



The Initial Stages of Electrodeposition of Re-Ni Alloys

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The early stages of Re-Ni alloy deposition from citrate electrolytes were studied in terms of the apparent faradaic efficiency (FE) of the deposition process, the composition of the deposits and their morphology. The deposition time was varied in the range of 0.05 to 60 seconds. The apparent FE of the deposition process was calculated as the ratio between the charge consumed in electrochemical stripping of the deposit and the charge consumed during electrodeposition. The apparent FE and Re-content in the deposits (measured by energy dispersive X-ray spectroscopy) were shown to decrease with deposition time. Anomalous values of the FE, well above 100%, were observed at short deposition times. Under these conditions, the deposition of material consisting of nanoparticles with diameters of 50–80 nm was observed by scanning electron microscopy studies, supporting the anomalous high deposition rates. This behavior is indicative of chemical reactions taking place at short times in parallel with electrodeposition. The effects of deposition time on the apparent FE and Re-content in the deposits are explained by the changes in catalytic activity of the cathode surface during deposition. © The Author(s) 2014. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution Non-Commercial No Derivatives 4.0 License (CC BY-NC-ND, <http://creativecommons.org/licenses/by-nc-nd/4.0/>), which permits non-commercial reuse, distribution, and reproduction in any medium, provided the original work is not changed in any way and is properly cited. For permission for commercial reuse, please email: oa@electrochem.org. [DOI: 10.1149/2.038405jes] All rights reserved.

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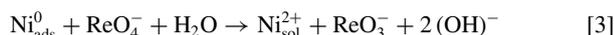
Electroplating and electroless plating of Re-based alloys has been investigated in our laboratory in recent years.^{1–7} Rhenium alone can be deposited, but the faradaic efficiency (FE) is very low and the layer formed is of poor quality and does not adhere well to the substrate. Addition of salts of one of the iron-group metals, (Me = Ni, Co or Fe) leads to high FE and high Re-content of the alloys formed.⁴

When alloy deposition is concerned, there are, by definition, at least two reactions occurring in parallel. Moreover, hydrogen evolution is commonly observed. In the particular case of electroplating of Re-Ni alloys, it is common to use citric acid as a complexing agent. This can give rise to several complexes of Ni with the citrate ions, depending on pH, as well as complexes of Re with citrate, and even a triple complex of Re-Ni-Cit. The overall reaction for deposition of Re is given by Eq. 1, in which 7 electrons are involved.



Thus, a detailed evaluation of all the steps would be extremely difficult, if at all possible. In several papers in the literature it was shown that this reaction follows the stepwise reduction of the ReO_4^- ion. Deposition of Re from acidic electrolytes was shown to proceed through formation of ReO_2 as an intermediate, followed by the complete reduction to the metal. Possible disproportionation of one of the intermediates has also been suggested as a route for electrodeposition.^{8–10}

The intriguing question is to understand the role of the divalent ion (Me) in inducing the deposition of metallic Re. In our recent papers we proposed the mechanism shown in Eqs. 2 and 3:



According to this mechanism, freshly deposited Ni^0 catalytically reduces the perrhenate ion from its complex with citrate to the 5-valent oxidation state in the rhenate ion, ReO_3^- , or directly to Re^0 .^{1–4} Summing up the last two equations one gets:



Eq. 4 shows that the nickel ion acts as a catalyst, and is not involved in the overall reaction. This should lead to the deposition of a pure Re coating. In practice, the alloys contained some nickel, the

content of which dependent on the composition of the electrolyte, and specifically the Ni/Re ions ratio in the bath. This can be readily understood, assuming one of two parallel pathways: (i) Reaction 2 could act directly to deposit Ni_{ads} ; or (ii) The rate of removal of Ni_{ads} from the surface (Eq. 3) is not fast enough, and part of the adsorbed Ni is incorporated in the deposited Re.⁸

The assumption that the surface is invariant during the deposition process is not valid, because new layers of metal are formed, and the nucleation and growth may follow different pathways depending on the composition of the bath, the temperature and the current density. Moreover, the catalytic activity of the surface may change during the deposition process. Thus, the initial stages of deposition can have peculiarities. Knowledge of the events taking place at the initial stages of alloy deposition is important for controlling the deposition process. Needless to say, the composition of the alloy deposit adjacent to the substrate, which is formed by electrolysis at very short times, could be of great interest because it may influence the strength of adhesion between the coating and the substrate.

The purpose of the current work is to study the initial stages of Re-Ni deposition, which are critical for understanding the catalytic mechanism and its control. The films deposited for different times were studied in terms of their composition and structure. While, in practice, metal deposition is usually a long process, on the scale of hours (deposition times were in the range of 20–100 minutes in our experiments reported earlier),^{1–4} we present here data concerning the FE and the composition of the alloy at short times of electrodeposition, on the scale of 0.05 to 60 seconds.

Anomalous values of the FE, well exceeding 100%, were observed, implying that chemical reactions, which do not involve electron transfer in the external circuit, must be taking place in parallel with electrodeposition. The composition of the alloy close to the substrate was also found to change significantly with deposition time.

Experimental

Deposition was conducted from stirred electrolytes containing nickel sulfamate, ammonium perrhenate and citric acid. The compositions of the baths are listed in Table I. All electrolytes contained 100 mM citric acid. The pH of the electrolytes was adjusted to $5.0 \pm$

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^dIn the rest of this paper, Ni will be used for Me, for convenience.

^eThe involvement of the citrate ions is ignored here for simplicity. The further reduction of the rhenate ion is also ignored, because we have no detailed information on the path taken for total reduction of the ReO_4^- ion.

Table I. Composition of electrolytes (all three electrolytes contained 100 mM citric acid).

Electrolyte #	Ni(SO ₃ NH ₂) ₂ , mM	NH ₄ ReO ₄ , mM
1	–	34
2	94	–
3	94	34

0.1 by addition of concentrated (5 M) solution of NaOH. The temperature was held at $70 \pm 1^\circ\text{C}$.

