Direct Plating of Steel with Pyrophosphate Copper

by S.B. Feng & S.B. Shang*

In order to enhance adhesion between a pyrophosphate copper plated layer and an iron substrate, the concepts of critical initial current density (D_{KC}) and activation potential (φ_A) are discussed. By controlling the initial current density, the plated layer may obtain good adhesion. Potential-time curves were measured at constant current. The curves showed that the cathode was first polarized to the activation potential when the applied initial current was greater than D_{KC}, and the iron substrate surface was activated. It then was polarized to the deposition potential of the copper ion. Direct pyrophosphate copper plating technology is described. The plate adhesion reached 71.8 MPa (10,400 lb/in^2) and was close to that of cyanide copper plating. This technology may replace cyanide as a copper pre-plating technology.

Pyrophosphate copper plating technology can completely eliminate cyanide pollution of the environment and threats to human health.[1-3] In addition, the crystal structure of the deposit is uniform and compact. The current efficiency is close to 100%. The throwing power of the solution is close to that of cyanide.[4-8] This technology has been used in industry. However, the great disadvantage of this technology is poor adhesion between the plated layer and an iron substrate. Thus, it cannot be used to electroplate directly without a strike layer.

In this study, we found that the tendency for immersion deposition of copper may be effectively prevented after the sample surface is adjusted in alkaline solution. When direct copper plating is carried out, each electrolyte composition exhibits a critical initial current density (D_{KC}). When the initial current density D_{KI} is greater than D_{KC}, good adhesion of the plated layer is obtained.[9] The complexing agent, copper salt concentration and temperature all influence the value of D_{KC}. That is to say that any factor increasing the polarization potential of copper may decrease D_{KC}. Potential-time curves present an electrochemical indication of whether the adhesion between the plated layer and the substrate is adequate.

Experimental procedure

Effect of initial current density on the adhesion of the plated layer

In the experiment, thin 50 × 30 mm (1.97 × 1.18 in.) iron plates for were used as substrates. Before testing, the samples were treated according to the following procedure:

1. Grind with #800 sand paper
2. Degrease
3. Rinse with distilled water
4. Chemically activate (1:1HCl)
5. Rinse
6. Immerse in sodium hydroxide (to avoid replacement copper)
7. Rinse
8. Electroplate for 15 min.

The bend-snap method was used to test adhesion of plated layer qualitatively. After repeated bending to the breaking point, good adhesion is said to exist if there is no evidence of flaking or peeling of the plated layer from the substrate.

Nuts & Bolts:
What This Paper Means to You

Pyrophosphate copper plating chemistry would be a viable substitute for cyanide copper processes, and all of its environmental and health concerns, if it weren't for the fact that you cannot plate directly on steel with it. A strike is needed, and generally a cyanide one at that. Here the authors provide a means of direct plating with an alkaline pretreatment. The adhesion test results show promise.

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Potential-time curves for an iron electrode in a common pyrophosphate copper plating solution

An electrochemical workstation** was used to generate the potential-time curves for an iron electrode in a pyrophosphate copper plating solution. A three-electrode system was employed. An iron rod, with a diameter of 3.44 mm (0.135 in.), was used as the working electrode. The cross-sectional end was used as the working surface, while the remainder of the rod was masked with epoxy resin. The thin copper plate was used as the auxiliary electrode. A saturated calomel electrode (SCE) was used as the reference electrode. Before testing, the working electrode was treated according to the following procedure:

1. Grind with #800 sand paper
2. Chemically activate (1:1HCl)
3. Rinse with distilled water
4. Immerse in sodium hydroxide (to avoid replacement copper)
5. Rinse again

Quantitative measurement of plate adhesion

Medium carbon steel plates were used as substrates. Samples 1 and 2 were plated in the direct pyrophosphate copper solution to a thickness of 80 μm (3.15 mil), controlling the initial current density. They were then plated continuously to a thickness of 2.5 to 3.0 mm (0.10 to 0.12 in.) in the acid copper solution. Samples 3 and 4 were pre-plated in the direct pyrophosphate copper solution for 5 min, then plated continuously to a thickness of 2.5 to 3.0 mm (0.10 to 0.12 in.) in the acid copper solution. Sample 5 was pre-plated in a cyanide copper plating solution for 5 min, then plated continuously to a thickness of 2.5 to 3.0 mm (0.10 to 0.12 in.) in the acid copper solution.

The method used to measure the adhesion of the pyrophosphate copper layer to the substrate is described in detail elsewhere.[10] The method of quantitative measurement involved the use of a tailor-made clamp with the material testing machine, as shown in Fig. 1.

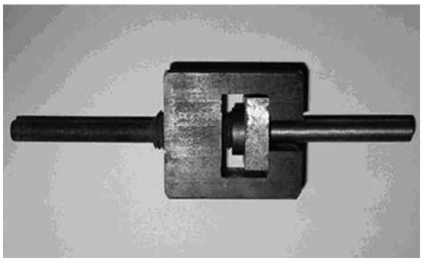

Figure 1—Clamp for the quantitative measurement of the bond strength of the plating layer.

