. Ian Burgess, Burke Barlow, Grzegorz Szymanski, Jacek Lipkowski, Babak Shobeir, and Bruce Love, "Pulsed Potential Dissolution Reduces Anode Residue Formation During Nickel Electroplating", *J.Electrochem.Soc.*, **2016**,163,C164-170..

Pulsed Potential Dissolution Reduces Anode Residue Formation During Nickel Electroplating

Burke C. Barlow,¹ G. Szymanski², J. Lipkowski², and Ian J. Burgess^{1,§}

¹Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan, S7N 5C9 Canada

²Department of Chemistry, University of Guelph, 50 Stone Road East, Guelph, ON N1G 2W1

[§]corresponding author : email (ian.burgess@usask.ca)

Abstract

The electrodisolution of nickel pellets with different controlled electrical variables was investigated in an effort to mitigate anodic residue in Watts bath based electroplating cells. During galvanostatic dissolution the anode potential was seen to oscillate between passive and transpassive potentials. In-situ microscopy and ex-situ characterization has shown that lacy-pit formation and large, partially perforated, pit covers form during the potential decay from transpassive levels and contributed significantly to anode residue. Constant potential measurements at large transpassive potentials reduced the anode residue but require large power consumption. Current transients during potentiostatic pulses were analysed and the critical time where pit propagation changed from superficial to quasi-hemispherical was determined. An alternative method of anode dissolution was devised using potential pulses and duty cycles that allowed average current densities comparable to industrial plating conditions to be achieved. By restricting the time spent at large transpassive potentials to 50 ms, anode residue was reduced more than six-fold in comparison to an equivalent galvanostatic dissolution run at a comparable current density.

Keywords : *nickel dissolution, pitting corrosion, anode residue, Watts bath, electroplating.*

Introduction

Nickel electroplating accounts for 35-40% of all electroplating activity [1] and continues to be an important means for the production of decorative and corrosion resistant components particularly for the automotive industry [2]. Once plated, the passivity of nickel is due to the presence of a 10 – 25 Å thick oxide layer that has been extensively investigated and found to consist of a nickel hydroxide outer layer with an inner layer of alternating lamellar nickel and oxygen sublayers [3-7]. The anode in an electroplating cell typically consists of a titanium basket containing Ni pellets or chips obtained by electrowinning [8] or the Mond process [9]. Generation of anode residue (undissolved Ni material) due to heterogeneous dissolution is a significant issue in nickel electroplating as it necessitates time-consuming and costly maintenance of the anode baskets. The presence of sulfide results in smooth, layer-by-layer Ni dissolution [10, 11] but many commercial electroplating applications must be conducted in standard Watts' baths where pitting is the dominant dissolution mechanism. By its very nature pitting is localized corrosion and it is proposed that the detachment of lace-like covers formed from highly spatially correlated pitting is a significant contributor to anode residue in commercial electroplating [12].

Several mechanisms have been proposed to explain the formation of lace-like, or large domains of partially covered pits. Wang *et al* proposed that iR drop within the pit leads to differential corrosion rates with the mouth of the pit being passivated and the pit core undergoing active dissolution [13]. The resulting flask shaped pit profiles eventually grow back toward the surface causing perforations in the oxide layer adjacent to the original pit opening. An alternative model relying on the chemistry of the pit solution rather than ohmic resistance was provided first qualitatively by Ernest *et al* [14] and then quantitatively by Laycock *et al* [15]. In this mechanism, enhanced diffusion of corrosion products at the mouth of the pit prevents the accumulation of a critical concentration that prevents film repassivation.

Restricted diffusion at the bottom of the pit allows it to actively corrode and a dissolution front propagates toward, and eventually through, the surface. Both the iR and the pit solution chemistry mechanisms propose that perforations in the pit cover result from the outward growth of the dissolving metal. Alternatively, new pit formation around an initiating pit can be explained in terms of an analysis of the solution chemistry and potential gradients found *outside* but in the near vicinity of a primary pit. Harb and Alkire found that such gradients extend to distances more than ten times the pit radius [16] and the local acidity resulting from the hydrolysis of dissolving Ni^{2+} can be lowered by up to six orders of magnitude compared to the bulk of the bathing solution [17]. Localized acidification and halide accumulation can result in the initiation of secondary pitting [18]. An autocatalytic process can then occur whereby the birth of new pits accelerates the effects described above leading to circular clusters of pits. In this sense, pitting is temporally and spatially correlated [18-21] and results in patterned domains of lacy-like pits such as those observed by Budiansky *et al* on stainless steel [22, 23]. The interplay between dissolution rate, diffusion processes, and the concentration of aggressive species determines pitting behaviour and strongly influence the mechanical properties of the dissolving metal *vis a vis* anode residue formation. In this work we compare the pitting properties of anodic Ni subjected to potentiostatic and galvanostatic conditions using scanning electron microscopy (SEM), white-light interference microscopy (WLIM), and in-situ optical monitoring. Our results indicate that the anode's morphology and tendency to produce residue due to mechanical instability can best be controlled using potential pulse dissolution.

