Electrodeposition of Nanoporous Nickel Layers Using Inductive Voltage Pulses

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Abstract. We used inductive voltage pulses for electro-deposition of porous nickel thin film onto steel electrode. Short pulses (tp<1 μs) with variable amplitude (to ensure electrodeposition current density in region 124-224 A/dm²) were applied to electrode and resulting coating were analyzed with electrochemical and microscopic methods. At lower current densities only smooth nickel coatings growth, while at higher current densities the bubbles appear and porous layer was formed. Electrochemical impedance spectra of smooth and porous layers are measured in deionized water and in 1M KOH solution. The capacity in equivalent scheme is proportional to electrode surface, and from impedance spectra it is calculated that porous layer has 20 times larger active surface comparing to smooth layer (in KOH solution). From electrochemical measurements it is estimated that more efficient hydrogen evolution reaction occurs on electrode with porous nickel layer obtained at 223 A/dm². It is shown in this work that inductive short pulse method can be used to obtain nano-porous nickel coatings on electrodes for efficient electrolysis cell.

1. Introduction
The pulse electrolysis in scientific literature is recognized as a powerful method to obtain electrochemical coatings [1]. Compared to constant voltage electrolysis, where only the value of applied potential can be changed, the more power parameters are changed in pulse electrolysis – the length of pulse, pulse tracking frequency, pulse polarity, pulse amplitude etc. By changing the characteristics of the pulse power, also changes the structure of obtained coatings – they are smoother and with better adhesion, as it is commonly recognized and explained by specific peculiarities of pulsed electric double layer[2]. Double layer is divided into two parts: the pulsating layer and diffusion layer. The concentration of active ions is periodically changing in the pulsating layer, reaching maximum at the momentum when pulse appears, and the minimum of the pulse ended. The layer thickness is proportional to the pulse duration, so the pulsating thin layer is duplicating the electrode surface very well, resulting in a smooth coating [3]. It is also observed that coating hardness increased by increasing the peak current [4], and if very high hardness internal stresses occur on the surface, it may be so high that the coating cracks. Generally, electro-coating crystallization process takes place in two steps. In the first step, the metal ion discharge and in the second step the metal atom is generated. The second step takes place in two scenarios: the metal atom is included in the bran of crystal and crystal growth, or new kernel is formed. The second scenario occurs when the crystal growth rate is so slow that generated metal atoms they can not add. It is shown that the radius of the surface of generated kernel is inversely proportional to the over-voltage. This suggests that increasing the over-voltage, the grain radius is decreasing [5]. When the pulse rate is high, Nernst diffusion layer non-stationary mass transfer is dominating, and higher is metal ion concentration gradient in the
interface. The stationary mass transfer is dominating in the DC or pulse electrolysis at low frequencies [6]. Although pulsed electrolysis is widely used to obtain different coatings, there are not found many research works directed to pulse power applying to water electrolysis.

We have considered the inductive voltage electrolysis process [7,8], and raised the hypothesis that such a process is separating the charging current of cell geometric capacitance and double layer from the current of electrochemical reactions, and found that this type of pulse is limited by the energy before it is supplied to the electrochemical cell.

In this work, the nickel layer was grown up of stainless steel wire as working electrode in electrolysis cell with inductive voltage pulses. Changing the voltage pulse amplitude, different types of films are obtained smooth and porous. For each sample the specific surface area, exchange current, Tafel slope and the equilibrium potential are measured and compared with smooth wire.

2. Experimental

We used nickel plating solution (80g NiSO₄·7H₂O, 80g NiCl₂·6H₂O and 45g H₃BO₃ in 1 litter water), stainless steel wire 316L as working electrode (diameter 1 mm, length 10 mm), nickel sheet with large surface area as counter electrode and standard calomel electrode as reference electrode. Thin nickel film was grown onto the working electrode in two ways: using direct current mode or inductive voltage pulse mode. Stainless steel wire was mechanically polished, washed with acetone and rinsed in deionised water before experiment. Then electrode was placed in 5M KOH solution at a temperature 60 °C for 5 minutes, again washed with deionised water and rinsed in nickel plating solution. Inductive voltage pulses were generated by the generator, which is detailed in our previous publications [7,8]. Different coatings were obtained adjusting the pulse amplitude. Typical coating time 2 min in all cases was used. After coating, the samples were rinsed with deionised water. The impedance spectrum of each sample in deionised water was measured with HP potentiostat-bridge within a frequency range from 100Hz to 40MHz, using modulation with pulse amplitude of 20mV and DC component 0V. This was done in order to judge the specific surface area of electrode in dependence from the type of plating. The impedance spectrum of all coatings in 0.1 M KOH solution also was measured with the same settings to measure the double layer capacitance of electrode/electrolyte interface for each coating. Potentiostat PGZ301 VoltaLab is used to measure VA curves in 1M KOH aqueous solution for each sample, using voltage scanning from -250 to -2500mV with scan rate 50 mV/s and the Tafel slope value and exchange current were determinate. To study the morphology of nickel coatings, scanning electron microscopy (SEM, Hitachi S-4800, Institute of Physical Chemistry, University of Latvia) was used.