The initial stages of deposition were studied on Pt electrodes (with an exposed surface area of 0.12 cm^2), and the current densities were in the range of 4.2 to 50 mA cm^{-2} . Regular three-electrode cells (Metrohm) were employed, with Pt-foil counter electrodes and a saturated calomel reference electrode (SCE). An Applied Research 273 potentiostat was used. Surface preparation of electrodes for deposition was conducted in $0.5\text{ M H}_2\text{SO}_4$, applying a potential cycled from -0.2 V to $+1.6\text{ V}$ vs. SCE and a linear potential scan of 50 mV s^{-1} , until a reproducible pattern was obtained.

The deposition times were varied in the range of 0.05 to 60 s . The deposition potential as a function of current density in galvanostatic mode is presented with jR_{sol} compensation. The values of the residual solution resistance in any given cell configuration were measured using "Power Suite" software. All potentials reported in this work were measured vs. SCE.

The apparent FE of the deposition process was calculated as the ratio between the charge consumed in electrochemical stripping of the deposit and the charge consumed during electrodeposition. Electrochemical stripping of the deposits was conducted by scanning the potential from open circuit to $+1.1\text{ V}$ in the same electrolyte where deposition was conducted. The scan rate was 50 mV s^{-1} . The charge consumed in electrochemical stripping was calculated as the difference between the charges consumed in the 1st and in the 2nd potential scans (cf. Fig. 1).

For comparison between the initial and the following stages of the deposition process, electroplating was conducted for times up to 1200 s , on Pt foil and Cu foil substrates, and the FE was determined by mass gain after deposition, using the electrochemical equivalent of both metals and their atomic concentration in the alloy. The area of the electrode in these measurements was 0.5 cm^2 .

The composition of the deposits was determined by energy dispersive X-ray spectroscopy (EDS), conducted either in a JSM-6300 scanning electron microscope (SEM) equipped with an Oxford EDS detector, or in a LEO 982 (Zeiss-Leica) high-resolution SEM equipped with Thermo NORAN (USA) spectrometer. The energy of the primary electrons was 20 keV . SEM micrographs were acquired with a Quanta 200 FEG ESEM, at 12.5 keV and a working distance of 8.8 mm .

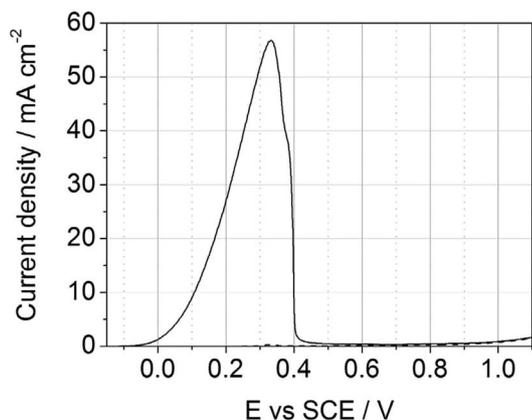


Figure 1. Typical stripping voltammograms. Solid line -1^{st} potential sweep; dotted line -2^{nd} potential sweep. Deposition conditions: Electrolyte #3, deposition at 50 mA cm^{-2} for 2 s . The very small charge related to the 2^{nd} sweep is referred to as background.

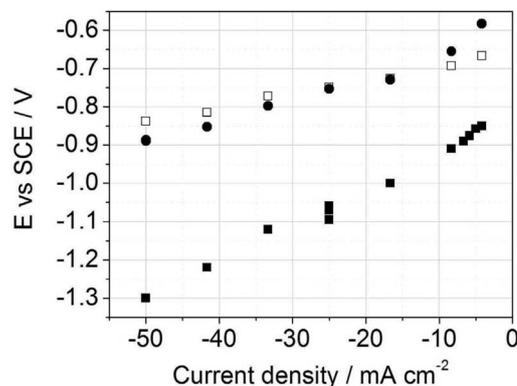


Figure 2. The effect of c.d. on deposition potential for electrolytes #1 (●), #2 (■) and #3 (□). Compensated for the potential drop due to the solution resistance.

Results and Discussion

Potentials vs. current density during galvanostatic deposition.— The deposition potential dependence on the applied current density (c.d.), obtained galvanostatically for the three electrolytes listed in Table I, is presented in Fig. 2. At the lowest c.d., 4.2 mA cm^{-2} , the values of deposition potential for electrolytes #1, #2 and #3 were -0.58 V , -0.85 V and -0.67 V , respectively. It is seen that alloy deposition occurs at a potential closer to that of pure Re reduction than to that of pure Ni reduction. At the highest current density tested, 50 mA cm^{-2} , the potentials of deposition from the electrolyte containing only Ni are much more negative, yielding values of -0.89 V , -1.30 V and -0.84 V , for electrolytes #1, #2 and #3, respectively. It should be noted that when Re is deposited (either alone or in the presence of Ni ions), the system is highly depolarized, compared to that when only Ni is deposited. Similar behavior has been reported in the literature for ammoniacal citrate baths.¹¹

Stripping voltammograms.— The comparison of typical voltammograms obtained after deposition and stripping in electrolytes #1, #2 and #3 is shown in Fig. 3. The stripping current densities observed for electrolyte #3 that contains both Ni^{2+} and ReO_4^- exceed dramatically those for electrolytes #1 and #2 that contain only ReO_4^- or only Ni^{2+} , respectively. This is consistent with the fact that the FE in electrolyte #3 is found to be very high, while in solutions #1 and #2 it is much lower. In the inset in Fig. 3, the same data are shown on a different scale, where the line for electrolyte #3 is partially out of scale, but the lines for electrolytes #1 and #2 are seen within the full potential range.

