

Optimization of the parameters for nickel electrowinning using interference microscopy and digital image analysis

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Abstract Ni electrodeposition experiments at a constant current density 220 A/m^2 were performed to determine the optimum concentrations of chloride and an organic additive used for an industrial Ni electrowinning. White light interference microscopy was used to acquire digital images of the morphology of the electrodeposited nickel. The scaling analysis was employed to parameterize the morphological information encoded in the images. The standard deviation of the surface height, δ , the critical scaling length, L_c , and the optical roughness, $4\delta/L_c$, were determined as a function of the chloride concentration and the amount of organic additives. These parameters were plotted as a function of the two compositional variables. These three-dimensional plots allowed us to find conditions corresponding to the minimum of $4\delta/L_c$, at which the deposited nickel is well leveled.

Keywords Nickel · Electrodeposition · Electrowinning · Scaling analysis · Interference microscopy · Digital image analysis

Introduction

Electrochemical deposition of metals is widely used in hydrometallurgy. Production of Cu, Ni, Zn, and noble metals traditionally involves electrowinning, i.e., electrochemical reduction of metal compounds obtained by leaching of ore or purifying of the metal produced in a smelter by anodic dissolution and electrodeposition on a cathode in a process called electrorefining.

Physical properties of electrodeposited metals often depend on their morphology, i.e., grain size, surface roughness, surface defects, etc. These factors also affect physical appearance of metals and consequently their market value. The morphology of electrodeposits strongly depends on parameters used in electrodeposition, such as current density, pH, temperature, and the electrolyte composition [1, 2]. Therefore, strong attention has been given to the optimization of electrochemical process parameters and compositions of electrolytes in order to achieve the most favorable morphology of the electrodeposited metal.

For a long time, the morphology of electrodeposited metals has been assessed using descriptive analysis of images obtained with the help of optical or electron scanning microscopy. Significant advances in surface imaging techniques such as the atomic force microscopy (AFM) and the scanning tunneling microscopy (STM) introduced new tools to study the morphology of electrodeposited metals. These techniques provide numerical images of the surface in three-dimensional (3D) coordinates. The numerical format of these images allows one to apply scaling analysis in order to extract parameters that characterize surface roughness and periodicity of surface features in the direction parallel to the surface. Monitoring evolution of these parameters with the electrodeposition time allows one to predict the morphology of industrially

Dedicated to Prof O.A. Petrii on the occasion of his 70th birthday and in recognition of his contribution to electrochemistry.

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produced metal with a laboratory experiment of a relatively short duration [3–8]. Parameters extracted from the scaling analysis also provide useful information concerning the mechanism of the surface growth [9].

In previous studies, AFM and the scaling analysis of AFM images were employed to study the metal deposition processes [6, 10–12]. Despite high lateral resolution of images obtained with AFM, this techniques cannot be applied to image surfaces if the roughness of the electrodeposited metal exceeds 5 μm . Under condition of industrial metal deposition, this limiting roughness is frequently achieved after less than 1 h of electrolysis. The duration of industrial electrolysis is typically several days. Therefore, AFM can be used for the analysis of the surface morphology of electrochemically produced metals at early stages of the deposition only.

Recently, white light interference microscopy (WLIM) equipped with achromatic phase shifter has offered a new opportunity to perform digital 3D imaging of surfaces with high lateral resolution and over a wide range of surface heights [13, 14]. Modern WLIM instruments allow imaging of a surface area that is $1,000 \times 1,000 \mu\text{m}$ wide and the height of the imaged objects up to 100 μm . The objective of this paper is to illustrate the power of imaging with WLIM combined with the scaling analysis to predict the morphology of nickel electrodeposited at conditions mimicking industrial nickel electrowinning. We will also show how to use this technique to optimize the electrorefining parameters such as concentrations of chloride and an organic leveling agent in the electrolyte.

Experimental

Nickel was electrochemically deposited onto stainless steel plates (substrates) from synthetic electrolyte containing Ni^{2+} (55 g l^{-1}), Na^+ (20 g l^{-1}), H_3BO_3 (7 g l^{-1}), Cl^- (from 0 to 30 g l^{-1}), and sulfate ions to balance charge. Leveling agent (Levelin), a proprietary organic compound supplied by our industrial partner, was added to the electrolyte in range of concentrations 0–40 ppm.

