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The influence of some parameters on the surface roughness of thin copper foils using statistical analysis

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Abstract

The influence of nucleation potential, nucleation time, growth potential and substrate roughness on the surface roughness of thin copper foils deposited electrolytically on titanium substrates from a 83 g dm^{-3} Cu^{2+} and 140 g dm^{-3} H_2SO_4 solution at a temperature of 65 °C, using $2k^4$ factorial design, was studied. A mathematical model to determine the average surface roughness, a quality parameter of thin copper foils, was established. Statistical adjustment of the model enables its use in accurate prediction (error lower than 5%) of the average surface roughness of thin copper foils. The initial steps of copper nucleation and growth are particularly important for the quality of thin (18 μm) copper foils, because during its manufacture, a rapid and homogeneous covering of the entire surface of the electrode becomes fundamental in order to obtain foils with a low surface roughness and a low degree of pinholes per unit area. Mechanisms for copper nucleation on titanium, based on the Thirsk and Harrison model for different experimental conditions, were determined with the aid of potentiostatic current transients. It was shown that the roughness of the thin copper foils is a function of not only the growth process, but also the nucleation process and that the lowest surface roughness is related to a pre-nucleation step at −0.590 V for 10 ms on a titanium substrate polished with 600-grit paper.

1. Introduction

The electrochemistry and crystallization of copper in acid solutions of copper sulfate have been extensively studied, but only in conditions related to the processes of electrowinning and electrorefining [1–8]. However, for copper foil production, the information available in the literature is relatively scarce [9–18]. This fact, allied to the need for high-quality copper foils, justifies further study on the subject. Although the electrolytic reaction for copper foil production is fundamentally the same as that for electrolytic copper production, the operational conditions and parameters for the processes are different. During the continuous deposition of copper foil on titanium drums, current density and copper concentration are much higher, while sulfuric acid concentration is lower [16–18]. Moreover, the cathodic cycle of an electrorefining process of copper is about 7–14 days [19], while during the continuous process of electrolytic copper foil, the electrodeposition time does not go beyond a few minutes, which is the residence time of a determined point of the drum in the electrolytic cell. Moreover, quality requirements of copper foil, such as integrity, surface roughness and physical properties are very strict.

Although copper nucleation on inert substrates has been studied [9–14], the experimental conditions were quite different from those used in thin film copper production. Moreover, only limited attention has been given to the initial stages of the nucleation process [12, 13], which are fundamental not only to produce thin copper films, but also to provide useful information, which can be applied in starter sheet production for copper electrorefining.

As thin copper foils have largely been used in the production of printed circuit boards and since the profile of these foils is one of the most important parameters that affects chemical attack during printed circuit board manufacture [15], a more detailed study on how process parameters affect surface roughness was initiated. Considering that chemical attack takes place at the grain boundaries, reduced grain size is fundamental for an effective and uniform chemical attack [20]. Additionally, Chaing et al. [21] reported that anisotropic grain growth should be inhibited and nucleation intensified in order to obtain good quality copper foils.

A two-level factorial design with four factors ($2k^4$) [22–25] was used in an attempt to investigate how the surface roughness of copper foil deposited electrolytically on titanium substrate of different surface rough-

ness, from acidic copper sulfate solution at 65 °C, is affected by process parameters and their interactions.

The choice of the experimental parameters considered and their respective levels were based on preliminary tests and on research conducted by Dutra and O'Keefe [12, 13], Sun et al. [7], Delplancke et al. [9] and Zhang et al. [10]. Dutra and O'Keefe [12] reported that saturation nuclei density is strongly potential dependent; increasing with increasing cathodic potentials up to −900 mV vs Hg/Hg_2SO_4, when mass transport limitations strongly affect the initial stage of nucleation. Additionally, they stated that saturation nuclei density in the potential range tested, was achieved after a very short time. Furthermore, they concluded that no significant nucleation was observed after a few milliseconds. Because of these findings the intensity of nucleation potential and nucleation time were two out of four process parameters studied. Sun et al. [7] and Zhang et al. [10] stated the importance of the substrate surface nature on the surface roughness of copper foil. They observed that mechanical polishing resulted in nucleation densities that varied with substrate smoothness and explained that mechanically polished titanium may have an air-formed oxide layer. This blocking film has just a few defects available as active sites for nucleation. On the other hand, they noted that on substrates mechanically polished with 600-grit emery paper a fine, dense uniform pattern emerged with sufficient surface defects to favor homogeneous copper deposition. The use of 400-grit emery paper was introduced in order to study the influence of substrate roughness on the quality of deposited copper foils.

