Effect of the Oxide Layer at the Coating/Substrate Interface on Plating Adhesion

S.B. Feng[*] & F.H. Hu
Department of Chemical Engineering
Zhengzhou University of Light Industry
Zhengzhou, P.R. China

The potential-time curves under constant current and cyclic voltammetry curves were measured, and the potential activation process of cyanide copper plating on an iron substrate was demonstrated, including the basic cyanide makeup without copper ions. The initial stage of pyrophosphate copper plating on iron was also studied. The results show that the deposition potential of copper is positive and copper deposits on inactive surface areas of the electrode. The adhesion of the plated layer is very poor. Analysis by the combination of argon ion sputtering and x-ray photoelectron spectroscopy was used. The oxygen content at the interface between the copper layer and the iron substrate was examined and the existence of an oxygen layer was proven. The process of reduction of the oxide on the bright iron electrode along with the negative potential shift in 5% KCl solution were studied by cyclic voltammetry (CV) and surface-enhanced Raman spectroscopy (SERS). The results indicated that two types of oxide were deoxidized on the iron surface under different potentials. By adding a complexing agent and controlling the initial current density, the adhesion of the plated layer was close to that obtained with cyanide copper plating.

Keywords: *Potential activation, x-ray photoelectron spectra, surface-enhanced Raman spectroscopy, non-cyanide plating*

Introduction

"Potential activation" is a phenomenon which can activate a substrate surface by controlling the magnitude of the potential in the initial stages of electrodeposition. It is thought that the electrode process will first complete the activation of the substrate surface when the deposition potential of the metal ion is more negative than the activation potential of the substrate surface, before reaching the deposition potential of the metal ion. When the plated layer is deposited on the activated substrate surface, adhesion is good. On the contrary, where metal is deposited on a passive substrate surface, adhesion is very poor. However, different preplating processes may change the character and structure of the passive layer, and the activation potential φA of the substrate surface may be changed. Different electrolyte compositions and electrodeposition conditions may change the deposition potential φD of the metal ion. Therefore, plate adhesion may be improved by making φD negative to φA. In cyanide copper plating, the deposit exhibits good adhesion because the deposition potential of the metal ion is initially more negative than the activation potential of the substrate surface, and the substrate is completely activated, after which the metal is deposited on the active surface. By applying potential activation theory to non-cyanide copper plating, specifically pyrophosphate copper, we propose that by adjusting the solution composition and operating conditions to reduce the deposition potential of copper, the deposition potential of copper can be made more negative than activation potential of the oxide layer on the iron surface. In this work, potential surface activation was realized, and the adhesion of non-cyanide copper closely approached that of cyanide copper.

Purpose of the work

In this work, we have applied the principles of "potential activation" theory to the electrochemistry of the plated metal-substrate combination to optimize the characteristics of the initial stages of electrodeposition. Specifically, we have addressed non-cyanide copper plating on steel. Our aim is to implement a more environmentally compatible plating process, and ultimately promote cleaner processes in the plating industry.

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[*] *Corresponding author:*
Dr. Fengshao Bin
Department of Chemical Engineering
Zhengzhou University of Light Industry
Dongfeng Lu No. 5
Zhengzhou, 450002, P.R. China
Phone: (86) 371-63557339
Fax: (86) 371-63556510
E-mail: kara.hu@yahoo.com.cn

Experimental

Potential-time curves of iron electrode in cyanide solutions and common pyrophosphate copper plating solution

A CHI660A Electrochemical Workstation was used to measure and produce the potential-time curves for an iron electrode in two cyanide solutions (one a copper plating solution and the other without copper ions) and a pyrophosphate copper plating solution. A routine three-electrode system was employed. A thick iron rod, approximately 3.44 mm in diameter, was used as the working electrode. Its cross-section was used as the working surface, and the remaining areas were masked with epoxy resin. A 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 sandpaper.
2. Chemically activate in 1:1 HCl solution.
3. Rinse with distilled water.
4. Adjust pH with sodium hydroxide (in effect avoiding replacement copper).
5. Rinse with distilled water again.
6. Test.

X-ray photoelectron spectroscopy (XPS) and surface-enhanced Raman spectroscopy (SERS)

The pyrophosphate copper plated layer on steel was first examined. The oxygen 1s (O1s) chemical states were analyzed by x-ray photoelectron spectroscopy (XPS) using sputtered argon ions. The oxide activation on the iron electrode in 5% KCl solution was studied by cyclic voltammetry (CV) and surface-enhanced Raman spectroscopy (SERS).

