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J. Electrochem. Soc. 2009, Volume 156, Issue 8, Pages D326-D330. doi: 10.1149/1.3147263

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Journal of The Electrochemical Society, **156** (8) D326-D330 (2009) 0013-4651/2009/156(8)/D326/5/\$25.00 © The Electrochemical Society



A Kinetic Study on Nickel Electrodeposition from Sulfate Acid Solutions

I. Experimental Results and Reaction Path

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In this work a systematic study on the kinetics of Ni electrodeposition in acid sulfate media over a wide pH range was carried out. Two distinct electrodeposition behaviors were experimentally detected as a function of pH. Accordingly, it is suggested that Ni electrodeposition takes place through different intermediates: In the lower pH range, $Ni(I)_{ads}$ species predominates at the electrode surface, and its formation is deactivated with increasing pH, whereas in less acid solutions, Ni electrodeposition occurs via two species, $[Ni(OH)]_{ads}^{+}$ and $[Ni(OH)]_{ads}^{+}$. The chemical nature of $Ni(I)_{ads}$, $[Ni(OH)]_{ads}$ and $[Ni(OH)]_{ads}^{+}$ species is discussed on the basis of the interfacial pH behavior.

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Manuscript submitted January 29, 2009; revised manuscript received April 20, 2009. Published June 22, 2009.

Nickel electrodeposition has been extensively investigated due to its vast importance as a surface finishing process that satisfies most of the required properties for decorative, magnetic, and anticorrosive applications. Nickel coatings are normally used for the corrosion protection of steel and brass, and their properties have been associated with the electrolyte composition and electrodeposition parameters. Much work has also been dedicated to the electrodeposition mechanism of Ni as well as Ni-containing alloys. In this latter case, the establishment of a codeposition model should be supported by the corresponding individual deposition mechanisms.

The mechanism of Ni electrodeposition from acid solutions¹⁻¹² occurs through different elementary steps that depend on the electrolyte composition and pH. In one of these approaches,⁹ two consecutive one-electron charge-transfer reactions with the anion participation were considered. From this model, the formation of an adsorbed complex intermediate for Ni electrodeposition was proposed. Some other studies have indicated the participation of a Ni monohydroxide ion, NiOH⁺, in charge-transfer steps in aqueous solutions.¹⁰⁻¹²

By using electrochemical impedance spectroscopy, Wiart,³ Epelboin et al.,⁴ and Chassaing et al.⁵ studied the mechanism of Ni electrodeposition from chloride, sulfate, and Watts solutions at different pH values. It was verified that the type of anion strongly influences the electrode kinetics.⁴ Important surface interactions between Ni²⁺ and H⁺ were also observed, particularly in sulfate solutions. These interactions, together with the anion influence, were considered to account for the impedance results. The interpretation was carried out in terms of adsorbed intermediates as well as of the potential dependence of growth sites. The existence of an adsorbate, Ni(I)_{ads}, which would behave as an intermediate for Ni electrodeposition as well as a catalyst for the slow formation of H^{*}_{ads} species, was suggested. It was also considered that H^{*}_{ads} acts as an inhibitor for hydrogen evolution, and it was concluded that the electrode active area is closely related to the degree of coverage by this species.

Efforts to describe the participation of H^+ in the Ni electrodeposition process have been made in many investigations.^{3,13-21} By interfacial pH measurements during Ni and Ni alloy electrodeposition,^{8,20,21} an alkalination at the vicinity of the electrode was verified. This was generally attributed to a catalyzing effect of the Ni species on the hydrogen reduction reaction.

