### **A Novel Chromium Plating from Trivalent Chromium Solution**

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Chromium deposition process from a novel Cr(III) solution based on a couple of carboxylic acids as complexing agents has been described. This process not only produce a bluish-white color of deposit visually indistinguishable from that of Cr(VI) plating, but also maintain a constant deposition rate over a prolonged period. It was found that the nature of a Cr(III) complex had a great influence on the deposition process including the deposit color, deposition rate and a sustained deposition process. It is proposed that an excessive hydrogen evolution on overall deposition process is detrimental to the deposit color and deposition rate because it causes a rapid rise of pH and thus the precipitation of a series of Cr(III) hydroxides on the cathode. The mixed Cr(III) complex obtained by the couple of carboxylic acids can promote chromium deposition reaction, suppress a rapid rise of pH in the cathode layer, and keep a sustained deposition process at lower current densities. The effects of solution constituents and compositions, pH and temperature on the deposit color, deposition rate and surface morphology have been investigated and discussed.

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### Introduction

Over the last 50 years considerable attempts have been made on the Cr(III) solution based on varied ligands including dimethylformamide,<sup>1-3</sup> hypophosphite,<sup>4-5</sup> glycolic acid,<sup>6-7</sup> formate,<sup>8-10</sup> thiocyanate<sup>11-15</sup> and amino-substituted carboxylic acids.<sup>16-17</sup> However, the commercial progress on a viable trivalent chromium bath as a replacement for traditional hexavalent chromium bath has been very slow because of a much less quality of trivalent chromium plating especially on the colour and thickness.<sup>18-19</sup>

Traditional Cr(VI) bath can produce a thin layer of bright chromium plating with wear and tarnish resistance for decorative usage and a thick chromium plating with good functional properties such as hardness, corrosion and wear resistance. But Cr(III) plating process can not provide the same properties of plating as that of Cr(VI) plating due to the quite different chemical and electrochemical nature between Cr(VI) and Cr(III) electrolyte.<sup>20</sup> For example, Cr(VI) has a higher solubility, a highly acidic solution but the deposition potential of Cr(VI)/Cr is highly positive. On the contrary, Cr(III) has a limited solubility, a very negative deposition potential for Cr(III)/Cr and a easy hydrolysis of Cr(III) and its complexes in a high pH environment especially in the vicinity of cathode. It was reported that an excessive hydrogen evolution caused a rapid rise of pH and the formation of a series of Cr(III) hydroxides which might be co-deposited and produced a dark colour of chromium plating, and finally terminated the deposition reaction.<sup>21-22</sup>

It is almost impossible to deposit chromium plating from a simple aqueous Cr(III) solution due to the formation of a very stable  $[Cr(H_2O)_6]^{+3}$  complex. One of possible solutions to this problem is to use an appropriate ligand to form a Cr(III) complex with the highly chemical and electrochemical reactivity. But the most characteristic features of Cr(III) complexes are its kinetic inertness, which cause a lower rate on the complex substitution reactions and finally a fast drop on the rate of deposition reaction.<sup>23-24</sup> Therefore, ligands play an important role on the success of chromium deposition process from Cr(III) solution. Over twenty ligands mainly from carboxylic acids have been tried and studied in this study. It is found that some carboxylic acids can be considered to be appropriate Cr(III) ligands for the formation of Cr(III)

complexes with good stability and solubility. These ligands can also act as an auxiliary buffer while released on the cathode. It was found that a mixed Cr(III) complex produced by a couple of carboxylic acids not only produced a bluish-white colour of plating visually indistinguishable from that from Cr(VI) bath but also maintained a sustained deposition process over a prolonged period.

This paper describes the deposition process from the Cr(III) solution based on the couple of carboxylic acids. The influence of Cr(III) concentration, the ratio of these two carboxylic acids, pH, temperature and current density has been studied. The morphology of chromium plating is examined by atom force microscope.

