Tungsten alloyed with transition metals, such as Ni, can be readily electrodeposited and are recognized for their corrosion resistance,1–2, wear resistance3–4 and hardness,5–6 having unique applications as materials for microelectromechanical systems (MEMS).11,12 and as cathodes for hydrogen generation.13,14 There are numerous parametric studies addressing the effect of electrodeposited parameters on the deposit composition, structure and resulting property as reviewed by Brenner15 and Tsytarsu et al.,16 but few mechanistic reports of electrodeposited W alloys with transition metals.16–19

Induced codeposition refers to the reduction behavior of W and Mo ions in the presence of iron-group elements (i.e., Fe, Co and Ni) from water. Both W and Mo ions in aqueous electrolytes can’t be fully reduced alone. However, in the presence of iron-group elements, both W and Mo ions can indeed be fully reduced to their zero valence states. An early model of induced codeposition by Holt and Vaaler20 describes the reduction of tungstate species as being catalyzed by the solid state of the iron-group element. Clark and Lietzke21 suggest that the electrodeposition of W alloys occurs via a partly reduced tungstate film on the cathode, followed by the catalytic reduction of this film by hydrogen with the solid form of iron, cobalt, or nickel. Without the iron-group metal inducing element the tungstate ion is partially reduced, and due to its low overpotentials to hydrogen evolution, cannot further reduce. Pertaining to the codeposition of Ni-Mo alloys, Fukushima et al.22 presented a mechanism, where molybdate was first reduced to Mo(IV) as an oxide or hydroxide, then further reduced to metallic Mo by adsorbed hydrogen in the presence of the solid, codeposited Ni, in a similar approach to Clark and Lietzke. In the mechanism raised by Chassaing et al.,23 an oxide of MoOxNi1 was identified ex situ by Auger electron spectroscopy, AES, and energy-dispersive X-ray spectroscopy, EDAX, when the applied potential was not large enough for complete reduction, e.g. at −1.35 V vs SSE. When the applied potential was more negative than −1.5 V vs SSE, an alloy was deposited with Ni3Mo stoichiometry. The approach by Podlaha and Landolt17–19 for Mo ion induced codeposition, assumed that the iron-group reduction reaction was an independent reaction from Mo ion reduction, hydrogen was not considered to be a reducing agent, and the iron-group species in the electrolyte, e.g., Ni(II), catalyzed the reaction via a mixed-metal adsorbed intermediate, such as [Ni(ClMo4)O4]−. Adsorbed intermediates containing Ni and Mo species have also been confirmed by in situ surface Raman spectroscopy by Zeng et al.,24 and Niu et al.25 In our recent work regarding Ni-W-Mo deposition,19 the Podlaha-Landolt mechanism was modified, replacing the governing catalytic species to the adsorbed Ni(I) intermediate, which was more consistent with reaction order data. An alternative view by Eliaz and Gileadi17,18 for Ni-W codeposition, suggested that soluble complex species containing both nickel and tungstate species, [(Ni)(HWO4)(Clit)]2−, is responsible for induced codeposition, not an adsorbed intermediate.

In the mechanisms of Fukushima et al.,22 Chassaing et al.,23 Podlaha and Landolt,17–20 and Sun et al.,21 the reaction intermediates that were suggested contained metal oxides. The intermediate metal oxides are expected to be semiconductive materials, with bandgap energies possibly smaller than the energy of UV light. Related materials that contained partially reduced tungsten and nickel, such as WO2 and NiO, are p-type semiconductors,29 and have bandgap energies of 0.6 eV29 and 3.25 eV30, respectively. The bandgap can also be influenced by film thickness or particle size; e.g., Patil and Kadam31 reported a decrease in the bandgap energy from 3.58 to 3.4 eV with NiO thickness, from thin (0.028 μm) to thick (0.23 μm) films. Hence, mixed-metal oxide intermediates during Ni-W codeposition are expected to be very thin, on the order of nanometers, and with bandgap values similar to those of the elemental oxide counterparts.

