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**Electrochemical Dissolution of Nickel Produced by the Mond Method under
Alternating Temperatures and Nickel Carbonyl Gas Pressures.**

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Abstract

The dissolution mechanism of nickel grown using the carbonyl process was investigated using laboratory Ni samples. These samples were purposely engineered to form an alternating

lamellar structure of Ni layers grown under two limiting conditions. Three layers formed from low nickel carbonyl gas concentrations (5%) at a decomposition temperature of 280 °C (LC/HT) were deposited between four layers formed from high nickel carbonyl gas concentrations (40%) at a decomposition temperature of 200 °C (HC/LT). These lamellar structures were used to simulate the two extremes found within an industrial decomposition chamber for nickel pellets grown using the Mond process. Cyclic voltammetry and fluctuations in the electrode potential were recorded during the 120 minute constant current dissolution experiment. Complementary scanning electron microscopy (SEM) and white light interference microscopy (WLIM) measurements were used to monitor the changes in surface morphology, texture and roughness as a function of the dissolution time. The electrochemical measurements showed that the dissolution of the sample proceeded in the transpassive regime at overvoltages above 300 mV. Large oscillations were observed in the chronopotentiogram, which suggests that the passive layer breaks down and then regrows on the surface of the nickel samples. SEM and WLIM images revealed that pits with lacy coverings were formed during the initial stages of nickel dissolution. With increasing dissolution time, the LC/HT regions dissolved at a significantly faster rate than the HC/LT regions and the lacy covers were more readily removed causing the transition to an open pit dissolution mechanism. At longer dissolution times the formation of trenches at boundaries between the lamina was observed. The average depth and width of the trenches increased as a function of dissolution time. The results from the lamellar samples used in this study clearly show preferential dissolution at boundaries between the lamina. In addition it shows that dissolution of the LC/HT regions proceeds faster than the dissolution of the HC/LT regions.

1. Introduction

High purity nickel needed for industrial electroplating can be obtained from refined ore using either electrolytic or carbonyl purification methods. The carbonyl process, which was discovered by Ludwig Mond in 1890, [1,2] involves flowing heated carbon monoxide gas (50-60 °C) over refined nickel. The CO gas bonds to the nickel forming a volatile $Ni(CO)_4$ complex, which is a very toxic gas. The process is completed when the temperature is raised between 200-280 °C causing the $Ni(CO)_{4(g)}$ to decompose forming high purity $Ni_{(s)}$. The decomposed CO gas is then reused in the carbonyl process. [1,2] The overall reaction of the Mond process is shown below:

Commercial application of the Mond process makes use of a nickel decomposer whereby pellets are gradually grown by pre-heating seed pellets to the desired nickel carbonyl gas decomposition temperature and passing them through a chamber where a layer of pure nickel is deposited onto the surface. This layer-by-layer deposition process is repeated roughly 300 times to produce approximately 10-mm diameter nickel pellets. Some of these pellets will be further processed by compressing the pellets into nickel chips. [3] During industrial electroplating, the pellets or chips are placed into a titanium basket, which is enclosed by a permeable polypropylene bag. The pellets are anodically dissolved at a constant current density in an electroplating bath with concurrent nickel plating occurring at the cathode.

In the production of nickel pellets, the composition of the laminar structure is always changing due to varying temperatures and $Ni(CO)_{4(g)}$ partial pressures within the decomposition chamber. The different compositional properties of each layer affect the overall dissolution behavior of the pellet. The aim of this research is to investigate the anodic nickel dissolution

behaviour of Ni produced by the carbonyl method in an attempt to understand its dependence on $\text{Ni}(\text{CO})_{4(\text{g})}$ gas decomposition conditions. Morrison *et al* [4] investigated the dissolution of laboratory-made samples produced at a constant carbonyl gas pressure and a variable decomposition temperature. The research described in this paper is a study of a laboratory-made sample using variable temperature and gas concentration, which correspond to the two extreme operational conditions that can occur within the carbonyl decomposition chambers. Each layer equates to either low carbonyl gas concentration and high decomposition temperature or high gas concentration and low decomposition temperature. The approach employed in this study is to measure the rate of anodic dissolution of each layer and determine the structure of the partially dissolved nickel surface. Over the duration of the electrochemical dissolution experiments, white light interference microscopy (WLIM) will be used to examine the overall change in the roughness and surface morphology and scanning electron microscopy (SEM) will be employed to analyze texture and grain distribution of the surface.