Experimental

Reagents and Solutions

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (98%), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (98%), boric acid (99%), dimethylglyoxime (>99.0%) and HNO_3 (ACS Plus Grade) were purchased and used as received. All solutions were prepared using Milli-Q water ($\geq 18.2 \text{ M}\Omega\text{cm}^{-1}$). Watt's electrolyte of composition 0.21 M NiCl_2 + 1.0 M NiSO_4 + 0.53 M $\text{B}(\text{OH})_3$ was used for all experiments unless otherwise noted.

Electrochemical Measurements

All electrochemical experiments were conducted at room temperature using a three electrode cell with a nickel pellet working electrode (Vale Canada), nickel quasi-reference electrode and copper foil cathode unless otherwise noted. Reported current densities were determined using the geometric area of the polished electrode. All working electrodes were fashioned from spherical nickel pellets (99.8% Ni, Vale Canada) which were attached to a nickel wire and cast in an insulating epoxy. The electrodes were polished using abrasives followed by successively finer diamond suspensions (15 μm , 6 μm , 1 μm). Final polishing was done on a Giga 0900 vibratory polisher using 0.05 μm alumina slurry (Pace Technologies) and all electrodes were then aged overnight in air to allow the natural passive oxide to develop. Data collection was done using National Instruments DAQ cards and software written in-house using LabVIEW. Polarization curves and collection of current transients were performed using a HEKA PG 590 Potentiostat. Pulsed electrodisolution experiments were carried out using a Solartron 1287 electrochemical interface in potentiostatic mode. The desired square potential wave was generated in LabVIEW and fed to the potentiostat's external input. The resulting current waveform was numerically integrated using Simpson's rule after each full cycle to provide the charge per pulse. By integrating over the entire pulse sequence (step from 0.0 V to 1.2 V and the return step) the contribution of double layer charging to the total charge should be negligible. The continuous

summation of the net charge per cycle was used to monitor the extent of electrodissoolution and to calculate the average current during the experiment.

In Situ Optical Microscopy

An *in-situ* cell for optical microscopy was designed using a petri dish fitted with a No. 0 glass coverslip (MatTek). The working electrode was mounted in the petri dish using a double-sided Kapton gasket to create an electrolyte reservoir and a cavity thickness of approximately 260 μm . Nickel wire (0.5mm, 99.98%) was embedded in the cell as a counter electrode with a circular geometry around the working electrode. Images were captured using an AccuScope 3035 series inverted metallurgical microscope equipped with a 10MP digital camera.

Scanning Electron Microscopy (SEM) and White-light Interference Microscopy (WLIM)

Scanning electron microscope images were collected on a Jeol 840A microscope operated in high vacuum mode using secondary electron signal with an accelerating voltage of 15 keV.

GRZEGORZ - PLEASE INSERT WLIM DETAILS HERE

Residue Collection and Measurement

In order to quantify the residue from multiple nickel pellets in one experiment, four-pellet anodes were fabricated as described above and polished to a 6 μm diamond suspension finish. For the electrodissoolution experiments the anode assembly was surrounded by a polypropylene mesh bag in order to capture residue detached from the anode during the experiment. Upon completion of the experiment the anode assembly and bag were transferred to a Buchner funnel with a coarse fritted disc and rinsed serially with copious amounts of Milli-Q water to completely remove any trace of nickel ions. The anode bag and filter funnel were then treated with 4 M HNO_3 to dissolve metallic nickel residue. A quick and simple quantitative test for aqueous nickel species was adapted from literature procedures [24]. Office paper was treated with a solution of dimethylglyoxime (saturated, 95% ethanol) and allowed to dry. To ensure all solutions had a $\text{pH} > 8$, small additions of NH_3 were spiked into

each sample prior to spotting. A 20 μl aliquot was pipetted onto the paper and allowed to dry. The intensity of the coloured nickel dimethylglyoxime complex was compared to that of standards to give an indication of the dissolved nickel from anode residue. The detection limit of this method was found to be $< 2.5 \text{ mg L}^{-1}$. Results of this simple test were confirmed using flame atomic absorption. Anode residue was quantified as the ratio of the mass of detached Ni from the dissolution bag to the mass of Ni deposited at the cathode.

