JOURNAL OF APPLIED ELECTROCHEMISTRY 19 (1989) 37–42

Effect of iron(III) and lead(II) on the quality of copper electrodeposited from a pyrophosphate bath

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Received 9 October 1987; revised 12 July 1988

The results of a study on the quality of copper electrodeposited from a pyrophosphate bath in the presence of iron(III) and lead(II) are presented. The electrochemical measurements and the analysis of the deposits revealed that the discharge potentials are sensitive to the concentrations of the cations which are present in the copper deposit over the range 2.26–3.12 P_2O_7/Cu (P/C) molar ratios (at 50° C). Under industrial operating conditions, i.e. for current densities of between 12 and 20 $A\,dm^{-2}$, the morphology of the deposit is also profoundly modified inasmuch as these metals, which do not form alloys with copper, inhibit the growth of crystal seeds and/or the formation of new ones. Consequently at the higher concentrations of Fe(III) and Pb(II) the deposit becomes non-coherent.

1. Introduction

The galvanic pyrophosphate copper bath is reliable, long lasting and easy to run; it produces a very good quality deposit. It is widely used in industry for the protection of ferrous materials and in the manufacture of brass-plated steel cord for radial tyres and high-pressure plastic pipes. Because of the need for continuous operation (the wires cross the bath at a speed of 40–60 $m\,min^{-1}$), high cathodic current densities (10–20 $A\,dm^{-2}$) are used and the presence of traces of impurities can cause dramatic changes in the morphological characteristics of the deposit. The most common anion impurities are chloride, sulphate, phosphate and nitrate (the latter being used as a depolarizing agent) and cation impurities are iron(III) and lead(II).

In a previous paper [1] we reported the results of a voltammetric study of the effects of the anionic species and ammonia (used in low concentrations as brightener). Here the results pertaining to iron(III) and lead(II) are presented. After a few days these two cations always appear in the bath in concentrations normally stabilized at between 100 and 1000 ppm.

Taking into account bath composition, working pH and temperature (8.8 ± 0.1, 50 ± 0.5° C), the predominant species should be $Fe(P_2O_7)_2^{5-}$ and $Pb(P_2O_7)_2^{6-}$ [2].

The iron(III) ion probably originates from a previous acid pickling bath (H_2SO_4 10%) and/or from the chemical corrosion of the plant's ferrous parts (pumps, pipes, heat exchanger and so on). The lead(II) ion may derive mainly from a previous patenting bath, where the wire, after heat treatment above the transformation temperature, is quenched in molten lead, in order to obtain a high strength steel wire with a pearlitic structure. Small amounts of lead can result from the dissolution of the anodes since this element is usually present in industrial electrodes, even if in minute concentrations (< 0.1%).

Preliminary tests revealed that these cations exert a detrimental effect on the deposit quality. Hence the object of this study was to investigate whether this drawback could be overcome by varying the P_2O_7/Cu molar ratio (subsequently denoted P/C).

2. Experimental details

2.1. *Reagents*

All reagents were analytical grade. Solution stocks were prepared from $K_4P_2O_7 \cdot 3H_2O$ and $Cu_2P_2O_7 \cdot 5H_2O$ maintaining the copper concentration constant (0.455 $mol\,l^{-1}$) and varying total pyrophosphate so as to obtain the required P/C (see Table 1). Iron(III) and lead(II) were added as pyrophosphate salts (iron: starting with $FeCl_3 \cdot 6H_2O$ the compound $Fe_4(P_2O_7)_3 \cdot 9H_2O$ was separated, recrystallized and dissolved in a pyrophosphate excess; lead: $PbCO_3 \cdot Pb(OH)_2$ – the carbon dioxide was eliminated by treatment with $H_4P_2O_7$ and then the required amount of $K_4P_2O_7$ was added). The pH was adjusted to 8.80 ± 0.02 by adding $H_4P_2O_7$ (or sometimes, HCl).

2.2. *Electrochemical measurements*

The cell [3] consisted of a three-electrode system: working electrode platinum 1 cm^2, mounted in resin, polished with emery paper, diamond paste, nitric acid, degreased and washed with acetone, ethanol and water; reference electrode: saturated calomel electrode (SCE) (all reported potential values are referred to this electrode); counter electrodes: two bars of graphite placed symmetrically on each side of platinum electrode.