The objective of this work is to study how some process parameters influence the copper foil quality, more specifically, its average surface roughness and also investigate the feasibility of obtaining smooth deposits without the presence of addition agents, such as chloride ion and glue.

2. Experimental details

2.1. *Electrodeposition system*

The electrochemical tests were carried out in conventional Pyrex cells. The electrochemical cell was a 150 cm^3 jacketed glass beaker with an acrylic cover, enabling a constant temperature (±0.5 °C) level. The working electrode was a titanium plate, polished with 400- or 600-grit emery paper, with an exposed area of 1 cm^2. The counter electrode was an electrolytic copper plate and the reference electrode, a copper wire (0.310 V vs NHE). All the potentials quoted in this study are given with respect to the normal hydrogen electrode, unless otherwise mentioned. The electrolyte was prepared from analytical grade cupric sulfate pentahydrate and sulfuric acid to give a stock solution of 83 g dm^{-3} copper and 140 g dm^{-3} sulfuric acid. All experiments were carried out without stirring at a temperature of 65 °C, unless otherwise stated.

2.2. *Electrochemical tests*

All electrochemical tests were carried out with the aid of an EG&G PAR model 273A potentiostat/galvanostat connected to a microcomputer with M270 software. In all electrochemical tests the ohmic drop was compensated through a positive feedback technique available in the M270 software.

2.2.1. *Voltammetry*

The cyclic voltammograms on titanium electrodes, at 65 °C, were started at the open circuit potential (around 0.510 V vs NHE), driven in the cathodic direction up to −0.690 V and back to the open circuit potential with a scan rate of 20 mV s^{-1}.

2.2.2. *Potentiostatic current transients*

Potentiostatic pulses at different potentials during different times were applied. A very short initial pulse was applied to the cell to promote nucleation. These pulses were 0.010, −0.290 or −0.590 V, while electrolytic growth was conducted at 0.060 or −0.040 V during 275 or 150 s respectively, until a charge of 66 C was achieved. Since the results of preliminary tests had shown that growth at potentials more cathodic than −0.040 V favored the formation of dendrites, the growth potential was studied at two levels below this critical level: 0.060 and −0.040 V.

2.3. *Factorial design*

The process parameters for copper foil manufacturing were the intensity of nucleation potential ($P1$), nucleation time ($T1$), growth potential ($P2$) with its corresponding growth time in order to keep the electric charge constant, and average substrate roughness ($R_{a,subs}$). The titanium plates polished with 600- and 400-grit emery paper have an average roughness of approximately 0.09 and 0.16 μm, respectively. A $2k^4$ factorial design was employed for the study of the influence of the process parameters.

2.4. *Surface roughness*

After each run the copper foils were thoroughly washed with distilled water, dried and their average surface roughness determined with a DEKTAK II profilometer. The average surface roughness definition used in this paper was the mathematical average of deposit surface roughness, expressed by Equation 1:

$$R_a = \frac{\sum h}{n} = \frac{h_1 + h_2 + \cdots + h_n}{n} \quad (1)$$

where, R_a is the average surface roughness, h_i, the measured deposit roughness, n, the total number of the measured deposit roughness.

3. Results and discussion

3.1. *Electrochemical tests*

Cyclic voltammograms related to the reduction of Cu^{2+} ions on titanium substrates, with and without previously deposited copper nuclei, for 2 ms, at three different potentials are presented in Figure 1. Well-defined plateaux are evident from −0.090 V up to approximately −0.490 V, after which the current begins to rise, probably due to the deposit surface roughness or cathodic hydrogen evolution. In the presence of previously formed nuclei, a faster current density growth was observed with a corresponding onset deposition overpotential decrease from 0.102 to 0.046 V, with a previous nucleation at −0.590 V for 2 ms. The more cathodic the potential used in the pre-nucleation the lower the onset deposition overpotential for copper on the cathodic substrate, which should lead to a faster growth and a more homogeneous deposit on titanium substrates, indicating that previously formed nuclei favor faster deposition. Additionally, the observed limiting current density was slightly higher for tests with previously deposited nuclei at more cathodic potentials.