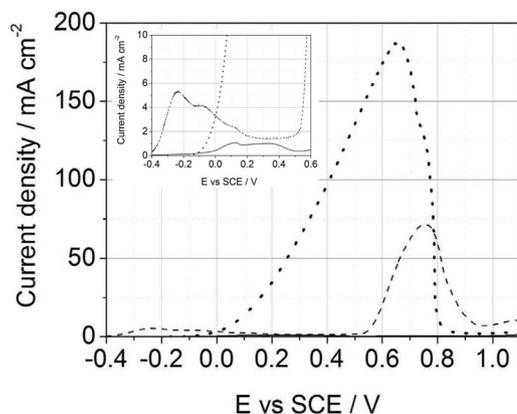


Figure 3. Linear anodic stripping voltammograms in three electrolytes. Deposition at 50 mA cm^{-2} for 30 s . Solid line (see inset) - electrolyte #1, dashed line - electrolyte #2, dotted line - electrolyte #3.

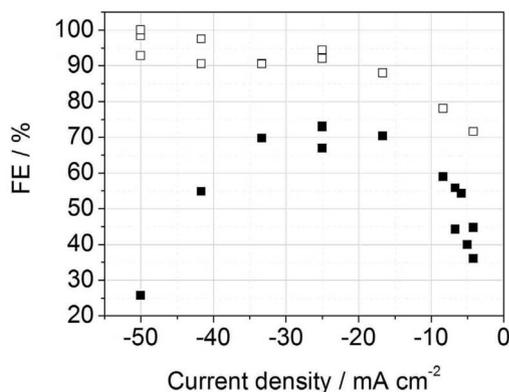


Figure 4. Effect of c.d. on FE for electrolyte #2 (■), and for electrolyte #3 (□). Electrochemical stripping of the deposit was done by potential scanning from open-circuit potential to +1.1 V. Deposition time: 30 s.

The effect of the current density on the faradaic efficiency.— No clear tendency in the change of FE with c.d. was observed in deposition from solution #1. The FE is very low (between 0.9% and 1.8%), which is consistent with our earlier observations,¹ showing that metallic Re cannot be electrodeposited efficiently in the absence of an alloying element such as an iron-group metal.

In Fig. 4 the effect of current density on the FE for deposition from electrolytes #2 (black square points) and #3 (open square points) is shown. For deposition from electrolyte #2, the FE was found to be lower than for deposition from electrolyte #3, both at the lowest and at the highest c.d. tested (35% and 25%, respectively), and a maximum of about 70% is evident. The existence of a maximal FE is in agreement with the diffusion control of the Ni deposition process from citrate electrolytes at high deposition current densities.¹² The increase of current densities beyond 35 mA cm^{-2} causes intensive hydrogen evolution, while the Ni deposition is limited by partial mass transport control. The behavior of solution # 1 is not shown in Fig. 4, since the values of the FE were very low.

The value of the FE in solution # 3 is of the highest interest, because it contains both ions of electrolytes #1 and #2, allowing efficient deposition of Re-Ni alloys.¹ At the highest c.d. used, the FE approaches 95%. The FE determined for deposition from electrolyte #3 exceeds significantly not only the FE of deposition from electrolyte #1, but also that from electrolyte #2. It remains nearly constant until the c.d. is reduced to about 25 mA cm^{-2} , and decreases with decreasing c.d. down to about 70% at the lowest c.d. tested.^f

The effect of deposition time on the faradaic efficiency of Re and Ni.—Re deposition (electrolyte #1).— The FE exhibits some tendency to increase with deposition time for deposition from electrolyte #1. However, the values obtained in this electrolyte are very low: the FE increases from 1% at 30 s to 3.5% at 240 s. When measured by mass gain at a long deposition time of 1.5 h, the FE reached only 6%.

Ni deposition (electrolyte #2).—No trend was found in the change of the FE over time for deposition in the range of 10 s to 180 s. Deposition at 50 mA cm^{-2} yielded a FE of about 26%. The FE measured by mass gain for a deposition time of 900 s and a c.d. of 25 mA cm^{-2} reached 71%, which is consistent with the value obtained by anodic stripping of the layer deposited for 30 s (see Fig. 4).

The effect of deposition time and current density on deposition of Re-Ni alloys.—Potential transients.— Transients of the potential of the initial stages of deposition in electrolyte #3 are shown in Fig. 5. The values of the applied c.d. were 50, 25, 12.5 and 6.7 mA cm^{-2} . At

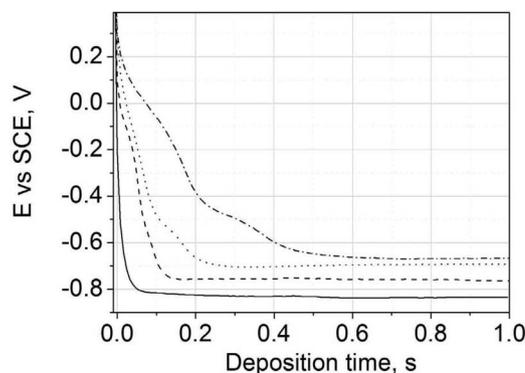


Figure 5. Transients of potential of deposition in Re-Ni electrolyte (#3) at different current densities — 50 mA cm^{-2} ; - - - 25 mA cm^{-2} ; ····· 12.5 mA cm^{-2} ; -·-·- 6.7 mA cm^{-2} .

all four current densities, a steady-state potential was reached within 0.6 s from the onset of current. The steady-state potential became more negative with increasing c.d. At 50 mA cm^{-2} steady-state is established after 0.05 s, while at 25, 12.5, and 6.7 mA cm^{-2} it occurs after 0.15, 0.25 and 0.55 s, respectively.

