid (II)	0.3 - 0.5M
Boric acid	0.2 - 0.8M
Aluminum (III) salt	0.2 - 0.6M
Carboxylic acid (III)	0.2 - 0.6M
Potassium chloride	1.0 - 3.0M
pH	1.0 - 3.0
Temperature	20 - 35°C

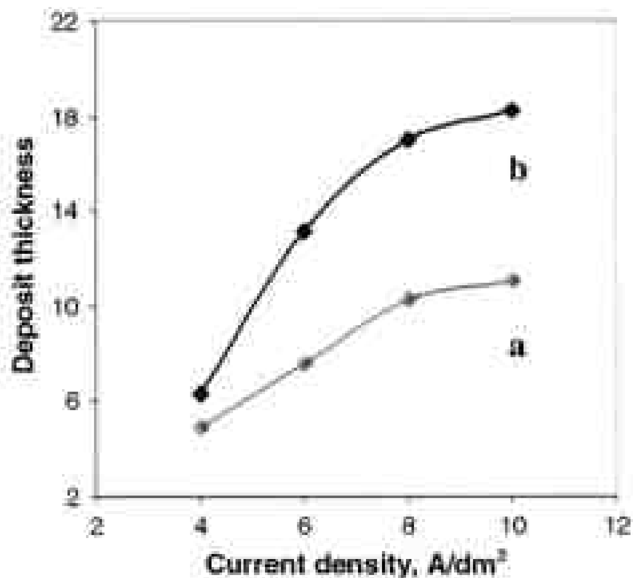

Fig. 1—Plating thickness vs. current density at 0.4M Cr(III). a) 30 min; b) 60 min.

These not only provide the means for continuous chromium deposition; they also promote high deposition rates and plating efficiencies over a prolonged period. A group of buffers was selected and used in this solution, including boric acid, aluminum salt and yet another carboxylic acid (III). The buffers maintain a stable solution pH in a range from 1.5 to 3.0. They prevent the precipitation of Cr(III) hydroxides over a prolonged period. We found that the mixed carboxylic acids and the buffers played a critical role in obtaining thick chromium deposits from this Cr(III) solution.

In this paper, the deposition process for producing a thick chromium plating from this Cr(III) solution will be described. The effects of Cr(III) concentration, carboxylic acids, buffers and deposition conditions have been studied in detail.

Experimental Procedure

The basic composition of the Cr(III) solution is shown in Table 1. All reagent-grade chemicals were used to prepare the solution. Cr(III) salts, carboxylic acids (I) and (II), boric acid and conductive salts were dissolved in deionized water. The solution was heated to 80°C, stirred for two hours, then cooled to room temperature and allowed to stand for at least five hours. The solution pH was adjusted between 1.5 to 3.0 by the addition of sodium hydroxide or potassium hydroxide.

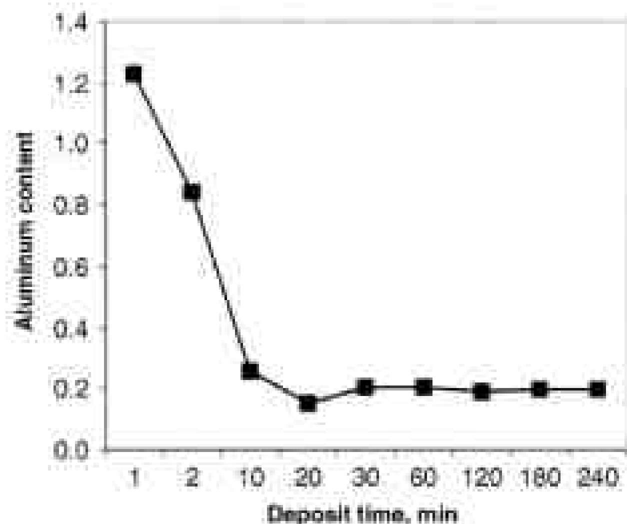

Fig. 3—Aluminum content vs. deposition time at 0.8M Cr(III), 15 A/dm².

