Cathode Polarization in Trivalent Chromium Plating

By Zhenmi Tu, Zhelong ***Yang, Jingshuang Zhang, Mao-Zhong An and Wen-Liang Li***

It Is well known that trivalent chromium plating technology has many advantages. Although the technology has been applied in production, some problems remain; for instance, the plated film cannot be thickened at will and its glossiness lacks a bluish hue. Accordingly, these factors may, to some extent, prevent the technology from being further applied in industry. In order to elucidate the problems, the authors investigated the technology by using chemical and electrochemical methods, as well as XPS analysis, were successful and have drawn some useful conclusions from the findings. The findings may be of great practical and theoretical significance for further improvement of the new technology, including improvement of the properties of the plated film and by extending the scope of application.

Research on trivalent chromium plating technology has been significant and the technology has found its way into production. The main advantages of the technology are low toxicity and easy treatment of spent liquids. In addition, it has good throwing and covering power. Plating can be performed at room temperature and is not affected by current interruption. There are disadvantages, however: The plated film cannot be thickened at will. Generally, its thickness is limited to several pm. Also, the glossiness of the plated film is slightly inferior, especially when the film is thicker.

In order to resolve these problems, various factors were explored that influence the increase of film thickness, including variation of pH of the cathode surface. The key reason for the problems appears to have been found, laying the theoretical basis for further improvement of the quality of the plated trivalent chromium film.

Experimental Procedure

A series of measurements of the various relationships of the plating process was made in an unstirred plating solution, the constituents of which are shown in the table. Shown also are the physical conditions of each set of the measurements.

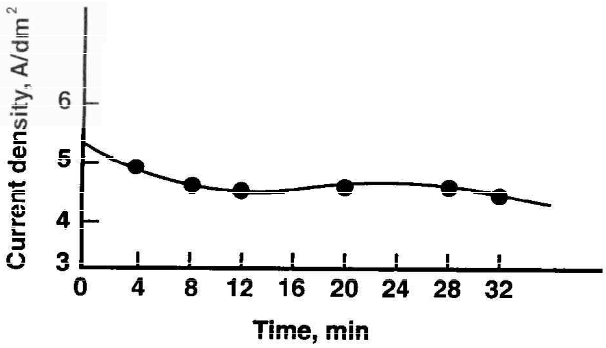


Fig. 1—Relationships of current and plating time.

For measurement of the specification curve of potential and pH, 50 mL of the trivalent chromium plating solution were mixed with sodium hydroxide or hydrochloric acid to obtain solutions with various pH values. Then, the pH and the potential of a microstibium (micro-antimony) electrode vs. SCE were measured simultaneously.

Table
Constituents of the Plating Solution
And Physical Conditions of Measurements

Trivalent chromium	0.44 mol/L
Formate	0.6 mol/L
Acetate	0.2 mol/L
Ammonium chloride	2.5 mol/L
Potassium chloride(optional)	1.0 mol/L
Ammonium bromide	0.1 mol/L
Boric acid	0.6 mol/L
Brightener and wetting agent	1-2 mL/L
pH	3-3.5
Current density, D_k	6-12 A/dm^2
Anode (compacted graphite)	

Current vs. Plating Time (constant voltage)
Constant potential: 1.30 V (vs. SCE)
pH of plating solution: 3.30
Temp 20 °C

Potential vs. Plating Time (constant current)
Potential at a distance of 20 μm from the cathode surface (vs. SCE)
pH 3.30
D_k: 10 A/dm^2
Temp 20 °C

Film Thickness vs. Plating Time
pH 3.0
D_k: 10 A/dm^2
Temp 15 °C
The appearance and thickness of the film were observed and measured by a scanning electron microscope.

Current Efficiency vs. pH
Temp 20 °C
D_k: 10 A/dm^2
Time: 10 min
pH (variable)

Deposit Velocity vs. pH
Temp 15 °C
Time: 3 min
D_k: 10 A/dm^2
pH (variable)
Thickness: (measured by SEM).

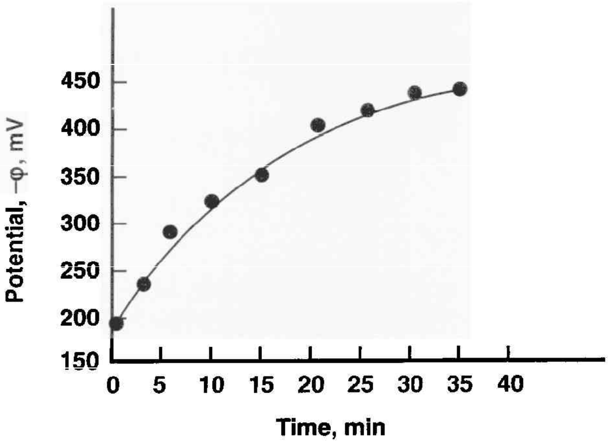


Fig. 2—Relationship of potential and plating time.