#### **Experimental Procedure**

The basic composition of the Cr(III) solution was shown in the Table1. All reagent grade chemicals were used to prepare this solution. Main salts either Cr(III) sulphate or Cr(III) chloride, a couple of carboxylic acids or its salts, boric acid, and conductive salts such as potassium or sodium salts were dissolved in deionised water. The solution was heated up to 80°C and stirred for about 2 hrs, then cooled to room temperature. Solution pH was adjusted in a range from 2.0 to 3.0 by the addition of sodium or potassium hydroxide. After that, the solution must be held to stand for more than 12 hours before plating test. Before plating, solution pH was adjusted again in a range from 2.0 to 3.0.

#### Table 1

#### The Basic Composition of This Solution

Chromium(III) salts	0.4 - 0.6M
Carboxylic acid (I)	0.2 - 0.3M
Carboxylic acid (II)	0.2 - 0.3M
Boric acid	0.8 – 1.0M
Sodium sulphate	0.4 - 0.6M
Sodium lauryl sulphate	0.5 - 1.0M
pH	2.5 - 3.5
Temperature	25 – 35 °C

Plating was carried out in Hull cell and rectangular cell. The anode was a platinized titanium mesh. The cathode was polished brass plate and its non-working area was insulated. The pre-treatment process of this cathode consisted of degreasing it in a heated base solution, dipping it in 5% (v/v) sulphuric acid and then rinsing it with distilled water.

The colour of chromium plating was examined visually and compared with that of hexavalent chromium. The plating efficiency and deposition rate was measured by weighing brass plate before and after plating. The morphology of chromium plating was examined by atom force microscope and the plating composition was measured by energy dispersive X-ray spectrometry.

### **Results and Discussions**

### *Effects of the ratio between the couple of carboxylic acids*

A different ratio of carboxylic acid(I) to carboxylic acid(II) has a much influence on the plating efficiency at varied current densities, as showed in Fig.1. At a high ratio of carboxylic acid(I) (curve 4&5), the plating efficiency was high at 4A/dm<sup>2</sup> but decreased rapidly with increasing the current density from 5 to 12A/dm<sup>2</sup>. At a high ratio of carboxylic acid(II) (curve 1&2), the plating efficiency was low at 4A/dm<sup>2</sup> and gradually increased with a further increase in the current density. The highest plating efficiency was attained at the ratio of 1:1 (curve 3) and remained stable at higher current densities. On the other hand, the high ratio of carboxylic acid(I) produced a bright plating with a little dark colour at low current density but a more dark plating with a lot of pits at higher current densities. With gradually increasing the ratio of carboxylic acid(II), the plating becomes more bright and smooth. This is because varied ratio between carboxylic acid(I) and carboxylic acid(II) can provide Cr(III) complexes with a different stability. Since carboxylic acid(II) has a stronger complexing ability to Cr(III) than that of carboxylic acid(I). A Cr(III) complex with lower ratio of carboxylic acid(II) has a weak stability which would cause an easily precipitated Cr(III) hydroxides at higher current densities.<sup>25</sup> These precipitates will cover the deposition reaction areas and retard the normal growth process of chromium plating. An increase in the ratio of carboxylic acid(II) will enhance the stability of Cr(III) complexes and efficiently prevent the formation and precipitation of Cr(III) hydroxides at higher current densities. But a highly stable Cr(III) complex will greatly decrease the kinetics of deposition reaction, which cause a hydrogen evolution instead of chromium deposition reaction taking place on cathode. The Cr(III) complex at ratio of 1:1 may have an appropriate balance between the stability and reactivity of Cr(III) complexes and therefore produce a higher plating efficiency and more bright plating.