Results and Discussion

Dynamic Polarization Behaviour

Linear scan voltammetry at 1 mV/s was used to determine the main features of the dissolution of Ni samples in room temperature Watts bath. Figure 1a shows that active dissolution is constrained to a very narrow range of potentials ($0 \text{ V} < E < +0.1 \text{ V}$). Polarization above the anodic limit of the active region places the Ni in a passive state characterized by a very low positive current density. The demarcation between passive and transpassive dissolution occurs at roughly 0.35 V and pits can be observed under optical microscopy for Ni samples biased at potentials above $\sim 0.40 \text{ V}$. Figures 1b and 1c provide *in-situ* optical microscope images of the Ni surface after polarization at 0.05 V for 300 mins and 0.60 V for 60 mins respectively. Biasing the anode at the active potential provides the surface with a pebbled look resulting from preferential dissolution of grain boundaries. The surface is free of pitting and the ridges seen in the figure arise from the carbonyl process used to produce the Ni pellet. The entire surface is in focus indicating that the surface is relatively flat. In contrast biasing at the weakly transpassive potential generates clusters of pits that lead to large, partially detached covers (*viz.* lower right side of Figure 1c). The underlying pit must be fairly deep as it is not possible to simultaneously focus on both the original surface and the bottom of the highly dissolved area.

Galvanostatic Dissolution

Industrial electroplating of Ni typically uses constant current conditions. In an effort to establish the pitting behaviour under such conditions, we performed galvanostatic experiments with a current density of 4.0 mA cm^{-2} [25]. Figure 2a shows the corresponding chronopotentiometric trace for a representative experiment. Immediately after the current is applied, the potential spikes to transpassive levels followed by a slow decay (on the order of minutes) to values close to the transition between transpassive and passive behaviour. The rate of dissolution at these lower potentials is obviously sufficient to maintain the required current density until the potential subsequently spikes again into the transpassive regime and slowly decays, a process that repeats several times over the duration of the electrolysis. The oscillations indicate that the pits formed in the excursions to high potentials must slowly re-passivate causing the need for a higher driving force and the genesis of new pits in the Ni surface. This dissolution behaviour can be better illustrated with the help of *in-situ* optical microscopy. Optical imaging of the Ni surface reveals that open pits appear more or less in a stochastic and random pattern on the surface (although more pronounced pits are found at the anode edge) the moment the current is applied, *i.e.* during the initial potential excursion into the transpassive regime (Figure 2b). Most of these pits remain constant in size (within the resolution afforded by the relatively low optical magnification used) whereas a smaller number seem to propagate below the oxide surface (Figure 2c) concurrent with the potential drop to a near-constant level close to the passive-transpassive boundary. Thus, a relatively small fraction of the anode supplies almost all the current and the remainder of the surface remains passivated. This is sustained until the rate of dissolution supplied by undercutting is insufficient and new growth sites must be initiated by subsequent potential spikes to transpassive values. A high density of new pits tend to be found near regions of undercut surface (Figure 2d). Figure 2e provides an SEM image of one such area after galvanostatic dissolution. The image reveals clusters of pits that form a circular pattern around a larger,

primary pit providing the area in question with a lace-like appearance. Such patterns are well known to form on stainless steel [14, 15, 26-28], Fe [26, 29, 30] and on Ni [13, 31]. It is desirable to eliminate the formation of large domains of partially perforated Ni (i.e. lacy-pit regions) as they contribute to residue formation during anodic dissolution [12].

Potentiostatic Dissolution

Two limiting scenarios might be envisioned to achieve more uniform dissolution of the Ni anode i) galvanostatic conditions that ensure that the anode potential is restrained within the active potential region at all times and ii) dissolution conditions that provide dense and homogeneous distributions of shallow and uniformly sized pits. Prohibitively low current densities render the first option impractical without the addition of undesired sulfur-containing species to the plating bath. The second scenario could most easily be achieved by entirely dissolving the anode at very large transpassive potentials rather than oscillating between passive and transpassive regimes. The optical/SEM images in Figure 3 reveals that sustained potentiostatic polarization at large potentials provide uniform anode textures devoid of lacy-pit domains. However, operating at large potentiostatic polarizations, or at large constant current densities that restrict the potential to high transpassive potentials requires high power consumption and may not always be desirable for electroplaters concerned with deposition performance at the cathode. In order to determine more moderate conditions that provide low anode residue it is necessary to first understand the time-dependence of pit formation and growth under potentiostatic conditions.

Current transients for a potential step from 0.0 V to 1.2 V were acquired with 50 μ s resolution and a representative trace is shown in Figure 4. The general features of Figure 4 are remarkably repeatable with only the magnitude of the longer time currents varying slightly from pulse to pulse. The current transient in the presence of chloride ions (main figure) reveals complex behaviour, marked by a sharp rise, followed by an exponential decay

that leads to a constant non-zero current density of approximately 7 mA/cm² that persists for several hundreds of milliseconds. The sharp rise in the current transient is not simply due to double-layer charging as an equivalent experiment performed in the absence of chloride reveals a much smaller peak current density (see inset of Figure 4). We attribute the initial current spike to the near instantaneous generation of many nanoscale pits due to breakdown of the passive film, most likely caused by oxide film breaking and/or chloride adsorption mechanisms [3, 18]. The current decay is the result of repassivation of a large number of the pit nuclei whereas a smaller number grow beyond a critical size and become stable or metastable pits. This is consistent with the adapted classical nucleation theory previously used to describe local breakdown of passive films [32, 33] and the exponential decrease with time in the nucleation rate of metastable pits [34].