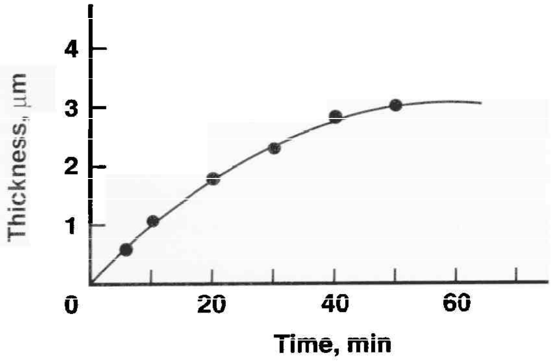


Fig. 3-Relationship of film thiickness and plating time.

The microstibium electrode was also used for measurement of pH near the cathode during plating. Solution pH was measured and the distance between the microstibium electrode and the development electrode (cathode surface) was adjusted to 20 µm, using a 100X microscope. The physical conditions were:

Research electrode-copper sheet, 11.5 x 20 mm
Auxiliary electrode—graphite, 23 x 20 mm
Reference electrode-saturated calomel (SCE)
Current-0.23 A
Temp-25 ℃
pH—3.3

Potential variation was measured for 15 rein, from the beginning of plating. Plated specimens were measured by a multifunction electron spectroscope.[a]

Results and Discussion

From the curve in Fig. 1, it can be seen that when the potential is constant, the reaction current decreases rapidly at the beginning. After 20 rein, however, the reduction is slower although it continues to decrease. After about 30 rein, the reduction finally reaches a standstill.

In Fig. 2, the curve shows that when the current is constant, it becomes more and more negative as plating time continues. From Fig. 3, it is found that film thickness increases quickly at the beginning of electroplating. As plating continues, the increase slows gradually, until it almost comes to a stop after 30 to ***40*** min. It has also been observed by SEM that when plating time grows longer, cracking of the film surface increases and glossiness is reduced.

From Fig. 4, it can be seen that when the pH of the plating solution increases, the current efficiency rises at the beginning of plating, but reaches a peak when the pH is equal to about 2. If the pH continues to increase, the current efficiency begins to decrease gradually, dropping to about 3 percent when pH = 5.

When pH = 2, the deposit velocity is greatest (Fig. 5), but falls sharply as the pH increases, mainly because hydrogen evolution increases and current efficiency decreases, which is in agreement with the result shown in Fig. 4.

These experimental results demonstrate that during trivalent chromium plating, the deposit velocity of chromium is rapid at the beginning but, as plating time continues, it slows gradually and finally comes to a standstill after about 30 min. This is the reason that the plated film can reach a thickness of merely 3 to 4 pm. The fact that the film can no longer be thickened is also verified by the electrochemical reaction to the variation of the cathode potential and the current. When the current is constant, the specification curve of the cathode potential and the plating time (Fig. 6) show that, as plating time increases, the cathode potential tends to become more and more negative, cathode polarization increases, and afterward becomes stable gradually. When the potential is constant, the reaction current decreases rapidly at the beginning as plating time increases; after this, it also becomes stable gradually.

In addition, it is clear that the cathode current efficiency and deposit velocity are closely related to the PH. When the pH

---

[a] Model PH 155 ESCA/SAM, Perkin-Elmer Corp., Norwalk, CT.

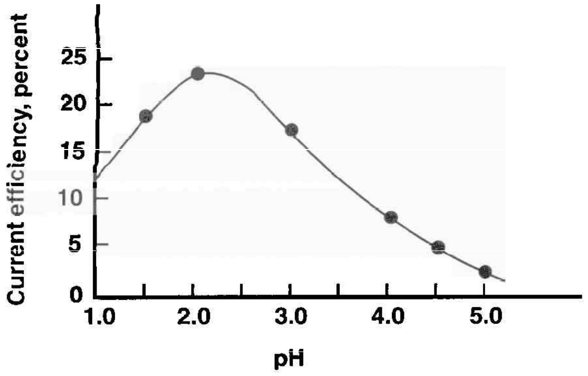


Fig. 4—Relationship of current efficiency and pH.

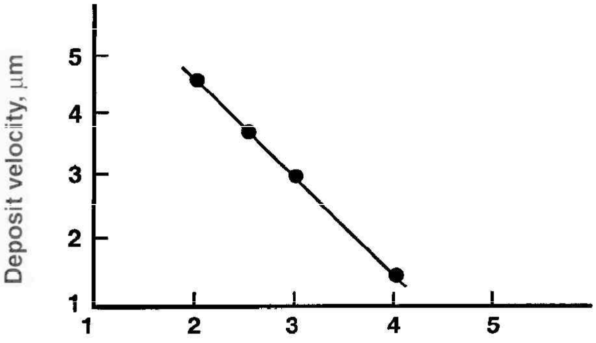


Fig. 5—Relationship of deposit velocity and pH.