 Fig.1
 Effects of the ratio on the couple of carboxylic acids at 0.4M Cr(III)

 Carboxylic acid(I)/carboxylic acid(II) :
 (1) 0.0M / 0.4M (2) 0.10M / 0.30M (3) 0.2M / 0.2M (4) 0.3M / 0.1M (5) 0.4M / 0.0M

*Effects of the ratio of the couple of carboxylic acids to chromium concentration* 

A different ratio of the couple of carboxylic acids to Cr(III) concentration has a great influence on the plating efficiency, as shown in Fig.2. Increasing the ratio to 1.5:1 and 2:1 caused a substantial drop on the plating efficiency in a current density from 4 to 5  $A/dm^2$ . With further increasing current density to 12  $A/dm^2$  the plating efficiency at the ratio of 1:1 gradually decreased. But the plating efficiency at ratio of 1.5:1 and 2:1 rapidly increased to a maximum value and then slowly decreased. This means that a higher ratio of carboxylic acids to Cr(III) will produce highly stable complexes with a less reaction kinetics, which retards the rate of deposition reaction at lower current densities but largely increase the stability of Cr(III) species and keep a high rate of deposition reaction at higher current densities. It was also found increasing the ratio from 1:1 to 2:1 had no marked improvement on the plating brightness. Though increasing the ratio from 1:1 to 2:1 largely increased the limit current density up to 25 A/dm<sup>2</sup>, which was unable to effectively prevent the occurrence of black deposits at such higher current densities on a prolonged period.



## Fig.2 Effects of ratio on Cr(III)/carboxylic acids

Cr(III)/carboxylic acids : (1) 0.4M / 0.4M (2) 0.4M / 0.6M (3) 0.4M / 0.8M

Effects of chromium concentration



**Fig.3** Effects of Cr(III) concentration Cr(III) concentration : (1) 0.2M (2) 0.4M (3) 0.6M

The effect of Cr(III) concentration from 0.2 to 0.6M at 1:1 ratio of Cr(III) to total carboxylic acid was showed in Fig.3. With increasing Cr(III) concentration from 0.2 to 0.6M, the plating efficiency increased. The decrease of plating efficiency at a lower Cr(III) concentration is probably due to a faster depletion of Cr(III) species in the diffusion layer which results in hydrogen evolution instead of deposition reaction taking place at cathode. Since the amount of Cr(III) in the diffusion layer mainly depends on the diffusion rate of Cr(III) from the bulk solution into diffusion layer. The higher concentration of Cr(III), the faster diffusion rate and the higher concentration of Cr(III) in the diffusion

layer. It was found that the increase of Cr(III) concentration from 0.4 to 0.8M could significantly increase the limit current density up to 20 A/dm<sup>2</sup> and keep a high deposition rate over a prolonged period.

### Effects of other constituents

Other constituents such as boric acid. conductive salts are essential to this plating process. Boric acid was added as a buffer to keep the solution pH stable in a suitable range on the plating process. In the absence or at a concentration of boric acid less than 0.4M only a black and poor coverage of plating was produced. Increasing the concentration of boric acid from 0.4M to its saturation could increase the plating efficiency and produce a bright and good covered plating. Alkali metal salts such as sulphates or chlorides of sodium and potassium could be used as conductive salts to increase solution conductivity and improve current distribution on the plating process. It was found that the use of potassium salts instead of sodium salts could increase the limit current density. The concentration of alkali salts was usually in a range from 1 to 2M.

On the other hand, small amount of additives was added in this solution and tried to make a further improvement on the plating process especially on enlarging limit current density. It was found that the addition of wetting agent such as sodium lauryl sulphate and triton-x-100 in a range from 0.05 to 0.1 g/l could decrease the pits on plating and produce a bright deposit with better coverage. The deposition process with the addition of other organic additives such as saccharin, glycerol, polyethylene glycol, thiourea, formaldehyde, ammonium bromide, sodium fluoride and DMF were studied. It was found that the addition of saccharin, glycerol or polyethylene glycol could not markedly improve the plating brightness but increase the deposition rate at higher current densities for a short period. The addition of sodium fluoride and DMF could also increase the limit current density but at higher current densities a black deposit occurred for plating time longer than 2 hours. It was found that the presence of thiourea, formaldehyde and ammonium bromide also could not produce a sustained deposition process at higher current densities. On the other hand, the addition of small amount of thiourea would largely decrease deposition rate and deepen a dark colour of plating due to the co-deposition of sulphur in chromium plating.