Anomalous faradaic efficiency.—A plot of the apparent FE obtained in electrolyte #3 at 50 mA cm^{-2} , as a function of deposition time in the range of 2 to 60 s, is shown in Fig. 6. The corresponding changes in the composition of Re in the deposited layer are shown in Fig. 7. In both cases, the points represent the average values for three measurements at each deposition time. The longest deposition time shown is 60 s, because both the FE and the concentration of Re in the alloy seem to level off beyond that. The FE decreases sharply with increasing deposition time at short times.

Similar dependences were observed for 25 mA cm^{-2} and for 12.5 mA cm^{-2} . At deposition time of 2 s, the FE was found to be about 220%, 180% and 135%, for 50, 25 and 12.5 mA cm^{-2} , respectively. The values of the FE obtained at deposition for 60 s are consistent with those determined by mass gain at deposition time of 300 to 900 s, yielding values of 90–95% for 50 mA cm^{-2} and 79–85% for either 12.5 or 25 mA cm^{-2} .

For low current densities (6 to 8 mA cm^{-2}), the results of stripping experiments at short deposition times were highly scattered, and the values of the apparent FE did not exceed 100%. At deposition times higher than 10 or 20 s, the FE stabilized at about 75–80%. These values are consistent with the values obtained by mass gain in long (1200 s) experiments.

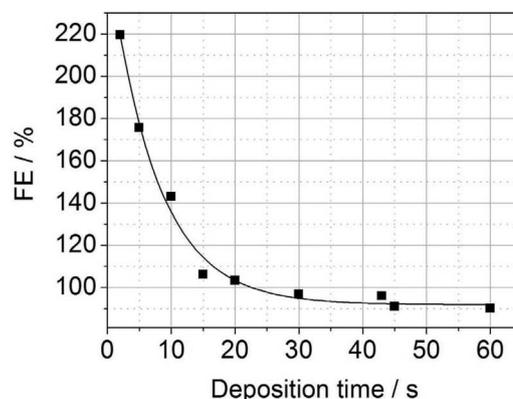


Figure 6. The effect of deposition time on the FE. Electrolyte #3, deposition at 70°C and 50 mA cm^{-2} . Each point is the average of three independent measurements. Line is fitted by least square.

^fNote that the data in Fig. 4 were taken following cathodic deposition for 30 s, where the FE has already been reduced to below 100% (cf. Fig. 6)

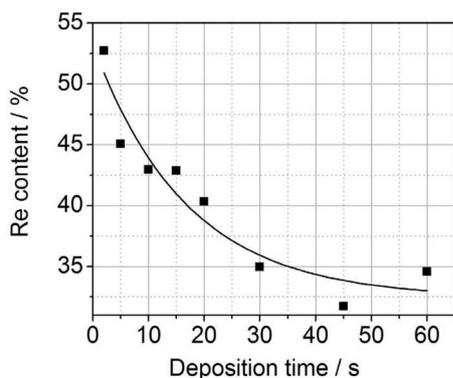


Figure 7. The effect of deposition time on the at% of Re in the plated alloy. Electrolyte # 3, deposition at 70°C and 50 mA cm⁻². Each point is the average of three independent measurements. Line is fitted by least square.

For 50 mA cm⁻², reducing the deposition time to 0.05 s led to calculated values of the apparent FE of about 3900%, as seen in Fig. 8. For deposition at a lower c.d. of 12.5 mA cm⁻² for 0.2 s, the apparent FE was found to be about 580%.

The observation of a FE exceeding 100% is rather rare, but it has been observed in a few cases and attributed to chemical reactions occurring in parallel to electrolytic charge transfer.^{13–16} However, such high values of the anomalous FE have not been reported yet, to the best of our knowledge.

Effect of deposition time on the anodic stripping charge.—Figure 9 shows the charge measured during anodic stripping plotted vs. deposition time. The dependences for 50, 25 and 12.5 mA cm⁻² are linear. Extrapolation of the straight lines to zero time crosses the ordinate significantly above zero. This is a clear indication of a chemical reaction taking place in parallel with the electrochemical reduction. It should be noted that the experimentally obtained values of anodic stripping charge in the range of 0.05 to 2 s are somewhat lower than those found by the linear extrapolation plots (cf. inset of Fig. 9).

The anodic stripping charge corresponding to zero time represents the part of the chemical process in the overall cathodic reaction. This part increases with c.d. (Fig. 9). However, for each c.d., it decreases with increasing deposition time, and is negligible at long times. In our previous studies^{1–5} electrodeposition was routinely conducted for long times, in the range of 20 to 80 minutes. A plot of the amount deposited was found to be a linear function of time (and, hence, of the cathodic charge passed at constant current density), as expected. Moreover, extrapolation to zero time was found to lead to the origin of the coordinates.¹

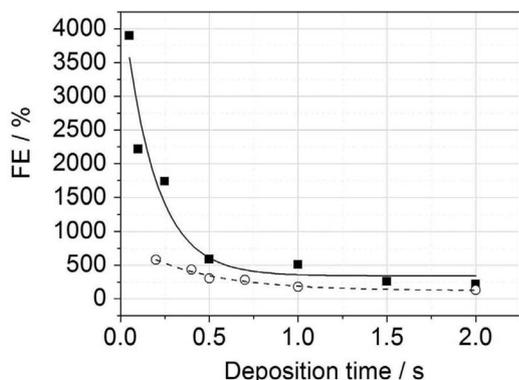


Figure 8. Variation of the FE with time in the range of 0.05 to 2.0 s. (■) $j = 50 \text{ mA cm}^{-2}$; (○) $j = 12.5 \text{ mA cm}^{-2}$.