The substrate was degreased in a warm soap solution and copiously washed with water. When stated in the text, the substrate was polished using first 600-, 800-, and 1200-grade sandpaper (Buehler) and next with 1 and 0.3 μm Al_2O_3 powder (Leco). Otherwise, the substrate was used “as received” (not polished). The surface of the substrate was insulated with Teflon tape except the area $1 \times 1 \text{ cm}$ exposed to electrolyte during electrodeposition.

The deposition was carried out in an electrochemical cell made of Teflon. Cell was immersed into water bath in order to maintain constant temperature of the electrolyte $60 \pm 1 \text{ }^\circ\text{C}$. The pH was measured by means of the EA-920 pH-meter

(Orion) with temperature compensator and adjusted to 4.0 ± 0.1 by adding H_2SO_4 .

A bar cut from nickel was used as an anode. A 1 cm^2 of the anode surface was exposed to the electrolyte. The rest of surface was insulated with Teflon tape. All experiments were carried out in galvanostatic mode at current density 220 A/m^2 using the EG&G PAR 273A potentiostat/galvanostat. This was the current density used by our industrial partner for nickel electrowinning. At pH 4, the current efficiency was 97% or higher.

After each deposition, the cathode was rinsed with deionized water, dried, and stored in a desiccator. For each plating condition, samples of electrodeposited nickel were collected for a series of electrodeposition times. The white light interference microscope WYKO NT3300 (Veeco Metrology, Tucson, Arizona) was used to capture images of the surface of electrochemically deposited nickel using different magnifications (5, 10, 27, and 104).

Results and discussion

The method

Figure 1 shows a representative WLIM image of the electrodeposited nickel. It shows that the surface consists of characteristic conical shaped grains. The grain consists of a cluster of multiple overlapping nuclei. The height of an average grain can be taken as being equal to four times the limiting standard deviation of the surface heights, and the width of the grain can be taken as an average distance between the grains. These parameters can be determined from the scaling analysis of the image.

Figure 2 describes principles of the method that was used for scaling analysis of images obtained by means of

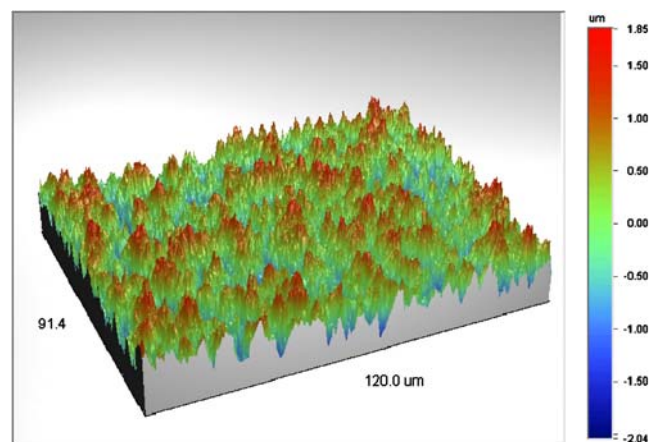


Fig. 1 Representative WLIM data for electrodeposited nickel for 180 min. from the synthetic electrolyte in presence of 24 g/l of Cl^- and 2 ppm of the organic additive at the current density 220 A/m^2 and temperature $60 \text{ }^\circ\text{C}$

WLIM. The root mean square (rms) of the surface heights or the standard deviation of the surface heights was calculated within the square which side length was L , shown in bottom right corner of the inset to Fig. 2. Then the square was moved step by step across the imaged surface using 1 pixel increment, and standard deviations of surface heights were calculated for each new position of the square. The standard deviations corresponding to all positions of the square were then averaged to determine the average rms roughness of the surface (ξ_L) for a given scaling length L defined as [6, 8, 10]:

$$\xi_L = \left\langle \sqrt{\frac{1}{L^2} \sum_{x,y} [H(x,y) - \langle H(x,y) \rangle]^2} \right\rangle \quad (1)$$

where $H(x,y)$ is the value of the surface height measured with respect to an arbitrary reference plane at a point whose surface coordinates are x and y .