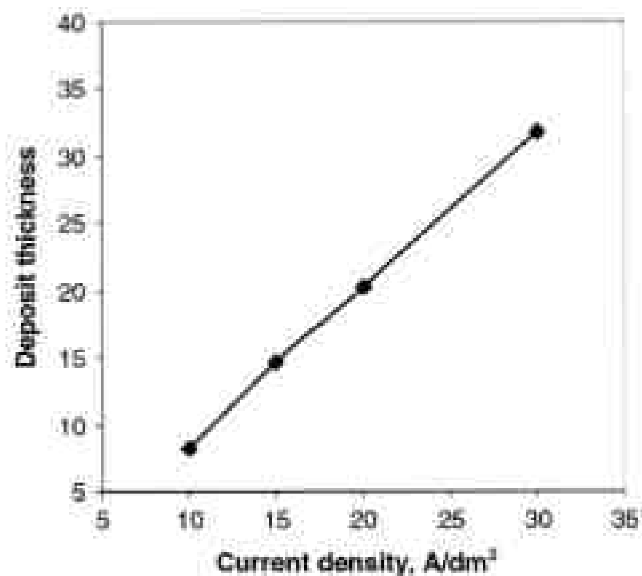

Fig. 2—Plating thickness vs. current density at 0.8M Cr(III), 30 min.

The aluminum salt and carboxylic acid (III) were added. The solution was again heated to 50°C, stirred for one hour and cooled to room temperature. The solution pH was readjusted between 1.5 to 3.0. The solution was allowed to stand overnight before any plating test.

Plating was carried out in a double-cell by using a Nafion® cation exchange membrane to separate the anode and cathode compartments. The anode consisted of a platinized titanium mesh or lead plate. The anolyte was either a 0.5M H_2SO_4, 0.5M K_2SO_4 or 0.5M Na_2SO_4 solution. The cathode was a brass plate, whose non-working area was insulated. The pretreatment of the cathode consisted of degreasing it in alkaline solution, activating it in a five volume percent sulphuric acid solution and rinsing it with distilled water.

The thickness of the chromium deposit was measured by weighing brass plate before and after plating, or by measuring the cross section with a scanning electron microscope (SEM). The surface morphology of the deposit was examined with the SEM. The aluminum content of the chromium deposit was measured by electron diffraction analysis by X-rays (EDAX). The hardness was measured by a Vickers hardness tester under a load of 100g on the cross section perpendicular to the substrate.

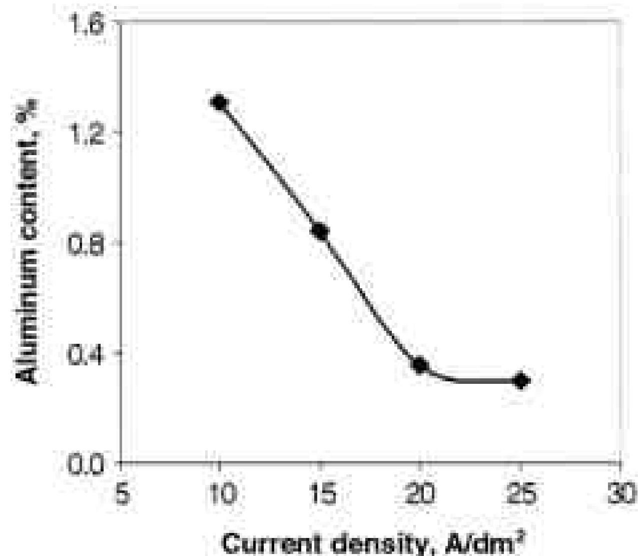

Fig. 4—Aluminum content vs. current density at 0.8M Cr(III) and deposition time 2 min.