2. Experimental

Vale Canada (Mississauga, Ontario) provided a laboratory-grown carbonyl purified nickel sample (denoted CN2). The sample was synthesized using two different growth conditions. Each condition was set to mimic the extremes during the industrial process where one region was grown with a low nickel carbonyl gas concentration (5%) and high temperature (280°C) (LC/HT), and the other region was grown with a high nickel carbonyl gas concentration (40%) and low temperature (200°C) (HC/LT). These conditions were alternated during the overall growth of the sample creating a lamellar-type structure. The growth times for each layer

occurred in roughly 30 minute intervals. Due to the significant difference in the $\text{Ni}(\text{CO})_4$ gas concentration, the lamina Ni film grown at the lower gas concentrations was five to six times thinner than that of the higher gas concentration layers. The LC/HT and HC/LT layer thicknesses were roughly 45-60 and 275-300 μm , respectively. The sample was cut in the direction perpendicular to the surface of the laminae. Selective dissolution of the CN2 sample was investigated by encasing the remaining portion of the sample in an epoxy resin and attaching a titanium wire to the back of the sample to allow for galvanostatic control during the anodic dissolution. The sample was then cut and polished to a mirror finish in order to monitor the initial grain structure of the laboratory-grown Ni sample. At this stage, the procedure previously described by Moula *et al* [5] was used to perform the dissolution experiments. The morphology of the polished Ni sample was investigated by scanning electron microscopy (SEM) and white light interference microscopy (WLIM). These techniques were also used to monitor changes in the surface morphology and texture throughout the 120-minute duration of anodic dissolution. The dissolution conditions used in the previous paper by Moula *et al* [5] were also applied in this work. A Watts nickel plating bath ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (240 g/L), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (20 g/L), H_3BO_3 (20 g/L) was used as the supporting electrolyte. The Watts bath was maintained at a temperature of 60 °C and pH of 4 and the dissolution was performed at a current density of 0.8 A/dm^2 , which was controlled and monitored with a potentiostat/galvanostat (HEKA PG590, Germany). Ten minute intervals were used for the first two dissolutions (10 and 20 minutes total dissolution). The next two dissolutions were completed at 20 minute intervals (40 and 60 minutes total dissolution) and the final dissolution was collected following a 60 minute interval (i.e. a total dissolution time of 120 minutes). After each interval, the samples were removed from the

electrochemical cell and rinsed with Milli-Q water. The nickel samples were then dried in argon and imaged via SEM and WLIM to examine the changes in surface structure.

3. Results/Discussion

3.1 Pristine Sample

Figure 1: SEM images (backscattering mode) of (a) the CN2 laboratory-grown sample showing lamellar structure of the HC/LT and LC/HT layers. A close-up view of (b) HC/LT and (c) LC/HT layers showing different grain structures.

Prior to the nickel dissolution, the pristine sample was characterized using both SEM and WLIM. Similar characteristics were observed in the WLIM and SEM images of the initial state (i.e. before the onset of anodic dissolution) of the CN2 sample (we refer to it as the pristine sample); however, only the backscattered SEM images are presented as they provide much better detail of the surface texture and grain structure. Figure 1 shows two distinct regions within the pristine CN2 sample, which correspond to the different $\text{Ni}(\text{CO})_4$ gas decompositions conditions. The HC/LT (40% gas concentration and 200°C) and LC/HT layers (5% gas concentration and 280°C) conditions were alternated giving rise to the lamellar structure consisting of 4 HC/LT and 3 LC/HT layers (i.e. 7 layers total). The wide area view in Figure 1a shows the narrow LC/HT band surrounded by two broad HC/LT bands. These bands have distinct grain structures. Figure 1b shows a zoomed region of the HC/LT layer within the CN2 sample and reveals a mosaic of large grains along with several tiny pinhole structures at the surface. The zoomed image of the LC/HT layer (Figure 1c) shows a more porous surface structure with much smaller grain sizes.

Figure 2: First cyclic voltammetry curve recorded at the pristine CN2 sample recorded in the Watts solution at a sweep rate of 5 mV s⁻¹. The initial scan direction was toward negative potentials starting from 0 V. The reference electrode was a nickel sheet immersed in the Watts solution.