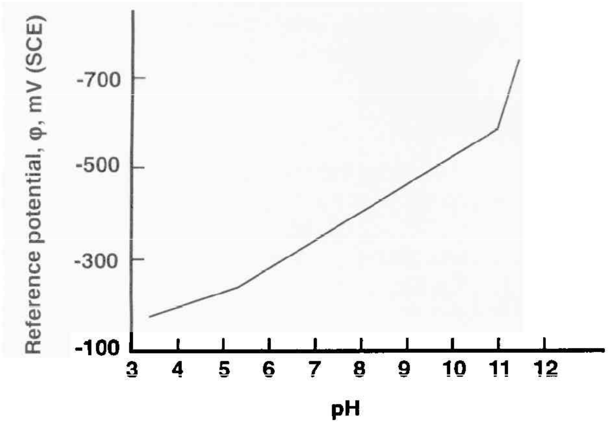


Fig. 6—Specification curve of pH and potential.

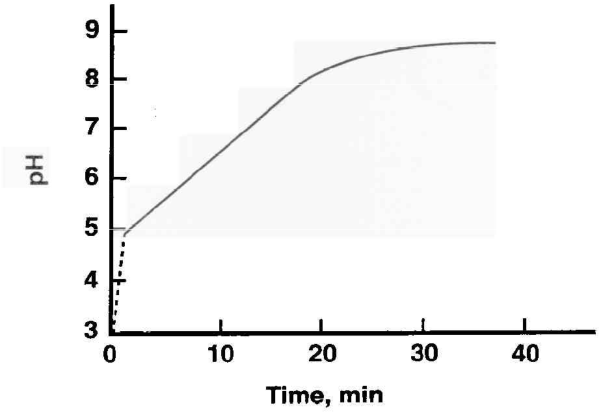


Fig. 7—Variation of pH at a distance of 20 µm from the cathode.

increases to 5, the current efficiency is about 3 percent. It follows that the variation of the pH at the cathode surface is the most likely reason that the film thickness is prevented from increasing any further,

In the experiments, the total plating time was 45 min. It was found that the pH value near the cathode varied and, as plating time continued, it rose gradually. After 24 min the value became stable at about 8.4. A portion of the plating solution was then titrated with sodium hydroxide. At that pH, it was found that some solid deposit began to emerge. Analysis determined it to be chromic hydroxide.

The main deterrent of increase in film thickness is the variation of pH at the cathode surface. When this variation is measured at a distance of 20 µm from the cathode by a microstibium electrode (Fig. 7), it is found that the efficiency of hydrogen eduction increases so much (about 80 percent) that the hydrogen ions at the cathode surface are consumed rapidly as plating time continues. Therefore, the pH rises quickly. It can reach 8.5 after about 2 min. In fact, the pH nearer the cathode surface is still higher. Because the volubility of chromic hydroxide is very small ($K_{sp} = 5.4 \times 10^{-31}$), sedimentation of chromic hydroxide will be facilitated when pH is high.

As the plating solution is titrated by alkali and the pH reaches 8.4, precipitation of solid chromic hydrate is noticeable. This shows that when the pH at the cathode surface is equal to 8.4, colloidal chromic hydroxide appears. This colloidal chromic hydrate and/or chromium oxide film covers the cathode surface, and its concentration and thickness increase as plating time continues and the pH increases. Chromic hydroxide and/or chromium oxide (impurity) are mixed in the chromium sedimentary deposit. This may also promote the increase of cathode polarization, the decrease of chromic deposit efficiency, and increase of impurities in the plated film. All these factors will influence the normal growth of crystals in the plated film, and finally lead to prevention of growth of the sedimentary deposit, except for the eduction of hydrogen and side reactions. When the appearance of the plated surface was observed by SEM, serious map cracking and even part of the film cast-off were discovered.

Analysis of the trivalent chromium plated film by XPS shows that Cr^0, Cr^{+3} and oxygen were present in the plated film. Further, the trivalent chromium and oxygen content in the external film are higher than those in the inner part of the film. The analytical results obtained by XPS showed that the plated film surface which had been cleaned contained metallic chromium, trivalent chromium and oxygen (Fig. 8). After the film was sputtered by argon for 15 rein, it still contained Cr^0, Cr^{+3} and oxygen, although the oxygen content was obviously lower.