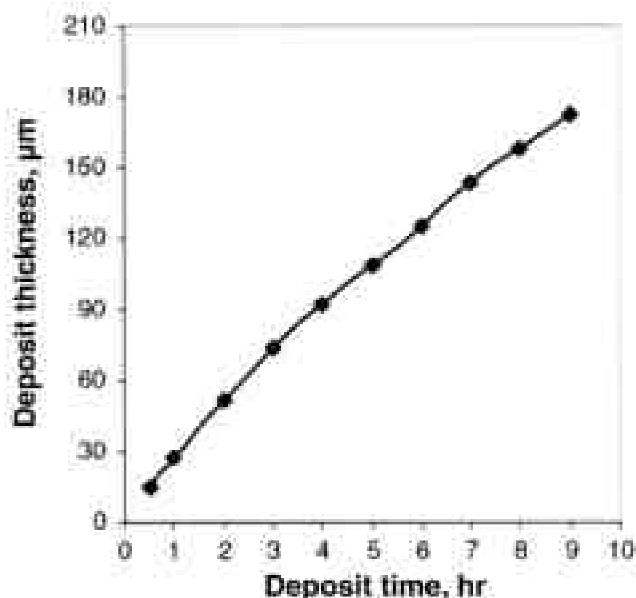

Fig. 5—Plating thickness vs. plating time at 0.8M Cr(III), 15 A/dm².

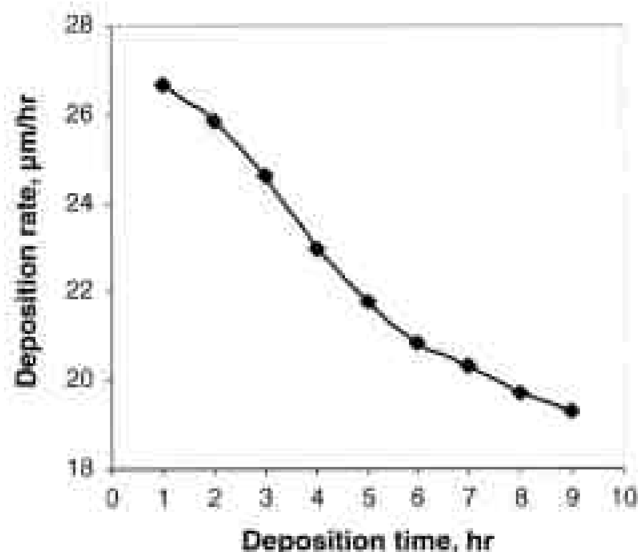

Fig. 6—Average deposition rate vs. plating time at 0.8M Cr(III), 15 A/dm².

Results & Discussion

Effect of Cr(III) Concentration

It was found that Cr(III) concentration had a significant effect on sustaining the deposition rate and increasing the limiting current density. The limiting current density and deposition rate were decreased at lower Cr(III) concentrations. At the concentration of 0.4M Cr(III), as shown in Fig. 1, the deposition rate increased markedly in the lower current density range from 4.0 to 8.0 A/dm² and gradually decreased beyond 8.0 A/dm². A black deposit was produced above 10.0 A/dm². On the other hand, the lower concentration did allow a lower deposition rate over a prolonged plating period.

The higher the Cr(III) concentration, the higher the limiting current density and deposition rate for this Cr(III) solution. When the Cr(III) concentration was increased above 0.8M, the limiting current density was 30 A/dm² and the deposition rate reached 35 μm in 30 min, as shown in Fig. 2.

A plausible explanation for the effect of Cr(III) concentration on the diffusion rate of Cr(III) species from the bulk solution into the cathode diffusion layer is as follows. Higher Cr(III) concentrations will increase the diffusion rate and produce more electroactive Cr(III) species. A higher deposition rate can thus be maintained.[18] In a dilute Cr(III) solution, the failure to transport sufficient Cr(III) species into the cathode diffusion layer will result in a lower rate of formation of electroactive Cr(III) species and the deposition rate is decreased. Although the higher Cr(III) concentration is beneficial to the deposition process, the ability to increase the Cr(III) concentration is limited by lower solubility and higher viscosity. Taking this into account, an optimum Cr(III) concentration in this solution is about 0.8M.