Potentiostatic current transients, for copper nucleation on titanium substrates, previously polished with either 600- or 400-grit emery paper are shown in Figure 2. A fast current increase at the beginning of the pulse and a trend to current stabilization after about 1 ms, depending on the applied pulse potential, were observed. This behavior indicates that most of the nuclei are formed during the first half of the pulse, and that during the second half, nuclei growth should predominate, which is in accordance with results of Dutra and O'Keefe [12]. On the other hand, Figure 2 shows that the nucleation density saturation on substrates mechanically polished with 600- and 400-grit emery paper was different. On substrates polished with 600-grit paper nucleation density saturation was not achieved at any applied potential, however, on substrates mechanically polished with rougher 400-grit paper, nucleation density saturation was achieved at −0.290 V corresponding to 1.28 A cm^{-2} after 2.0 ms, since for more cathodic potentials (−0.590 V) no further current density increase was attained. This behavior is probably related to the different surface finishing, since the rougher substrate, obtained with the 400-grit paper polishing, presents a smaller number of energetically active sites, although these sites seem to be more active than those present on a smoother substrate. Consequently, with even a less cathodic potential, nuclei saturation is achieved on rougher substrates.

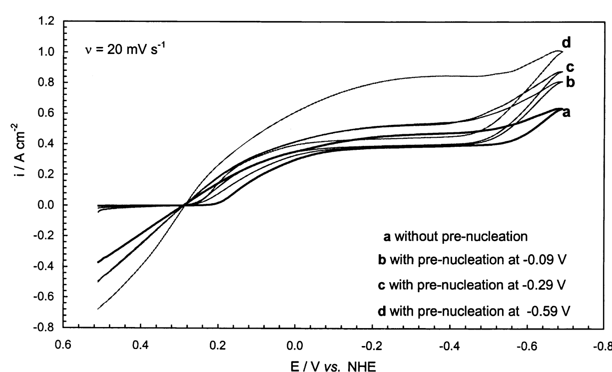

Fig. 1. Cyclic voltammetry on titanium substrates with and without previous nucleation at 65 °C.

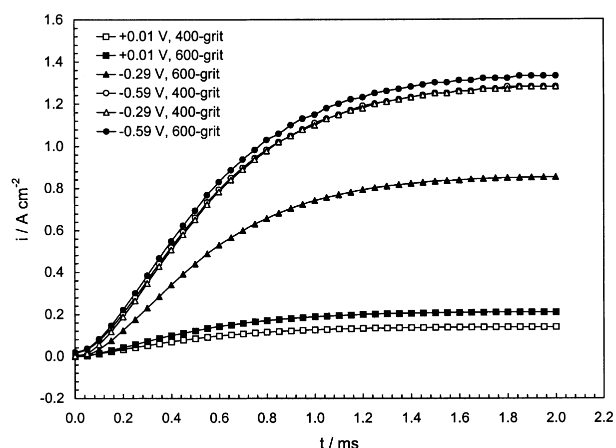

Fig. 2. Potentiostatic current density transients of 2 ms, for the copper nucleation on titanium polished with 600- and 400-grit emery paper.

In the nucleation and growth model of an isolated nucleus proposed by Thirsk and Harrison [26], current density (i) is proportional to a power (n) of time (t). In a logarithmic form, according to Equation 2, n permits the determination of the nucleation mechanism and the constant a is associated with the nucleation rate.

$$\log i = n \log t + \log a \tag{2}$$

The $\log i$ vs $\log t$ behavior for copper nucleation on titanium substrates is presented in Figure 3. Straight lines with slopes between 0.9 and 1.4 and correlation coefficients close to 0.99 may be observed. The n value indicates the possible forms of the nucleation and growth mechanisms of isolated crystals (Table 1), according to the Thirsk and Harrison model [26]. A n value close to 1.5 indicates progressive nucleation, 3D growth and a diffusion control mechanism. For n close to 1.0 there are three possible mechanisms: instantaneous nucleation with 2D growth under kinetic control, progressive nucleation with 1D growth and needle formation under kinetic control and progressive nucleation with 2D growth under diffusion control. The most probable mechanism can be determined with the aid of scanning electron microscopy (SEM) and voltammetric