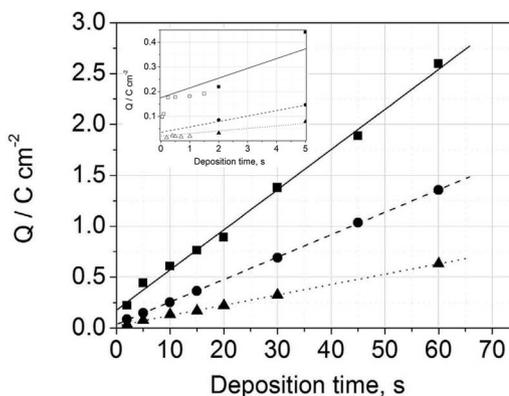


Figure 9. Plots of the anodic charge during stripping as a function of the deposition time, in the range of 2.0–60 s. ■ – 50 mA cm⁻²; ● – 25 mA cm⁻²; ▲ – 12.5 mA cm⁻². Linear fitting plots: — 50 mA cm⁻²; - - - 25 mA cm⁻²; ····· 12.5 mA cm⁻². Inset: Same data but plotted in the range of 0.05–5.0 s. Experimental □ and △ at very short deposition times, for 50 mA cm⁻² and 12.5 mA cm⁻², respectively.

The apparent FE reaches extremely high values at very short deposition times, which are close to the time needed for the potential to shift from its open circuit value to its steady-state plateau (cf. Figs 5 and 8). However, if a chemical reduction is taking place, there should be some deposition at open circuit, which would be detected during anodic stripping. Yet, none was observed, even when the electrodes were dipped in solution for as long as 60 min. These observations indicate that the electrochemical reaction turns on the chemical reaction by shifting the potential to negative values. The dependence of the apparent FE and anodic stripping charge on c.d. (Figs. 8 and 9) supports this statement.

Effect of deposition time on the deposit composition.—Figure 7 shows the effect of the deposition time on Re-content in the films obtained by deposition in electrolyte #3 at a c.d. of 50 mA cm⁻². Similar dependences (not shown here) were observed for c.d.'s of 25 mA cm⁻² and of 12.5 mA cm⁻². The Re-content is high (45–55 at%) for short times, and declines to 25–35 at% for a deposition time of 60 s. The data obtained at 60 s are close to those obtained for the films deposited for 300 to 900 s.

One can expect that the decline of the apparent FE would also lead to the decline of the Re-content, since the decrease in the FE corresponds to a decrease in the rate of the chemical reaction, which is another route to deposit the metal. However, the rates of decline are not necessarily identical, since there are two metals involved, and the parallel chemical reaction may not affect the rate of deposition of the two metals equally.

The effect of electrolyte composition on the anomalous FE and on the Re-content in the deposits.— We considered above the apparent FE and Re-content declining with deposition time for electrolyte #3 (Table I). In order to check the generality of this phenomenon in different citrate electrolytes containing ReO₄⁻ and Me salt, the early stages of deposition were studied in a few Re-Ni electrolytes (#4 to #7) and one Re-Co electrolyte (#8). The electrolyte compositions and the Re-content in the deposits produced from them at 50 mA cm⁻², 70°C and pH 5.0 ± 0.1, are shown in Table II. All electrolytes contained 34 mM NH₄ReO₄. The molar concentrations of components in electrolyte #8 were equal to those in electrolyte #3; however, Ni(SO₃NH₂)₂ was replaced by CoSO₄. In electrolytes # 4 to #7, the concentrations of Ni(SO₃NH₂)₂ and citric acid were varied. The pH of the electrolytes was adjusted by addition of a concentrated solution of NaOH.

Figure 10 illustrates the influence of deposition time on the apparent FE for different electrolytes. The values of FE observed in electrolyte #8 are very close to those observed in deposition from Re-Ni electrolyte #3 (cf. Fig. 6). Almost the same dependences of FE on depositions time were found for electrolytes #6 and #7. Although

Table II. The effect of electrolyte composition on the Re-content in the deposits for different deposition times. All electrolytes contained 34 mM NH_4ReO_4 . In electrolyte #8, $\text{Ni}(\text{SO}_3\text{NH}_2)_2$ was replaced by CoSO_4 .

Electrolyte #	$\text{Ni}(\text{SO}_3\text{NH}_2)_2$, mM	Citric acid, mM	Citric acid/ Ni^{2+}	Deposition. time, s	Re, at%
4	94	340	3.6	5	100
				60	100
5	34	100	2.9	5	85
				15	80
				178	79
				340	66
				900	67
6	94	188	2.0	2	75
				5	76
				10	68
				15	63
				300	56
				900	52
7	130	100	0.8	2	32
				5	32
				10	29
				300	18
				900	19
8	94	100	1.1	2	19
				5	21
				10	19
				30	17
				60	15
				900	14.5

the FE decreased with deposition time for electrolyte #5, the values did not exceed 100%, unlike those for electrolytes #6, #7 and #8. The values of the FE observed in deposition from electrolyte #4 were very small, of the order of a few%, and increased slightly with deposition time.

The variation of the ratio of the concentrations of citric acid and either $\text{Ni}(\text{SO}_3\text{NH}_2)_2$ or CoSO_4 in these electrolytes in the range of 0.8 to 2.0 (Table II) did not change the fact that the FE for short deposition times (2–10 s) was well above 100%. The increase of this ratio resulted in the decrease of FE, weakening its dependence on deposition time (cf. electrolyte #5 in Fig. 10), and even changing its character (cf. electrolyte #4, Fig. 10).

Within the range of a molar ratio of 0.8–2.0, the Re-content in the deposits was more sensitive to the electrolyte composition (Table II and Fig. 7) than the apparent FE at short deposition times. The

Re-content increased with the ratio of Citric acid/ $\text{Ni}(\text{SO}_3\text{NH}_2)_2$, and declined with deposition time for all electrolytes, except electrolyte #4 (only Re was found in the deposits obtained from this electrolyte). The Re-content in Re-Co deposits also decreased with deposition time; however, it was lower than in Re-Ni deposits produced from electrolyte #3 at all deposition times.