The SEM images provide structural information about the pristine Ni sample whereas the electrochemical behaviour was characterized by cyclic voltammetry (CV). Figure 2 displays a typical cyclic voltammogram of the pristine CN2 sample using a scan rate of 5 mV s⁻¹. The nickel surface displays an active region between -200 mV and 50 mV and a passive region between 50 mV and 300 mV. As the voltage is increased to potentials more positive than 300 mV, a transpassive current response is observed. For comparison purposes, a blue line has been added to the CV to represent the current density of the subsequent dissolution experiment (0.8 A dm⁻²), This current density is typical for industrial electroplating applications.[5]

3.2 Dissolution

3.2.1 Changes of potential of the nickel electrode with time

Following initial characterization of the surface, anodic dissolution of the CN2 sample was investigated using a constant current of 0.8 A dm⁻². In order to gain insight into the dissolution mechanism, the potential of the working electrode (CN2 sample) was monitored over the dissolution time. A plot of potential versus time recorded at the initial stages of the dissolution is presented in Figure 3. A distinct initial spike in the potential to values within the transpassive region, followed by a drop to potentials between 300-350 mV is observed. Comparing this plot with the CV obtained in Figure 2, it can be concluded that the dissolution was initiated by the breakdown of the passive layer and later continued at potentials bordering between the passive and transpassive regions. At dissolution times longer than 5 minutes, small and irregular oscillations between 300 and 400 mV begin to occur. This behavior implies that after the initial breakdown of the passive film, further dissolution was controlled by a continuous

regrowth and breakdown of the passive layer. Barlow *et al* have shown that each potential spike into the transpassive region results in the dissolution of nickel from new localized areas on the nickel surface. [6]

Figure 3: Potential vs. time plot showing the initial 10 minutes of CN₂ dissolution at 0.8 A/dm² current, in Watts electrolyte at 60° C.

The mechanism responsible for the breakdown and formation of the passive film has been discussed extensively [7-21]. The passive film has a bilayer structure that consists of an outer nickel hydroxide layer and an inner layer of nickel oxide. [8,10,11] Three primary mechanisms of the passive layer breakdown; namely the adsorption mechanism, penetration mechanism and film breaking mechanism have been discussed in several studies focussed on metal passivity and pit initiation. [12–21] The penetration mechanism describes the translocation of anions to the metal surface through the passive layer, which initiates the dissolution reaction and the transfer of metal cations back through the passive film into the bulk electrolyte. [10,12,14,20] The film breakdown mechanism describes the diffusion of anions from the electrolyte through the passive film resulting in either the formation of a pit or the growth of a metal-anion complex beneath the

oxide film. The passive layer on top of this metal-anion complex will either collapse or fracture upwards, thus breaking passivity and allowing for open pit formation to occur. [10,20] In the adsorption mechanism, the breakdown is caused by a noticeable potential drop at the interface between the electrolyte and oxide layer. This forces metal cations to transfer across the oxide film into the electrolyte, thinning the passive layer in the process. [10,20] Furthermore, it has also been demonstrated that the presence of Cl^- ions, at significant concentrations, inhibits repassivation and assists with further passive film breakdown and dissolution of metal surfaces. [14]

After the initial 10-min dissolution, the experiment was interrupted and the surface of the sample was examined with SEM and WLIM. The sample was then re-immersed into the electrolyte and the anodic dissolution was continued for another 10 min. Figure 4(a) shows the potential transient recorded during the second 10-min dissolution interval (i.e. between 10 and 20 min). The initial potential spike is significantly smaller than that of the pristine CN2 sample shown in Figure 3 indicating that the passive layer was weaker. After the initial spike, the potential again dropped to a value between 300 and 400 mV. At the end of this second dissolution, the nickel sample was once again removed from the electrolyte and examined by SEM and WLIM. The results of this analysis correspond to the 20-min dissolution and will be discussed below. The nickel sample was placed back into the electrochemical cell and the same current density and procedure was repeated for 40, 60 and 120 minute dissolution times. The potential transients recorded for the 20 to 40, 40 to 60 and 60 to 120 minute electrolysis intervals are presented in Figure 4(b), (c) and (d), respectively. Interestingly, each transient shows different characteristics after each dissolution time. After 20 minutes of dissolution (Figure 4a), there were no significant oscillations observed after the initial potential spike to ~475 mV,

however the average potential increased slightly from ~300 mV to ~350 mV vs. the Ni reference electrode as time progressed suggesting that the surface became slightly more passivated. After 40 minutes of dissolution (Figure 4b), the potential-time curve shows significant oscillations during the 20-min dissolution time interval. The frequency of these oscillations significantly increases during the final 6 minutes of the dissolution period. The high initial potential spike (~1.0 V) and significant oscillations suggest that breakdown and repassivation of the oxide film at the nickel surface is the primary mechanism for the dissolution process.