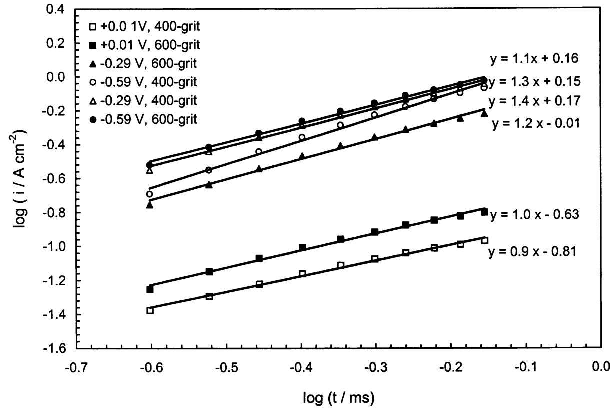

Fig. 3. Logarithmic relationship between current density and time for copper nucleation on titanium polished with 600- (full marks) and 400-grit emery paper (empty marks), at different potentials.

curves, which indicate diffusion control for the more cathodic potentials and mixed control around 0.010 V.

3.2. *SEM analysis*

The morphology of the copper nuclei deposited on titanium substrates, polished with 600- and 400-grit paper, at different potentials, after 2 and 10 ms, is presented in Figures 4 and 5 respectively. Electrocrystallization theory [27] establishes that initial nuclei size, before grain growth, depends on the applied potential, since there is a critical value of free energy related to a critical nucleus radius to be overcome, and this critical radius will be smaller for higher potentials. Figure 4i and ii, show that the higher the applied cathodic potential, the smaller the nuclei size, and also a significantly higher number of nuclei was obtained. In Figure 4iii, which provides a better overview of the nuclei presented in Figure 4ii, a very uniform substrate coverage with small crystals is observed. In Figure 4iv, obtained after 10 ms, no further nucleation is observed, but only crystal growth from less than 0.5 (Figure 4ii) up to about 1.5 μm mean diameter. Additionally, these SEM images indicate the presence of progressive nucleation, since different nuclei sizes are observed. At 0.010 V, the predominance of needle-like crystals confirm the proposed nucleation mechanism presented in Table 1. For higher cathodic potentials, the nucleation remained progressive but the growth type changed from 1D to 2D or/and 3D, under diffusion control. At an intermediate potential (−0.290 V) a mixture of needle-like and irregularly shaped grains indicated a gradual

Table 1. Current–time relationships and possible nucleation mechanisms for the nucleation of copper on titanium at 65 °C for different potentials on substrates polished with 600- and 400-grit emery paper

Potential /V	Substrate finishing /μm	Time interval /ms	Equation ($Y = nX +$ const.)	Possible nucleation mechanisms*
+0.010	0.09	[0.15–0.85]	$Y = 1.0X - 0.63$	Progressive, 1-D needle, kinetic control.
−0.290	0.09	[0.15–0.85]	$Y = 1.2X - 0.06$	(1) Progressive, 1D needle, kinetic control.
				(2) Progressive, 2D and 3D, diffusion control.
−0.590	0.09	[0.15–0.85]	$Y = 1.1X + 0.16$	Progressive, 2D and 3D, diffusion control.
+0.010	0.18	[0.15–0.85]	$Y = 0.9X - 0.81$	Progressive, 1D needle, kinetic control.
−0.290	0.18	[0.15–0.85]	$Y = 1.3X + 0.15$	Progressive, 2D and 3D, diffusion control.
−0.590	0.18	[0.15–0.85]	$Y = 1.4X + 0.17$	Progressive, 2D and 3D, diffusion control.

*According to Thirsk and Harrison model [26] and SEM micrographs.