The measurements at 50 ± 0.5° C were carried out

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Table 1. Discharge potential of copper (0.455 M) for different concentrations of pyrophosphate ion (pH = 8.80 ± 0.02, 50 ± 0.5° C, in N_2 atm, magnetic stirring)*

	P/C	−E (*mV vs SCE*)		*P/C*	−E (*mV vs SCE*)
(6.2)	2.26	335(7)	(7.2)	2.63	396(11)
(6.4)	2.35	335(1)	(7.4)	2.72	416(23)
(6.6)	2.41	360(7)	(7.6)	2.78	429(9)
(6.8)	2.48	379(1)	(7.8)	2.85	417(17)
(7.0)	2.57	371(7)	(8.5)	3.12	466(29)

Values averaged over a minimum of 4 and a maximum of 18 separate measurements (standard deviation in parentheses).

* pH adjusted with $H_4P_2O_7$; adjusting the pH with HCl the following results are obtained:

P_2O_7/Cu molar ratio, (P/C) = 2.26, $E = -311$; P/C = 2.57, $E = -355$; P/C = 2.85, $E = -371$; P/C = 3.12, $E = -420$ mV vs SCE.

under a N_2 atmosphere with continuous magnetic stirring of the solution, starting from −0.05 V vs SCE and progressing towards more negative values with a scanning rate of 0.5 mV s^{-1}.

The electrolysis experiments were performed at constant current (2 mA corresponding to 0.2 A dm^{-2}) and the deposits were dissolved (a few drops of HNO_3), diluted and analysed. The duration of electrolysis and current intensity were such that the concentrations of the species in solution were not significantly altered.

All experiments were carried out using an Amel apparatus (models 550, 564, 667) equipped with a Perkin-Elmer recorder (model 023) and an MGW-Lauda thermostat.

2.3. *Atomic absorption measurements*

All analytical determinations of copper, iron and lead were carried out with Perkin-Elmer A. A. spectrophotometers (mod. 603 and 5000) using standard Merk solutions. The deposits were diluted in water, distilled twice in a quartz distiller and stored in polyethylene containers.

2.4. *Diffractograms*

The diffractometric measurements were taken with a Jeol J SDX-60 A4 spectrometer, equipped with an X-ray copper anode source ($CuK\alpha_{av}$ = 1.54179 Å) supplied with 40 mA at 40 kV. The scanning rate was 0.25 degree min^{-1} with high signal expansion (8×10^3–4×10^4). The signals were integrated using a Salmoiraghi planimeter evaluating the area values with about 3–5% reproducibility.

2.5. *XPS–SEM determinations*

The XPS spectra were recorded with a VG-Escalab MKII spectrometer (Vacuum Generator Instrument, UK), equipped with twin anode X-ray sources (AlKα = 1486.6 eV and Mgkα = 1253.6 eV), a hemispherical electrostatic analyser and a turbomolecular and titanium sublimation pump fitted with liquid nitrogen cold trap. The residual pressure operating in these conditions was usually less than 5×10^{-7} Pa. Binding energies were calibrated using the signal of the Au $4f_{7/2}$ electrons of gold (83.8 eV) and, as internal standard, that of C1s electron of carbon (285.0 eV). The raw data were recorded both in analog and digital modes using an appropriate scan number so as to obtain optimum signal-to-noise ratio. The raw experimental data were processed using an Apple-II computer and VGS-1000 software; in this way the following operations were performed: (a) background subtraction; (b) curve smoothing; (c) resolution of the multicomponent signals into single peaks

3. Results and discussion

3.1. *Electrochemical results*

3.1.1. Preliminary measurements. From a series of preliminary measurements using a solution containing copper(II) ions and the pyrophosphate ion (i.e. in the absence of iron(III) and lead(II) ions) it emerged that by varying the P/C between 2.26 and 3.12 (spanning the ratio of 2.57 usually used in industrial processes) the discharge potential[†] tends towards increasingly negative values (Table 1). This was expected inasmuch as the discharge potential is a function of both the copper(II) ion concentration (kept constant throughout the tests) and the pyrophosphate concentration [4–6]. By adjusting the initial pH with HCl instead of $H_4P_2O_7$ slightly less negative potentials were found, due to the formation of an adsorbed chloride coating. In fact it has been proved [1] that this ion competes with pyrophosphate in the coordination to copper.

3.1.2. Measurements in the presence of Fe(III) ion. The potential vs current curve recorded in the presence of the Fe(III) ion exhibits two distinct inflections. These values do not usually differ by more than 100 mV (Table 2).

The first inflection, which is not always well defined can be attributed to the onset of the reduction process of the Fe(III) ion. Both values tend towards more negative potentials with increasing P/C and less negative potentials with increasing Fe(III) concentrations.

