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SHORT COMMUNICATION

Influence of phosphorous acid on the nucleation and growth of copper

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1. Introduction

Much research has recently been devoted to copper electrodeposition under conditions related to electrorefining [1–19]. Most work has been related to the control of electrocrystallization to obtain high purity cathodes with a high deposition yield. The main studied parameters are plating current density, temperature, substrate surface treatment and additive concentrations. The inhibiting or activating effects of these additives are described in the literature [20–30], particularly for copper electrodeposition.

In industrial practice, in sulfuric acid electrolytes, low concentrations of three additives (gelatin, thiourea and chloride ions) are generally used simultaneously. A very strict control of their concentrations is needed to maintain during the growth good deposit structure, purity and morphology. It is of interest to study new additives that could be used at relatively high concentration in order to ease the on-line additive concentration control. Moreover, a small change in the new additive concentration should not have a detrimental effect on the copper electrodeposition.

In a weak acid electrolyte, phosphorous acid (H_3PO_3) presents this type of behaviour for nickel electrocrystallization [31]. The purpose of this research is to determine whether phosphorous acid has the same effect for copper electrocrystallization in an acid electrolyte.

2. Experimental details

2.1. *Electrolysis*

A rectangular channel cell with uniform distribution of limiting current densities (except small edge effects) was designed to control the hydrodynamics during electrodeposition [3]. An electrolyte containing $40\,g\,dm^{-3}$ Cu^{2+} (as $CuSO_4.5H_2O$) and $180\,g\,dm^{-3}$ sulfuric acid was used. Phosphorous acid was added to obtain concentrations of 0, 1, 5 and $10\,g\,dm^{-3}$. The electrolyte flowed parallel to the electrodes. A fully developed forced turbulent flow was obtained with an electrolyte flow rate of $1.5\,m\,s^{-1}$. A mercury/mercurous sulfate reference electrode (MSE: +0.656 V vs SHE) was used. Two temperatures (25 and 60 °C) were studied.

The cyclic voltammetry experiments were made in the channel cell using a Tacussel PIL 101 T coupled with a Tacussel PJT 35-2 apparatus. The voltammograms were begun at the rest potential, then the scans were driven in the cathodic direction to –800 mV vs MSE before reversing to the initial potential. Two scan rates (1 and $10\,mV\,s^{-1}$) were used. Very small differences were observed in the voltammograms for these two scan rates and accordingly, only the results obtained at $10\,mV\,s^{-1}$ are presented. For the galvanostatic experiments, a GW 3010 H power source was used. Two current densities (1 and $10\,A\,dm^{-2}$) were studied. Deposits of $5\,\mu m$ thick were produced.

Electrolytic copper was used as electrode substrate. The anodes were mechanically polished with 800 SiC paper and rinsed in distilled water. Two different cathode pretreatments were used. Pretreatment A was based on a mechanical polish up to 1200 SiC paper followed by an electrochemical polish in a phosphoric acid bath in order to obtain a mirror-like surface. Pretreatment B was based on pretreatment A followed by an activation (anodic dissolution during 60 s at 100 mV above the rest potential) in the channel cell. The results were not markedly different for the two pretreatments and accordingly, only results obtained for substrates after activation are presented here.

2.2. *Analysis*

Surface micrographs of the copper deposits were obtained with a scanning electron microscope (SEM) Jeol JSM 820. To estimate the consumption of the inhibitor, the composition of the deposits was studied by energy dispersive X-ray spectroscopy (EDS) with a Tracor Northern 5525 microanalysis system coupled with the electron microscope.

The texture of the deposits was analyzed by X-ray diffraction with a Siemens D5000 apparatus. The cross sections were observed with an optical microscope Reichert–Jung MeF3A after embedding the deposits in Mecaprex resin, polishing with 1200 SiC paper and etching in an ammonia-water peroxide solution. The metallographic structures of the deposits were estimated according to Fischer–Winand's classification [3].

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3. Results

Figure 1 shows the influence of increasing concentrations of phosphorous acid on the copper cyclic voltammograms. The higher the inhibitor concentration, the more noble the electrode potential and the higher the current density for a constant value of the electrode potential. Simultaneously, the second wave that appears at low phosphorous acid concentration tends to disappear at high inhibitor concentration.