The ξ_L were calculated for a progressively increasing scaling length (size of the square) L . In scaling analysis, logarithm of ξ_L is then plotted as a function of logarithm of the scaling length L . Several such plots are shown in Fig. 2. They correspond to images acquired at different deposition times. In the logarithmic coordinates, ξ_L initially increases linearly with L . In fact, the scaling theory predicts that in this range, $\xi_L \propto L^\alpha$, where α is the static exponent, and its value should be independent of the electrolysis time. The magnitude of parameter α reveals the dominant mechanism of the surface growth. The static exponent is related to the smoothing coefficient $n=2(\alpha+1)$, that can be independently determined from the spectral power density analysis of the images (Fourier transform analysis of the image). The parameter $n=4$ indicates that the deposition is controlled by

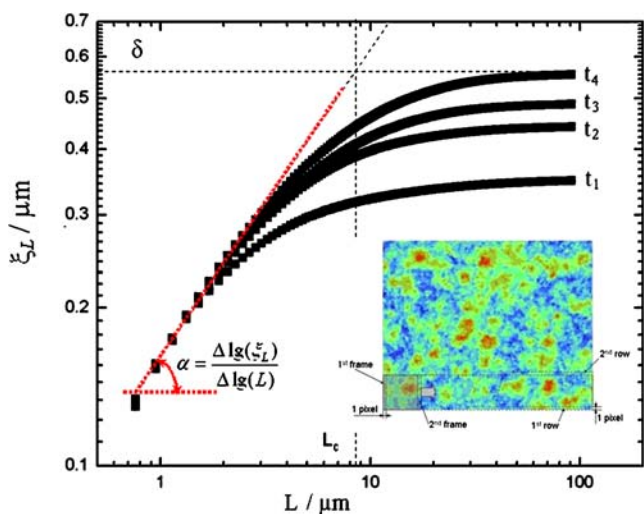


Fig. 2 Scaling analysis of the image of Ni deposited from the synthetic electrolyte in presence of 24 g/l of Cl^- and 6 ppm of the organic additive at the current density 220 A/m^2 and temperature 60 °C. Deposition time t_1 – t_4 are 60, 120, 180, and 300 min, respectively

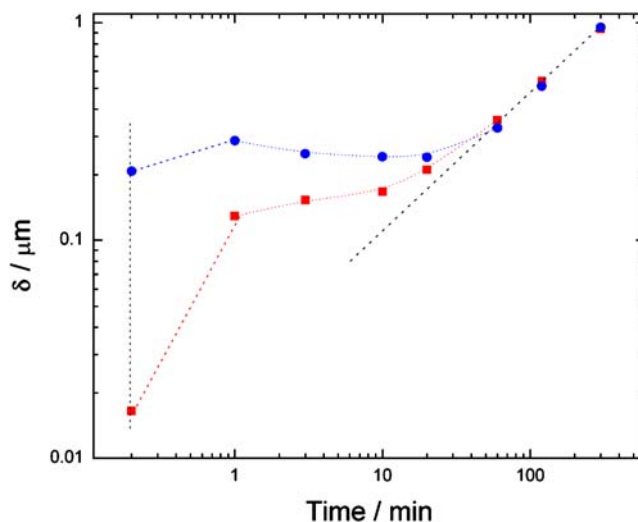


Fig. 3 Dependence of the limiting surface roughness δ vs deposition time for Ni deposited from the synthetic electrolyte in presence of 24 g/l of Cl^- and 0 ppm of the organic additive at the current density 220 A/m^2 and temperature 60 °C at “mirror finished” (squares) and “as received” (circles) stainless steel substrates

surface diffusion, while $n=3$ indicates that the smoothing of the surface is due to the so-called volume flow which can be identified as the progressive nucleation mechanism.