After the induction period, the current rises again before exhibiting an inflection and approaching a nearly constant current at $t > 2.5$ s. Interpretation of the transient beyond the induction period requires consideration of corrosion pit growth kinetics. Much has already been determined about potentiostatic pitting phenomena by following current transients associated with individual pits [18, 34-37]. Studies on individual pit formation and growth consistently reveal that the initial dissolution current scales with a t^2 dependence [16, 34, 37, 38] irrespective of whether or not the pit eventually repassivates (metastable pit) or continues to grow (stable pit). This early time behaviour is attributed to the formation of covered hemispherical or near-hemispherical pits [35, 37]. If the pit cover fails before a critical point, mass transport of corrosion products is rapid, the pit repassivates causing the current density to almost immediately quench, and rather shallow and approximately hemispherical pits are left on the metal surface. Diffusion of the corrosion products into the bulk of the electrolyte is hindered if the pit retains a (partial) cover such that the solution in the pit remains sufficiently aggressive to prevent passivation. In this case the pit grows large enough to sustain corrosion

even after the pit cover is eventually lost [3, 18, 34, 37]. The progression of pit dissolution into stable growth is marked by a transition to new controlling kinetics dominated by either the ohmic drop within the pit [30, 36, 39] and/or the formation of salt films due to the precipitation of metal halide films [15, 37, 40, 41]. In both mechanisms single pit currents scale with $t^{1/2}$ making it difficult to know which is truly rate limiting [18]. Nevertheless, a distinctive feature in the current transients for stable pit growth is an inflection where the current converts from a t^2 to a $t^{1/2}$ dependence [34, 37].

The red lines in Figure 4 are fits to Equation 1

$$j = A(t - \tau)^x + B \quad \text{Equation 1}$$

where j and $t - \tau$ are the current density and offset transient time, A and B are constants, and x is either 2 or $1/2$. For $0.2 \text{ s} < t < 0.75 \text{ s}$, the experimental transient fits very well to Equation 1 with $x = 2$, whereas for $t > 1.2 \text{ s}$ very good agreement is found for $x = 1/2$. Intermediate times reflect the transient's inflection which marks the point where pit growth changes from small, roughly hemispherical pits to the propagation of much larger pits that spread deeply into the underlying nickel. The agreement between Figure 4 and the expected behaviour determined for individual pit measurements is somewhat remarkable considering the amount of ensemble averaging. The sudden step to a large overpotential likely means that the majority of nuclei are formed from the electrostrictive stress created by the initial potential pulse. The contribution of metastable pits (current quenching) to the total transient is negligible due to the large overpotential [37]. Single pit transients with sufficient time resolution consistently exhibit fluctuations that are attributed to additional nucleation events around the growing pit [36]. We presumably do not observe such fluctuations because the number of these events is very small and they are randomly distributed throughout the time course of the transient.

Pulsed-Potentiostatic Dissolution

To examine the size and distribution of the pits formed as a function of time after a potential step to 1.2V, a series of pulsed experiments were performed. A potential step sequence was applied whereby the anode was biased at 1.2 V for different pulse times ranging between 50 ms and 700 ms followed by a step to 0.0 V (just cathodic of the active region of potentials) for 500 ms to re-passivate the surface and allow corrosion products to diffuse into the bulk electrolyte. This pulse sequence was repeated 100 times before the sample was removed and the resulting pits were analyzed by white-light interference microscopy (WLIM). In comparison to SEM, WLIM can provide accurate measurements of the depth of features allowing a much better assessment of the three-dimensional geometry of the pits formed by pulsed potential dissolution. A relatively small number of pulses allows a sufficiently low pitting density such that individual pits can be discerned and a quantitative assessment of pit size can be made. Figures 5a and 5b show representative WLIM images for pits formed for 200 ms and 700 ms pulse times. The pits arising from the shorter pulse time are densely distributed on the surface whereas the prominent pits for 700 ms pulse times are rather sparse. The impression of low pit density in Figure 5b is an artifact caused by the larger vertical scale needed to represent the relatively small number of deep pits which in turn obfuscates a very large number of shallow re-passivated pits. These shallow pits can be clearly seen and quantified by artificially adjusting the vertical scale. Figure 5c provides plots of the measured pit depth *versus* pit radius for the two pulse times. The average pit depth for the shorter pulse time is considerably smaller than the corresponding radius of the pit opening as evidenced by the 0.07 +/- 0.03 slope of the trend line. This demonstrates that shorter pulses restrict nickel dissolution from the anode to a depth of ca. 100 nm and result in a surface stippled with many shallow pits. Excursions to transpassive potentials for less than several hundred milliseconds are insufficiently long enough for pit growth to propagate into the bulk of the metal. In contrast, allowing pit growth to continue for 700 ms after the potential step to

1.2 V generates prominent, three-dimensional pits. The trend line for 700 ms pulses in Figure 5c has a slope close to unity (1.0 ± 0.1). This is consistent with a pitting growth mechanism whereby any oblong pits formed at early times that survive beyond the critical re-passivation stage progress into a radial growth regime. The transition to hemispherical growth occurs at times greater than 200 ms which agrees well with the onset of the current transients' t^2 dependence (see Figure 4).