Table 2
Aluminum Composition vs. Plating Time

Time, min	Aluminum, %
1	1.2306
2	0.8358
10	0.2561
20	0.1487
30	0.2009
60	0.2011
120	0.1867
180	0.1911
240	0.1965

Effect of Complexing Agents

It is impossible to deposit chromium metal from a simple Cr(III) electrolyte because of the formation of a very stable $[Cr(H_2O)_6]^{+++}$. Therefore, appropriate ligands are necessary to substitute for water molecules and form an electroactive Cr(III) complex. An easily-deposited Cr(III) complex should have a suitable thermodynamic stability and promote high electrochemical kinetics in the chromium deposition process.[24-25] Over twenty kinds of potential ligands, mostly carboxylic acids, were selected and studied. We found that using these mixed carboxylic acids not only enhanced the deposition process but also maintained a suitable stability of Cr(III) species. A high deposition rate was sustained over a prolonged period.

In previous work,[26] we studied the influence of the concentration ratios of a) carboxylic acid (I) to carboxylic acid (II) and b) of the mixed carboxylic acids to Cr(III). It was found that an optimum ratio of carboxylic acid (I) to carboxylic acid (II) was 1:1. The ratio of the mixed carboxylic acids to Cr(III) ranged from 1:1 to 2:1. We found that increasing this mixed carboxylic acid to Cr(III) ratio increased the limiting current density. However, the deposition rate decreased rapidly because a more stable Cr(III) complex formed. In general, a more stable Cr(III) complex is associated with a lower rate of formation of electroactive Cr(III) species, and thus the deposition rate is decreased.[27] On the other hand, even a more stable Cr(III) complex was unable to prevent the precipitation of Cr(III) hydroxides because of the lower deposition rate and build-up of pH over a prolonged period. Excepting at lower deposition rates, increasing the ratio of the mixed carboxylic acid to Cr(III) would increase the solution viscosity and the amount of insoluble deposits. Therefore, a strong buffer was necessary to prevent the precipitation of Cr(III) hydroxides during deposition.

Effects of Buffering Agents

During a prolonged plating process, the most important factor is the control and stabilization of the solution pH, particularly in the cathode diffusion layer. It has been reported that pH