Despite many studies, there are still some significant gaps in the

models proposed to explain the mechanism of Ni electrodeposition. So far, none of the available models has fully described all the kinetic aspects, especially those associated with a wide acid pH range. As an example, by using electrochemical impedance analysis, Ordine et al.⁸ recently verified that the interfacial processes that take place during Ni electrodeposition from sulfate solution at pH 4 generate a faradaic capacitive loop followed by an inductive one. This behavior cannot be explained by the reaction path proposed by Epelboin et al.,⁴ the most widespread model based on electrochemical impedance data, which describes an inductive-capacitive faradaic relaxation sequence. In the model of Epelboin et al.,⁴ the inductive loop was associated with the relaxation of Ni(I)_{ads} at the electrode surface and the low capacitive process was related to a blocking effect due to the adsorbed hydrogen. Because this blocking effect always gives a capacitive feature in impedance diagrams, the inversion in the diagrams observed experimentally at pH 4 by Ordine et al.⁸ cannot be taken into account by that model.

Therefore, the objective of the present work is to perform a systematic study on the kinetics of Ni electrodeposition in sulfate media in pH ranging from 1 to 6. Potentiostatic polarization curves, electrochemical impedance spectroscopy, and interfacial pH measurements were used as the experimental tools, the results of which are presented and discussed in Part I of this paper. The goal is to provide a deeper insight into the electrode reaction mechanism, aiming to give a more comprehensive model of Ni electrodeposition, whose main features are also described here. In Part II of this paper, the reaction model is fully described and transcribed into mathematical expressions to permit the simulation of the experimental results. Moreover, the Ni electrodeposition mechanism validated for a large pH range is useful for further studies, particularly for Ni alloy electrodeposition.

Experimental

The electrolyte used in this work consisted of 1.2 M $NiSO_4$ · $6H_2O$ solution, whose pH varied from 1 to 6. The solutions were prepared from analytic grade chemicals and double-distilled water, without other substances such as additives, complexing agents, or supporting electrolyte. The pH of the solution was adjusted with additions of 1.2 M H₂SO₄. All the experiments in the pH range 4–6 were performed with a large volume of electrolyte (4 L), which was circulated between the containing flask and the cell by a peristaltic pump. The solution entered the cell through a capillary distant enough from the working electrode, thus avoiding disturbances to the flow pattern. This procedure was carried out to guarantee the stability of the solution pH during the electrochemical measurements.

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Figure 1. Potentiostatic cathodic polarization curves obtained in the 1.2 M NiSO₄·6H₂O solution at different pH values: (**II**) 6, (**O**) 5, (**A**) 4, (**D**) 3, (**O**) 2, and (\triangle) 1.

A conventional three-electrode cell (600 mL) using a Pt rotating disk electrode (RDE) with 0.2 cm² as the working electrode was employed. All experiments were performed at 650 rpm of electrode rotation speed. The counter electrode was a cylindrical Pt grid (300 cm²), and a saturated Hg/Hg₂SO₄ electrode (SSE) was used as reference. The potential values in this work are always given against this reference. All experiments were performed in an open cell and at room temperature.

Cathodic potentiostatic polarization curves and electrochemical impedance measurements, in both potentiostatic and galvanostatic modes, were carried out by a model Asservissement Electronique rotating electrode device. The polarization curves were obtained through a model PGSTAT30 Autolab electrochemical interface using the linear sweep polarization staircase (stationary current) method with 30 mV of potential step. A PG19 Omnimetra potentiostat and a Solartron SI1254 frequency response analyzer, coupled with a PC, were used in the impedance measurements. The signals were filtered by means of a model VBF-8 Kemo filter in low pass mode. In most of the experiments, the impedance diagrams were obtained in the frequency interval of 40 kHz to 1.3 mHz with the amplitude ranging from 5 to 15 mV, always ensuring linearity. The polarization curves were corrected from the ohmic drop through the high frequency limit of the electrochemical impedance plots. A chemical analysis of the deposits obtained in some polarization conditions was performed through atomic absorption spectrometry to estimate the efficiency of the electrodeposition process, whose calculation was done by Faraday's law.