Effect of deposition time and current density on the surface morphology of the coating.— Figure 11 shows the effect of the deposition time on the evolution of surface morphology of the Re-Ni films deposited at 70°C and 50 mA cm^{-2} for 2, 5, 10, and 60 s. The deposit formed within 2 s consists of non-uniformly distributed grains with diameters of 50–80 nm. The presence of such grains supports the anomalous high rates of deposition of the Re-Ni films. These grain sizes agree rather well with the evaluation of the thickness of the deposited film. Deposition under the same experimental conditions for 300 s yields film thickness of about 2.5 μm , based on mass gain (FE of about 95%). Taking into account that the FE at 2 s is 220% (cf. Fig. 6), the thickness of the film deposited in 2 s should be about 38 nm. Grain coalescence and coarsening occurred as the deposition time was increased; yet, the grain size remained at the submicron scale.

Figure 12 demonstrates the effect of current density on the surface morphology of the Re-Ni films deposited for 2 s at 70°C at either 12.5 or 25 mA cm^{-2} . The film formed under the lower current density has a lower surface coverage and slightly smaller grains.

The electrodeposition process.— In recent years we have been studying the mechanism of induced co-deposition from aqueous solutions of alloys of Tungsten^{17–23} and Rhenium^{1–4} with the iron-group metals. The sources of the refractory metal in solution were WO_4^{2-} and ReO_4^- , respectively. Although these two ions are iso-electronic, the mechanism by which the iron-group metal can enhance the rate of deposition of the corresponding alloy was found to be quite different. Most importantly, the highest concentration of W in the alloy was limited to 50 at%,⁸ while in the case of Re a much higher concen-

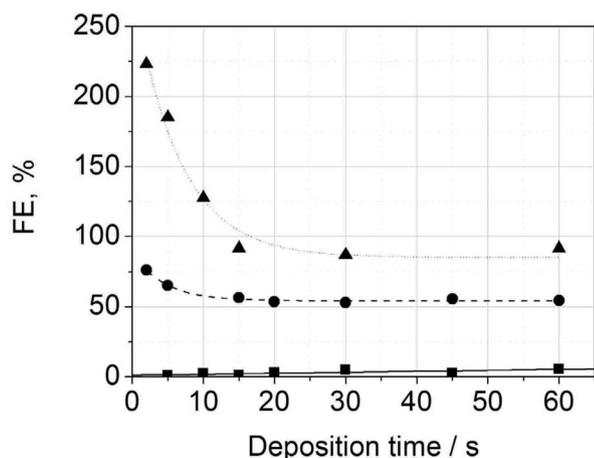


Figure 10. Effect of deposition time on FE in the different electrolytes. Deposition at 70°C and 50 mA cm^{-2} ■ – electrolyte #4; ● – electrolyte #5; ▲ – electrolyte #8 (compositions: see Table II).

⁸In one case, an alloy with 67 at.% W was detected, but the FE for deposition of this alloy was too low to be of practical interest.