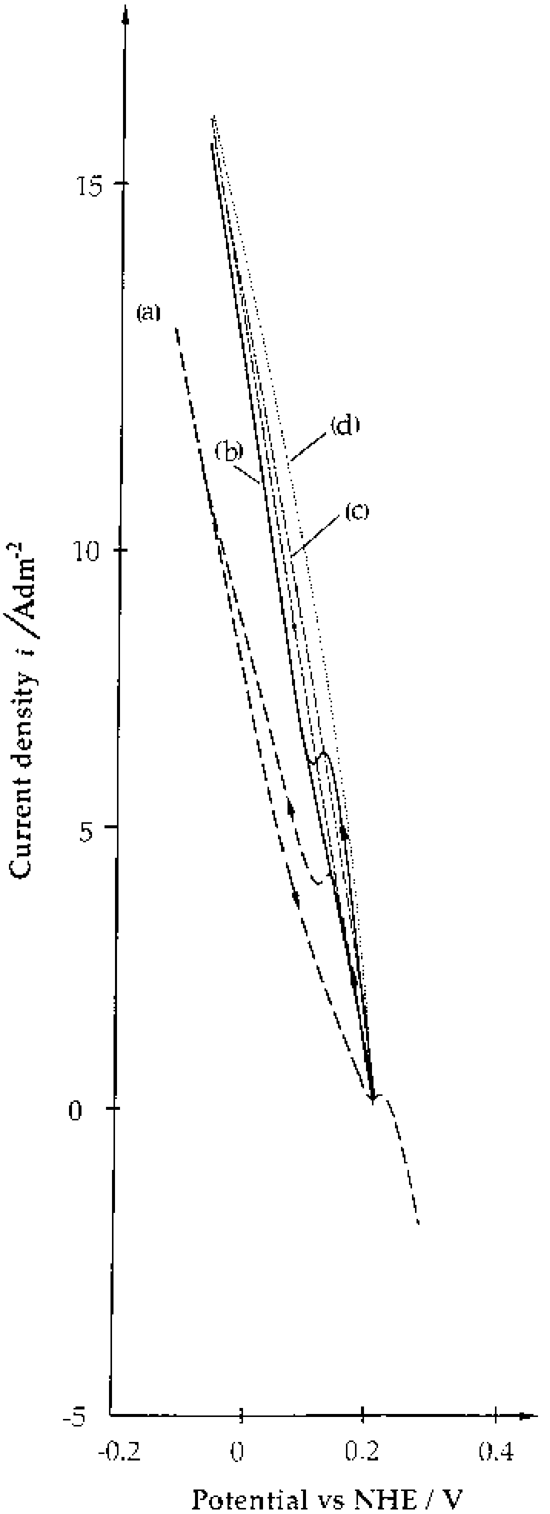

Fig. 1. Potentiokinetic polarization curves (10 mV s^{-1}, 25 °C, 40 g dm^{-3} Cu^{2+}, 180 g dm^{-3} H_2SO_4): (a) 0, (b) 1, (c) 5 and (d) 10 g dm^{-3} H_3PO_3.

The chronopotentiometric curves observed during the constant current electrolysis are presented in Figs 2 and 3 for the two studied current densities at 25 and 60 °C. The electrode potential decreases rapidly during the first minutes of electrolysis and then stabilizes. This effect is less pronounced for high inhibitor concentration and high temperature. Indeed in these cases, the electrode potentials are stable from the beginning of the electrolysis. The electrode potential is stable for more than 3 h. This shows that the phosphorous acid is not consummed during electrolysis. For the two studied temperatures and current densities, the deposition overpotentials are always lowered by addition of increasing concentrations of phosphorous acid. The activating effect of this additive is thus clearly observable on these chronopotentiometric curves. This activating effect is more pronounced at low temperature (25 °C) than at high temperature (60 °C) and at low current density (1 A dm^{-2}) than at high current density (10 A dm^{-2}).

Tables 1 and 2 summarize the influence of phosphorous acid additions on the orientation of the deposits, as measured by X-ray diffraction. Without additive, for the selected experimental conditions (current density and temperature), a preferential orientation of the (2 2 0) crystallographic planes parallel to the substrates is observed. Addition of phosphorous acid, even at high concentration, does not change this preferential orientation. These results are confirmed by the metallographic structures of the deposits. In the studied experimental conditions (see Fig. 4), a BR (base reproduction) structure [3] is always observed with a small trend to a field oriented texture (BR-FT texture). The phosphorous acid additions have only a very small influence on the growth of the copper crystals. Twins are only observed for additive concentrations higher than 5 g dm^{-3}. The influences of the electrolyte temperature and the plating current density are weak. The deposits are uniform and present large regular terminating crystal faces (see Fig. 5). Phosphorous acid shows only a weak levelling effect at very high concentration (10 g dm^{-3}).