The chemical analysis of the deposits revealed the iron presence under all the test conditions here investigated but that its concentration is not proportional to that in the bath. In any case, with increasing P/C and for Fe(III) ion concentration not exceeding 1–2 g l^{-1}, the amount of iron present in the deposit is extremely small (0.1–0.2%).[‡]

3.1.3. Measurements in the presence of Pb(II) ion. The potential vs current curves also exhibit two distinct

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[†] Evaluated as the intercept between residual current and proportional discharge.

[‡] Obviously in the reference tests, in the absence of added Fe(III) this element is not present in the metallic deposit in amounts of analytical significance.

Table 2. Discharge potential and composition of the deposit in the presence of Fe(III) for different concentration of ion pyrophosphate (pH = 8.80 + 0.02, 50 + 0.5° C, N_2)*

Fe^{3+} ($g\,l^{-1}$)	P/C							
	2.26		2.57		2.85		3.12	
	−E (mV vs SCE)	Fe (%)	−E (mV vs SCE)	Fe (%)	−E (mV vs SCE)	Fe (%)	−E (mV vs SCE)	Fe (%)
0.5	296(6) 360(8)	0.2	322(3) 384(6)	0.3	325(5) 437(17)	0.2	334(4) 421(38)	0.1
1.0	348(1)	–	–	–	335(5) 382(3)	0.2	–	–
2.0	303(7) 326(8)	0.2	–	–	332(5) 383(3)	0.3	–	–
4.0	310(2)	0.8	–	–	322(3) 371(12)	0.2	–	–
6.0	294(3)	1.3	289(0) 247(6)	0.3	324(3) 370(3)	0.6	314(6) 395(19)	0.2

Values averaged over 8–10 separate measurements (standard deviation in parentheses).
* pH adjusted with $H_4P_2O_7$.

inflections in the presence of the Pb(II) ion (Table 3). The potential values straddle that recorded with the pure galvanic bath and tend towards more negative values with increasing Pb(II) ion concentration.

The Pb(II) codeposits along with Cu(II) and its concentration in the deposit is higher than for the iron and does not depend on the P/C. For the cathodic current density (0.2 A dm^{-2}) and temperature (50° C) used in the tests, the amount of codeposited metallic lead does not appear to substantially depend on the Pb(II) ion concentration in the galvanic bath. By contrast (Fig. 1) electrolysing at much higher current densities (10–20 A dm^{-2}), i.e. in conditions similar to industrial processes, the percentage of lead detected in the deposits is proportional to the concentration of this impurity and depends, moreover, on the working temperature.

3.1.4. Measurements in the presence of both Fe(III) and Pb(II) ions. The measurements were conducted at P/C = 2.85 with 500 ppm of Fe(III) and 50 ppm of Pb(II) with and without the nitrate ion (2 g l^{-1}) and ammonia (0.5 g l^{-1}). The potential vs current curves feature two inflections and yielded: −329 (6) and −400 (6) mV in the absence of nitrates and ammonia; −326 (6) and −430 (17) mV vs SCE in their presence. Therefore nitrates and ammonia shift the discharge potential of copper towards more negative values but not that of the Fe(III) and Pb(II) ions (1000 ppm) and elevated current densities (20 A dm^{-2}) revealed that in this case the percentage of iron in the deposit is also considerably lower than that of lead. Increasing the P/C does not diminish these percentages to any great extent (Table 4).

Table 3. Discharge potential and composition of the deposit in the presence of Pb(II) for different concentrations of pyrophosphate ion (pH = 8.80 ± 0.02, 50 ± 0.2° C, N_2 atmosphere)*

Pb^{2+} ($g\,l^{-1}$)	P/C			
	2.26		2.85	
	−E (mV vs SCE)	Pb (%)	−E (mV vs SCE)	Pb (%)
0.5	312(1) 350(19)	1.6	337(3) 459(5)	1.8
0.05	318(2) 378(18)	1.8	337(2) 495(32)	1.8

Values averaged over 3 and/or 6 measurements (standard deviation in parentheses).
* Adjusted with $H_4P_2O_7$.