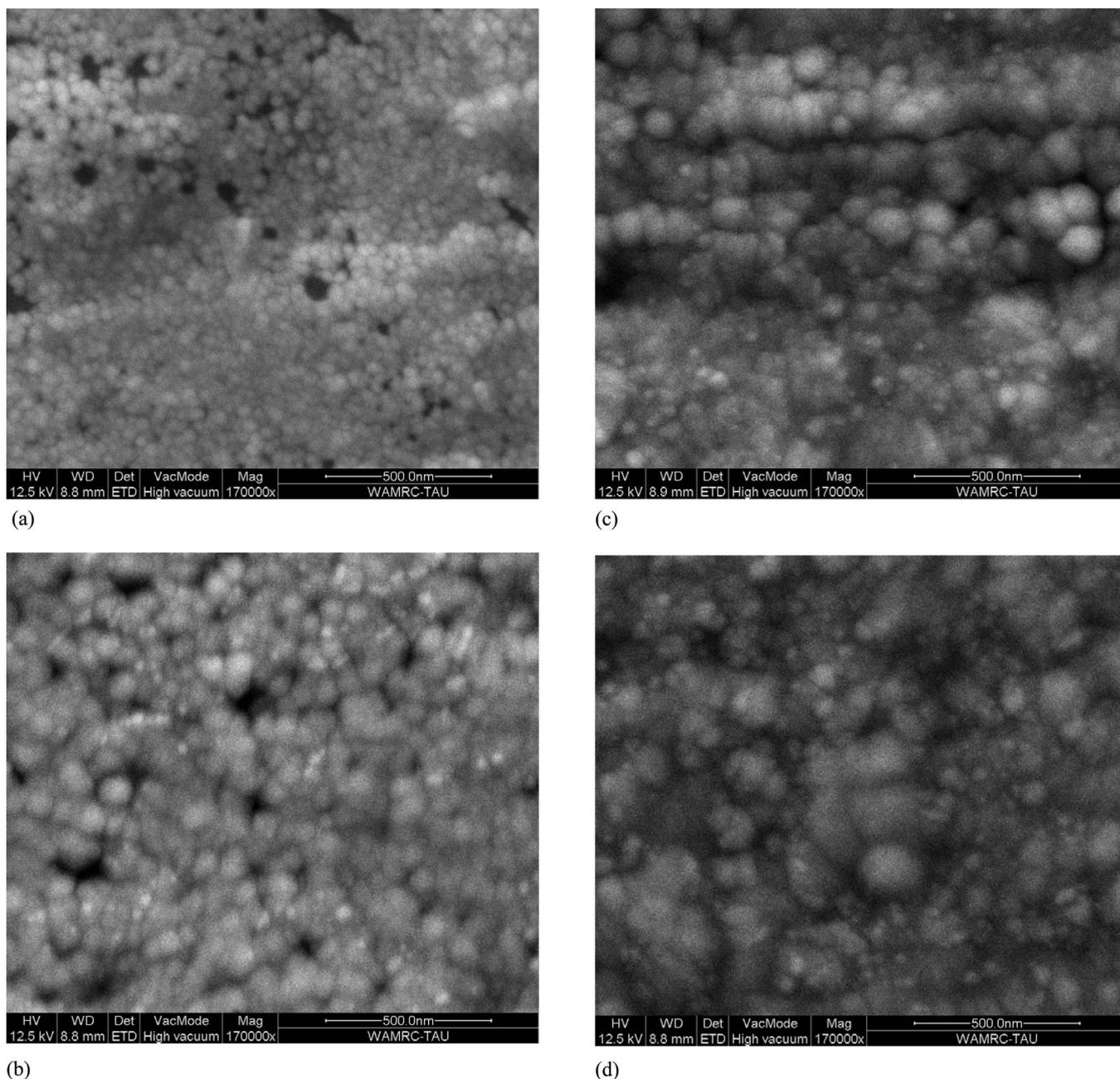


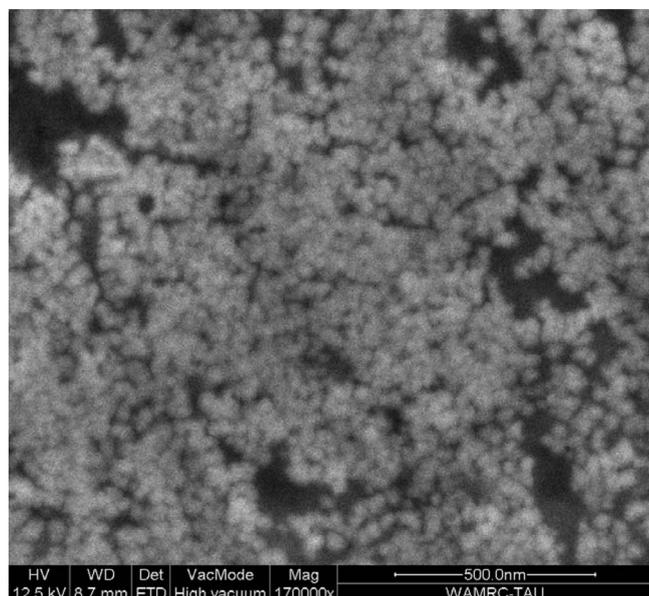
Figure 11. Morphology of the Re-Ni films deposited from electrolyte #3 at 70°C and 50 mA cm⁻² for 2 s (a), 5 s (b), 20 s (c), and 60 s (d).

tration of Re in the alloy, approaching 100 at%, could be obtained. In most experiments, electroplating was conducted for 60 minutes, and the thickness of the deposits was in the range of 5 to 25 μm , depending on the composition of the electrolyte and other parameters of the experiment.

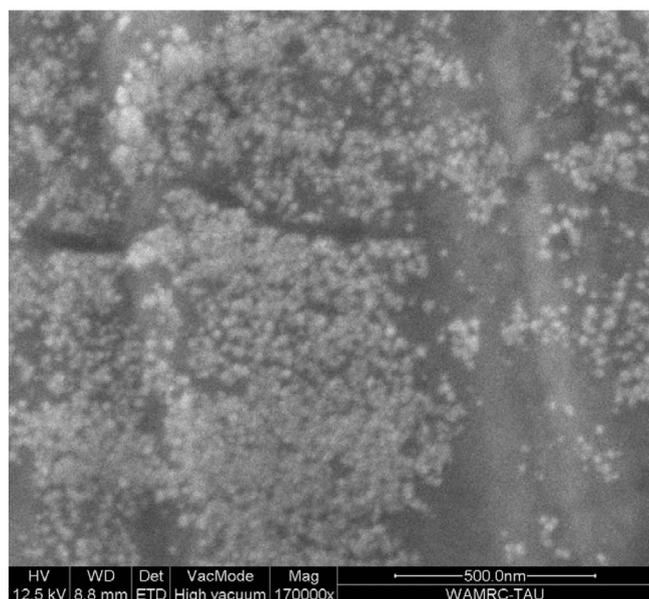
In the current work we studied the deposition process of alloys of Re in the early stages of deposition. The above considered results of electrochemical experiments indicate a catalytic character of the Re-Ni alloys deposition. As shown by the data presented in Figs. 1–4, both Re and Ni deposition are intensified in the simultaneous presence of ReO_4^- , $\text{Ni}(\text{SO}_3\text{NH}_2)_2$ and citrate ions. Electrodeposition without citrate does not yield a FE higher than 100% and does not show a variation of the FE with deposition time, as discussed above. Hence, the citrate ions must play a major role in the electrodeposition process.

The fact that the FE exceeds 100% in different electrolytes and under different experimental conditions shows that a chemical reaction is taking place, in parallel with the electrochemical deposition of the Re-Me alloy. This chemical reaction occurs without the flow of electrons through the external circuit. It should be noted, however, that no reaction was taking place until the deposition current was turned on (even if the Pt working electrode was in contact with the solution for an hour).

Although the experiments were conducted galvanostatically, one has to consider the change in potential caused by applying a constant current density. This is represented in Fig. 5, where the potential is shifted from about +0.34 V to a stable value of -0.84 V, at 0.05 s and 50 mA cm⁻². Figure 5 also shows the effect of the applied current density on the sudden change of potential, which could influence the rate and extent of the removal of the adsorbed species. These



(a)



(b)

Figure 12. Morphology of the Re-Ni films deposited from electrolyte #3 at 70°C for 2 s at 25 mA cm⁻² (a) and 12.5 mA cm⁻² (b).

rapid changes in potential can desorb most species from the surface, activating it for the chemical reduction reaction. But then, as soon as the electrodeposition process is started, it could carry different adsorbates (e.g. fractions of the citrate ions, different lower-valent oxides of Re, etc.), which gradually block the surface and reduce the rate of the parallel chemical reactions. This will reduce the FE to its steady-state value at long times, which is about 95% in this particular composition of the electrolyte. In other words, the change of catalytic activity of the cathodic surface with time is responsible for the decay of chemical reactions rate and hence decreasing the apparent FE.