3. Results

4. Voltage oscillograms taken during deposition of thin nickel layer using pulses of different amplitude conditions are shown in Figure 1. The current density values marked in figure 1 is the current pulse peak values during deposition. In the case of current densities 207, 213 and 223 A/dm², in addition to nickel loading reaction, gas evolution at the working electrode was noticed. As a result of gas evolution, obtained coating was porous and homogeneous over the entire deposition surface. Gas bubbles certainly contributed in additional recovering of the nickel loading process simply mixing the electrolyte around the electrode. Gas bubble encapsulation in deposited nickel layer is responsible for the formation of pores in the coating. Obtained electrode coatings appeared homogeneous over the entire surface, since the release of gas after visual inspection were relatively uniform during all coating time. In voltage oscillograms the rapidly growing voltage region appears followed with slow changing region (Figure 1). As already discussed in our previous works [7,8], fast growing front is purely capacitive charging of electrochemical cell, while the slow discharge is related to the electrochemical reaction. In other words, at starting very short-time region is only charging process and electrochemical processes are turned off. The energy supply to the cell ended up charging when voltage pulse front reach the maxima, and since energy is supplied to the capacity, small decrease of it
during the process may further increase the potential on it. Two reasons can be to decrease the geometric capacity of cell: gas bubbles are blocking the surface, and erosion occurring on nickel grains. Since both of these processes are electrochemical reactions, the flat voltage increases the beginning of the electrochemical reaction start time for Ni coating process (this time is set around 1 microsecond). In addition to the slow voltage growth region in oscillograms, previously debated fact is confirmed, that during the inductive voltage pulse electrolysis, the energy supplied to the interface metal - electrolyte is determined prior to the pulse inducing magnetic field in primary circuit coil. Hence it is easy to deal with power of pulse electrolysis system – firstly calculate the reactive power of coil in primary circuit which will determine the power of electrolysis system in secondary circuit.

SEM images shows that gas bubbles during pulse coating are encapsulated and later remains as pores, while in DC mode the coating is smooth (Figure 3).

Figure 1. Voltage oscillograms taken during pulse plating with different peak currents.

Figure 2. Voltage and current oscillograms taken during pulse plating with peak current 213 A/dm².

Figure 3. SEM images of Ni coatings: a), b) - a porous coating with inductive voltage pulses, c), d) - smooth coating with DC voltage mode.
From impedance spectra the capacitance of electrode/electrolyte interface is calculated for porous pulse plated and smooth DC plated Ni coatings. In case of smooth steel electrode in water the value 5.08 pF is obtained what is very close to measured value 9.64 pF. In case of porous coating rough estimation gives value 2 times larger comparing with smooth layer. Impedance measurements of electrodes without in with different coatings in an alkaline solution gives evidence that the double layer capacity of porous coating is six times larger than that of smooth coating. It means that the difference between surfaces of porous and smooth coatings is already about 20 times.

From electrochemical measurements it is estimated that more efficient hydrogen evolution reaction occurs on electrode with porous nickel layer obtained at 223 A/dm² (Table 1).

Table 1. Parameters of Tafel equation for porous nickel coating and smooth steel (accordingly SCE).

| Material                                      | E₀ [mV] | I₀ [μA/cm²] | b [mV/dec] |
|-----------------------------------------------|---------|-------------|------------|
| Steel (smooth)                                | -998    | 50,2        | 158        |
| Porous nickel coating (mode 213 A/dm²)        | -934    | 16,08       | 142        |
| Porous nickel coating (mode 223 A/dm²)        | -926    | 18,17       | 135        |

5. Conclusions
A variety Ni layer structures on stainless steel wire is obtained using inductive voltage pulses. The porous layer is formed in pulse coating mode because of encapsulation of small gas bubbles in the volume of coating film. The main difference with DC mode is that in pulse mode the immediately after rapid voltage rise the interface is charging followed by a slow voltage decrease. The authors explain this by the surface of the capacity reduction as a result of the constant power supplied to the cell voltage increase. Capacity reduction on the surface can be attributed to two reasons: the erosion of nickel grains, which reduces the surface area and gas bubbles blocking the surface. Since both of these processes are electrochemical reactions, the flat voltage increases the beginning of the electrochemical reaction start time for Ni coating process (this time is set around 1 microsecond). The highest measured HER kinetics parameters has sample obtained at highest current 223 A/dm², observed for porous nickel coating obtained in the pulse mode and having the equilibrium potential of -926 mV (SCE), 18.17 μA/cm² – the exchange current value and 135 mV/dec - Tafel slope. As the great advantage of such a porous Ni layer on the metal surface in pulse mode plating the films are the high power density and high voltage amplitude obtained at the same time.

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