Intensity modulated photocurrent spectroscopy (IMPS) is a technique conventionally used to characterize the semiconductive/electrolyte interface. IMPS was included in a comprehensive review by Peter in 1990 that summarized dynamic techniques at semiconductor electrodes.32 The first use of IMPS and its interpretation with meaningful models, in contrast to equivalent circuit models, was presented by Peter,33 Li and Peter,34 Ponomarev and Peter,35 Schlichthör,37 and Oksam38 that captured the features of electronic–hole pair recombination and charge transfer when incident light is modulated under an applied potential, thus making it possible to extract the corresponding rate constants and to discriminate between different processes. It has been used to characterize photoactive materials, for example, to determine the kinetics of photoinduced hydrogen evolution on p-InP semiconductors,36 p-Si(110) and p-Si/Re electrodes,39 examine photoelectrochemical reactions at passive iron electrodes,40 investigate kinetics of oxygen reduction on p-GaAs,41 oxygen evolution on α-Fe2O3 electrodes,42 and hydrogen evolution and to examine electron transport in nanostructured solar cells materials such as CuInS2–TiO2,43 CdS,44 TiO2,45 dye-sensitized TiO2 nanorod photoelectrodes,46 dye-sensitized TiO2 solar cells47,48 and molecular semiconductors.49

The IMPS response is generated by modulating the intensity of light in a sinusoidal fashion over a wide range of frequency. For semiconducting materials, a response in current is generated due to the incident light, or photocurrent, in contrast, a metal would not generate a response to a change of incident light. In an analogous manner to electrochemical impedance spectroscopy (EIS) the real and imaginary components of the ratio of photocurrent to the intensity of light are determined and plotted on either a Bode or Nyquist plot representing the transfer functions for IMPS.

UV light is used in the IMPS presented here. A response is only generated if the intermediate species have a bandgap energy smaller than the energy of the UV light source (3.4 eV). Two other factors could affect IMPS spectra: the absorbance of the electrolyte and the
blockage of light by hydrogen gas bubbles. Typical electrolytes for Ni-W contain ammonium hydroxide and it is known that the ammonium ion adsorbs light in the UV range. Thus, selecting an ammonium ion free electrolyte helps to deliver UV light through the electrolyte. However, eliminating ammonia can significantly decrease the current efficiency of W and Mo alloy induced codeposition, generating problematic hydrogen gas bubbles from the side reaction. The electrolyte used here is adapted from conditions reported for Co-W alloy electrodeposition having high current efficiency in boric acid-citrate electrolytes that do not contain ammonia species, and had been similarly used for Ni-W codeposition in a previous work.

If indeed the intermediates formed during the process of Ni-W electrodeposition have semiconductive properties, and are located at the electrode surface, then IMPS can be a useful tool to detect them in situ. Thus, this work is the first application of the IMPS technique to investigate intermediates during Ni-W electrodeposition onto a metal substrate. In addition, to the best of the authors’ knowledge it is the very first example of using IMPS to probe an intermediate during electrodeposition in general.

**Experimental**

A three electrode single, compartment cell with a flat quartz window was used. The Ni-W electrolyte contained 0.375 M sodium citrate, 1 M boric acid, 0.075 M sodium tungstate, 0.1 M nickel sulfate and pH was 7. Elemental Ni electrodeposition was also examined from the same electrolyte and at the same pH. The working electrode was sputtered gold onto a polycarbonate film and supported by a copper current collector. The reference electrode was Ag/AgCl and the counter electrode was a platinum wire. IMPS and the pretreatment before it were conducted using a Zahner IM6ex and Zahner PP210 systems. IMPS was performed in a frequency range of 500 Hz to 3000 kHz. The LED generated UV light has a wavelength of 365 nm, (3.4 eV), and under modulation, the average intensity was 30 W/m^2 with an amplitude of 10% of the average light intensity. Both Ni-W and pure Ni IMPS were performed at variable applied potentials. Before each IMPS scan, there was a 10 min pretreatment at the same applied potential as the IMPS experiment, followed immediately by the light modulation.

The composition of the deposits was characterized using a Kevex, Omicron X-ray fluorescence (XRF) spectroscopy instrument. XRF analysis was obtained with a Rh tube at 40 kV, 1.5 mA, in air, and with a collection time of 60 s. A minimum of three analyzes per sample were completed and the average value reported.