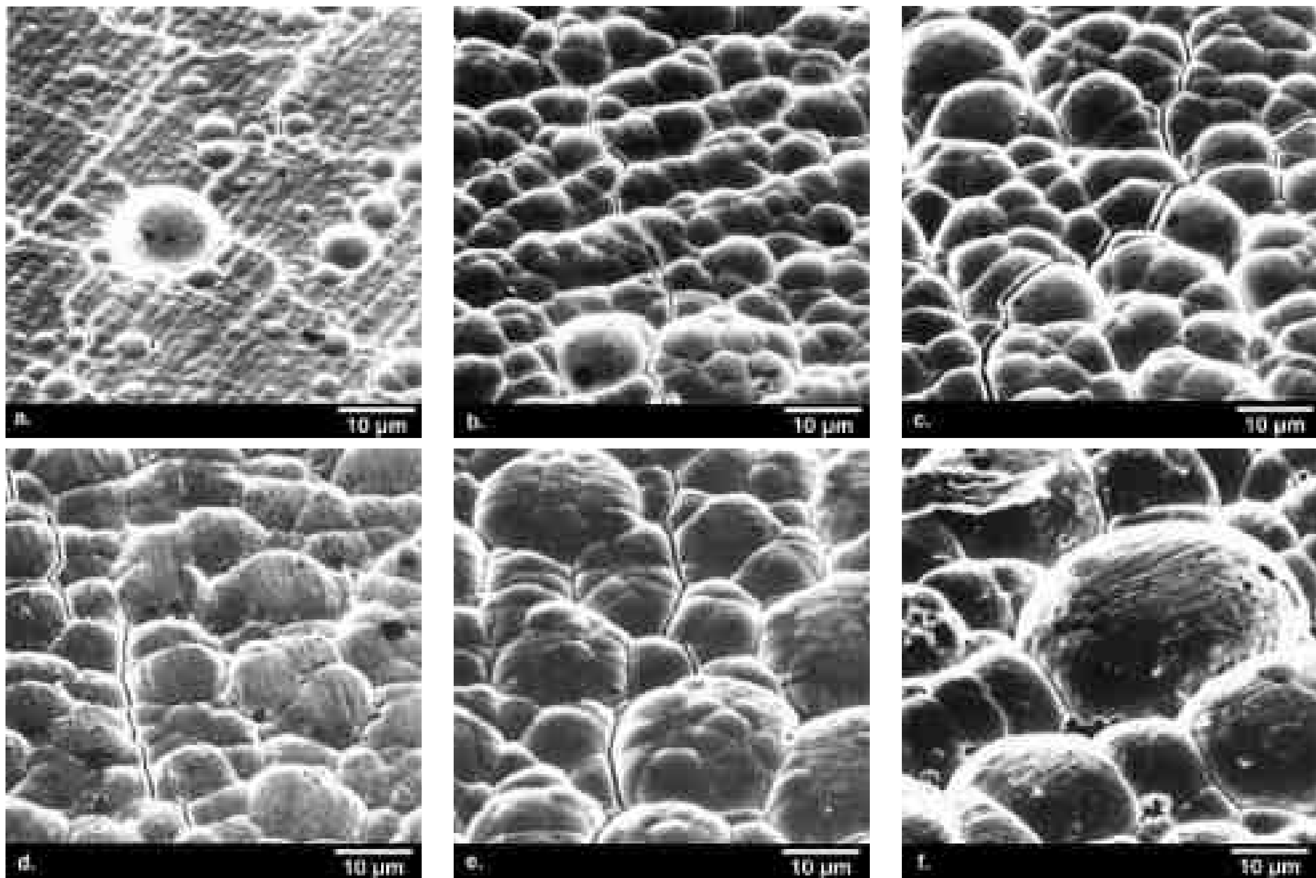

Fig. 7—SEM photographs of hard chromium plating produced at 15 A/dm² with a) 0.5 hr; b) 2 hr; c) 3 hr; d) 4 hr; e) 5 hr; f) 9 hr.

can rapidly increase from 3.3 to 8.4 in the cathode diffusion layer after the deposition time of more than 20 minutes.[22] At that pH value, the formation and precipitation of Cr(III) hydroxides is inevitable. The normal growth of chromium deposit would thus be inhibited.

After much experimentation, a group of buffers, including boric acid, aluminum salt and carboxylic acid (III) were used in solution. The combined use of these buffers prevented the build up of solution pH and the precipitation of Cr(III) hydroxides. A constant deposition rate was maintained over time. Each buffer was necessary in this solution and played a particular role in stabilizing solution pH during deposition. Without the buffers, or in a solution containing only boric acid, plating could only be carried out either at a lower pH range of 0.5 to 1.0 or at lower current densities. These operating conditions, however, were unable to maintain a sustained deposition process because of the lower deposition rate and an excessive hydrogen evolution.

By introducing aluminum salt and carboxylic acid (III), two main problems for obtaining thick chromium plating from this solution were solved. First, at higher current densities, this solution had much stronger buffering capabilities than those containing only boric acid or other kinds of buffers. The pH could be stabilized in a range of 1.5 to 3.0 over prolonged deposition. Second, the tendency for precipitation of Cr(III) hydroxides and the formation of a black chromium deposit on the cathode had been diminished. The pH for the formation of aluminum hydroxides is 3.0, but the pH for the formation of Cr(III) hydroxides is about 4.0. It is probable that a thin insoluble film, primarily of Al(III) hydroxides, was produced before the Cr(III) hydroxides formed in the cathode diffusion layer. Such a thin film could hinder the entrance and growth of large molecular-sized Cr(III) hydroxides to a deposition site, yet allow the entrance of the electroactive Cr(III) species and the deposition reaction taking place on the cathode.