Figure 4: Potential vs. time plots recorded during: (a) 10 to 20 minutes, (b) 20 to 40 minutes, (c) 40 to 60 minutes, and (d) 60 to 120 minutes dissolution intervals at 0.8 A/dm² current density, in Watts electrolyte at 60° C

The dissolution between 40 and 60 minutes shown in Figure 4c resembles the trend presented in the 20 minute dissolution plot (Figure 4a) with a similar initial voltage of ~400 mV.

Extended periods of rather stable galvanostatic dissolution potentials (no oscillations) were also reported by Barlow et al [6] for related carbonyl nickel samples using lower current densities. After an elapsed time of 50 minutes, an increase in oscillation was once again observed, however, the amplitude and frequency of these oscillations is significantly lower than those observed in the 40 minute dissolution plot (Figure 4b). Figure 4d shows the final dissolution of the CN2 sample, which most closely resembles the characteristics of the 40 minute dissolution plot shown in Figure 4b. After the initial voltage spike, the potential remains fairly constant with small oscillations until the dissolution time reaches approximately 80 minutes where the amplitude of the oscillations become significantly larger. After 95 minutes, the frequency and amplitude of the oscillations increased further, indicating that significant breakdown and repassivation is occurring at the nickel surface. This can also be seen in the work of Moula *et al* [5]. However, the lack of systematic changes in the transient profiles shown in Figure 4 suggest that the interruption of the dissolution, cleaning and drying of the sample may lead to irreproducible changes in the structure of the passive layer.

Figure 5: Changes of the electrode potential with time of the CN2 sample during uninterrupted dissolution during 120 minutes, at 0.8 A/dm² current density, in Watts electrolyte at 60° C

Therefore, an independent study was conducted to determine if the initial spikes and changes in each of the potential vs time plots were causing irreproducibility by interrupting the dissolution. Figure 5 shows the initial spike in potential, consistent with the beginning of the dissolution and a decay of the potential to a lower stable potential for a short time. After 13 minutes, the oscillations resume, they become stable and constant throughout the remainder of the 120 minute dissolution. Overall, the potential oscillations, that are consistent with the breakdown and repassivation of the surface, were observed in all dissolution experiments. To understand the physical changes in the surface morphology, SEM and WLIM studies were performed at different intervals throughout the course of the dissolution.

3.2.2 SEM Characterization Studies

Figure 6: SEM images of the CN2 sample after 10 minutes of dissolution: (a) a wide area view of a single LC/HT band surrounded by two HC/LT bands. This image was used to calculate the pit density within the clusters. Zoomed images of the HC/LT and LC/HT areas are presented in (b) and (c), respectively.

Figure 6 shows the backscattered SEM images of the nickel sample surface acquired after 10 minutes of dissolution. Figure 6a shows two layers of the HC/LT bands with a LC/HT band in