**Results and Discussion**

Assuming that the electrodeposited intermediates species, which may be adsorbed species, possess semiconductive properties and are thus photoactive, the light modulation in an IMPS experiment reflects changes in the photogenerated charge flux at the semiconductor-electrolyte surface. With a bias that favors reduction of the metal ions to create the intermediate species, and hence the semiconductor, a simple model borrowed from the approach of Ponomarev and Muñoz et al., can be used to represent two competing processes: (1) direct charge transfer from the semiconductor to the interface with a rate constant, \( k_1 \), that drives the reactions, and (2) electron-hole pair recombination with a rate constant, \( k_2 \). It is assumed that the illumination intensity is low enough so that both \( k_1 \) and \( k_2 \) are independent of the light intensity. A sketch of the interfacial region and these two governing processes are shown in Figure 1 with the expected response represented on a Nyquist plot. The transfer function of the modulated photoresponse to the modulated minority carrier current, \( \Delta I_{ph} / \Delta g \), at different light modulation frequencies, \( \omega \), for the working electrode is given as,

\[
\frac{\Delta I_{ph} (\omega)}{\Delta g (\omega)} = \frac{k_1 + \frac{C}{C_{SC}} \omega}{k_1 + k_2 + i\omega}
\]

where, the ohmic resistance has been neglected. The total capacitance is determined by the semiconductor space charge capacitance, \( C_{sc} \), and a Helmholtz-like capacitance, \( C_H \), that excludes the adsorbed metal oxide intermediates.

\[
\frac{1}{C} = \frac{1}{C_H} + \frac{1}{C_{SC}}
\]

It is assumed that there are no surface states, and thus no surface state capacitance. Separating the real and imaginary components,

\[
\text{Re} \left[ \frac{\Delta I_{ph} (\omega)}{\Delta g (\omega)} \right] = \frac{k_1 (k_1 + k_2) + \omega^2 \frac{C}{C_{SC}}}{(k_1 + k_2)^2 + \omega^2}
\]

\[
\text{Im} \left[ \frac{\Delta I_{ph} (\omega)}{\Delta g (\omega)} \right] = \frac{\frac{C}{C_{SC}} \omega (1 - \frac{C}{C_{SC}}) k_1 + k_2}{(k_1 + k_2)^2 + \omega^2}
\]

produces a semicircle on a Nyquist plot, Figure 1, where the real axis intercepts are, at low frequency, \( \omega \to 0 \), and at high frequency, \( \omega \to \infty \), \( \frac{C}{C_{SC}} \), the frequency at the apex is related to the rate constants, according to \( \omega_{max} = \frac{1}{2 \pi t_{max}} \). In order to guide the applied potentials for deposition, a cyclic voltammetry plot is shown for the Ni-W and Ni electrolytes (Figure 2) without illumination. Under UV illumination, at an amplitude of 50 mV/s, without UV illumination (with a steady dc UV illumination at 30 W/m^2 the polarization was unchanged).
intensity of 30 W/m², there was no significant change to the total current density. The total current density is larger for the Ni-W electrolyte than the Ni electrolyte at a given potential, as expected due to the additional metal reduction reaction and also a larger expected side reaction. No significant mass transport peak was observed in the range of –0.4 to –1.1 V vs Ag/AgCl for both Ni and Ni-W electrodeposition, as desired, since the study targets the kinetic regime. When the applied potential was –0.6 V vs Ag/AgCl, the overall current density was close to zero for Ni-W deposition, potentials more negative to this value is thus required for deposition.

In Figure 2, at an applied potential of –1 V vs Ag/AgCl, there is a significant cathodic current in both electrolytes containing Ni-W and Ni that is due, in part, to electrodeposition as evidenced by clearly observable gray deposits under dc condition, and confirmed by XRF analysis. Therefore the dynamic IMPS experiment at this applied potential, shown in Figure 3, is reflective of processes occurring during electrodeposition. The IMPS performed at –1 V vs Ag/AgCl for Ni-W and Ni electrodeposition followed a 10 min pretreatment at this steady state applied potential. A semicircular IMPS spectrum was observed, with modulated light intensity, \( \Delta P(\omega) \), which is directly proportional to \( \Delta g(\omega) \). It indicates that there are indeed photoactive species formed during electrodeposition. The response is larger for Ni-W compared to Ni. The low frequency intercepts of both Ni-W and Ni spectra are at the origin. According to Equation 3, this intercept is equal to \( k_1 \approx 0 \), thus, \( k_1 \ll k_2 \), indicating that the dominate process is recombination. In other words, the light modulation does not alter the electrochemical reaction. To confirm this finding, Ni-W was electrodeposited at –1 V vs Ag/AgCl for 30 min, in the dark and under UV illumination at 30 W/m². In the dark, the deposit composition was 36 ± 1 wt% W, and under UV illumination it was 36 ± 3 wt% W, essentially equivalent, and thus verifying that the light experiment did not alter the deposition.