Deposition time and current density had an influence on the aluminum composition in the chromium deposit. At 15 A/dm², the aluminum composition decreased markedly in the first 20 minutes of electrolysis. It then remained constant at about 0.2% up to 4 hours, as shown in Fig. 3. At the earlier deposition time of two minutes, shown in Fig. 4, the aluminum composition decreased rapidly by increasing the current density from 10 to 25 A/dm².

The use of carboxylic acid (III) is a key factor in obtaining

Table 3
Aluminum Composition vs. Current Density

Current Density, A/dm²	Aluminum, %
10	1.3036
15	0.8358
20	0.3569
25	0.2926

Table 4
Plating Hardness Before & After Heat Treatment

Sample	Thickness, micron	Before Heat, VHN	After Heat, VHN
1	110	719	1025
2	180	658	1131
3	220	711	1126
4	280	785	1079
5	350	616	1046
6	450	674	1103

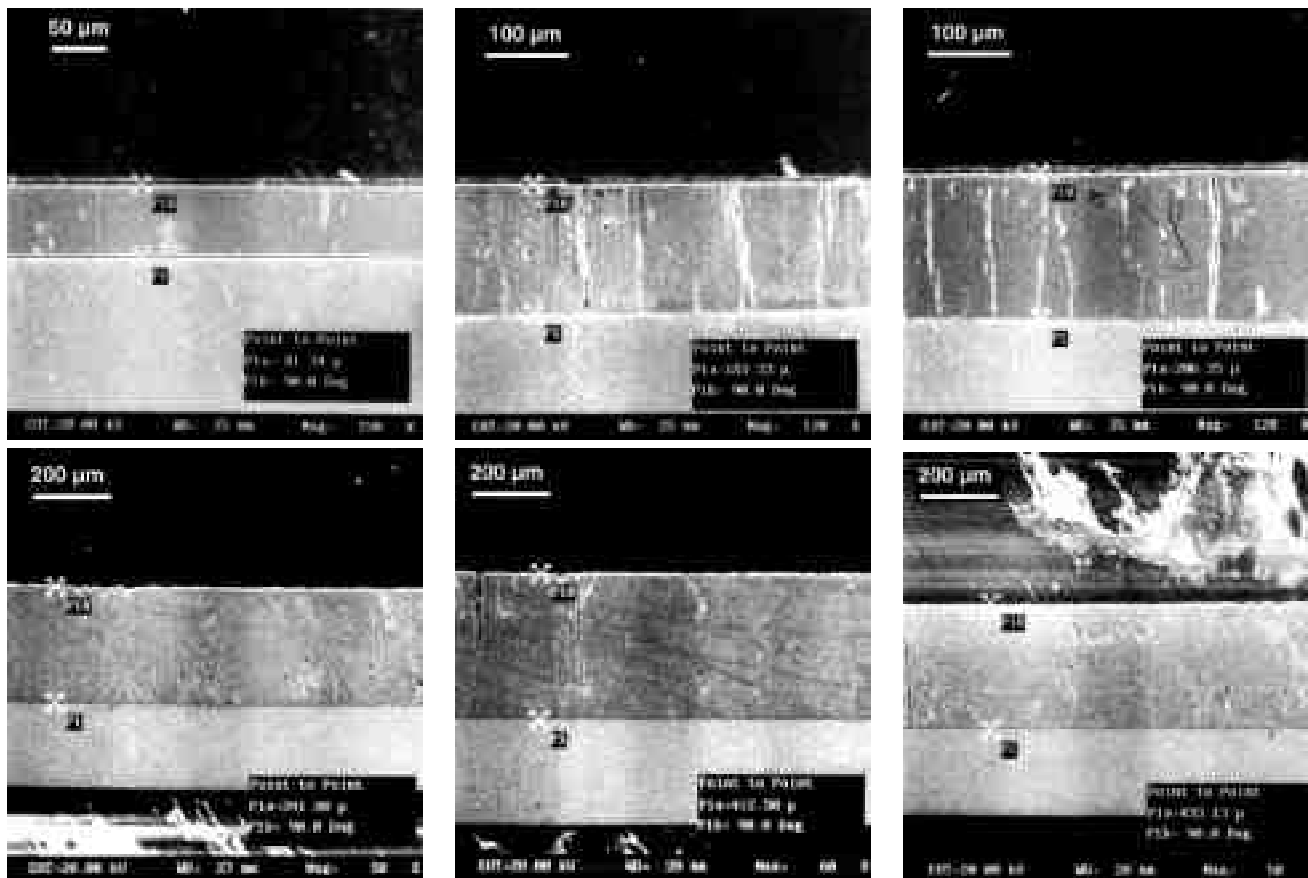

Fig. 8—SEM photographs on the cross section of hard chromium plating produced from Cr(III) solution.

thick deposits from this Cr(III) solution. It overcomes the eventual peeling of the chromium plating during prolonged electrolysis. In the solution containing only the aluminum salt and boric acid, the deposit peeled after one hour. This was not the case if carboxylic acid (III) was added. The carboxylic acid (III) may form a stable Al(III) complex that prevents a thin cathode layer film from growing into a thick one. A thicker film will significantly retard the entrance of electroactive Cr(III) species and decrease the deposition rate. Deposit adhesion can be adversely effected because of the presence of one layer of non-metallic Al(III) hydroxide between the chromium deposit and the substrate. On the other hand, the carboxylic acid (III) itself may be regarded as a strong buffer that prevents a rapid pH rise in the cathode diffusion layer, preventing precipitation of Al(III) hydroxides.

Boric acid has a marked role for improving the coverage of deposits over a prolonged plating period. The appropriate concentration range for the boric acid is from 0.2 to 0.8M. The aluminum salt and carboxylic acid (III) concentrations are 0.2 to 0.6M.

Effects of Deposition Conditions