At sufficiently large values of L , the parameter ξ_L attains a limiting value called the limiting roughness (δ). The values of L at which ξ_L reaches the plateau is called the critical scaling length (L_c). The critical scaling length measures periodicity of surface features in the direction parallel to the surface. It is a measure of the average distance between the grains on the surface of the electrodeposited metal. Figure 2

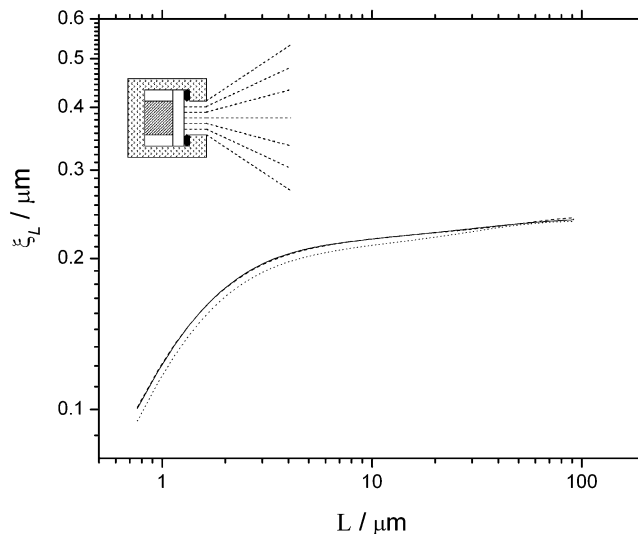


Fig. 4 Scaling analysis of images taken at three different spots of electrode after 300 min of nickel deposition with electrode configuration shown in the insert. Ni deposited from the synthetic electrolyte in presence of 24 g/l of Cl^- and 25 ppm of the organic additive at the current density 220 A/m^2 and temperature 60 °C. (Note that two of three curves are almost identical)

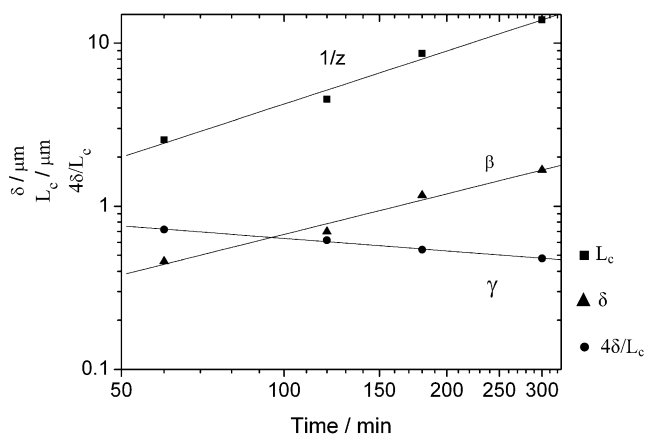


Fig. 5 Plots of the limiting roughness δ (triangles), critical scaling length L_c (squares) and the aspect ratio $4\delta/L_c$ (circles) as a function of the deposition time for Ni deposited from the synthetic electrolyte in presence of 15 g/l of Cl^- and 20 ppm of the organic additive at the current density 220 A/m^2 and temperature 60 $^\circ\text{C}$

shows that both δ and L_c depend on the deposition time. The theory predicts that the time dependence of the limiting roughness is described by $\delta \propto t^\beta$, where β is the dynamic or the growth exponent. The time dependence of the critical scaling length is described by: $L_c \propto t^{1/z}$, where $1/z$ is the roughness exponent. The aspect ratio $4\delta/L_c$ is the ratio of the height to the width of a periodic feature on a surface (the ratio of the grain height to the grain width). The scaling theory predicts that the aspect ratio depends on time as $4\delta/L_c \propto t^\gamma$, where γ is the optical roughness or aspect ratio exponent.