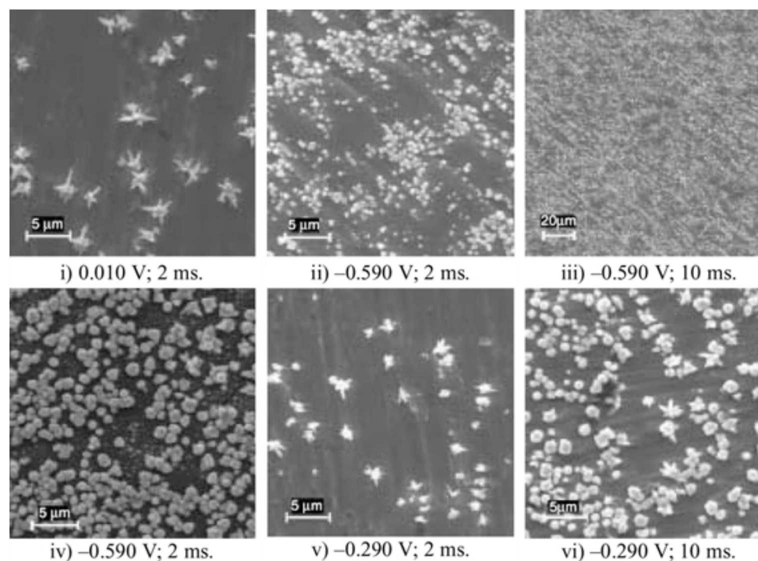

Fig. 4. SEM micrographs of copper crystals deposited on titanium polished with 600-grit paper, at 0.010 and −0.590 V, during 2 and 10 ms.

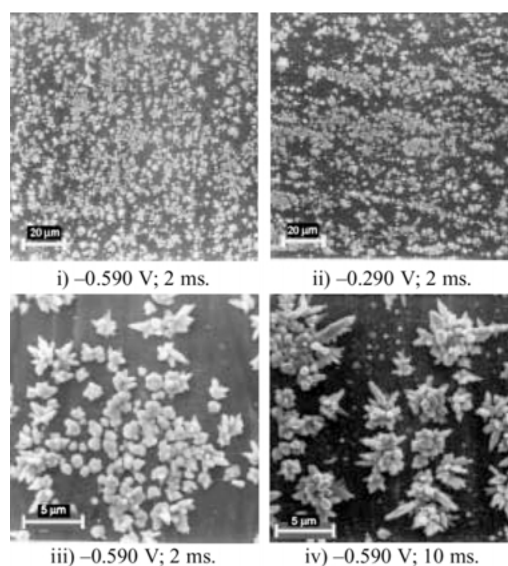

Fig. 5. SEM micrographs of copper crystals deposited on titanium polished with 400-grit paper, at −0.290 and −0.590 V, during 2 and 10 ms.

change of the nucleation mechanism as the cathodic potential was increased, as indicated in Figure 4v and vi. For an increased nucleation time the needle predominance tends to be smaller and the appearance of nodules is favored, as observed in Figure 4vi.

The suggested mechanisms for copper nucleation on a rougher titanium substrate (Figure 5) did not change significantly from those proposed for the smoother substrate, except for the larger predominance of needle-like crystals and the onset of some dendritic growth, observed at −0.290 and −0.590 V for longer nucleation times (Figure 5ii–iv), probably caused by the non-uniform current distribution on the large grains obtained on the rougher substrate, as the surface coverage obtained at −0.590 V, on the rougher substrate, was smaller and the grains considerably larger, as seen in Figures 4iv and 5i. Comparing Figure 5i and ii, it can observed that nucleation density at −0.290 and at −0.590 V did not increase significantly, since saturation was already achieved as observed previously in Figure 2.

The morphology of copper foils deposited on titanium substrates under different conditions is presented in Figure 6. For the substrates finished with 600-grit paper (Figure 6i–v), the copper foil obtained at low cathodic nucleation potential (0.010 V) followed by deposition at −0.040 V presented the roughest surface (3.4 μm), inappropriate for foil production, as can be seen in Figure 6i. However, when just the nucleation step was changed to −0.590 V (Figure 6ii) a considerably smoother surface (1.5 μm) was obtained, indicating the importance of the nucleation step on the surface roughness of the foil. For a lower deposition potential (0.060 V) and a nucleation step of 2 ms at −0.590 V a 0.76 μm surface roughness was achieved, indicating that both, the nucleation and deposition potentials, may influence the final surface roughness of the foil. When the nucleation was carried out at −0.590 V for 10 ms and the deposition potential was 0.060 V (Figure 6iv and v), the lowest surface roughness was achieved (0.18 μm), indicating that smoother foils can be obtained easily, even without stirring and the presence of additives, but only if a fairly complete initial coverage with stable crystals, favoring an even current distribution, is prepared initially. On a rougher substrate, a low copper foil surface, around 0.22 μm, was obtained