To investigate the surface evolution of pulsed electrodes in long time electrodisolution experiments samples were pulsed a total of 10^4 times and characterized by SEM. Figure 6 shows SEM images of the electrode surface for pulse times at 1.2 V ranging from 50 ms to 700 ms. As above, the anode is biased for 500 ms at 0.0 V between each pulse. Increasing the number of pulses 100-fold greatly increases the extent of nickel dissolution and individual pits are no longer discernable in the images. However, a progression from a smooth surface for 50 ms pulses to a roughened and porous-looking surface for pulse times > 300 ms can be clearly observed. For 50 ms pulses the surface shows enhanced dissolution at nickel grain boundaries suggesting that film breaking nucleation is more probable in the oxide surface above grain boundaries in the substrate metal. In fact this bears a remarkable resemblance to *in situ* observations of electrodes held at a constant potential in the active region of polarization (*c.f.* inset of Figure 1) and is qualitatively similar to the dissolution of sulfur activated nickel [42]. The results shown in Figures 5 and 6 indicate that the duration the anode remains at a large transpassive potential likely plays a critical role in residue formation. Allowing the pulse time to progress into the region of three-dimensional (hemispherical) pit growth will generate large domains of porous nickel and lacy pits that will delaminate from the anode and provide a primary source of undissolved nickel residue. However, much more uniform and superficial pitting can be obtained by restricting the time the anode is polarized at 1.2 V to short times. For the first 200 ms after the potential step, pits

remain shallow even though there is substantial dissolution current, especially in the first 50 ms. The exponential decay of the initial current and its direct relation to the number of active pit nuclei [32] suggests that limiting the potential pulse duration to very short times (~ 50 ms) will ensure that the ratio of nucleation events to dissolution current is high while still preventing the pit nuclei formed from having sufficient time to progress to hemispherical growth. On the basis of the results presented above the use of short duration transpassive potential pulses should result in an anode surface that closely resembles layer-by-layer dissolution.

To test this hypothesis the amount of residue produced by galvanostatic dissolution was compared to that formed from pulsed-potential dissolution using 50 ms pulse durations at 1.2 V and a 45% duty cycle (i.e. 60 ms at 0.0 V between pulses). The duty cycle was chosen such that the average current density of the potential-pulsed dissolution (3.3 mA cm^{-2}) closely matched that of the galvanostatic experiment (3.6 mA cm^{-2}). The cumulative charge passed was monitored and both experiments were terminated after an essentially equivalent amount of charge was past after ~ 3.5 days of electrolysis. The estimated percent dissolution of the original anode pellets was less than 5% by mass. Figure 7 shows SEM images of the resulting electrode surfaces after electrodisolution for galvanostatic and potentiostatic pulsed methods. Low magnification images for both conditions show pits and larger depressions in the anode surface as well as remnants of the initial outer layer. However, Figure 7a clearly shows that the galvanostatic dissolution produces a lacy oxide pit cover that can be seen to cover a large portion of the original surface. The partially torn cover in the centre of the image reveals a large, hollowed-out depression indicating that large pits have clearly propagated underneath the original oxide cover of the anode. In contrast the low magnification image of the pulsed surface (Figure 7b) shows no evidence of either large undissolved covers or lace-like pits. Although the presence of depressions in the anode

indicates that the whole surface doesn't dissolve uniformly, the absence of a lace-like appearance, perforated covers, or patinas of the original oxide surface reveals that the pulsed dissolution procedure does not lead to any noticeable undercutting or delamination of the oxide surface which is thought to be a significant source of anode residue. It is also important to note that the surface textures on depressed (highly dissolved) areas as well as what remains of the initial surface (weakly dissolved) are indistinguishable for the pulsed sample. On the other hand the pit exterior and interior textures are drastically different after galvanostatic dissolution. The higher magnification SEM image in Figure 7c shows the texture of the surface of the pit interior of the galvanostatic sample. Qualitatively, it shows a much rougher and more porous surface in comparison to an equivalent image of the outermost surface of the Ni. Figure 7d provides a high magnification image of the depressed region of the pulsed sample. It shows a different texture altogether and is qualitatively much smoother and less porous compared to the image shown in Figure 7c. Intuitively, one would expect that a rough, highly porous, textures would be much more prone to detach from the anode as a result of any mechanical perturbation (*e.g.* addition of new Ni pellets to the dissolution basket, gas evolution, convective forces) proving a secondary source of anode residue. In fact we were able to quantify this by collecting the residue generated from a composite anode comprised of four randomly selected Ni pellets using the conditions described above. Both the galvanostatic and pulsed-potential dissolution was repeated a total of three times and the collected residue was analyzed using atomic absorption spectroscopy. The results shown in Figure 8 confirm that the pulse-potential dissolution method decreases anode residue by a factor of 6.5. The reduction of the residue by pulsed-potential dissolution is very encouraging but the implications of the method on the cathode performance have yet to be fully studied. The texture, morphology, crystallography and hardness of metal deposits are known to depend on pulsed *versus* constant deposition conditions [43-45] and it is presently unclear