Effect of initial current density on plate adhesion

In the experiment, thin 30 × 50 mm iron panels were used as substrates. Before testing, the samples were treated by the following procedure:

1. Grind with #800 sandpaper
2. Degrease.
3. Rinse with distilled water.
4. Chemically activate in 1:1 HCl solution.
5. Rinse with distilled water.
6. Adjust pH with sodium hydroxide.
7. Rinse with distilled water.
8. Electroplate for 15 min.
9. Test.

Plate adhesion was qualitatively determined by a bend test. Repeated bending to fracture, with no peeling of the plated coating was considered to be evidence of good adhesion.

Quantitative measurement of adhesion of plating layer

We used the method described in the *Proceedings of the Third International Congress on Metallic Corrosion* to measure the plate adhesion of pyrophosphate copper. The plated layer was peeled with a specially-made clamp in a tensile testing machine. Carbon steel panels were used as substrates. Samples 1 and 2 were direct-plated in pyrophosphate copper for 0.08 min while controlling the initial current density. They were then plated continuously for 2.5 to 3.0 min in the acid copper solution. Samples 3 and 4 were preplated with pyrophosphate copper for 5 min, then plated continuously for 2.5 to 3.0 min in the acid copper solution. Sample 5 was preplated in cyanide copper for 5 min, then plated continuously for 2.5 to 3.0 min in the acid copper solution. Finally, the plate adhesion of the samples was measured quantitatively.

Results

Potential-time curves of iron electrode in cyanide and pyrophosphate copper plating solutions

The cyanide copper plating solution composition was 40 g/L CuCN, 70 g/L NaCN and 10 g/L NaOH. Potential-time curves for the iron electrode in the cyanide solution at 35°C are shown in Fig. 1. It can be seen that the iron electrode is thought to be under potential activation between -1.20 and -1.25 V_{SCE}, respectively, in cuprous cyanide solution (curve a) and cyanide solution without copper ions (curve b). The deposition potential of the copper ion (-1.30 V_{SCE}) and the hydrogen evolution potential (-1.36 V_{SCE}), in curve (b), are all negative to the activation potential of iron. Therefore, the oxide on the iron substrate was deoxidized before copper deposition (curve a) or hydrogen evolution (curve b) could take place.

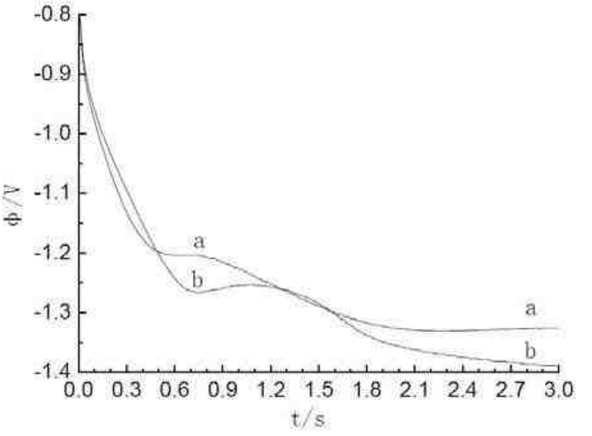

Figure 1—*Chronopotentiometry curves for the iron electrode in a cyanide electrolyte: (a) with copper ion; (b) without copper ion.*

The pyrophosphate copper plating solution composition was 47 g/L $Cu_2P_2O_7$ and 300 g/L $K_4P_2O_7$. Potential-time curves for the iron electrode in the pyrophosphate solution at pH 8.5 and 35°C are shown in Fig. 2. The four curves shown were obtained at different current densities: (a) 0.1 mA, (b) 0.5 mA, (c) 2.0 mA and (d) 3.0 mA. From the figure, the respective deposition potentials of copper ion were (a) -0.6 V_{SCE}, (b) -1.05 V_{SCE}, (c) -1.35 V_{SCE} and (d) -1.4 V_{SCE}. The obvious difference between curves a and b versus curves c and d is that smooth steps of potential activation appear prior to copper deposition in curves c and d, indicating deoxidation. This process is thought to be activation of the oxygen layer on the iron surface. We define the lowest current density where surface activation occurs as the critical current density, D_{KC}. When polarization is performed below the critical current density D_{KC}, the iron surface will not be activated. Conversely, above this value, the iron surface will be activated. We define this potential as the activation potential of iron in this solution and call this phenomenon potential activation.