For the pH measurements at the electrode/electrolyte interface, a working electrode of the type proposed by Deligianni and Romankiw²¹ and adapted by Deslouis et al.²² was applied. It consisted of a 75 mesh Pt grid (3.5 cm^2) held at the end of a flatbottomed glass electrode (Orion model 8135 BN) using a Teflon adaptor. The electrode was connected to a pH meter, thus measuring the pH of the solution retained in the mesh. The assembled electrode was motionless, and the solution was stirred to guarantee a uniform bulk pH, as detailed elsewhere.²³ Under these conditions, surface pH and current measurements were recorded simultaneously as the electrode was potentiostatically polarized.

Results and Discussion

Figure 1 shows the cathodic polarization curves obtained in the solution with the pH values ranging from 1 to 6, plotted against $E-E_{\rm OCP}$. Open-circuit potentials (OCPs) ($E_{\rm OCP}$) of the Pt electrode in the respective solutions are given in Table I. Independently of the pH value, two distinct regions are observed as a function of the potential ($E-E_{\rm OCP}$) in the curves of Fig. 1. In the first one, at low values of $E-E_{\rm OCP}$, the current varies slowly with cathodic polarization. In this region, the efficiency for metallic deposition is extremely low, and, consequently, the H⁺ reduction prevails. With further polarization increase, the current densities show a sudden

Table I. OCPs of the Pt RDE in the 1.2 M NiSO₄·6H₂O solution at different pH values.

Solution pH	OCP (V _{SSE})
1	0.201
2	0.196
3	0.157
4	0.098
5	0.028
6	0.003

increase that confers a noticeable change to the slope of the curves, which starts to vary sharply with the potential. High efficiency in metallic deposition was only detected at this branch of the curves for all solution pH values investigated. For simplicity, hereafter in this text the curves are divided into two parts regarding the cathodic reaction predominance: part 1, associated with the low slope region, wherein H⁺ reduction prevails, and part 2, the high slope region of the curve, mainly related to Ni electrodeposition.

The two parts of the polarization curves are affected differently by the solution pH. In part 1, a decrease in current values with increasing pH is observed. The beginning of part 2 occurs at different $E-E_{OCP}$ regarding the solution pH, showing two distinct tendencies. Indeed, for the curves obtained in the solution with the pH ranging from 1 to 3, the increase in pH caused a shift in part 2 to more negative potentials. This means that Ni electrodeposition is inhibited with increasing pH from 1 to 3. This result agrees with those reported by Epelboin et al.⁴ for Ni electrodeposition in sulfate solutions at pH 1.5 and 3. By contrast, for the curves obtained in the solution at the pH interval 4-6, an opposite behavior is observed in Fig. 1. The activation of the metallic deposition is verified when the solution pH increases from 4 to 6. Note that Ni electrodeposition kinetics in sulfate solutions at $pH \ge 4$ has not been effectively investigated. The results in Fig. 1 clearly indicate that this process may occur through two different mechanisms as a function of the pH range.

Aiming to better understand the role of a simultaneous hydrogen evolution during Ni electrodeposition, cathodic polarization curves were obtained in 1.2 M Na₂SO₄ solution. Figure 2 depicts typical curves obtained at pH 3 in both Ni²⁺-containing and Ni²⁺-free ($E_{OCP} = 0.07 V_{SSE}$) solutions using the Pt RDE electrode. Higher current densities can be observed for the Ni²⁺-free (Na₂SO₄) solution at the $E-E_{OCP}$ range corresponding to -0.9 to -1.4 V if compared to the curve for the Ni²⁺-containing solution. Because H⁺ reduction is the major reaction in this region, this behavior suggests



Figure 2. Potentiostatic cathodic polarization curves at pH 3 obtained in (\blacksquare) 1.2 M NiSO₄·6H₂O and (\bigcirc) 1.2 M Na₂SO₄ solutions (OCP = 0.07 V_{SSE}).



Figure 3. Potential dependency of both (\bigcirc) interfacial pH and (\blacksquare) current density obtained in the 1.2 M NiSO₄·6H₂O solution at different pH values: (a) 6, (b) 5, (c) 4, (d) 3, (e) 2, and (f) 1.

an inhibitory effect on such reaction by the presence of Ni^{2+} ions in the solution. This result is in accordance with the model proposed by Epelboin et al.,⁴ as discussed below.