The plating conditions, including pH, temperature and current density played an important role in the chromium plating process. Temperature was generally maintained between 25 to 45°C. Below this range, the solution viscosity increased. Large amounts of insoluble deposits were also produced. Higher temperatures accelerated the rate of hydrogen evolution and increased the instability of the mixed Cr(III) complexes.

The appropriate pH ranged from 1.5 to 3.0. Above a pH of 3.0, the deposition rate greatly decreased and a black deposit was produced. At a pH below 1.0, significantly more hydrogen evolution took place on the cathode, at the expense of chromium deposition. This decreased the current efficiency and plating coverage.

A suitable current density range for producing thick deposits was between 10 and 30 A/dm^2. Although the limiting current density could be increased by lowering the pH or raising the ratio of carboxylic acids to Cr(III), these methods enhance hydrogen evolution rather than chromium deposition.

The process allowed sustained deposition to continue for more than 20 hours, provided the Cr(III) concentration and other conditions were kept within range. In the first nine hours of plating, the thickness increased markedly, as shown in Fig. 5. Beyond nine hours, we found that the average plating rate gradually decreased. Figure 6 shows that, during the first several hours, the average plating rate was high and it decreased markedly with a further increase of plating time. It is likely that a sustained deposition reaction will consume a large quantity of Cr(III) species, which may in turn decrease the rate of formation of electroactive Cr(III) species, leading to a drop in the deposition rate.

An ion exchange membrane had to be used to separate the cathode from the anode on the plating process. It enhanced the stability of the solution constituents and sustained the plating process. At the anode, the membrane completely eliminated the oxidation of some easily oxidizable constituents, including the oxidation of Cr(III) species and some reductive carboxylic acids. Such oxidation will generally produce poor deposit quality and shorten the working life of the Cr(III) bath. An ion exchange membrane can also prevent the evolution of toxic gases such as chlorine at the anode.