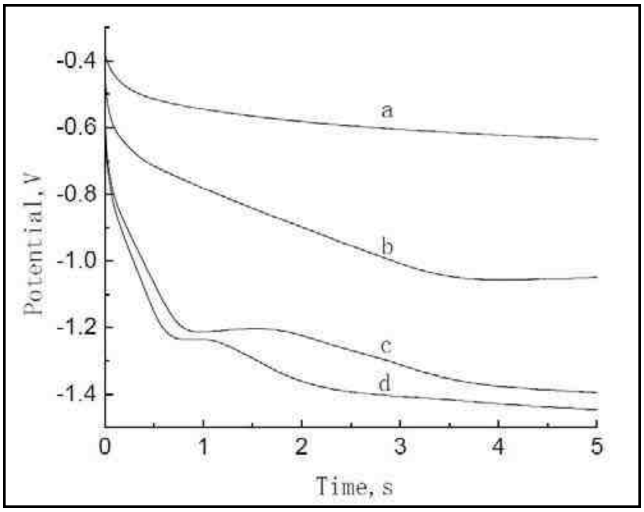

Figure 2—*Potential-time curves for the iron electrode in the pyrophosphate copper plating solution: (a) 0.1 mA; (b) 0.5 mA; (c) 2.0 mA; (d) 3.0 mA.*

X-ray photoelectron spectroscopy and surface-enhanced Raman spectroscopy (SERS) testing

The change of oxygen percentage with sputtering time (and therefore depth below the surface) is shown in Table 1. The oxygen concentration at the plated surface was 6.34%, and it decreased gradually with sputtering time. The oxygen content within the plated layer reached a minimum of 1.5% at a depth corresponding to 1,110 sec of sputtering, but it increased to 2.94% after 2,430 sec, corresponding to the interface between the iron substrate and the copper layer. The results show the existence of oxygen between the plated layer and the iron substrate, and that this was the cause of the poor adhesion that was observed.

Table 1

Change of oxygen percent along with different sputtered time

Sputtering time, sec	0	600	1,100	2,430
Oxygen content, %	6.34	1.87	1.50	2.94

Figures 3 and 4 show that the change of the oxide on iron electrode along with the potential moving towards negative in 5% KCl solution.

The Raman spectroscopy results shown in Fig. 3 show three iron oxide peaks at a potential of -0.6 V_{SHE}, and two peaks disappear at -0.9 V_{SHE} because of the oxide reduction reaction. The remaining peak (at 671 cm^{-1}) was further reduced as the potential decreased to -1.2 V_{SHE}. More evidence can be seen from the cyclic voltammetry results in Fig. 4, showing two reduction peaks at -0.9 and -1.2 V_{SHE}, respectively. The results indicate that the iron oxide can gradually be deoxidized under different applied potentials, and thus activate the iron substrate.

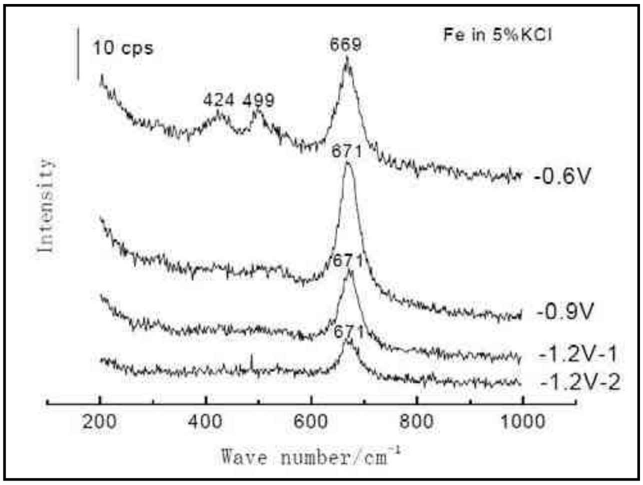

Figure 3—*Surface-enhanced Raman spectroscopy of an iron electrode in 5% KCl solution.*

Effect of initial current density on plate adhesion

Initially, the copper pyrophosphate plating solution composition and operating conditions were as follows:

Copper pyrophosphate ($Cu_2P_2O_7$)	23 g/L
Potassium pyrophosphate ($K_4P_2O_7$)	134 g/L
Nitrilotriacetic acid [$N(CH_2COOH)_3$](NTA)	25 g/L
Ammonium citrate [$(NH_4)_2HC_6H_5O_7$](AC)	15 g/L
pH	8.5
Temperature	35°C

The effect of the initial current density D_{KI} on the plate adhesion is shown in Table 2.