Preliminary experiments

Preliminary experiments were performed to determine the effect of the substrate roughness on the roughness of electrodeposited nickel. For that purpose, two types of stainless steel substrates were prepared. The first was the “mirror-like” sample polished first with sand paper and then with alumina powders as described in the experimental

section. The second type of substrate was “as received”, i.e., without any polishing. Figure 3 plots values of the optical roughness δ for the two substrates as a function of the deposition time. Initially, the roughness of electrodeposited Ni was smaller at the “mirror finished” sample. However, after 60 min of electrodeposition, the two curves coincided. For deposition times longer than 60 min, the morphology of the electrodeposited Ni was no longer dependent on the preparation of the stainless steel substrate. Further, in the logarithmic coordinates, the dependence of the limiting roughness on the deposition time became linear consistently with the scaling theory. Therefore, in all further experiments, nickel was deposited on substrates with the surface roughness “as received” using deposition times 60, 120, 180, and 300 min. At 97% current efficiency, these deposition times are equivalent to the deposition of 26, 52, 78, and 120 micrometers of a perfectly smooth Ni film.

In order to ensure a uniform current distribution and hence a uniform roughness across the whole electrode surface, the stainless steel disk electrode (0.25 cm^2) was inserted into the cylindrical hole of a Teflon holder as schematically shown in the inset to Fig. 4. The main section of this figure shows that the scaling analysis of images taken at three different spots of the surface display vary small differences in the values of ξ_L and in the values of the limiting surface roughness δ . Therefore, the errors in the limiting surface roughness and the critical scaling length are small.

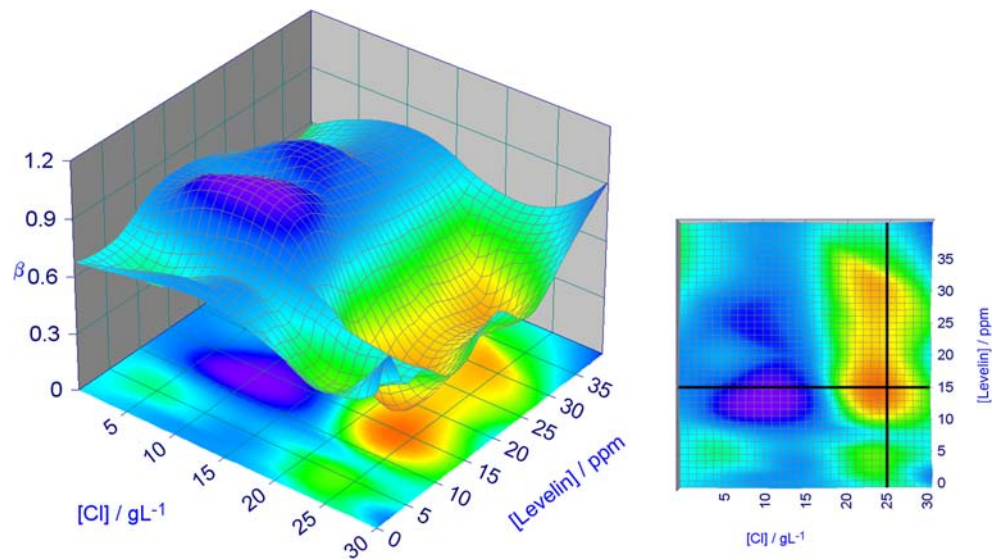
The representative time dependence of δ , L_c and $4\delta/L_c$ is shown in Fig. 5. The plots are linear, and their slopes give the scaling exponents β , $1/z$ and γ , respectively. These exponents show how the height, width, and the aspect ratio of surface features change with the deposition time. The relation between the values of parameters determined from the scaling analysis and the morphology of electrodeposited nickel is described in Table 1.

Table 1 shows that it is necessary to find electrolyte composition where γ and β are at minimum and $1/z$ parameter has a small value, if one wishes to have a mirror-like finish to the surface of electrodeposited nickel,

Table 1 Relation between the surface morphology and the magnitude of scaling parameters [14]

γ	$1/z$	β	Corresponding surface morphology
Small or negative	Small	Small	Surface with small grains and roughness. If L_c is smaller than wavelength of visible light, surface looks like a mirror. These conditions can be used for electropolishing. Internal stress is very small.
Small or negative	Large	Small	Surface has large grains but small roughness. These conditions correspond to leveling. Internal stress is small.
Large	Small	Large	Surface has needle-shaped structures with small distance between grains. The roughness is large, and internal stress is very significant.
Large	Large	Large	Similar to previous case but with a larger size of grains (“needle-like” or “cones”). Internal stress is significant.