The copper deposits are not contaminated by phosphorus and the atomic absorption analysis of the electrolytes before and after deposition shows no consumption of the phosphorous acid during electrolysis. All these facts support the negligible influence of this additive on the current yield that remains always between 98 and 99%.

4. Conclusions

Phosphorous acid has proved to be an activating compound instead of an inhibitor in the case of copper electrodeposition in sulfuric acid. It decreases the electrodeposition overpotential for the whole range of studied electrochemical parameters. Only

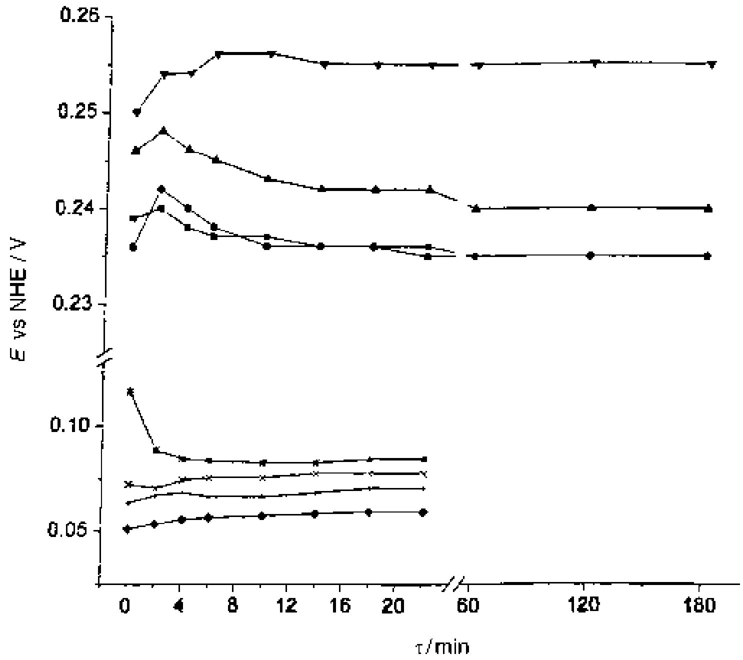

Fig. 2. Chronopentiometric curves (25 °C, 40 g dm^{-3} Cu^{2+}, 180 g dm^{-3} H_2SO_4). Legend: (■) add. 0 g dm^{-3}, 1 A dm^{-2}; (●) add. 1 g dm^{-3}, 1 A dm^{-2}; (▲) add. 5 g dm^{-3}, 1 A dm^{-2}; (▼) add. 10 g dm^{-3}, 1 A dm^{-2}; (♦) add. 0 g dm^{-3}, 10 A dm^{-2}; (+) add. 1 g dm^{-3}, 10 A dm^{-2}; (×) add. 5 g dm^{-3}, 10 A dm^{-2}; (*) add. 10 g dm^{-3}, 10 A dm^{-2}.

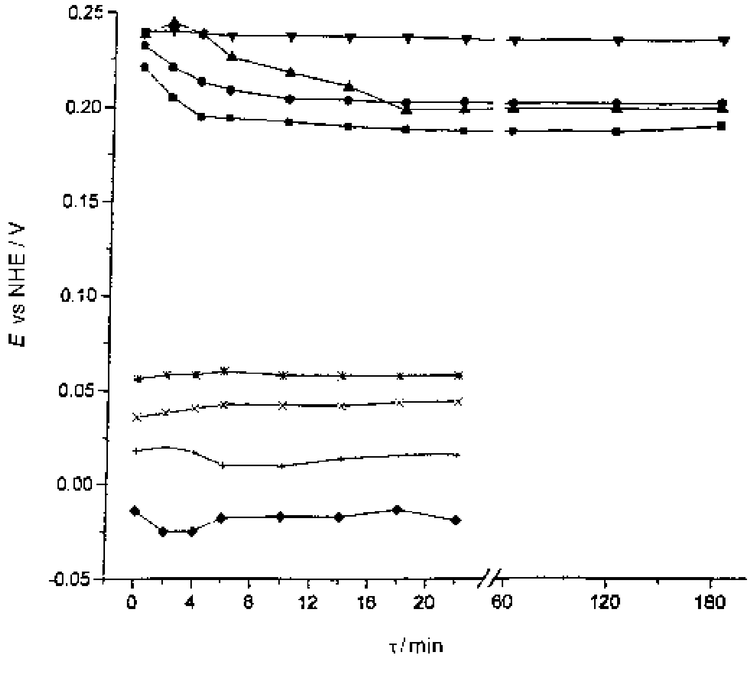

Fig. 3. Chronopentiometric curves (60 °C, 40 g dm^{-3} Cu^{2+}, 180 g dm^{-3} H_2SO_4). Legend: as for Fig. 2.