Figure 3 shows the potential dependence of both interfacial pH and current density for the 1.2 M NiSO₄·6H₂O solution at pH ranging from 1 to 6. For the solution at pH 6 (Fig. 3a), no significant alkalination is observed at the $E-E_{\rm OCP}$ range corresponding to part 1 of the polarization curve. However, the interfacial pH increases with increasing polarization along part 2 of the curve. This indicates that Ni²⁺ reduction, which is the main reaction in this potential range, takes place with some kind of simultaneous consumption of H⁺ ions. The interfacial pH obtained in the solutions at pH 5 and 4, Fig. 3b and c, respectively, starts to increase at $E-E_{\rm OCP}$ near -400 mV. Part 2 of the curve starts when the interfacial pH attains 6 for both solutions. This situation is similar to that of the solution at pH 6 (Fig. 3a), where no additional alkalination was detected at the electrode surface before part 2 of the curve. Furthermore, the highest interfacial pH verified in Fig. 3a-c is always close to 7.

For the solution at pH 3, an increase in the interfacial pH was only noticed at $E-E_{\rm OCP}$ of about -900 mV. With increasing polarization, a small drop is observed, and then the interfacial pH starts again to increase at a potential that matches the beginning of part 2 of the polarization curve, namely, wherein metallic deposition occurs with high efficiency. At much higher polarizations, the local pH reaches about 6.5.

The interfacial pH obtained in the solution at pH 2 and 1, Fig. 3e and f, respectively, does not show significant changes along the potential branch associated with part 1. The increase in local pH was only observed in part 2 of the polarization curves, wherein Ni electrodeposition prevails. Moreover, the maximum values obtained were about 4 and 3 for solution pH 2 and 1, respectively, that is, a variation of 1.0 in the interfacial pH.

The interfacial pH results corroborate the idea of the existence of a remarkable change in the mechanisms of Ni electrodeposition from sulfate acid solutions as a function of the pH range. For the solution pH in the range of 4–6, there is a significant surface alkalination at high polarizations, reaching values near 7. For the more



Figure 4. Impedance diagrams obtained in the 1.2 M NiSO_4 · $6H_2O$ solution at pH 1, 2, and 3 at the potential values corresponding to part 1 of the polarization curves in Fig. 1 (frequencies in Hz).

acid solutions, namely, 2 and 1, the interfacial pH does not exceed 4. The solution at pH 3 shows a transitional behavior.

Impedance measurements were performed at different points of the polarization curves in Fig. 1 and are presented in Fig. 4-8. For each diagram, the capacitive loop at high frequency is related to the charge-transfer resistance in parallel with the double-layer capacitance. As verified by the polarization results as well as by the interfacial pH data, two different behaviors were also detected. Figure 4 shows the typical impedance diagrams obtained in the solution at pH 1, 2, and 3 and at potential values corresponding to part 1 of the polarization curves. In the low frequency domain, only one capacitive loop near 0.004 Hz exists, which is associated with the H⁺ reduction as the main cathodic reaction in this potential range. As expected, this feature becomes less important as the solution pH increases, given that the rate of H⁺ reduction decreases.⁴

Figure 5 presents typical impedance diagrams obtained in the solution at pH 1, 2, and 3 at the potential range corresponding to part 2 of the polarization curves (Fig. 1). At the beginning of this region, independently of the pH value, the diagrams show the same qualitative behavior: an inductive loop at about 1 Hz followed by a capacitive loop at 0.02 Hz, as can be seen in Fig. 5a-c, respectively, for pH 1, 2, and 3. With increasing polarization, for pH 1 and 2, this behavior did not change, in conformity with the results of Epelboin et al.⁴ However, for pH 3, at higher current densities, as shown in Fig. 5d, there is a noticeable modification in the kinetics: The dia-



Figure 5. Impedance diagrams obtained in the 1.2 M NiSO₄· $6H_2O$ solution at (a) pH 1, (b) 2, and (c) 3 at the beginning of part 2 of the corresponding polarization curves and at (d) pH 3 at higher polarization (frequencies in Hz).