Conclusions

The primary reason why trivalent chromium plating technology cannot increase film thickness at will, as plating time continues, is the result of rapid increase of the pH at the cathode surface. This leads to increase of the hydrates of chromium mixed in the

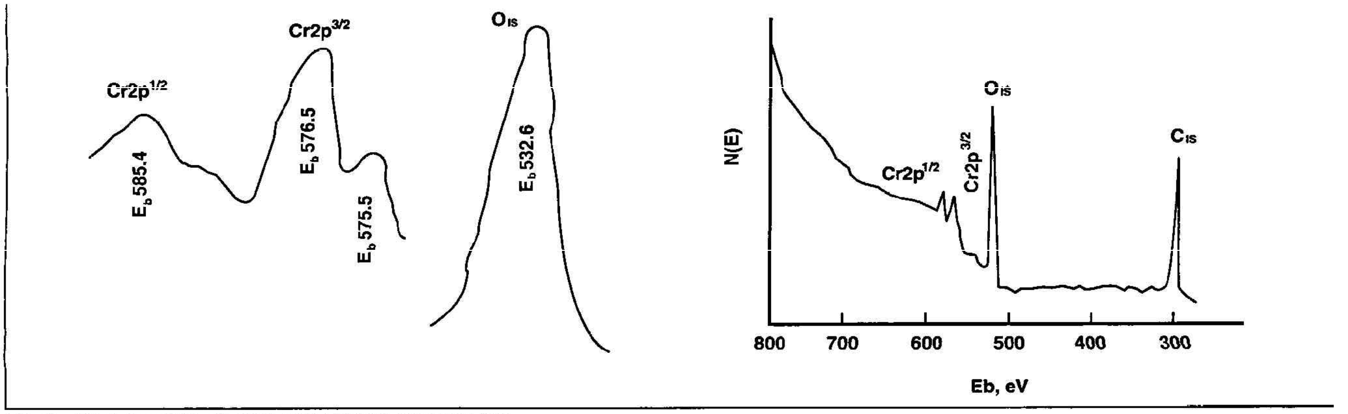
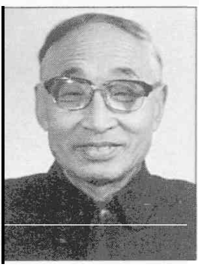


Fig. 8—X-ray spectrum diagram of the plated chromium film.

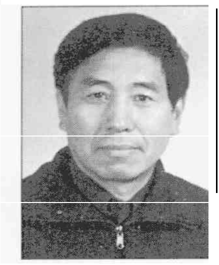
plated film, which influences the normal generation of crystals. Consequently, the increase of film thickness is restrained, the film surface becomes coarse, with map cracking, and its glossiness is reduced.

References

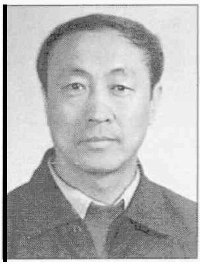
1. Zhenmi Tu, ***Shanghai Electric Plating, No. 4, 1981.***
2. Kuofu Keng and Shingji Yaomiz, ***Metal Surface Technology,*** Zhelong Yang, Trans. 32,569 (1981).
3. Zhenmi Tu and Zhelong Yang, ***Academic Journal of Ordnance, No. 1 & No. 3, 1983.***
4. Zhenmi Tu and Zhelong Yang, ***Electroplating and Environmental Production, No. 5, 1985.***
5. A.T. Kuhn and C.Y. Chan, ***J. Applied Electrochem.,*** **13,189-**207 (1983).



Tu



Yang



Zhang

An

About the Authors

Zhenmi Tu is a professor at the Harbin Institute of Technology, Harbin 150006, P. R, China. His research includes electroplating, electroless plating, and metal finishing. He is an Adviser to the Electroplating Association of China, and vice-president of the Surface Treatment Association of Heilongjiang Province. He has published two books and more than 70 papers on metal finishing and related fields.

Zhelong Yang is a lecturer in the Department of Electrochemistry, Harbin Institute of Technology. His research interests include electroplating and electroless plating. He holds a BS from Harbin Institute of Technology and has published more than 40 papers on electroplating and related fields.

Jingshuang Zhang is a senior engineer in the Department of Applied Chemistry, Harbin Institute of Technology. He is a laboratory director and inventor. He holds a BS from Harbin Institute of Technology and has published more than 40 papers on metal finishing and surface treatment.

Mao-Zhong An is a lecturer in the Department of Applied Chemistry, Harbin Institute of Technology. His research interests include metal finishing and surface treatment, He has published one book and more than 25 papers. He holds an MS from HIT.

Wen-Liang Li is an engineer at the Zhuhai Eastbourne Chemical Power Development Center, Zhuhai City. His research interests include electroplating and metal finishing. He has published several papers on electroplating of alloys. He holds an MS from HIT.