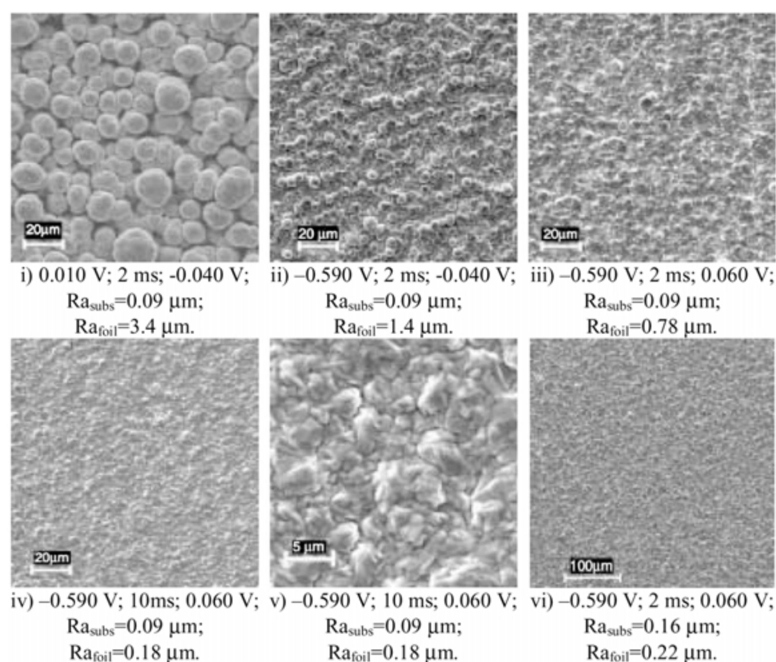

Fig. 6. Influence of nucleation potential, nucleation time, deposition potential and titanium roughness on the surface aspect and roughness of copper foils.

Table 2. $2k^4$ factorial design and foil surface roughness measurements

Test code	Nucleation potential	Nucleation time	Growth potential	Substrate roughness	Foil roughness	
	(1)/V	(2)/ms	(3)/V	(4)/μm	R_a/μm	$R_{a'}/\mu$m
1	−0.290	2	0.060	0.09	0.22	0.26
a	−0.590	2	0.060	0.09	0.76	0.80
b	−0.290	10	0.060	0.09	0.57	0.63
ab	−0.590	10	0.060	0.09	0.19	0.17
c	−0.290	2	−0.040	0.09	0.22	0.18
ac	−0.590	2	−0.040	0.09	1.50	1.20
bc	−0.290	10	−0.040	0.09	0.22	0.21
abc	−0.590	10	−0.040	0.09	0.23	0.23
d	−0.290	2	0.060	0.16	0.46	0.49
ad	−0.590	2	0.060	0.16	0.20	0.22
bd	−0.290	10	0.060	0.16	0.37	0.39
abd	−0.590	10	0.060	0.16	0.29	0.30
cd	−0.290	2	−0.040	0.16	0.45	0.42
acd	−0.590	2	−0.040	0.16	0.30	0.34
bcd	−0.290	10	−0.040	0.16	0.32	0.34
abcd	−0.590	10	−0.040	0.16	0.69	0.74

(Figure 6vi), under the same conditions except for the nucleation time, which was shorter (2 ms). This behavior may be due to the fact that a similar nuclei size may be obtained on titanium polished with 600-grit paper at −0.590 V for 2 ms and on titanium finished with 400-grit paper at the same potential for 10 ms, as can be seen in Figures 4iii and 5iii respectively.