3.2. *Diffractometric analysis results*

The data shown in Table 5 refer to the analysis of the signals pertaining to the reflections of the crystal faces (111), (200), (220), (311) and (222) of polymicrocrystal samples of copper electrodeposited on a nickel holder

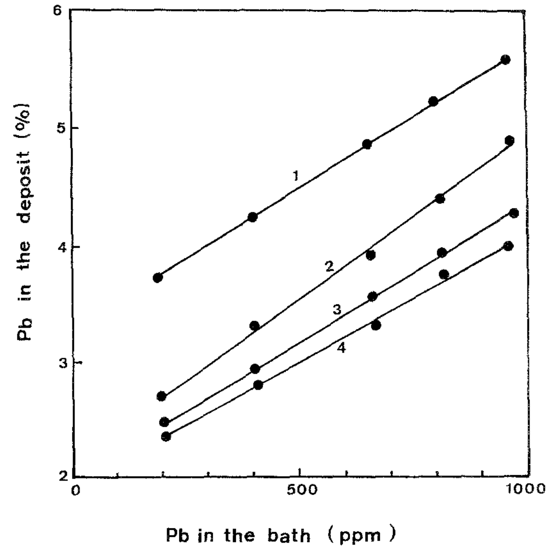

Fig. 1. The percentage value of Pb in the copper deposit (T = 50 ± 0.2° C, pH = 8.8 ± 0.1) is proportional to the Pb^{2+} concentration in the pyrophosphate bath. Cathodic current densities: (1) 8.6; (2) 13.2; (3) 16.1; (4) 19.3 A dm^{-2}.

Table 4. Analysis of the deposit obtained with electrolysis at 50° C and 20 A dm^{-2}. Fe(III) 1000 ppm, Pb(II) 1000 ppm

P/C	*Density* (*kg l*$^{-1}$)	*Cu* (%)	*Fe* (%)	*Pb* (%)
2.22	1.234	96.2	0.2	3.6
2.35	1.257	97.3	0.2	2.5
2.48	1.282	96.6	0.1	3.3
2.57	1.288	97.5	1.0	1.6
2.72	1.302	96.9	0.8	2.3
2.85	1.326	97.0	0.2	2.7
2.92	1.338	98.6	0.7	0.7

with and without Fe(III) and Pb(II) ions. The thickness of the deposit never exceeded 8 μm; nevertheless the orientation effect of the holder is negligible. In fact it is known [7] not to exceed 1000 Å. The percentage area and full width at half maximum of the reflections were calculated. The signal of the face (222) was always rather weak and consequently, in certain cases, was not used. The experimental results were then processed using the Cauchy–Gaussian equation [8]:

$$\frac{K}{(\delta s_0)L} = 1 - \left[\frac{2eS}{(\delta s_0)}\right]^2 \qquad (1)$$

which, setting $\delta s = (2/\lambda)\cos\theta\, d\theta$, gives:

$$\frac{(\delta 2\theta)^2}{\tan^2\theta_0} = \frac{k\lambda}{L}\,\frac{(\delta 2\theta)}{\tan\theta_0 \sin\theta_0} + 16e^2 \qquad (2)$$

(where L = average size of the side of the microcrystal perpendicular to the reflecting face; $e = \delta L/L$, average stress along the same side; θ_0 = position of the peak of each reflection; $k = 1$ (in first approximation); $\lambda = 1.54179$ Å; 2θ = area-to-height ratio of each signal).

With the above equation the values of L and e can be estimated for internal comparative purposes between a certain number of experiments performed under different conditions (and therefore not in absolute terms). The correlation coefficients r, of the straight lines $(\delta 2\theta)^2/\tan^2\theta_0$ vs $(\delta 2\theta)/(\tan\theta_0 \sin\theta_0)$ were always more than 0.97. The values shown in Table 4 are averaged over at least three independent measurements.

All measurements were carried out on deposits obtained with cathodic current density of 12 and 20 A dm^{-2}. Moreover, the reference measurements were executed at galvanic bath densities ranging from 1.21 to 1.60 kg l^{-1} (at 20° C). The average dimensions of the microcrystals obtained are not affected to any great extent by solution density but are highly sensitive to current density. In fact these preliminary tests yielded the following results: at 12 A dm^{-2} $L = 320 \pm 35$ Å and at 20 A dm^{-2} $L = 230 \pm 60$ Å. In all the reference tests the copper deposit was coherent, pinkish and smooth.

Tests were taken performed in the presence of Pb(II) and Fe(III) using a galvanic bath with density of 1.295 kg l^{-1} at identical cathodic current densities.

As can be observed from Table 4, the codeposition of lead causes an appreciable reduction of the crystal grain (average values of L at 12 A dm^{-2}, $L = 170 \pm 10$ Å, at 20 A dm^{-2}, $L = 150 \pm 20$ Å).