Fig. 6 Dependence of the dynamic exponent on chloride and organic additive concentrations for nickel deposited from the synthetic electrolyte at the current density 220 A/m^2 and temperature 60°



or a large value, if one wishes to produce a well-leveled material. Below, we will apply this analysis to find the optimum concentrations of chloride and the organic additive for the electrowinning of Ni.

Optimization of the chloride and organic additive concentration

Over 40 combinations of chloride and Levelin concentrations in the synthetic electrolyte have been investigated in order to determine how these components influence the morphology of electrodeposited nickel. Chloride concentration varied from 0 to 30 g/l, and Levelin concentrations covered the range from 0 to 40 ppm. For every combination of chloride and Levelin concentrations, the images were acquired of samples obtained for four deposition times. The

scaling analysis of these images was performed, and the scaling parameters β , $1/z$ and γ were calculated. Figure 6 shows dependence of the dynamic exponent on chloride and Levelin concentrations in 3D coordinates. It shows that the roughness exponent changes with the electrolyte composition in a complex manner. The right-hand side of Fig. 6 shows the contour map of β projected onto the plane that is defined by the concentrations of the two components. The contour map indicates that β has the global maximum at $\sim 10 \text{ g/l}$ of Cl^- and 12 ppm of Levelin. Ni produced at this electrolyte composition has the roughest surface. The global minimum is observed at 25 g/l of Cl^- and 15 ppm of Levelin. At this electrolyte composition, the electrodeposited Ni has the smoothest surface.

Further, the 3D surface of β shows that the minimum is deep, narrow along the chloride-concentration axis, and broad along the Levelin-concentration axis. This behavior

Fig. 7 Dependence of the roughness exponent on chloride and organic additive concentrations for nickel deposited from the synthetic electrolyte at the current density 220 A/m^2 and temperature 60°

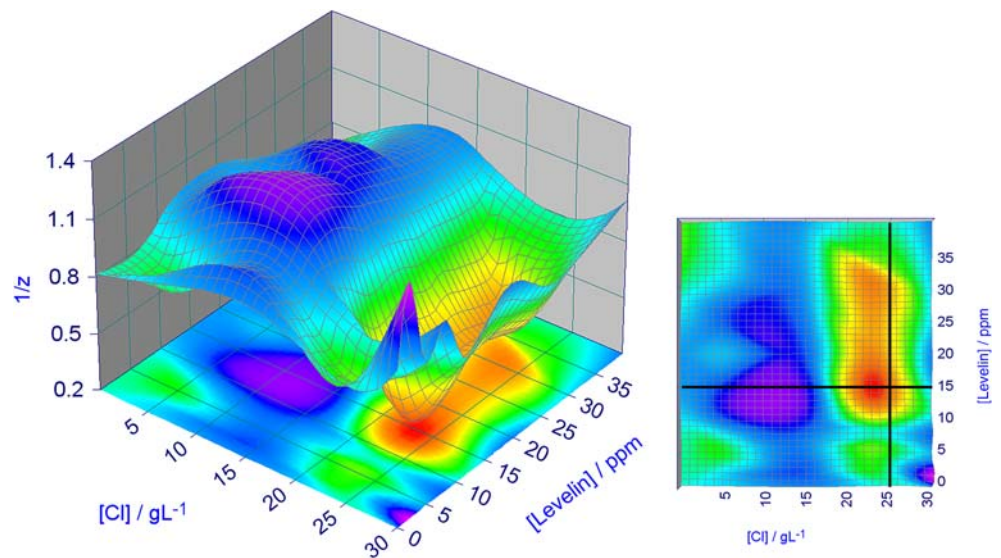
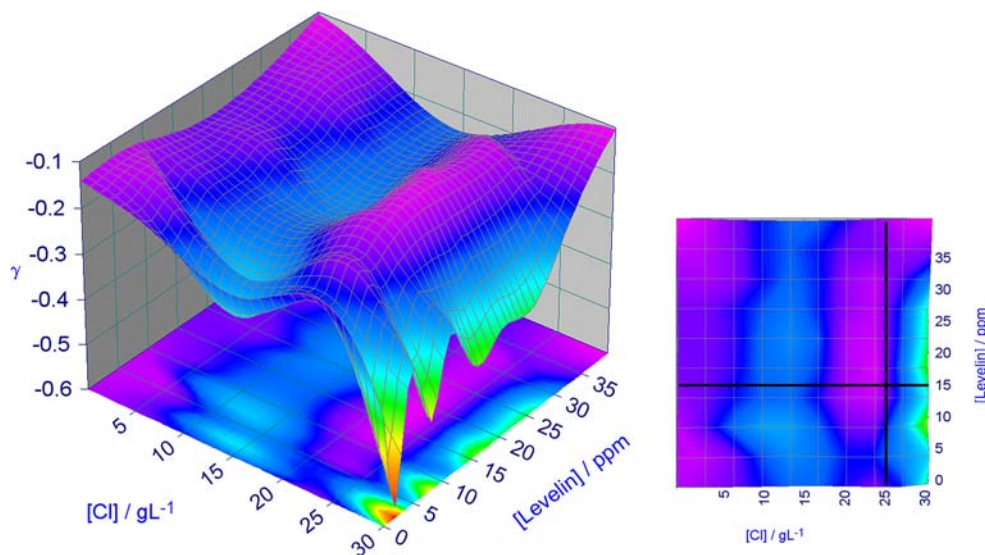