In the IMPS spectra, the maximum frequency, \( f_{\text{max}} \), provides a measure of the recombination rate constant, \( k_2 \), under the assumptions made in this model. During Ni-W deposition, \( f_{\text{max}} \) is 97 kHz thus, \( k_2 = 6.1 \times 10^5 \) s⁻¹, a relatively fast recombination rate. At the same potential, during Ni deposition, \( k_2 = 1.2 \times 10^5 \) s⁻¹. There is a larger difference in values at the real intercept at high frequency that provides a measure of \( C_{\text{SC}} \). The ratio of the total capacitance to the space charge capacitance, \( C_{\text{SC}} + C_H \gg C_H \), and therefore the total capacitance is

![Figure 3. IMPS spectra of (a) Ni-W and Ni electrodeposition at –1.0 V vs Ag/AgCl, directly following a 10 min dc pretreatment at the same potential onto a gold substrate, and (b) expanded axes for Ni electrodeposition.](image)

![Figure 4. IMPS spectra of Ni-W at different applied potentials (a) –0.6 V, OCP, (b) –0.85 V, (c) –0.9 V, (d) –0.95 V, (e) –1.0 V (also shown in Figure 3a), and (f) –1.05 V vs Ag/AgCl, directly following a 10 min dc pretreatment at each potential onto a gold substrate.](image)
dominated by the Helmholtz layer, \( C \approx C_{\text{H}} \). The Ni-W intercept is 1.31 \times 10^{-5}, while that of Ni is 1.27 \times 10^{-6} \, \text{m}^2 \, \text{V}^{-1} \, \text{m}^{-1}, almost one order of magnitude difference. Since the semiconducting response is a reflection of the surface intermediates, the large change in the capacitance would be expected for different amounts and types of surface intermediates.

Figure 4 compares the Ni-W IMPS at different applied potentials, including OCP (−0.6 V vs Ag/AgCl), and more negative applied potentials where deposition occurs. At OCP there is no response, as expected, since there is no net reduction reaction and hence no adsorbed intermediates. There is a general increase in the magnitude of the photoresponse with potential between −0.6 V to −0.9 V vs Ag/AgCl, and thus the imaginary and real components of the transfer function increase. Between −0.95 and −1.05 V the IMPS response is of similar magnitude, and remains relatively constant with potential. Figure 5 summarizes the values of \( f_{\text{max}} \) and the high \( f \) intercept, which is proportional to \( C_{\text{H}} \). There is a maximum in the values at −0.9 V vs Ag/AgCl, where recombination is the quickest and the space charge capacitance is the lowest. Inspection of the Ni polarization curve shows that at potentials more positive to −0.9 V vs Ag/AgCl, Ni deposition without W is not appreciable (Figure 2). When the applied potential is more negative than −0.9 V vs Ag/AgCl the reduction of Ni ions increases exponentially, and in this region the values of \( f_{\text{max}} \) and \( C_{\text{H}} \) become almost independent of potential. Oskam et al. have shown that when recombination is complete the maximum frequency in IMPS remains constant with potential, similarly observed here when the applied potential is −1.05 < \( E \) < −0.9. A change in \( f_{\text{max}} \) with potential can reflect a partial recombination process, although it is not consistent with other features of the IMPS spectra. The increase in the maximum frequency and capacitance ratio observed when \( E = −0.9 \) V vs Ag/AgCl, cannot be due to a partial recombination because the low frequency intercept remains zero, indicating that recombination is also complete at this potential. An increase in the recombination rate constant can increase with charge carrier concentration, and can arise in this case from the electrochemically generated intermediates during reduction. This is also consistent with a wider space charge region and thus a smaller \( C_{\text{H}} \) and larger \( C_{\text{SC}} \). Thus, the peak in \( f_{\text{max}} \) and \( C_{\text{H}} \) are attributed to a change in the total amount of photoactive intermediates, such as adsorbed metal oxide intermediates, at the surface.

Figure 6 is a measure of the steady state deposit elemental composition without UV illumination. There is a gradual increase in the amount of W in the deposit with the applied potential. At the applied potentials of −0.85 V and −0.9 V deposits from the W-free, Ni electrolyte did not yield a Ni deposit. Metallic Ni deposits were observed however in the range −1.05 < \( E \) < −0.9. Thus deposition of W at −0.85 V and −0.9 V is unexpected if the nickel species that catalyzes the reduction of tungstate ions requires the zero valence state of Ni (i.e., solid Ni), and supports the assumption that either soluble Ni species or partially reduced Ni(I) ions can catalyze the W reduction reaction. In addition, Ni ions reduce at more noble potentials when codeposited with W, suggesting a coupled reaction rate that could be akin to underpotential deposition.