the center. After 10 min of dissolution, the surface of the CN2 sample is much rougher than at the initial state observed in Figure 1. The grain structure of the pristine CN2 sample is no longer visible and has been replaced by large clusters of pits. The SEM images show a more pronounced dissolution in the LC/HT band while micro pit formations are visible in different regions across the HC/LT bands. Figures 6b and 6c show magnified images of the two lamina surfaces. The HC/LT band (Figure 6b) shows a roughening of the surface with multiple micro pit formations. The LC/HT band (Figure 6c) shows very different characteristics. Due to pronounced dissolution of this band, open pits with partial covers (lacy covers) attached to the top of some pits could be seen in this image. The lacy covered pits and open pit clusters begin as the passive layer thins in a localized area creating a single pit [21,22]. There are two explanations of the mechanism of lacy cover formation. The first assumes that the attack is coming from the solution side. Once the first pit has formed, it begins to grow with the assistance of a high concentration of localized Cl^- anions, which inhibit repassivation and allow for increased Ni^{2+} diffusion from the surface [14,23]. Further breakdown of the surrounding passive layer is achieved due to the increase of the local H_3O^+ concentrations, as a result of hydrolysis of Ni^{2+} and reformation of the oxide layer due to the reaction between Ni^{2+} and water. [5] The egress of H_3O^+ ions from the pit creates a hemispherical diffusion wave that assists in the breakdown of the passive layer and initiates secondary pitting leading to the creation of the pits clusters seen in Figure 6a [3, 22-25]. The secondary pits contribute further to the increase of the H_3O^+ concentration. This creates an autocatalytic process where the growth of the pit cluster occurs in a circular pattern. This phenomenon has been observed in the corrosion of stainless steel [24,25] and during the anodic growth of TiO_2 nanotubes. [26,27] The second mechanism proposed by Pistorius and Burstein [38] and developed further by Ernst et al [29] and Laycock et al [30]

assumes that solution chemistry within the pit plays a critical role in lacy cover formation. The model is based upon evidence that a minimum concentration of corrosion products (for example nickel salts such as NiCl_2) is required to form precipitated films on the pit surface and prevent repassivation. Since the length-scale for diffusion into the bulk of electrolyte is small near the pit opening, the concentration of corrosion products falls below the critical value and the pit repassivates near its mouth. At the same time, the inner volume of the pit has restricted diffusion of corrosion products and continues to corrode causing the pit to undercut the metal surface. As shown in the computational modeling of Laycock et al [30], this mechanism results in growth of the pit back towards the metal surface and the formation of new pit openings. As this process is repeated, it leads to the formation of a perforated pit cover over a central hemisphere. Recently Davenport and co-workers [31] performed X-ray tomography studies and provided visualization of pit formation with lacy covers.

The formation of lacy covers is observed on the majority of the CN2 surface. However, as mentioned in the LC/HT regions the lacy covering has already begun to collapse. In contrast, only the initial stages of pit clustering are seen in the HC/LT regions.

Figure 7: Density of pits within a cluster plotted as a function of a radius from the center of the cluster.

Figure 6a shows distinct, quasi-circular pit clusters of different radii. The distribution of pits within a cluster is analyzed in Figure 7 which shows the pit coverage as a function of radius r from the center of the cluster. The pit density is larger in the central area of the pit and then becomes more uniform. For example, clusters 1, 3 and 4 showed a 10-15% higher pit density within a radial distance of 2 μm . At radial distances higher than 4 μm , clusters 1 and 3 showed relatively constant pit density, while in cluster 4 the pits density continues to decrease slowly with distance from the cluster center. This behaviour is consistent with radial diffusion of corrosion products propagating outward from the pit center.

To understand the structure of lacy covers that are observed after 10 minutes of dissolution, adhesive carbon tape was used to remove the loosely bound nickel from the surface. Figure 8 (a) shows the image of the tape with lacy covers detached from the CN2 sample. The two stripes seen on the adhesive tape correspond to the LC/HT lamina and show significantly

greater amounts of the detached material compared to the HC/LT regions, which left only a few small pieces of detached material. Figure 8 (b) is a magnified image of a material removed from the LC/HT region. It shows the interior of the lacy cover facing the solution of the pit with quasi-concentric rings surrounding the central hole. These rings are consistent with predictions of the formation of concentric rings in the undercut metal by the model proposed by Laycock *et al* [30]. They are also consistent with quite uniform distribution of the pit density seen on the solution side of the cover illustrated by Figure 7.

Figure 8: Lacy cover removed from the surface of the CN2 sample using the carbon tape after 10 minutes of dissolution (a) image shows distinct areas with more removed material corresponding to the LC/HT regions (b) magnified image of material removed from the LC/HT band showing the interior of the lacy cover.

They are also consistent with tomography images of the pit growth published by Davenport and co-workers [31]. Therefore the model of the lacy cover formation proposed by Laycock *et al* [30] may explain the present results.

Figure 9: SEM images (backscattered mode) of the CN2 sample after 20 minutes of dissolution time: (a) wide area view of multiple HC/LT (wide bands) and LC/HT (narrow deep bands). The zoomed in view of the (b) HC/LT and (c) LC/HT regions.