how nickel electrodeposited at the cathode during potential pulsing will compare to galvanostatically deposited Ni. However, by weighing the mass of Ni deposited on the copper cathode for both the galvanostatic and pulsed-potential dissolutions we can report that the two methods had an identical cathodic efficiency of $98 \pm 1 \%$.

Summary and Conclusions

Electro-dissolving commercial nickel samples using different electrochemical dependent variables (current or potential) has been performed in an effort to understand the causes of the Ni anode residue formation. Low residue levels can be achieved if the anode is under galvanostatic or potentiostatic conditions that force the dissolution to occur completely under active conditions (i.e. low current densities and low polarizations). Alternatively, keeping the anode polarized at large transpassive potentials and consequently high current densities (or vice versa) also mitigates the amount of residue. Neither of these approaches is feasible from a practical perspective. If the anode's potential oscillates in an uncontrolled fashion between passive and transpassive regimes (typical of industrially-relevant constant current dissolutions) the nickel surface develops lacy pits, exhibits undercutting and generates an open texture that is very susceptible to residue formation. We have provided an alternative approach that relies on controlled potential-pulses to provide low-residue dissolution while maintaining functional average current densities.

By analyzing the current transients for potential steps from a potential close to the open-circuit potential to a large transpassive value we have been able to provide important details about the pitting behaviour of nickel anodes. The current transient at short time scales is dominated by pit initiation likely caused by electrostriction. Following an induction period, surviving nuclei enter a complex growth regime that is dominated at short times by hemispherical growth leading to aggressive dissolution of Ni material below the anode surface. By limiting the time of the pulse to values before nucleated pits exhibit substantive

growth into the underlying nickel and controlling the duty cycle of the pulse sequence we can effectively mimic layer-by-layer (active) dissolution while maintaining significant average current densities. Our method generates a factor of 6.5 less residue compared to a galvanostatic experiment that passes the same amount of charge with a comparable current density. The practical implementation of pulsed-potential dissolution requires future consideration of other factors such as the overall power consumption, scalability, and importantly the quality of the nickel deposited on the cathode.

Acknowledgments

This work was supported by Vale Canada and the Natural Sciences and Engineering Research Council (NSERC) of Canada.

Figure Captions

Figure 1. a) Polarization curve (1 mV s^{-1}) for nickel anode in room temperature Watts bath. The active and transpassive dissolution regions are highlighted. The active current has been expanded by a factor of 100-fold in the inset. Optical, in-situ images ($200 \text{ }\mu\text{m}$ scale bars) of the Ni electrode after holding the potential at b) 50 mV for 5 hrs and c) 600 mV for 1 hr. The large indents in panel b) are fiducial marks made *a priori* with a nanoindenter.

Figure 2. In-situ monitoring of the Ni anode surface during galvanostatic dissolution at 4.0 mA cm^{-2} . Panel a) shows the corresponding chronopotentiogram. Optical microscopy images ($200 \text{ }\mu\text{m}$ scale bars) were taken at indicated times and are shown in panels (b-d). An SEM image of a perforated pit cluster is shown in panel e).

Figure 3. SEM images of Ni anode surface after sustained potentiostatic polarization at 1.0 V for X minutes.

Figure 4. Current transient after stepping the anode potential from 0.0V to 1.2 V in chloride-containing Watts bath. Solid red lines are fits to Equation 1. The inset provides magnification of early times for chloride-containing Watts bath (black line) and chloride-free Watts bath (red line scaled by a factor of 10).

Figure 5. WLIM images of Ni surfaces after 100 pulses to 1.2 V. The duration per pulse at the high potential was a) 700 ms and b) 200 ms. The pit depth to pit radius is plotted in panel c).

Figure 6. SEM images showing the Ni anode surface after 10,000 pulses to 1.2 V for different times a) 50 ms b) 299 ms c) 300 ms d) 500 ms e) 700 ms. The potential was held at 0V for 500 ms between pulses.

Figure 6. Low-magnification SEM images of Ni anodes after 3.5 days of electrodisolution under a) galvanostatic conditions ($j = 3.3 \text{ mA cm}^{-2}$) and b) potential pulse conditions (50 ms pulse to 1.2 V following 110 ms at 0.0 V, $j_{\text{avg}} = 3.6 \text{ mA cm}^{-2}$). Panels c) and d) are high magnification of images a) and b) respectively.