## Effects of pH and temperature and current density

The influence of solution pH on the plating efficiency and brightness was studied at 5  $A/dm^2$ . A bright, uniform and adherent plating was produced in a pH range from 1.5 to 3.0 but the plating became a dull, loose and poor covered at pH larger than 3.0. As shown in Fig.4, an optimum pH range for this bath is in a range from 1.5 to 3.0 and the highest current efficiency was attained at about 2.0. When solution pH was larger than 3.0, the plating efficiency dramatically decreased and the plating became a less bright and more dark. This is probably that the increase of solution pH may enhance the precipitation of Cr(III) hydroxides and then reduce the plating brightness and deposition rate <sup>21</sup>. At a low pH from 0.5 to 1.5, only a black and poor covered plating was observed and the plating efficiency substantially decreased due to a much higher rate of hydrogen evolution instead of chromium deposition taking place at a lower pH.



## Fig.4 Effects of solution pH at 5A/dm<sup>2</sup>, 5 minutes

The influence of temperature from 20 to 45°C on the plating efficiency and colour was examined at 5 A/dm<sup>2</sup>. As illustrated in Fig.5, with increasing from 20 to 35°C the plating efficiency slowly increased to a maximum and then decreased sharply with further increasing to 45°C. Bright and uniform plating was produced from 20 to 35°C but the plating became less bright and had more blacks and bits on the plating over 35°C. At higher than 45°C, there was no plating

produced on cathode except for the evolution of hydrogen at 5 A/dm<sup>2</sup>. But at higher current densities the deposition reaction took place on cathode and the plating had many pits and easily peeled off. This is because high temperature generally accelerates the rate of hydrogen evolution and thus causes a faster rise of pH near the environment of cathode. On the other hand, the stability of Cr(III) complexes is diminished due to an increase on the hydrolysis and olation of Cr(III) complexes at a higher temperature, which causes the potential of deposition becoming more negative and difficult. Therefore, a higher temperature will hinder the chromium deposition process, decrease the plating efficiency and enhance the precipitation of Cr(III) hydroxides on the cathode.



## Fig.5 Effects of temperature at 5A/dm<sup>2</sup>, 5 minutes

This chromium plating process can provide more bright plating with good coverage and adhesion in a lower current density from 3 to 5A/dm<sup>2</sup> but the deposition rate is low about 0.1 to 0.4 micron/per minute. On the other hand, the limit current density and deposition rate can be largely increased either by increasing Cr(III) concentration and the ratio of the couple of carboxylic acids to Cr(III) or by decreasing solution pH. For example, a thick plating with thickness up to 80 microns was obtained at a higher current density from 15 to 30 A/dm<sup>2</sup>, Cr(III) concentration from 0.6 to 0.8M, the ratio of the couple of carboxylic acids to Cr(III) from 1:1 to 2:1 and pH in a range from 0.5 to 1.5.

#### Structure and Surface Morphology

Atom force microscope is used to observe the morphology of the plating

produced from 2 to 10 minutes at 5A/dm<sup>2</sup>. When the plating time exceeded 15 minutes, the plating began to lose its brightness and became a blur. The morphology of plating obtained at 2, 5 and 10 minutes is showed in Fig.6. It can be seen that the typical morphology of plating obtained from this solution is nodular structure. The chromium crystals at the initial stage of deposition process are fine-grained and uniform. With increasing plating time and thickness, these fine-grained crystals gradually grow up and micro-cracks occurred on the plating structure. It was found that the morphology of crystal growth was mainly determined by the structure of substrate, which lead to the morphology on the growth process of these crystals to be a pattern of striated lines. Fig.7 showed that the morphology of the plating obtained at 5 and 10 minutes. It can be seen that these crystals grow perpendicular to the substrate and form a pattern of striated lines. With increasing plating time the volumes of these crystals markedly increase and the interfaces among the striated lines become more wide and deep. The morphology of plating obtained from Cr(VI) solution is showed in Fig.8. It is found that there is no much difference on the morphology of plating between Cr(VI) and this Cr(III) solution but these chromium crystals produced from Cr(VI) solution seem to be a less nodular and more prismatic shape compared with these from this Cr(III) solution.