Fig. 8 Dependence of the optical roughness exponent on chloride and organic additive concentrations for nickel deposited from the synthetic electrolyte at the current density 220 A/m^2 and temperature 60°



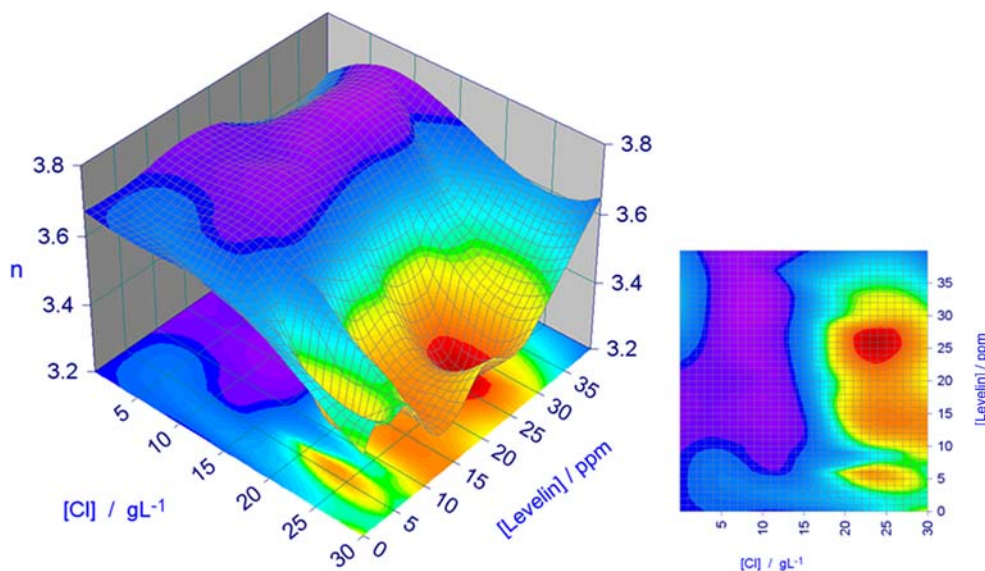
indicates that a small variation of Cl^- concentration, on the order of $\pm 5 \text{ g/l}$ around the value corresponding to the global minimum, may have a profound influence on the roughness of the electrodeposited Ni. In contrast, similar changes in the amount of the organic additive will have a small influence on the morphology of the electrodeposited metal.