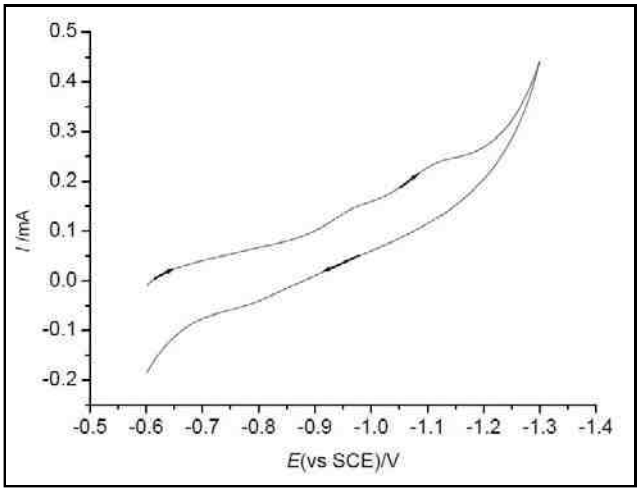

Figure 4—*Cyclic voltammetry (CV) of an iron electrode in 5% KCl solution.*

Table 2

Effect of D_{KI} on plate adhesion with the initial pyrophosphate copper bath composition

D_{KI}, A/dm^2	0.00	1.00	2.08	3.07	3.80	5.00	6.00
Adhesion	Poor	Poor	Poor	Good	Good	Good	Good

The solution composition was then changed to:

Copper pyrophosphate ($Cu_2P_2O_7$)	56 g/L
Potassium pyrophosphate ($K_4P_2O_7$)	384 g/L,

with all other parameters unchanged. The results are shown in Table 3.

It can be seen from Tables 2 and 3 that each electrolyte composition had a critical initial current density D_{KC}, 3.0 A/dm^2 and 0.9 A/dm^2, respectively. When D_{KI} is larger than D_{KC}, good plate adhesion is obtained. D_{KC} increases with increasing copper pyrophosphate concentration, decreases with increasing complexing agent concentration and increases with increasing temperature.

By adding complexing agent and decreasing the main salt concentration, polarization of the copper ions may be increased, and D_{KC} is reduced below 0.1 A/dm^2. As long as D_{KI} is controlled within the proper range of applied current, good adhesion between the plated layer and the iron substrate can be ensured. The compositions and operating conditions for direct pyrophosphate copper plating are as follows:

Copper pyrophosphate	19 - 23 g/L
Potassium pyrophosphate	300 - 350 g/L
Complexing agent	60 - 70 g/L
pH	8.2 - 8.8
Temperature	10 - 35°C
Cathodic current density	0.5 - 1.0 A/dm^2
Anode	Electrolytic copper plate
Agitation	Cathode movement

Quantitative measurement of adhesion of plating layer

The clamp used for quantitative adhesion measurement is shown in Fig. 5. The quantitative plate adhesion results are shown in Table 4.

In the table, Sample 1 has the same value as Sample 3. The peel test showed no separation of the acid copper from the pyrophosphate copper, and iron substrate material remained attached to the pyrophosphate copper. Peel failure occurred within the substrate, showing that the adhesive strength was actually greater than the measured value. The plated layer of Sample 4 peeled, but fractured along the cross-section. Again, the adhesion of the plated layer was actually larger than the measured value. It can be seen from Table 4 that the adhesion values for pyrophosphate copper plating (Samples 1-4) approximated those obtained for cyanide copper plating (Sample 5).