Figure 8. Comparison of anode residue for galvanostatic ($j = 3.3 \text{ mA cm}^{-2}$) and pulsed potential electrodisolution ($j_{\text{avg}} = 3.6 \text{ mA cm}^{-2}$).

References

- [1] T. Lampke, H. Steger, M. Zacher, S. Steinhäuser, B. Wielage, Status quo und Trends der Galvanotechnik, *Materialwissenschaft und Werkstofftechnik*, 39 (2008) 52-57.
- [2] D.L. Snyder, Electroplating nickel/chromium for the automotive industry, 95 (1997) 29-30.
- [3] S. Hans-Henning, Mechanisms of Pitting Corrosion, *Corrosion Mechanisms in Theory and Practice*, Third Edition, CRC Press 2011, pp. 349-393.
- [4] M. Keddam, H. Takenouti, N. Yu, Transpassive Dissolution of Ni in Acidic Sulfate Media: A Kinetic Model, *Journal of The Electrochemical Society*, 132 (1985) 2561-2566.
- [5] B. MacDougall, M. Cohen, Mechanism of the Anodic Oxidation of Nickel, *Journal of The Electrochemical Society*, 123 (1976) 1783-1789.
- [6] P. Marcus, V. Maurice, H.H. Strehblow, Localized corrosion (pitting): A model of passivity breakdown including the role of the oxide layer nanostructure, 50 (2008) 2698-2704.
- [7] D. Zuili, V. Maurice, P. Marcus, Surface Structure of Nickel in Acid Solution Studied by In Situ Scanning Tunneling Microscopy, *Journal of The Electrochemical Society*, 147 (2000) 1393-1400.
- [8] R.R. Moskalyk, A.M. Alfantazi, Nickel sulphide smelting and electrowinning practice: A review, *Mineral Processing & Extractive Metallurgy Review*, 23 (2002) 141-180.
- [9] D.S. Terekhov, N.V. Emmanuel, Direct extraction of nickel and iron from laterite ores using the carbonyl process, *Processing of Nickel Ores and Concentrates*, 54 (2013) 124-130.
- [10] S. Ando, T. Suzuki, K. Itaya, Layer-by-layer anodic dissolution of sulfur-modified Ni(100) electrodes: in situ scanning tunneling microscopy, *Journal of Electroanalytical Chemistry*, 412 (1996) 139-146.
- [11] T. Suzuki, T. Yamada, K. Itaya, In Situ Electrochemical Scanning Tunneling Microscopy of Ni(111), Ni(100), and Sulfur-Modified Ni(100) in Acidic Solution, *Journal of Physical Chemistry*, 100 (1996) 8954-8961.
- [12] A.S. Morrison, G.;Moula, G.; Barlow, B.; Burgess, I.J.; Shuebair, B.; Huang, H.; Lipkowski, J., Electrochemical Dissolution Behaviour and Residue Formation of Laboratory Grown Carbonyl Nickel Simulating Industrial Carbonyl Nickel Pellet Growth, submitted to *Electrochimica Acta*, (2015).
- [13] M. Wang, H.W. Pickering, Y. Xu, Potential Distribution, Shape Evolution, and Modeling of Pit Growth for Ni in Sulfuric Acid, *Journal of The Electrochemical Society*, 142 (1995) 2986-2995.
- [14] P. Ernst, N.J. Laycock, M.H. Moayed, R.C. Newman, The mechanism of lacy cover formation in pitting, *Corrosion Science*, 39 (1997) 1133-1136.
- [15] N.J. Laycock, S.P. White, J.S. Noh, P.T. Wilson, R.C. Newman, Perforated Covers for Propagating Pits, *Journal of The Electrochemical Society*, 145 (1998) 1101-1108.
- [16] J.N. Harb, R.C. Alkire, Transport and Reaction during Pitting Corrosion of Ni in 0.5M NaCl: II . Flowing Fluid, *Journal of The Electrochemical Society*, 138 (1991) 3568-3575.
- [17] G. Butler, H.C.K. Ison, A.D. Mercer, Some Important Aspects of Corrosion in Central Heating Systems, *British Corrosion Journal*, 6 (1971) 31-38.
- [18] G.S. Frankel, Pitting Corrosion of Metals: A Review of the Critical Factors, *Journal of The Electrochemical Society*, 145 (1998) 2186-2198.
- [19] T.T. Lunt, S.T. Pride, J.R. Scully, J.L. Hudson, A.S. Mikhailov, Cooperative Stochastic Behavior in Localized Corrosion: II. Experiments, *Journal of The Electrochemical Society*, 144 (1997) 1620-1629.