Furthermore, at Pb(II) ion concentrations higher than 500 and 200 ppm for the two current densities used, the deposit turns black and non-coherent.

As for iron, the most prominent effect is an increase in the average dimensions of the microcrystals, especially at 20 A dm^{-2}. The deposit remains coherent and bright up to 1000 ppm of Fe^{3+} ion electrolysing at 12 A dm^{-2} and up to 500 ppm at 20 A dm^{-2}. At higher concentrations the deposit is black and non-coherent.

The values of $(\Delta L/L)100$, representative of the average stress of the deposited microcrystals in the tests with lead(II), are consistent with the average values obtained in the reference measurements (0.17 ± 0.07 against 0.13 ± 0.08 for the references). As for Fe(III) at 12 A dm^{-2} for coherent deposits we obtained $(\Delta L/L)100 = 0.06 \pm 0.002$ whilst for non-coherent deposits this value rises to 0.16 ± 0.01. On the contrary, at 20 A dm^{-2} the average stress of the microcrystals is much higher both for coherent and black deposits: $(\Delta L/L)100 = 0.26 \pm 0.09$.

In the tests run in the copresence of Fe(III) and Pb(II) (Fe/Pb ratio by weight from 1.5 to 2.0), the average dimensions were always lower than the references (average values: 160 ± 16 Å for c.c.d. 12 A dm^{-2} and 190 ± 90 Å for c.c.d. 20 A dm^{-2}) whilst the value of $e = \Delta L/L$ was practically negligible.

By contrast, all samples were composed of a black, non-coherent deposit except those obtained at 12 A dm^{-2} with lower concentrations of contaminating cations.

3.3. *XPS–SAM–SEM analyses*

The results of surface analyses on copper samples electrodeposited on Pt from a bath with P/C = 2.85 with and without Pb^{2+} are shown in Table 5. The reference data for $K_4P_2O_7 \cdot 3H_2O$ and $Cu_2P_2O_7 \cdot 5H_2O$ are consistent with the literature data [9–12].

The analysis of the sample (a), electrodeposited in the absence of Pb^{2+}, revealed the presence of a surface coating of Cu_2O which practically disappeared after sputtering with Ar$^+$ ions to remove only about 30 Å.

The analysis of samples (b) and (c) clearly showed the presence on the surface of metallic Pb. In addition, the signal due to this metal at 143.4 eV increased in intensity if the coating was pulverized. This demonstrates that the Pb is not alloyed but is segregated at the edges of the copper microcrystal grain whose surface is exposed by pulverizing the sample.

The XPS–SAM–SEM analyses of samples obtained by electrolysing solutions where Fe^{3+} and Pb^{2+} were copresent revealed that, even at low concentrations of these cations, the deposit, which appeared bright, was discontinuous under microscopic observation. Because the electron escape depth and the spot size for the same element are not identical, the comparison between the XPS and Auger spectra is a source of information.

In our XPS spectrum the predominant signal for the

Table 5. Results of diffractometric analysis of microcrystal copper samples electrodeposited from galvanic baths containing Fe(III) and/or Pb(II) (pH = 8.80 ± 0.02 adjusted with $H_4P_2O_7$; 50 ± 0.5° C; P/C = 2.57; NO^{3-} = 2 $g\,l^{-1}$; NH_3 = 0.5 $g\,l^{-1}$; execution of diffractogram, source CuKα; scan rate 0.25 deg min^{-1})

Solution composition		*c.c.d. 12 A dm^{-2}*			*c.c.d. 20 A dm^{-2}*		
Fe^{3+} (g l^{-1})	*Pb^{2+} (g l^{-1})*	L (Å)	*100e**	r	L(Å)	*100e**	r
†	†						
–	–	320(36)	0.14(8)	†	235(60)	0.12(7)	†
–	0.196	150	0	0.970	180	0.13	1.000
–	0.390	165	0.14	0.998	–	–	–
–	0.593	175	0.24	0.973	160	0.12	0.996
–	0.998	160	0.11	0.998	130	0	0.990
–	1.970	180	0.14	0.991	140	0	1.000
0.193	–	350	0.07	0.997	445	0.21	0.927
0.441	–	360	0.06	0.997	890	0.31	0.969
0.641	–	385	0.06	0.973	860	0.34	0.978
0.936	–	340	0	0.999	300	0.25	0.967
1.823	–	460	0.16	0.963	470	0.34	0.945
2.679	–	255	0.17	0.990	240	0.11	0.998
0.160	0.084	170	0.16	0.984	180	0	0.981
0.332	0.184	155	0	0.975	–	–	–
0.559	0.320	165	0.09	0.978	160	0	1.000
0.831	0.532	–	–	–	130	0	0.999
1.516	0.932	135	0	1.000	140	0	0.910

* $e = \Delta L/L$.