Results & Discussion

Effect of initial current density on the adhesion of the plated layer

The solution composition and operating conditions were as follows:

Copper pyrophosphate($Cu_2P_2O_7$)	23.0 g/L (3.1 oz/gal)
Potassium pyrophosphate ($K_4P_2O_7$)	134.0 g/L (17.9 oz/gal)
Nitrilotriacetic acid [$N(CH_2COOH)_3$](NTA)	25.0 g/L (3.3 oz/gal)
Ammonium citrate [$(NH_4)_2HC_6H_5O_7$](AC)	15.0 g/L (2.0 oz/gal)
pH	8.5
Temperature	35°C (95°F)

The effect of D_{KI} on the adhesion of the plated layer is shown in Table 1.

The solution composition was changed to:

Copper pyrophosphate($Cu_2P_2O_7$)	56.0 g/L (7.5 oz/gal)
Potassium pyrophosphate ($K_4P_2O_7$)	384.0 g/L (51.3 oz/gal)

Table 1
Effect of D_{KI} on plate adhesion – low copper formulation

D_{KI}, A/dm^2	0.00	1.00	2.08	3.07	3.80	5.00	6.00
D_{KI}, A/ft^2	0.0	9.3	19.3	28.5	35.3	46.4	55.7
Adhesion	Poor	Poor	Poor	Good	Good	Good	Good

All other values and conditions remained unchanged. The results are shown in Table 2. From the two tables, it can be seen that each electrolyte formulation had a critical initial current density, 3.00 and 0.90 A/dm^2 (27.9 and 8.4 A/ft^2), respectively. When D_{KI} was greater than D_{KC}, the plated layer showed good adhesion.

Factors influencing D_{KC}

The effect of potassium pyrophosphate concentration on D_{KC} is shown in Table 3. The solution was varied from 100 to 350 g/L (13.4 to 46.7 oz/gal) $K_4P_2O_7$, with all other conditions as before. The effect of copper pyrophosphate concentration on D_{KC} is shown in Table 4. The solution was varied from 23 to 70 g/L (3.1 to 9.3 oz/gal) $Cu_2P_2O_7$, with all other conditions unchanged. The effect of temperature on D_{KC} is shown in Table 5. The solution contained 70 g/L (9.3 oz/gal) $Cu_2P_2O_7$ and 450 g/L (60.0 oz/gal) $K_4P_2O_7$, all other conditions the same.

It can be seen from Tables 3 and 4 that D_{KC} increased with increasing copper pyrophosphate concentration and temperature and decreased with increasing complexing agent concentration. That is to say, D_{KC} declined with increasing polarization.

Potential-time curves for an iron electrode in common pyrophosphate copper solution

In this part of the study, the solution contained 47 g/L (6.3 oz/gal) $Cu_2P_2O_7$ and 300 g/L (40.0 oz/gal) $K_4P_2O_7$. The potential-time curves for an iron electrode in the solution at pH 8.5 and at 35°C (95°F) are shown in Fig. 2.

From the four curves obtained at different current densities, it can be seen that the deposition potentials of copper ion were -0.6 V_{SCE}, -1.05 V_{SCE}, -1.35 V_{SCE} and -1.4 V_{SCE}, respectively. The obvious difference between curves *a* and *b* and curves *c* and *d* is that smooth steps of potential activation appear before copper deposition in curves *c* and *d*. This indicated that the materials were deoxidized. This process is thought

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** *CHI 660A Electrochemical Workstation, Shanghai, China, available from CH Instruments, Austin, TX* to be activation on the oxygen layer on the iron substrate surface. We define the lowest current density at which activation occurs as the critical current density, D_{KC}. When polarization is applied below D_{KC}, the iron will not be activated. When polarization is applied above D_{KC}, the iron surface is activated. We define this potential as the activation potential of iron in this solution and call this phenomenon *potential activation*.

Cathodic polarization

The electrochemical workstation was used to measure the cathodic polarization curves for the solution at pH 8.5 and at 35°C (95°F). The solution contained 23 g/L (3.1 oz/gal) $Cu_2P_2O_7$ and 350 g/L (46.7 oz/gal) $K_4P_2O_7$. The effect of adding a complexing agent on cathodic polarization is shown in Fig. 3. The complexing agent consisted of nitrilotriacetic acid and ammonium citrate. It can be seen from the figure that cathodic polarization of solution increase with increased complexing agent concentration. Finally, we determined that the optimum range for the complexing agent was 60 to 70 g/L (8.0 to 9.3 oz/gal).

Direct pyrophosphate copper plating technology

Through adding complexing agent and decreasing the primary salt concentration, polarization of copper ion may be increased. As a result, D_{KC} declined to less than 0.1 A/dm^2 (0.93 A/ft^2). As long as D_{KI} is maintained within the range of the applied current, good adhesion between the plated layer and the substrate can be ensured.