- [20] L. Organ, Y. Tiwary, J.R. Scully, A.S. Mikhailov, J.L. Hudson, Interactions among metastable pits on heterogeneous electrodes, 52 (2007) 6784-6792.
- [21] B. Wu, J.R. Scully, J.L. Hudson, A.S. Mikhailov, Cooperative Stochastic Behavior in Localized Corrosion: I. Model, Journal of The Electrochemical Society, 144 (1997) 1614-1620.
- [22] N.D. Budiansky, J.L. Hudson, J.R. Scully, Origins of Persistent Interaction among Localized Corrosion Sites on Stainless Steel, Journal of The Electrochemical Society, 151 (2004) B233-B243.
- [23] N.D. Budiansky, L. Organ, J.L. Hudson, J.R. Scully, Detection of Interactions among Localized Pitting Sites on Stainless Steel Using Spatial Statistics, Journal of The Electrochemical Society, 152 (2005) B152-B160.
- [24] M. Salman, U. Shafique, Z. Waheed uz, R. Rehman, A. Yousaf, F. Azhar, J.M. Anzano, A rapid method for measurement of nickel and chromium at trace level in aqueous samples, J. Mex. Chem. Soc., 55 (2011) 214-217.
- [25] Unless otherwise specified, all current densities herein are calculated using the initial geometric area of the anode. Experiments were designed such that the geometric area of the anode did not significantly change.
- [26] R.P. Frankenthal, H.W. Pickering, On the Mechanism of Localized Corrosion of Iron and Stainless Steel: II . Morphological Studies, Journal of The Electrochemical Society, 119 (1972) 1304-1310.
- [27] J. Mankowski, Z. Szklarska-Smialowska, Studies on accumulation of chloride ions in pits growing during anodic polarization, 15 (1975) 493-501.
- [28] M.A. Streicher, Pitting Corrosion of 18Cr-8Ni Stainless Steel, Journal of The Electrochemical Society, 103 (1956) 375-390.
- [29] M.G. Alvarez, J.R. Galvele, The mechanism of pitting of high purity iron in NaCl solutions, 24 (1984) 27-48.
- [30] Y. Xu, M. Wang, H.W. Pickering, On Electric Field Induced Breakdown of Passive Films and the Mechanism of Pitting Corrosion, Journal of The Electrochemical Society, 140 (1993) 3448-3457.
- [31] M.I. Abdulsalam, H.W. Pickering, Effect of the applied potential on the potential and current distributions within crevices in pure nickel, 41 (1998) 351-372.
- [32] B. Baroux, A multistep birth and death model for local breakdown of passivity, Passivation of metals and semiconductors, 31 (1990) 447-452.
- [33] T. Okada, A two-step initiation hypothesis of pitting corrosion in passive metals, Passivation of metals and semiconductors, 31 (1990) 453-458.
- [34] G.S. Frankel, L. Stockert, F. Hunkeler, H. Boehni, Metastable Pitting of Stainless Steel, Corrosion, 43 (1987) 429-436.
- [35] R.C. Alkire, K.P. Wong, The corrosion of single pits on stainless steel in acidic chloride solution, 28 (1988) 411-421.
- [36] R.C. Newman, E.M. Franz, Growth and Repassivation of Single Corrosion Pits in Stainless Steel, Corrosion, 40 (1984) 325-330.
- [37] P.C. Pistorius, G.T. Burstein, Metastable Pitting Corrosion of Stainless Steel and the Transition to Stability, Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences, 341 (1992) 531-559.
- [38] D.E. Williams, J. Stewart, P.H. Balkwill, The nucleation, growth and stability of micropits in stainless steel, 36 (1994) 1213-1235.
- [39] G.S. Frankel, J.R. Scully, C.V. Jahnes, Repassivation of Pits in Aluminum Thin Films, Journal of The Electrochemical Society, 143 (1996) 1834-1840.
- [40] T.R. Beck, R.C. Alkire, Occurrence of Salt Films during Initiation and Growth of Corrosion Pits, Journal of The Electrochemical Society, 126 (1979) 1662-1666.

- [41] G.S. Frankel, J.O. Dukovic, V. Brusic, B.M. Rush, C.V. Jahnes, Pit Growth in NiFe Thin Films, *Journal of The Electrochemical Society*, 139 (1992) 2196-2201.
- [42] G.A. Di Bari, Electrodeposition of Nickel, *Modern Electroplating*, John Wiley & Sons, Inc.2010, pp. 79-114.
- [43] N. Ibl, Some theoretical aspects of pulsed electrolysis, *Surf. Technol.*, 10 (1980) 81-104.
- [44] V.M. Maksimovic, M.G. Pavlovic, L.J. Pavlovic, M.V. Tomic, V.D. Jovic, Morphology and growth of electrodeposited silver powder particles, *Hydrometallurgy*, 86 (2007) 22-26.
- [45] K.I. Popov, M.G. Pavlovic, G.Z. Removic, The effect of the pause-to-pulse ratio on the morphology of metal powder particles electrodeposited by square-wave pulsating overpotential, *J. Appl. Electrochem.*, 21 (1991) 743-745.