Figure 7 shows dependence of the roughness exponent $1/z$ on chloride and Levelin concentrations. The shape of the 3D surface of $1/z$ is qualitatively similar to the shape of the 3D surface of β shown earlier in Fig. 6. The global minimum is observed at the $\sim 24 \text{ g/l}$ of chloride and $\sim 15 \text{ ppm}$ of Levelin, very close to the global minimum on the 3D surface of β . The coordinates of the global maximum are $\sim 10 \text{ g/l}$ of chloride and $\sim 12 \text{ ppm}$ of Levelin, almost the same values as that corresponding to the global maximum of the roughness parameter β . The large values

of the exponent $1/z$ indicate that the correlation length between two features at a surface increases quickly with the deposition time. Small values of $1/z$ indicate that the correlation length or an average distance between two features (two grains) changes little with time. After prolonged electrodeposition of several days, typical for industrial electrowinning or electrorefining, small values of β and $1/z$ indicate that the metal will consist of large numbers of small grains (with a small width and height). The metal produced at conditions at which β and $1/z$ are large has large grains.

The leveling properties of a given electrolyte depend on whether the roughness or the correlation length increases faster with the deposition time. This property could be determined from the optical roughness coefficient plotted in Fig. 8. The optical roughness coefficients are negative

Fig. 9 3D map of the smoothing coefficient n as a function of chloride and Levelin concentrations



numbers, indicating that the aspect ratio of surface features (grains) decreases with the deposition time. Figure 8 shows that the optical roughness coefficient displays a shallow minimum at chloride concentrations between 10 and 15 g/l that is almost independent of the Levelin concentration. These are conditions at which surface features grow faster in the direction parallel than in the direction normal to the surface. After prolonged electrolysis, the surface of the metal produced under these conditions will be best leveled. Figure 8 also shows that γ decreases steeply at high chloride concentrations. The optical roughness coefficient is particularly low at ~ 30 g/l chloride concentration in the absence of the organic additives. This composition corresponds to very good leveling conditions for electrodeposition of Ni.

We have mentioned earlier that information concerning the mechanism of Ni electrodeposition can be gleaned from the magnitude of the smoothing coefficient n . Figure 9 is a 3D map of the smoothing coefficient that shows how it changes as a function of chloride and the organic additive concentrations. At low chloride and Levelin concentrations, the smoothing coefficient is close to 4, and this value indicates that surface diffusion is the prevailing mechanism of growth. However, at high chloride concentrations, the smoothing coefficient decreases to a value close to 3 which is characteristic for a growth controlled by progressive nucleation. In this concentration regime, the parameter n depends strongly on the Levelin concentration and displays the global minimum for Cl^- concentration ~ 25 g/l and Levelin concentration ~ 25 ppm. This is the composition of the electrolyte at which a strong electropolishing effect is observed.

Summary and conclusion

We have applied the WLIM to acquire digital images of electrolytically produced Ni at conditions simulating industrial Ni electrowinning. The digital format of the images allowed us to perform scaling analysis. In this way, the morphological information contained in the images was encoded into parameters such as the limiting surface roughness δ and the critical scaling length L_c or the ratio of the limiting surface roughness to the critical correlation length which gives the aspect ratio of surface features $4\delta/L_c$. We have analyzed how these parameters change with the electrodeposition time and demonstrated that their temporal

dependence is described by the following scaling law: $\delta \propto t^\beta$, $L_c \propto t^{1/z}$, and $4\delta/L_c \propto t^\gamma$, where β , $1/z$, and γ are the temporal exponents of the roughness, the correlation length and the aspect ratio, respectively. The temporal exponents provide useful information about the morphology of metal produced by a prolong electrolysis. For Ni electrodeposition at conditions mimicking industrial electrowinning, we have determined how these exponents vary with chloride and organic additive concentration in the electrolytic bath. We were able to determine concentrations of these two components that correspond to good leveling conditions (10 or 30 g/l Cl^- essentially independent on the organic additives concentration) and concentrations corresponding to good electropolishing conditions (25 g/l Cl^- and 15 to 25 ppm of the organic additive). We have demonstrated that the scaling analysis of digital images of electrodeposited metal can be used as a powerful tool for optimization of industrial processes.

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