3.3. *Average surface roughness measurements*

Table 2 shows the measured average surface roughness (R_a) and its replicate ($R_{a'}$) of the copper foils using factorial design. The process conditions of each manufactured copper foil are also indicated. The lowest average surface roughness, 0.18 μm, was obtained with a cathodic nucleation potential of −0.590 V during 10 ms and a cathodic growth potential of 0.060 V during 275 s on substrates polished with 600-grit emery paper. The highest average surface roughness, 1.35 μm, was obtained with a cathodic nucleation potential of −0.590 V for 2 ms and a cathodic growth potential of −0.040 V for 150 s on substrates polished with 600-grit emery paper. It can be concluded that the use of substrates polished with 600-grit emery paper (R_a = 0.09 μm) allied to high cathodic nucleation potential (−0.590 V) for longer nucleation times (10 ms), followed by growth (275 s) with a cathodic growth potential of 0.060 V may generate high quality copper foils. This occurs, because with a 10-ms pulse for the nucleation step, the achievement of good surface coverage with stable nuclei at 0.060 V was favored, and this lower cathodic growth potential also contributes to smoother copper foil deposition.

Figure 7 presents the Pareto diagram [22] of the effects of the variables and their interactions on the average surface foil roughness. The purpose of the diagram is to distinguish which parameters are significant and which are trivial, that is those on the left of the dashed vertical line, which indicates a 5% error level. The individual effect of the substrate roughness (4) is more significant than that of the growth potential (3), which is more significant than the effects of both nucleation time (2) and the intensity of the nucleation potential (1), which have an effect of the same extent. The interaction of the nucleation potential, the growth potential and the substrate roughness on one hand, and nucleation time and substrate roughness on the other hand, have an important influence on the foil roughness as can be seen clearly in Figure 7.

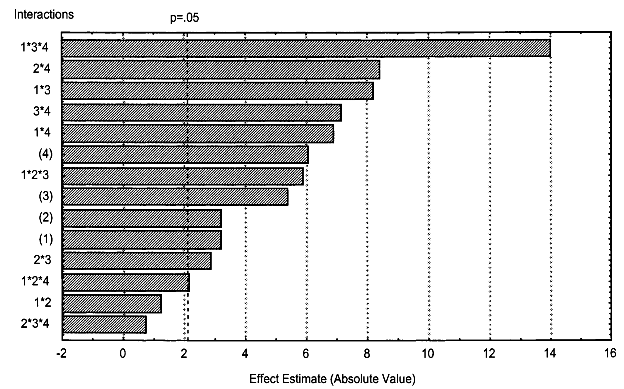

Fig. 7. Pareto chart of standardized effects; response variable: average foil surface roughness (R_a); process variables: (1) nucleation potential, (2) nucleation time, (3) growth potential and (4) average substrate roughness.

The so-called normal probability plot is a tool to assess how closely the set of residuals follows a normal distribution. In this plot the actual residual values are plotted along the horizontal X-axis; the vertical Y-axis shows the expected normal values for the respective values, after they were rank-ordered. If all values fall onto a straight line, as they do in Figure 8, the residuals follow a normal distribution, validating the statistical analysis.

Table 3, the ANOVA Table, shows the effect estimates of the variables and their interactions with a square

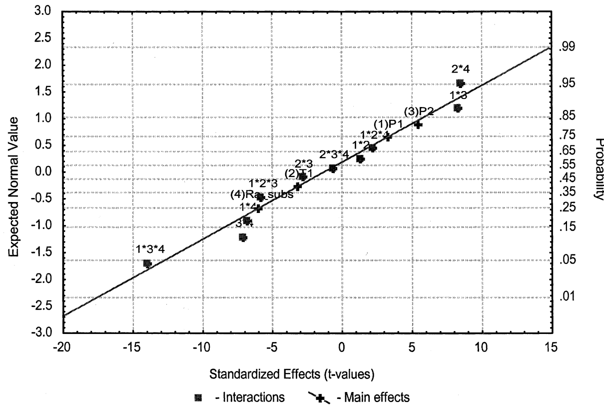

Fig. 8. Normal probability plot.