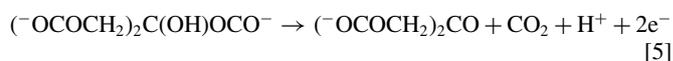
The change of catalytic activity of the cathodic surface with time can be explained in different ways. One possibility is that the Re-Ni alloy formed on the surface during deposition is less catalytic (or not catalytic at all) for the chemical reactions. Alternatively, it could be argued that the reduction of the ReO₄⁻ ion is a complex reaction, requiring the transfer of 7 electrons (cf. Eq. 1). Thus, it may take

a relatively long time for the concentrations of all intermediates to reach their steady-state value, and this time-delay is expressed by the decline of both the FE and the Re-content of the alloy over time.

The catalytic activity of the cathode surface and its decrease cannot be mainly explained by the changes of the catalytic activity of the nano-sized grains in the deposits and their growth with time. Although nano particles often exhibit high catalytic activity in different processes, their dependence on size manifests itself in substantially smaller range of sizes, of just a few nanometers,^{24–26} while the changes in the nano grains found in our case are of the order of tens of nanometers. Besides, the processes of coalescence and growth with deposition time are accompanied by the appearance of small nano-grains on the coalescent surface, as can be seen comparing Figs. 11a and 11d. Therefore, the changes of the catalytic activity of the cathode surface could be related to changes in the composition on the surface of the deposit rather than to the changes in the surface morphology.

The values of the FE during the initial stages of deposition decrease with decreasing deposition current density. This is not necessarily associated with the lower charge passed, but rather with the smaller shift of the potential (cf. Fig. 5), which yields a lower rate of the changes in the composition on the surface of the deposit.

In view of reductive properties of citrate, the participation of citrate in the catalytic chemical deposition of Re-Ni alloy can be assumed. The reaction of decarboxylation (accompanied by formation of acetone-1, 3-dicarboxylate, cf. Eq. 5) is believed to be a first stage in the processes of synthesis of nano-particles of Au, Pt and Ag, by chemical reduction with citrate.^{27–29} We suggest that this reaction is catalyzed by the products formed on the surface of the cathode, upon application of a current and the resulting potential shift. The electrons released during decarboxylation of citrate participate in the chemical reduction of perrhenate and Ni²⁺.



While observing a FE that exceeds 100% is unusual (although not unheard of), the composition of the alloy formed during the initial stages of deposition is of much greater importance. Thus, it is reasonable to assume that any process that changes the FE would also affect the composition of the alloy formed. This was indeed observed in our measurements, as seen in Fig. 7 and Table II. A gradient of the concentration of Re shown in Fig. 7 could be important in its influence on the adhesion of the deposited layer, on the morphology of the deposit, and on the likelihood of formation of cracks at the interface with the electrolyte.

It is important to determine if the anomalous FE can be related to a surface interaction, or whether it is due to the chemical reaction occurring in the bulk. Electrolysis at a rate of 50 mA cm⁻² for 2 s corresponds to 100 mC cm⁻², which would form a surface layer of about 30–40 nm. Thus, the anomalous FE must be associated with some bulk processes.

The observation of a FE of 3,900% (obtained when the deposition time was only 0.05 s) has never been reported in any system, to the best of our knowledge. The validity of this result was tested by repeating the experiment at 0.2 s deposition time, and with a smaller cathodic current density of 12.5 mA cm⁻² (cf. Fig. 8). This yielded a lower FE of 580%, which is still very high this value is in line with the lowering of the FE with increasing deposition time (cf. Fig. 6) and decreasing of the applied c.d. (cf. Fig. 8).

Summary

We note that very close to the surface of the substrate, there may be a gradient of the composition of the alloy, which could be of major importance in determining the properties of the deposited coating. We confirmed this behavior in the case of Re-Ni in different compositions of the electrolyte (cf. Table II), and with Ni²⁺ replaced by Co²⁺. However, whether a similar behavior exists in W-Ni and Mo-Ni, or in alloy deposition in general, is an open question. Moreover, it is not yet known whether the formation of this concentration gradient is

advantageous or detrimental to the formation of uniform and adherent coatings.

Conclusions

The initial stages of Re-Ni alloy deposition from citrate-containing electrolytes were studied, for the first time. The alloy deposition was shown to be depolarized compared to the deposition of Ni. The rate of alloy deposition and the apparent FE of the deposition process were much higher than those for the deposition of either pure Re or pure Ni.

Anomalous apparent FEs exceeding 100% were observed at very short deposition times. The values of the FE decreased with the deposition current density and with deposition time, reaching a steady-state value after about 60 s. The Re-content in the Re-Ni deposits decreased with deposition time in a manner similar to the decrease of FE. The above phenomena were observed only in the electrolytes containing all three components of the bath: Ni (SO₃NH₂)₂, NH₄ReO₄, and citric acid; the concentrations of nickel and citric acid having a profound influence on the Re-content in the deposits and on the values of apparent FE.

The plots of the anodic stripping charge vs. deposition time were linear for different deposition current densities and crossed the ordinate above zero. The anodic stripping charge at a deposition time equal to zero increased with current density. These dependences and anomalous FE confirm that a chemical reaction is taking place in parallel with the electrochemical process at short times. Along with this, there was no deposition taking place, until the deposition current was turned on, even after a long contact of the Pt working electrode with the electrolyte.

Based on these findings we suggest the catalytic character of the chemical and electrochemical reactions taking place during the deposition of Re-Ni alloys. Chemical reactions are triggered only after application of current, which causes a large shift of the potential. The changes in catalytic properties of the cathode surface with deposition time result in a decline in the rate of the chemical reactions. The citrate ions in solution play an important role in creating a parallel chemical

reduction, which only occurs at high negative potentials, generated by applying a high current density.

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