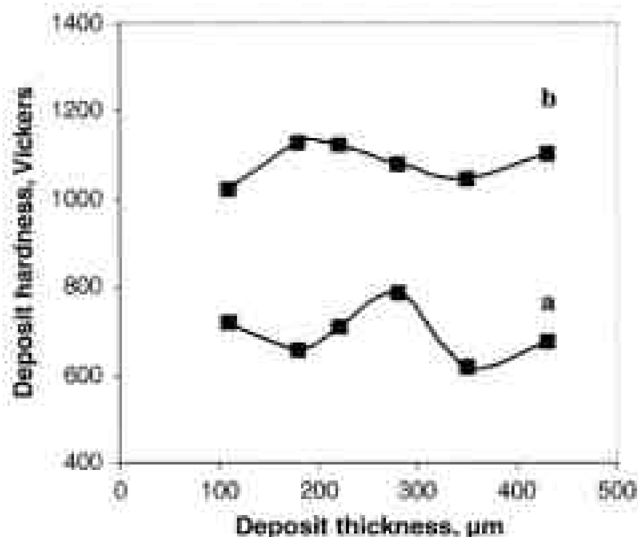

Fig. 9—Hardness of the chromium plating before and after heat treatment; a) before; b) after.

Surface Morphology & Hardness

We were able to produce chromium deposits with a thicknesses ranging from 50 to 450 µm from this trivalent solution. The deposit was semibright with a silver white color. A typical structure consists of a large number of nodular crystals surrounded by some microcracks, as shown in Fig. 7. In Figs. 5(a) to 5(e), it can be seen that with increasing plating time and deposit thickness, the nodular crystals grow markedly and the microcracks become wider and deeper. With a further increase of plating time of several hours, these nodular crystals continue to grow and finally evolve into a larger and smoother chromium crystal, as in Fig. 5(e). From Fig. 5(a) and 5(f), it can be seen that at lower current densities, both the chromium crystals and the micro-cracks are very small. By increasing the current density to 15 A/dm^2, these chromium crystals enlarge and the numbers of microcracks markedly increase.

Metallographic cross sections of the chromium deposits produced at varying times are shown in Fig. 8. Some of the microcracks are seen to cross the entire plating layer down to the substrate. In the other cases, some cracks are overlapped and covered by a further deposit growth and do not penetrate the entire thickness. We also found that the numbers of cracks was influenced by plating conditions.

We found that the deposit hardness obtained from this solution ranged from 550 to 800 VHN. After heat treatment ranging between 250 and 350°C for two hours, the hardness increased to about 1200 VHN, as shown in Fig. 9. It was also found that after heat treatment, the deposit structure was much smoother compared with the rough and somewhat brittle structure beforehand. It is possible that a mixture of Cr(III) hydroxides, hydrides and carboxylates were codeposited and encapsulated during plating. These compounds may be transformed into Cr(III) carbides and oxides after heat treatment, leading to the hardness increase.

Conclusion

A new trivalent chromium deposition process has been developed which allows sustained chromium deposition for up to 20 hours, providing a deposit with a thickness of up to 450 microns. The deposit thickness can be increased at will if the solution constituents and plating conditions are controlled in an appropriate range. The key to the success of this plating process lies in the combination use of carboxylic acids as Cr(III) complexing agents, and a group of buffers including boric acid, aluminum salt and a third carboxylic acid(III) to prevent the precipitation of Cr(III) hydroxides and stabilize the solution pH over a prolonged period. After heat treatment, the plating hardness can be increased up to 1200 VHN. An ion exchange membrane must be used to prevent the oxidation of some easily oxidized constituents at the anode and keep the stability of the Cr(III) solution and a sustained plating process over a prolonged period.

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