E = -1.00 V; $I = -0.21 mA cm^{2}$

1000 2000

pH=5

3000 4000

0.03

0.003

5000

 $Z_{\rm Re} / \Omega \ cm^2$ Figure 6. Impedance diagrams obtained in the 1.2 M NiSO₄·6H₂O solution

1500

75

E = -0.95 V; I = -0.21 mA cm

0.03

E = -1.05 V; $I = -0.21 mA cm^{-2}$

2000

300

200

100

0.05

3000

pH=6

0.005

4000

0.95

1000

pH=4

1500

100

50

 $-Z_{Im} / \Omega \ cm^2$

at pH 4, 5, and 6 at the potential values corresponding to part 1 of the polarization curves in Fig. 1 (frequencies in Hz).

gram displays a capacitive loop at 0.13 Hz, followed by an inductive one at 0.013 Hz in the low frequency domain. As verified by the interfacial pH measurements (Fig. 3d), this change in the impedance behavior is accompanied by a strong alkalination (pH \approx 6.5) at the electrode surface. This result cannot be described by the model of Epelboin et al.⁴ because it only accounts for an inductive–capacitive behavior of the type presented in Fig. 3a-c. Indeed, the capacitive loop at lower frequencies was attributed to a blocking effect induced by the hydrogen reduction, and this phenomenon is always capacitive.

Figure 6 shows impedance diagrams obtained in part 1 of the polarization curves (Fig. 1) at pH 4, 5, and 6. Different from what was observed for pH 1, 2, and 3 at the same corresponding region, in the pH conditions of Fig. 6 the behavior can be attributed to a hydrogen reduction reaction coupled with a very low efficient metallic deposition. An extremely thin metallic film obtained in such conditions was analyzed by a chemical analysis, the results of which revealed a Ni deposition efficiency of 0.94%.

The impedance diagrams obtained at the beginning of part 2 of the polarization curves (Fig. 1) in the solution at pH 4, 5, and 6 are shown in Fig. 7. These diagrams are analogous to that observed at high current densities for the solution at pH 3 (Fig. 5d). A capacitive loop followed by an inductive one is verified in the low frequency domain in all the diagrams of Fig. 7. This similarity can be associated with the alkalination degree of the electrode surface during high polarizations in the solution at pH 3 (Fig. 3d), which is comparable

15 V ; I = -5.0 mA cm

pH=5

3

-1.22 V ; I = -5.0 mA cm

'13

0.027 $-Z_{Im}/\Omega cm^2$ Cono 0.023 10 15 12 15 18 E = -1.17 V; $I = -5.0 mA cm^{-2}$ pH=6 6 186 5.9 2 000 0.027 0 -2∟ 0 Sec. 4 8 12 16 20 $Z_{Re}\,/\,\Omega\,cm^2$

Figure 7. Impedance diagrams obtained in the 1.2 M NiSO_4 · $6\text{H}_2\text{O}$ solution at pH 4, 5, and 6 at the beginning of part 2 of the corresponding polarization curves in Fig. 1 (frequencies in Hz).



Figure 8. Impedance diagrams obtained in the 1.2 M NiSO₄· $6H_2O$ solution at pH 4, 5, and 6 in part 2 of the corresponding polarization curves at current densities above 25 mA cm⁻² (frequencies in Hz).

to that for the solutions at pH 4–6 (Fig. 3a-c). However, the capacitive loop at medium frequencies seems to be pH dependent because its characteristic frequency changes from 0.53 Hz at pH 4 to 5.9 Hz at pH 6. By contrast, the inductive loop appears at a fixed frequency of about 0.02 Hz, independently of the pH in the range of 4–6. This behavior corroborates the results of Ordine et al.⁸ and, as already mentioned, cannot be described by the model of Epelboin et al.⁴

Higher polarizations in the solution at pH 4, 5, and 6 brought about a significant change in the kinetics of Ni electrodeposition. Indeed, in Fig. 8 the higher complexity of the diagrams is noteworthy if compared to those shown in Fig. 7, which were obtained at the corresponding pH values at lower polarizations in part 2 of the curves. The features observed can be related to the high interfacial pH (\approx 7) verified in the solution pH range 4–6 at high polarizations (Fig. 3a-c). Under these conditions, the presence of free OH⁻ species at the electrode surface that gives rise to a local precipitation of oxide–hydroxide products should be considered. This could be associated with the presence of the features verified in Fig. 8.