Conclusions

The modulation of UV light during the electrodeposition of Ni-W alloys produced a modulated current response reflective of semiconductive intermediates at the electrode surface. A simple model that assumes that the generated photocurrent can contribute to an electrochemical reaction at the electrode/electrolyte interface or be lost to recombination was used to interpret the IMPS results. The dominate process occurring during IMPS is electron-hole pair recombination and thus, the modulated light does not significantly change the deposit composition. In the potential range of −0.85 to −1.05 V vs Ag/AgCl, the values of IMPS, characterized by \( f_{\text{max}} \) and \( C_{\text{H}} \), reached a maximum at −0.9 V vs Ag/AgCl, which was due to the changes in the intermediate species generated in situ during alloy electrodeposition.

Acknowledgment

Financial support of this work has been provided by the National Science Foundation under grant # 0957448.

References

1. K. R. Sirimaran, S. G. S. Raman, and S. K. Seshadri, Mater. Sci. Eng. A, 460–461, 39 (2007).
2. A. Ogundipe, B. Greenberg, W. Braida, C. Christodoulatos, and D. Dermatas, Corros. Sci., 48, 3281 (2006).
3. A. Krolikowski, E. Płonska, A. Ostrowski, M. Doment, and Z. Stojek, J. Solid State Electrochem., 13, 263 (2009).
4. A. Chianpairoj, G. Lothongkum, C. A. Schul, and Y. Boonyongmaneerat, Corros. Sci., 53, 1066 (2011).
5. A. S. M. A. Haseeb, U. Albers, and K. Bade, Wear, 264, 106 (2008).
6. J. K. Dennis and D. Jones, Tribol. Int., 14, 271 (1981).
7. K. R. Sirimaran, S. G. S. Raman, and S. K. Seshadri, Mater. Sci. Technol., 22, 14 (2006).
8. M. Doment, H. Cesulis, and Z. Stojek, Electrochem. Acta, 45, 3389 (2000).
9. N. Eliaz, T. M. Sridhar, and E. Gileadi, Electrochem. Acta, 50, 2893 (2005).
10. N. Sunwang, P. Wangyao, and Y. Boonyongmaneerat, Surf. Coat. Technol., 206, 1096 (2011).
11. D. E. I. Armstrong, A. S. M. A. Haseeb, S. G. Roberts, A. J. Wilkinson, and K. Bade, Thin Solid Films, 520, 4369 (2012).
12. M. Haj-Taieb, A. S. M. A. Haseeb, J. Caulfield, K. Bade, J. Aktaa, and K. J. Hemker, Microsystem Technologies, 14, 1531 (2008).
13. M. P. Marceta Kaninski, D. P. Saponjic, I. M. Perovic, A. D. Maksic, and V. M. Nikolic, Applied Catalysis, A: General, 405, 29 (2011).
14. C. Fan, D. L. Piron, A. Slep, and P. Paradis, J. Electrochem. Soc., 141, 382 (1994).
15. A. Brenner, Electrodeposition of Alloys: Principles and Practice, p. 347, Academic Press Inc., New York (1963).
16. N. Tsytina, H. Cesulis, M. Doment, J. Sort, E. Pellicer, and E. J. Podlaha-Murphy, Surf. Eng. Appl. Electro., 48, 491 (2012).
17. N. Eliaz and E. Gileadi, Mod. Aspect. Electro., 42, 191 (2008).
18. N. Eliaz and E. Gileadi, ECS Trans., 2, 337 (2007).
19. S. Sun, T. Bairacinha, and E. J. Podlaha, J. Electrochem. Soc., 160, D434 (2013).
20. M. L. Holt and L. E. Vailer, *J. Electrochem. Soc.*, 94, 50 (1948).
21. E. Clark and M. H. Lietzke, *J. Electrochem. Soc.*, 99, 245 (1952).