Figure 9 is an SEM image of the CN2 sample after 20 minutes total dissolution. It shows increased roughening of the surface and open pit formation. Figure 9a shows a wide field of view of the CN2 sample with four HC/LT and three LC/HT regions. The LC/HT region dissolves much faster than the HC/LT region and deep trenches corresponding to the LC/HT bands are seen in the image. The HC/LT (Figure 9b) regions show an increased roughening along the smoother areas as well as an increased number of open pits with no lacy covering. Figure 9c shows a magnified image of the LC/HT region showing that the open pits propagate

deeply into the sample. The close up images also shows the remainder of a few lacy covers at the rim of an open pit.

Figure 10: SEM images (backscattered mode) of the CN2 sample after: (a) 40, (b) 60, and (c) 120 minutes of dissolution. Deep crevice lines correspond to LC/HT regions; the more uniform regions with some pits correspond to the HC/LT regions.

Figures 10 (a), (b) and (c) are images of the CN2 sample after 40, 60, and 120 minutes of dissolution, respectively. Preferential dissolution takes place at the LC/HT layers resulting in the formation of deep trenches. The depth and width of the LC/HT trenches increase with the dissolution time. This can be explained by restricted diffusion of corrosion products and/or an overall increase in H_3O^+ concentration (i.e. decreasing the pH) within the trenches, which allows for faster dissolution in the direction normal to the surface and widening of the trenches due to nickel dissolution at the HC/LT edge. In the HC/LT region the open pit formation becomes predominant leading to an increase in pit size and density, and consequently surface roughness, with time. It should be noted that the lacy covers of the pits are not visible in these images.

3.2.3 WLIM Characterization Studies

Figure 11: WLIM Images of the CN2 sample after (a) 10 minutes and (b) 20 minutes of dissolution. In each image the two LC/HT regions have the greatest depth (bluer color) and the HC/LT regions are red in color.

The SEM images, presented in the previous section, provide a qualitative description of changes in the surface topography as a function of dissolution time. However, 3D images of the surface obtained with WLIM provide an opportunity to quantify the effects of dissolution on the surface. WLIM was used to provide supplementary information about the surface. Figures 11 (a) and (b) show 3-D topographical WLIM images of the CN2 sample surface after 10 and 20 minutes of dissolution, respectively. The blue regions in both images correspond to the LC/HT bands while the red regions are indicative of the HC/LT bands. To ensure that the WLIM images were collected with a high resolution for accurate quantification, the wide area images displayed in Figure 11 were compiled by digitally stitching together several 90 by 120 μm images.

Figure 12: WLIM Images of the CN2 sample after: (a) 40, (b) 60, and (c) 120 minute dissolution. Distinct dark regions are the LC/HT regions and the brighter (red) regions are the HC/LC regions

The WLIM images of the 40, 60 and 120 minute dissolution are displayed in Figure 12 (a), (b), and (c), respectively. As the dissolution progresses, the surface becomes rougher and the depth of the LC/HT region significantly increases. Consistent with the SEM images presented earlier, the WLIM images show that the LC/HT region dissolves faster than the HC/LT region. In order to numerically quantifying the degree of roughness with dissolution time, scaling analysis of the WLIM images was performed using the procedure described by Moula *et al* [5].

Figure 13: (a) The limiting surface roughness (rms) calculated using scaling analysis on the WLIM images of the CN2 sample shown in Figures 11 and 12. The red line shows the total surface roughness calculations while the black line shows the roughness of the HC/LT regions (b) The average width of the LC/HT regions (the width of the trenches in Figures 11 and 12).

Scaling analysis allows one to quantify the surface roughness in terms of a quantity known as the limiting roughness. [32–34] To properly calculate the limiting roughness of the surface, the standard deviation of the surface heights within a given square with length L on the sample image is determined. This square is then moved in one pixel increments across the surface in both the X and Y-directions and the standard deviation is calculated at each new position. The average of these standard deviations gives the rms roughness of the surface (σ_L) corresponding to the square with length L . The calculation is then repeated by increasing the length of L until the rms roughness becomes independent of L which defines the limiting roughness. [32]

Figure 13 (a) shows the limiting roughness calculations for the entire surface (red points), and the limiting roughness of the smoother HC/LT regions (black points). After the first 10 minutes of dissolution, the roughness of the entire surface and that of the HC/LT region are similar. The roughness increases with dissolution time with the overall surface becoming significantly rougher at later dissolution times. However, the roughness of the HC/LT region is much smaller than the overall roughness. This can be explained by the significant dissolution of the LC/HT regions, which contributes predominantly to the increase in the overall surface roughness. After 40 minutes of dissolution, the overall roughness of the surface attains a plateau. The WLIM images quantitatively illustrate that nickel dissolution takes place predominantly in the LC/HT regime.