Table 3

Effect of D_{KI} on plate adhesion with the altered pyrophosphate copper bath composition

D_{KI}, A/dm^2	0.00	0.65	0.97	1.50	2.05
Adhesion	Poor	Poor	Good	Good	Good

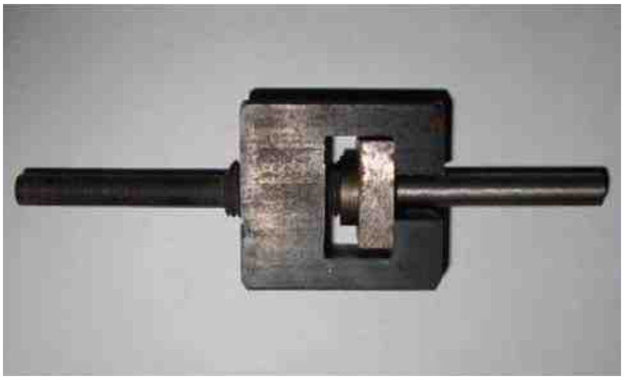

Figure 5—*Clamp for quantitatively measuring plate adhesion.*

Table 4

Quantitative plate adhesion results

Sample number	1	2	3	4	5
Adhesion, N/cm^2	> 6,300	7,180	> 6,300	> 9,550	8,330

Conclusion

The effects of the activation potential of the substrate and the applied potential in the initial process of electrodeposition on the adhesion between the plated layer and the substrate were explained by the "potential activation" phenomenon. The composition of interface between the plated layer and iron substrate has been characterized by x-ray photoelectron spectroscopy, and the cause of poor adhesion between film and substrate was found. Surface-enhanced Raman spectroscopy (SERS) has shown evidence for an activation process which reduces the oxide on the iron surface. By adding a complexing agent and decreasing the main salt concentration in a pyrophosphate copper bath, plate adhesion values for pyrophosphate copper were found to approach those produced by cyanide copper plating on iron.

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About the authors

Shaobin Feng is a professor in the Department of Chemical Engineering, Zhengzhou University of Light Industry, Zhengzhou, P.R. China. His major research interest is in surface treatments for copper and its alloys, as well as plating, electrochemistry and metal finishing. He has published one book and more than 50 papers on metal finishing and surface treatment. He received his BS degree from Harbin Institute of Technology (HIT). He obtained his MS from Beijing Normal University.

Fanghong Hu is a graduate student in the Department of Chemical Engineering, Zhengzhou University of Light Industry, Zhengzhou, P.R. China. Her research activities include copper plating, corrosion and protection of bronze and related fields. Her holds a B.S. degree from Zhengzhou University of Light Industry.

In Memoriam

Walter J. Dyber

Long time Connecticut Branch member of AESF, Walter J. Dyber, passed away on Tuesday, June 2, 2009 at the age of 91. Mr. Dyber began his electroplating career in 1936 as plater on the cadmium plating/chromate conversion finishing line of airplane parts at the original Pratt & Whitney Aircraft facility then located in Hartford, CT. Mr. Dyber joined AES as a Hartford Branch member on June 5, 1936.

After many years as a line plater at Pratt & Whitney, Mr. Dyber accepted a position as a sales representative for MacDermid, Inc. In 1955, Mr. Dyber moved to West Hartford, CT and assumed responsibilities as a sales executive with MacDermid. In his new role, Mr. Dyber travelled extensively to Asia to establish the company's infrastructure and customer base in that region of the world. Mr. Dyber had many friends in Asia and regaled AESF branch members with many stories related to his trips to Asia.

Mr. Dyber retired from MacDermid in 1980 but remained an active member at branch meetings for many years afterward. In addition to his activity with AESF, Mr. Dyber additionally pursued many philanthropic endeavors and needy causes. An avid sportsman as a younger man Mr. Dyber still enjoyed skiing into his seventies and spending weekends in Vermont at a farmhouse that he renovated himself. Mr. Dyber enjoyed a good game of golf well into his eighties.

Upon the formation of the Connecticut Branch of AESF, with the merger of the former Waterbury, Hartford and Bridgeport Branches, Mr. Dyber was honored as a Connecticut Branch honorary member. This honor was bestowed upon Mr. Dyber on November 10, 2005.

Mr. Dyber was predeceased by his first wife Beatrice and his second wife Carolyn. He leaves two sons, James Dyber of West Hartford and Michael Dyber of New Hampshire. At the time of his passing, Mr. Dyber was three-days shy of celebrating his 73rd anniversary as an AESF member.