The composition and operating conditions for direct pyrophosphate copper plating are as follows:

Copper pyrophosphate	19 to 23 g/L (2.5 to 3.1 oz/gal)
Potassium pyrophosphate	300 to 350 g/L (40.0 to 46.7 oz/gal)
Complexing agent	60 to 70 g/L (8.0 to 9.3 oz/gal)
pH	8.2 to 8.8
Temperature	10 to 35°C (50 to 95°F)
Cathode current density	0.5 to 1.0 A/dm^2 (4.6 to 9.2 A/ft^2)
Anode	Electrolytic copper plate
Agitation	Cathode rod

Table 2
Effect of D_{KI} on plate adhesion – high copper formulation

D_{KI}, A/dm^2	0.00	0.65	0.97	1.50	2.05
D_{KI}, A/ft^2	0.0	6.0	9.0	13.9	19.0
Adhesion	Poor	Poor	Good	Good	Good

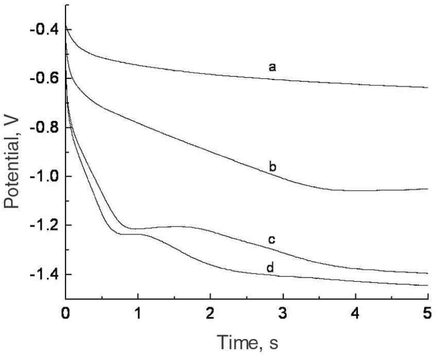

Figure 2—Potential-time curves for an iron electrode in the common pyrophosphate copper plating solution: (a) 0.1 mA; (b) 0.5 mA; (c) 2.0 mA; (d) 3.0 mA.

Table 3
Effect of potassium pyrophosphate concentration on D_{KC}

$K_4P_2O_7$, g/L (oz/gal)	150 (20.0)	200 (26.7)	250 (33.4)	350 (46.7)
D_{KC}, A/dm^2 (A/ft^2)	3.0 (27.9)	1.0 (9.3)	0.4 (3.7)	0.0 (0.0)

Table 4
Effect of copper pyrophosphate concentration on D_{KC}

$Cu_2P_2O_7$, g/L (oz/gal)	23 (3.1)	35 (4.7)	47 (6.3)	59 (7.9)	70 (9.3)
D_{KC}, A/dm^2 (A/ft^2)	0.0 (0.0)	0.4 (3.7)	0.5 (4.6)	0.6 (5.6)	10 (93)

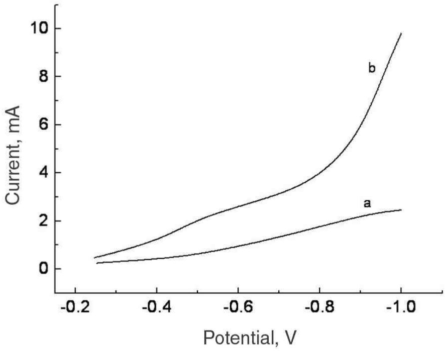

Figure 3—Effect of the complexing agent on cathodic polarization: (a) with complexing agent; (b) without complexing agent.

Table 5
Effect of temperature on D_{KC}

T, °C (°F)	5 (41)	10 (50)	15 (59)	20 (68)	25 (77)	30 (86)	35 (95)	40 (104)	45 (113)
D_{KC}, A/dm^2	0.0	0.0	0.0	0.6	0.7	1.0	1.5	3.2	10.0
D_{KC}, A/ft^2	0.0	0.0	0.0	5.6	6.5	9.3	13.9	29.7	92.9

Quantitative adhesion measurement

The quantitative adhesion test results are given in Table 6. The value for Sample 1 exhibited the same value as that of Sample 3. For the samples plated with acid copper over direct pyrophosphate copper, separation occurred within the coating. Only sample 4 showed no failure within the coating, but it separated along the profile. The pyrophosphate remained bonded to the iron substrate, indicating that actual copper-to-iron bond strength was greater than the value measured. The results in Table 6 also show that the strength of the pyrophosphate copper bond was close to that of the cyanide copper value (Sample 5).

Conclusions

1. The primary cause of poor adhesion of pyrophosphate copper plating iron is related to the fact that the deposition potential of copper is positive with respect to the activation potential of iron and copper deposits on the passivated iron.

2. Good plate adhesion was obtained by modifying the chemistry of the pyrophosphate solution, including an increase in the complexing agent concentration, a decrease in the copper concentration and appropriate control of the initial current density. Finally, making the copper deposition potential negative with respect to the activation potential of the iron surface, allowed direct copper deposition onto the activated iron substrate surface.

Table 6
Quantitative adhesion results

Sample No.	1	2	3	4	5
Adhesion, MPa	>63.0	71.8	>63.0	>95.5	83.3
Adhesion, lb/in^2	>9,140	10,400	>9,140	>13,900	12,100

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