Figure 13 (b) shows how the average width of the LC/HT regions (trenches) changes as a function of dissolution time. It appears that the width of the trenches grows over the first 40 minutes of dissolution and attains a limiting value that is approximately equal to the width of the LC/HT lamina at dissolution times greater than 40 min. The measured trench width after 10 minutes of dissolution has an average value of $\sim 57 \mu\text{m}$ and increases to $\sim 79 \mu\text{m}$ by 40 minutes and after 120 minutes of dissolution, the average width of the trench was $\sim 90 \mu\text{m}$. It should be noted that the width of the LC/HT regions after dissolution are larger than those measured in the pristine CN2 sample. This suggests that some dissolution must also take place at the border between the two bands.

Figure 14(a) Cross-sectional view of the CN2 sample after 120 minutes of dissolution time. The three LC/HT regions are circled in red. Magnified images showing the depth of the (b) left, (c) center and (d) right trenches formed by LC/HT regions dissolution.

Supplementary to the WLIM measurement, a cross-sectional SEM measurement was also performed to verify the depth and width of trenches on the sample after 120 minutes of dissolution. Figure 14 (a) shows the cross-section of the CN2 sample with all three LC/HT regions (circled in red), which clearly show that the dissolution of nickel penetrates deeply into the sample. Figures 14 (b), (c) and (d) reveal that the trench depths range between 110 and 130 μm . These numbers can be compared to the peak to peak roughness calculated from the WLIM images and equal four times the limiting rms roughness. Figure 13a shows that the peak to peak roughness amounts to $\sim 60 \mu\text{m}$ which is a half of the trench depth determined from the SEM image. This suggests that the plateau on the plot of limiting roughness shown in Figure 13a corresponds to the limit of the WLIM to measure the roughness on a surface with deep narrow trenches. In agreement with the WLIM measurements in Figure 13b, the width of the mouth of the trench is much larger than the width of the LC/HT lamina and gives the trenches a funnel-like appearance. This means that at the mouth of the trench the dissolution front extends into the

adjacent layers of HC/LC as well as extending deeper into the LC/HT region. In comparison, previous cross-sectional microscopy and x-ray radiography studies of large pits with semi-intact pit covers show a distinctly flask-shaped appearance [35]. In the present case the slower rate of dissolution along the internal boundaries with the HC/LT layers prevents propagation in the lateral direction. Furthermore, after extensive (120 minute) dissolution, any perforated covers at the surface of the trench have been lost and the lacy-pit mechanisms described above are no longer operative.

3. Summary and Conclusion

The investigation of the constant current dissolution of a laboratory made carbonyl nickel sample was performed to understand the dissolution mechanism of the sample. Two different conditions of the Mond process were used to create a laminar sample. The HC/LT layer was formed using a high concentration of carbonyl nickel gas (40%) and a low temperature (200 °C) to decompose carbonyl nickel. The LC/HT layer was formed using a low carbonyl nickel gas concentration (5%) and a high decomposition temperature (280 °C). The LC/HT layers were sandwiched between the HC/LT layers. During the dissolution, the electrode potential oscillated between values corresponding to the transpassive and the passive regions indicating that the dissolution involved repeated breaking and repassivation of the oxide layer. SEM and WLIM images showed that pits were formed at the surface. Initially, pits with lacy covers were formed. They were transformed into open pits at longer dissolution time. The two laminae were dissolved with different rates. The LC/HT regions dissolved much faster leading to the formation of deep trenches in the dissolving sample. The HC/LT region showed significant roughening but its dissolution was more uniform. The fact that the different layers of the CN2 sample exhibit significantly different dissolution behavior can lead to non-uniform dissolution of the industrial

pellets grown by the Mond process. The knowledge provided by this study allows for optimization of carbonyl Ni production conditions to promote the most uniform dissolution of Ni pellets in electroplating applications.

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