From the above set of experimental data, the main characteristics for the establishment of a reaction path can now be considered. The model proposed by Epelboin et al.⁴ properly described the experimental results obtained at $pH \le 3$, i.e., the polarization curves (Fig. 1) and impedance diagrams (Fig. 5a-c). According to this model, Ni(I)_{ads} is formed and the rate of its production is deactivated with increasing pH. This assumption accounts for the shift in part 2 of the polarization curves toward more negative potentials as well as for the inductive loop in the impedance diagrams obtained in this pH range. However, the diagram in Fig. 5d, obtained at pH 3 and at higher polarizations, corresponds to a transient behavior that is not predicted by the model. As already seen, the potential in which the diagram in Fig. 5d was obtained is associated with an interfacial $pH \approx 6.5$ (Fig. 3d). This behavior is analogous to those verified in the diagrams of Fig. 7 obtained at pH 4-6. Moreover, by interfacial pH measurements performed in this pH range (Fig. 3a-c), it was shown that part 2 of the polarization curves, wherein highly efficient Ni electrodeposition occurs, starts only when the interfacial pH arrives at 6. This means that once this interfacial alkalination level is attained, the production of an adsorbed intermediate of the type of $Ni(I)_{ads}$ suggested by the available model⁴ is no longer favored. Consequently, this model, as proposed by Epelboin et al.,⁴ must be adjusted to contemplate those changes in the mechanism due to the interfacial pH behavior. At this pH condition, the Ni(I)_{ads} kind of species must have OH- in its composition. Accordingly, the formation of the following adsorbed species should be considered

$$Ni^{2+} + H_2O + e \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} [Ni(OH)]^+_{ads} + H$$
[1]

$$[Ni(OH)]_{ads}^{+} + Ni^{2+} + 2e \rightarrow [Ni(OH)]_{ads}^{+} + Ni$$
 [2]

$$[Ni(OH)]^{+}_{ads} + e \underset{k_{3}}{\overset{k_{-3}}{\leftrightarrow}} [Ni(OH)]_{ads}$$
 [3]

$$[\text{Ni(OH)}]_{\text{ads}} + \text{Ni}^{2+} + 2e \rightarrow [\text{Ni(OH)}]_{\text{ads}} + \text{Ni}$$
 [4]

In view of Reaction 1, the higher the solution pH, the higher the rate for the $[Ni(OH)]^+_{ads}$ production would be. This means that the energy required for the beginning of a highly efficient metallic deposition would be lower with increasing pH. These considerations give a suitable explanation for the opposite behavior observed for the pH dependence of part 2 of the polarization curves obtained in the solution at pH 4-6 as compared to those at pH 1-3. As seen in Fig. 1, there is a positive shift in part 2 of the polarization curves at pH 4-6, while the opposite is verified for pH 1-3. This means that the Ni(I)_{ads} intermediate previously proposed by Epelboin et al.⁴ is easily obtained in the presence of H⁺, whereas $[Ni(OH)]^+_{ads}$ (Reaction 1) can be easily obtained in the presence of OH⁻ for higher pH values. At a higher pH range, Ni electrodeposition no longer proceeds through the $Ni(I)_{ads}$ intermediate, which should be replaced by $[Ni(OH)]_{ads}^{+}$ or $[Ni(OH)]_{ads}$, adsorbed at the electrode surface.