Table 1. Influence of phosphorous acid concentration on the X-ray diffraction analysis of the copper deposits (1 A dm^{-2} plating current density)

Solution	*Temp./°C*	*Relative X-ray intensities, I/I_0/%* for (*h k l*)*							
		(111)	(200)	(220)	(311)	(222)	(400)	(331)	(420)
0 g dm^{-3}	25	12	6	100	52	1	–	26	50
H_3PO_3	60	89	16	100	31	4	–	25	31
1 g dm^{-3}	25	13	6	100	62	1	–	31	64
H_3PO_3	60	17	4	100	59	–	–	26	53
5 g dm^{-3}	25	19	7	100	70	1	–	34	63
H_3PO_3	60	29	9	100	59	–	–	37	61
10 g dm^{-3}	25	17	8	100	61	–	–	18	56
H_3PO_3	60	38	31	100	78	2	–	36	72
Powder		100	46	20	17	5	3	9	8

[*] crystal plane orientation

Table 2. Influence of phosphorous acid concentration on the X-ray diffraction analysis of the copper deposits (10 A dm^{-2} plating current density)

Solution	*Temp.*/°C	*Relative X-ray intensities, I/I$_0$/%* for (*h k l*)* (111)	(200)	(220)	(311)	(222)	(400)	(331)	(420)
0 g dm^{-3}	25	2	–	100	2	–	–	5	–
H_3PO_3	60	4	1	100	42	–	–	10	29
1 g dm^{-3}	25	4	4	100	3	–	–	30	48
H_3PO_3	60	3	2	100	26	–	–	17	33
5 g dm^{-3}	25	7	4	100	12	–	–	15	22
H_3PO_3	60	4	2	100	7	–	–	19	18
10 g dm^{-3}	25	19	16	100	37	–	–	20	43
H_3PO_3	60	9	2	100	14	–	–	23	34
Powder		100	46	20	17	5	3	9	8

* crystal plane orientation

very weak effects are observed at high concentrations in solution such as a weak levelling effect and the formation of twins in the copper deposits associated with a modification of the metallographic structure for a BR type to a BR-FT type in Winand's classification. This is probably due to the fact that in the case of copper electrodeposition in sulfuric electrolytes, the cathode potential is not sufficiently cathodic to promote the decomposition of the phosphorous acid with coprecipitation in the deposit and modification of the crystal growth as is observed in the case of nickel electrodeposition [31].

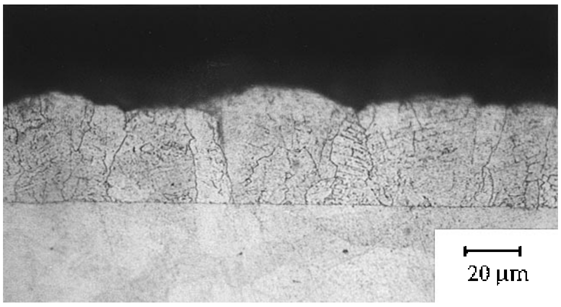

Fig. 4. Cross section of a BR (base reproduction) metallographic structure of a copper deposit in presence of phosphorous acid (40 g dm^{-3} Cu^{2+}, 180 g dm^{-3} H_2SO_4, 5 g dm^{-3} H_3PO_3, 1 A dm^{-2}, 60 °C).

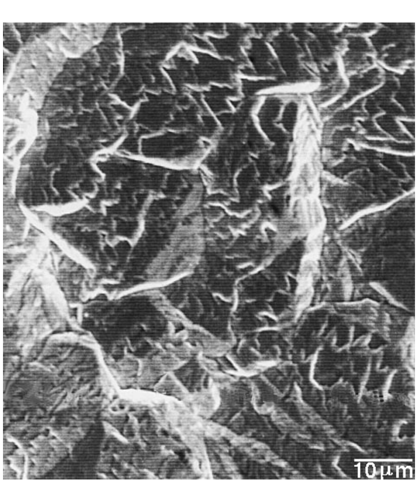

Fig. 5. Surface micrograph of a copper deposit in presence of phosphorous acid (40 g dm^{-3} Cu^{2+}, 180 g dm^{-3} H_2SO_4, 5 g dm^{-3} H_3PO_3, 1 A dm^{-2}, 60 °C).

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