correlation coefficient of 0.97 and a model adjustment for a confidence level of 95%. Additionally, Table 3 contains the regression coefficients of the multiple regression model, from which a mathematical equation for the average surface roughness estimation can be derived; where A_0 is the overall average and A_{i-j} are the regression coefficients from i to j. The figures shown in italics (Table 3) are not significant statistically, since their p-value (0.234 and 0.475, respectively) is higher than the error level of 0.05. The coded mathematical model considering the statistically significant parameters and their interactions, is presented in Equation 3:

$$\begin{aligned} R_a = {} & A_0 + A_1(P1) + A_2(T1) + A_3(P2) + A_4(R_{a,subs}) \\ & + A_5(P1)(P2) + A_6(P1)(R_{a,subs}) + A_7(T1)(P2) \\ & + A_8(T1)(R_{a,subs}) + A_9(P2)(R_{a,subs}) \\ & + A_{10}(P1)(T1)(P2) + A_{11}(P1)(T1)(R_{a,subs}) \\ & + A_{12}(P1)(P2)(R_{a,subs}) \end{aligned} \tag{3}$$

The final model can be determined by replacing the coded coefficients by their determinated values from Table 3, as shown in Equation 4:

$$\begin{aligned} R_a = {} & 0.434688 + 0.039688(P1) - 0.039687(T1) \\ & + 0.066563(P2) - 0.075312(R_{a,subs}) \\ & + 0.101563(P1)(P2) - 0.085313(P1)(R_{a,subs}) \\ & - 0.035313(T1)(P2) + 0.104063(T1)(R_{a,subs}) \\ & - 0.088437(P2)(R_{a,subs}) - 0.072812(P1)(T1)(P2) \\ & - 0.026563(P1)(T1)(R_{a,subs}) \\ & - 0.173438(P1)(P2)(R_{a,subs}) \end{aligned} \tag{4}$$

4. Conclusions

(1) There is a good agreement between electrochemical theory and the results obtained: the determined nucleation mechanisms (Table 1) are in accordance with the morphology and grain size observed in the SEM photographs. All the parameters and some of their interactions influence the average surface roughness of the copper foils.
(2) With very short nucleation steps, under high cathodic potentials, preceding grain growth, smooth foils can be obtained, confirming the importance of the pre-nucleation steps.
(3) The smoothest copper foil (R_a = 0.18 μm) was obtained with a 10-ms cathodic nucleation pulse of −0.590 V, followed by growth at 0.060 V during 275 s.
(4) The straight line obtained in the normal probability plot indicates a normal distribution of the residuals, validating the statistical analysis.
(5) Statistical analysis has shown that the interaction of the process variables: nucleation pulse, growth pulse and the substrate roughness, and also nucleation time and the substrate roughness, present the most relevant effect, among the selected parameters in this study, on copper foil roughness.

Table 3. ANOVA table for a confidence level of 95% with a correlation coefficient of 0.97 and regression coefficients (Rgr. Coeff.)

	SS	MS	F	p	$t(17)$	Rgr. Coeff.
(1)	0.050	0.050	10.2	0.005	35.0	0.434688
(2)	0.050	0.050	10.2	0.005	35.0	0.434688
(3)	0.142	0.142	28.8	0.000	3.2	0.039688
(4)	0.181	0.181	36.9	0.000	−3.2	−0.039687
1 × 2	0.007	0.007	1.5	0.234	5.4	0.066563
1 × 3	0.330	0.330	67.1	0.000	−6.1	−0.075312
1 × 4	0.233	0.233	47.3	0.000	*1.2*	*0.015312*
2 × 3	0.039	0.039	8.1	0.011	8.2	0.101563
2 × 4	0.347	0.347	70.4	0.000	−6.9	−0.085313
3 × 4	0.250	0.250	50.8	0.000	−2.8	−0.035313
1 × 2 × 3	0.169	0.169	34.5	0.000	8.4	0.104063
1 × 2 × 4	0.023	0.023	4.6	0.047	−7.1	−0.088437
1 × 3 × 4	0.963	0.963	195.6	0.000	−5.9	−0.072812
2 × 3 × 4	0.003	0.003	0.5	0.475	2.1	0.026563
Error	0.084	0.084			−13.9	−0.173438
Total SS	2.872	2.872			*−0.7*	*−0.010091*

SS: sum of squares, MS: mean of squares, F: F-test, p: pure error.

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