22. H. Fukushima, T. Akiyama, S. Akagi, and K. Higashi, *T. Jpn. I. Met.*, 20, 358 (1979).
23. E. Chassaing, Q. K. Yu, and R. Wiart, *J. Appl. Electrochem.*, 19, 839 (1989).
24. E. J. Podlaha and D. Landolt, *J. Electrochem. Soc.*, 143, 893 (1996).
25. E. J. Podlaha and D. Landolt, *J. Electrochem. Soc.*, 144, 1672 (1997).
26. Y. Zeng, Z. Li, M. Ma, and S. Zhou, *Electrochem. Commun.*, 2, 36 (2000).
27. Z.-J. Niu, S.-B. Yao, and S.-M. Zhou, *J. Electroanal. Chem.*, 455, 205 (1998).
28. N. Inagaki, *Plasma Surface Modification and Plasma Polymerization*, p. 175, Technomic Publishing Company, Inc., Lancaster, Pennsylvania (1996).
29. V. I. Shaposhnikov, D. B. Migas, V. N. Rodin, and V. E. Borsenko, *Physica Status Solidi B*, 248, 1471 (2011).
30. A. J. Varkey and A. F. Fort, *Thin Solid Films*, 235, 47 (1993).
31. P. S. Patil and L. D. Kadam, *Appl. Surf. Sci.*, 199, 211 (2002).
32. L. M. Peter, *Chem. Rev.*, 90, 753 (1990).
33. L. M. Peter in *Trends in Interfacial Electrochemistry*, NATO Advanced Study Institute, Reidel Dordrecht, 523-546 (1986).
34. J. Li and L. M. Peter, *J. Electroanal. Chem.*, 193, 27 (1985).
35. E. A. Ponomarev and L. M. Peter, *J. Electroanal. Chem.*, 396, 219 (1995).
36. E. A. Ponomarev and L. M. Peter, *J. Electroanal. Chem.*, 397, 45 (1995).
37. G. Schlichthörl, E. A. Ponomarev, and L. M. Peter, *J. Electrochem. Soc.*, 142, 3062 (1995).
38. G. Oskam, J. C. Schmidt, and P. C. Seardon, *J. Electrochem. Soc.*, 143, 2538 (1996).
39. E. Muñoz, R. Schreibler, R. Henríquez, C. Heyser, P. A. Verdugo, and R. Marotti, *Thin Solid Films*, 518, 138 (2009).
40. R. Peat and L. M. Peter, *J. Electroanal. Chem.*, 228, 351 (1987).
41. L. M. Peter, J. Li, R. Peat, H. J. Lewerenz, and J. Stumper, *Electrochim. Acta*, 35, 1657 (1990).
42. L. M. Peter, K. G. U. Wijayanthab, and A. A. Tahir, *Faraday Discuss.*, 155, 309 (2012).
43. C. Grasso, M. Nanu, A. Gossens, and M. Burgelman, *Thin Solid Films*, 480-481, 87 (2005).
44. S. G. Hickey and D. J. Riley, *J. Phys. Chem. B*, 103, 4599 (1999).
45. T. Oekermann, D. Zhang, T. Yoshida, and H. Minoura, *J. Phys. Chem. B*, 108, 2227 (2004).
46. B. H. Lee, M. Y. Song, S.-Y. Jang, S. M Jo, S.-Y Kwak, and D. Y. Kim, *J. Phys. Chem. C*, 113, 21453 (2009).
47. T. Oekermann, D. Schlettwein, and N. I. Jaeger, *J. Phys. Chem. B*, 105, 9524 (2001).
48. G. Franco, L. M. Peter, and E. A. Ponomarev, *Electrochem. Commun.*, 1, 61 (1999).
49. J. Kruger, R. Plass, M. Graetzel, P. J. Cameron, and L. M. Peter, *J. Phys. Chem. B*, 107, 7536 (2003).
50. O. Younes and E. Gileadi, *J. Electrochem. Soc.*, 149, C100 (2002).
51. E. J. Podlaha and D. Landolt, *J. Electrochem. Soc.*, 143, 885 (1996).
52. S. S. Belevskii, H. Cesulis, N. I. Tsyntsaru, and A. I. Dikusar, *Surf. Eng. Appl. Electr.*, 46, 570 (2010).
53. N. Tsyntsaru, A. Dikusar, H. Cesulis, J.-P. Celis, Z. Bobanova, S. Sidel’nikova, S. Belevski, Yu. Yapontseva, O. Bersiroya, and V. Kublanovskii, *Powder Metall. Met. Ceram.*, 48, 419 (2009).