† Values averaged over 7 separate measurements. Varying bath density between 1.226 and 1.605 kg l^{-4} the result varies within the limits of experimental error.

Fe 2p electrons fall at 712 eV and it is thus attributable to an oxidized form. Because the P 2p signals are absent and the O1s one is multicomponent in character, this species is an oxide and/or hydroxide. Furthermore the signal at 707.0 eV due to the metallic iron is also present. Vice versa in our AES spectrum the main signal in the Fe 2p region is that attributable to the metallic iron; however a reduction process due to the electron irradiation, and/or to the argon etching cannot be excluded.

Thus the Auger analysis seems to confirm the previous analytical date, i.e. the presence of metallic iron and lead randomly distributed both on the surface and in the bulk.

Table 6. Results of XPS analysis; binding energy values (eV)

Sample	*K 2p*	*P 2p*	*O 1s*	*2p3/2*	*Cu* *sat.*	*2p1/2*	*Pb 4f*
$K_4P_2O_7 \cdot 3H_2O$	292.4	132.8	530.3	–	–	–	–
$Cu_2P_2O_7 \cdot 5H_2O$	–	133.6	532.0	935.9	943.9	955.9	–
a	–	–	532.6	932.1	–	952.2	–
a 30 Å removed	–	–	532.0*	932.5	–	952.3	–
b	–	–	532.3	932.6	–	952.6	143.5 139.4
c surface	–	133.9*	530.6 532.0	932.8 933.2*	– 944.4*	953.6	143.2 139.2
c as powder	–	–	532.6 533.8	934.8	–	954.9	143.4 140.4
d surface (1)	–	–	530.3	932.5	–	952.5	–

Traces of chloride and potassium are present on the surface. *Traces, (1) Fe 2p3/2 at 712.3 eV.

(a) Copper electrodeposited on Pt from a bath at P/C = 2.85; T = 50 ± 0.5° C, pH = 8.80 ± 0.02 and c.c.d. 0.2 A dm^{-2}.

(b) As in (a) in the presence of 0.05 g l^{-1} Pb^{2+}.

(c) As in (a) in the presence of 0.5 g l^{-1} Pb^{2+}.

(d) As in (a) in the presence of 0.5 g l^{-1} Fe^{3+}.

4. Conclusions

Iron(III) and lead(II) are always present in the copper deposit both at low cathode current densities and electrolysing under conditions normally used in industrial processes. This is made possible by complexing the two cations by means of the pyrophosphate, which involves their discharge potential.

In the case of Pb(II) its discharge potential becomes practically identical to that of copper and the concentration of this element in the deposit is proportional to its concentration in the bath.

As far as Fe(III) is concerned, this element is also present in the electrodeposit even if in a non-proportional concentration. It appears in the metallic state in the Auger analysis and mainly in an oxidized form in the XPS spectra. Furthermore by increasing the P/C its percentage in the deposit can be relatively lowered while the P/C has little effect on the percentage of lead when electrolysis is performed at low cathodic current densities. By contrast, under industrial operating conditions, i.e. much higher cathodic current densities, the percentage of lead codeposited with copper is directly proportional to its concentration in the galvanic bath and depends, moreover, on current density and temperature.

Despite not providing absolute values of the microcrystal dimensions, the diffractometric analysis revealed that the codeposition of Fe and Pb alters the morphology of the copper coating considerably, even when, as happens at the lowest concentrations of these cations, it still appears smooth and coherent.

The effect of these two metals, if considered singly, is antithetic: while the lead that accumulates on the edges of the grain inhibits growth of the seeds, thus reducing the final dimensions of the microcrystals, the iron appears to hinder the formation of the seeds themselves. In any case, when the cations are copresent, they exert a combined effect, considerably lowering the maximum tolerable limit, as the deposit is smooth and useful for further mechanical working. The upper limit concentrations for a good-quality copper deposit depend largely on the plant duty conditions (i.e. P/C ratio, c.c.d. value, temperature, stirring and so on). In any case at medium-high c.c.d. values, concentrations of Pb(II) and Fe(III) below 200 and 1000 ppm are strongly recommended.

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