We analysed and compared the composition of plating from trivalent and hexavalent chromium by energy dispersive Xray spectrometry. Only four element peaks including chromium, copper, zinc and oxygen could be observed in the spectrum. The presence of oxygen could be due to easy formation of chromium oxide film on chromium surface, and copper and zinc are from substrate metal. The results show that there is no much difference on the composition of chromium and oxygen from trivalent and hexavalent chromium solutions.

# Chromium deposition process from a mixed Cr(III) complex

The deposition process from an aqueous Cr(III) electrolyte can be described as follows,<sup>26</sup> (a) the diffusion process of Cr(III) complexes from bulk solution into the cathode diffusion layer; (b) the formation process of electroactive Cr(III) species from an inert Cr(III) complex by the substitution and dissociation of Cr(III) complex in the cathode

diffusion layer; (c) the deposition process from electroactive Cr(III) species into chromium crystal on the cathode; (d) the diffusion and growth process of chromium crystal on the cathode. The second stage is generally considered to be the slowest and ratecontrolling step due to a lower rate on the substitution and dissociation of a Cr(III) complex, which depends on the characteristics of ligands, and the balance between kinetic reactivity and thermodynamic stability of Cr(III) complexes.<sup>27</sup> Too strong Cr(III) ligand produces a Cr(III) complex with much higher stability and lower reactivity, which greatly reduce the rate of substitution and deposition reaction. On the other hand, too weak Cr(III) ligand forms a Cr(III) complex with much lower stability which easily causes the precipitation of Cr(III) hydroxides and then prevent the normal growth process of chromium deposit. In our study a darker colour of deposit with a lower efficiency or no deposit was obtained from a Cr(III) complex formed by some strong ligands such as oxalic acid, malic acid, tartaric acid, citric acid, nitrolotriacetic acid and EDTA. The Cr(III) complex produced by weak Cr(III) ligands such as glycine, alanine, formic acid, glycolic acid provided a less dark colour of deposit at lower current densities.

A mixed Cr(III) complex formed by the couple of carboxylic acids may have some advantages over a Cr(III) complex obtained by a single lignad. Firstly, a mixed Cr(III) may possess an appropriate complex thermodynamic stability and highly kinetic reactivity which enhance the rate on the substitution and dissociation of a Cr(III) complex and finally increase the rate of deposition. Secondly, an easy release of the couple of carboxylic acids will provide a large quantity of carboxylic acids as auxiliary buffer to efficiently prevent a rapid rise of pH and the precipitation of Cr(III) hydroxides on the deposition process. Therefore, this Cr(III) solution formed by the couple of carboxylic acids not only produced a brighter plating visually indistinguishable from that from Cr(VI) bath but also continued this deposition process over a prolonged period at a higher deposition efficiency

### Conclusion

A novel Cr(III) solution based on a couple of carboxylic acids in combination has been developed. This plating process not only produces a bluish-white colour of deposit visually indistinguishable from that of deposit from Cr(VI) bath but also continues the deposition reaction over a prolonged period at high deposition rate and plating efficiency. This plating bath has stability on its chemistry and electrochemistry and can consistently produce a satisfied chromium deposit during a long period while plating conditions in a control range. This technology appears to open up a new opportunity for further increase use of trivalent chromium plating both for decorative and functional usage.

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### (a) 2 minutes

(b) 5 minutes



(C) 10 minutes

Fig.6 AFM photographs of Cr(III) deposits at 2, 5, 10 minutes





(a) 5 minutes

### (b) 10 minutes

### Fig.7 AFM photographs of Cr(III) deposits at 5 and 10 minutes



Fig.8 AFM photographs of Cr(VI) deposits at 5 minutes