From the impedance diagrams in Fig. 7, it can be suggested that the relaxation of $\left[\operatorname{Ni}(\operatorname{OH})\right]_{ads}^{+}$ is associated with the capacitive loop at medium frequencies (0.5-5.9 Hz), which becomes more evident when the pH increases within the pH 4-6 interval. Although not shown in this paper, for the solution in such pH range, this capacitive loop becomes bigger with increasing polarization probably as a result of the higher interface alkalination under these conditions (Fig. 3a-c). The relaxation of [Ni(OH)]_{ads} can be related to the inductive loop at around 0.02 Hz. Different from the capacitive loop, this inductive aspect does not show a potential dependence, as seen in Fig. 7. Accordingly, Ni electrodeposition in the sulfate solution with pH ranging from 4 to 6 would occur by $\left[\operatorname{Ni}(OH)\right]_{ads}^{\!\!\!+}$ and [Ni(OH)]_{ads} through Reactions 2 and 4, respectively. Taking into account these reactions, a further alkalination at the electrode surface is predictable. This conforms with the interfacial pH behavior, depicted in Fig. 3a-c, where values near 7 were detected at high electrode polarizations. This alkalination level would be high enough to bring about a local precipitation of oxide-hydroxide products. Consequently, the complexity of impedance diagrams should increase, as seen in Fig. 8, wherein different time constants come into view. The Ni electrodeposition mechanism in this case is clearly dissimilar, becoming a process in the alkaline medium. Under such conditions, the electrode behavior deserves a different description to reflect the mechanism of Ni electrodeposition in the alkaline medium. This qualitative discussion will be further detailed and justified by the simulation of the experimental results in Part II of this paper.

Conclusion

The polarization curves for the Ni sulfate acid solutions at the pH range 1-6 show two distinct regions. The first is particularly potential dependent and reflects the H⁺ reduction. Increasing polarization makes the current vary sharply with potential. Ni electrodeposition with high efficiency was only detected at this branch of the curves. Moreover, two different mechanisms as a function of the pH range were verified. Between solution pH 1 and 3, the increase in pH caused a deactivation of the Ni electrodeposition. However, in the pH ranging from 4 to 6, the opposite behavior was observed.

The interfacial alkalination in part 1 of the curves was basically due to the H⁺ reduction. In the high slope part of the curves, the interfacial pH increases during Ni electrodeposition, meaning that this occurs with a simultaneous H⁺ consumption. For the solution pH from 4 to 6, the high efficiency in Ni electrodeposition only started to occur when the interfacial pH was 6.

Impedance diagrams obtained in the solution with a pH ranging from 1 to 3 showed an inductive loop at 1 Hz followed by a capacitive loop. In contrast, the diagrams obtained in the pH interval from 4 to 6 presented a distinct behavior, in accordance to the trend verified from the polarization curves. The diagrams depicted a capacitive loop (1–5 Hz) followed by an inductive one (~ 0.02 Hz) in the low frequency domain.

From the proposed reaction path, different intermediates, as a function of the solution pH, are proposed to participate in the process. In conformity with the model of Epelboin et al.,⁴ between pH 1 and 3, Ni(I)_{ads} is formed and its production is deactivated with increasing pH. For the pH range 4-6, Ni electrodeposition takes place through two different intermediates: $[Ni(OH)]^+_{ads}$ and $[Ni(OH)]_{ads}$. The increase in both the bulk solution pH and the interfacial pH supports the formation of these adsorbed species in the pH range. Because the electrodeposition that occurs by these intermediates brings about a strong local alkalination, the formation and precipitation of hydroxide products were considered at the electrode surface. Accordingly, the complexity of the impedance diagrams obtained at high polarizations at this pH range is then justified.

Acknowledgments

The authors are grateful to the Brazilian agencies Conselho Nacional de Desenvolvimento Científico e Tecnológico, Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro, Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, Financiadora de Estudos e Projetos, and Fundação Universitária José Bonifácio for their support.

Universidade Federal do Rio de Janeiro assisted in meeting the publication costs of this article.

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D330