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THE PRESENT STATE OF RESEARCHES REGARDING ELECTROPLATING PROBLEMS
(Review)

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Abstract. *During the last years researches regarding galvanic electroplating problematic had an accelerated development due to environment protection reasons, because more of the present technologies will have to be changed by new ones of minor environmental impact. For example, in machine building industry, heavy metals (as cadmium) are replaced by new materials with superior properties and non-toxic. Alloys and composite materials are a convenient alternative.*

One of the greatly developed galvanic-technique branches is represented by functional electroplating under very hard working conditions. Human activity is extended in all places of the planet, so metals have to work under very corrosive conditions.

Decorative electroplating represents another branch in quick development. There are new and unexpected uses for electroplating materials. For example deposits of silk nickel have a silky aspect, a uniform appearance, corrosion resistance etc.

Galvanic electroplatings with nickel are used for fabrication of smaller and smaller mechanical micro-components. To control the quality of these micro-components is necessary to understand the relations between variables of the process and resulting properties. The influence of additives is intensively studied because these ones permit to obtain high quality deposits.

Keywords: *Galvanic electroplatings, nickel layers electrodeposited, nickel electroplating mechanism, nickel electro crystallization*

Actual directions in researches of nickel and nickel alloy electroplating

1. Actual directions in researches of nickel electroplating

At *Chagsha University, China* [4] was performed a new bath for nickel electroplating based on a solution with citrate. Tri-sodium citrate was used as complexion and blotter agent. There were compared blotting capacity of tri-sodium citrate and boric acid. The effects were investigated under different conditions and for different compositions of the bath. XRD analysis shows the finest crystalline structure as compared to Watts bath.

At *Technique University Dresda, Germany*, sub-micro-crystalline nickel (smc) electrodeposited was studied, through a method in PED (*pulse electrodeposition*) without additives. Fresh deposited layer was deformed at room temperature and for different amplitudes of plastic deformation forces and it was found that the interactions of dislocations with grain boundaries are responsible by diminution of internal stress observed on *smc* PED fresh prepared nickel [5].

In China, at Shanghai University, nickel was deposited from sulfamate bath for different current densities. It was studied corrosion behaviour in Nal solutions using potentio-dynamics polarization and *Electrochemical Impedance Spectroscopy-EIS*. The best corrosion resistance was obtained at 0.05 A/cm^2 current density. The corrosion potential and breaking potential decreased with the increasing of current density used in electrodeposition.

In China, at Shanghai University, electrodeposited nickel was prepared from a sulphamate bath at different current densities. Based on the microstructure, the corrosion behaviour of the electrodeposited nickel in 3.5% NaCl solution was studied using potentiodynamic polarization and electrochemical impedance spectroscopy (*EIS*). The electrodeposits with the best corrosion resistance are obtained at 0.05 A/cm^2 current density. The corrosion potential and breakdown potential decrease with increasing current density used to prepare electrodeposits [6].

At University of Nanjing, China, bright nickel was produced by a new technique with spherical hard particles filling between electrodes. The related theories and structure of the bright deposit were studied. It was found that the hard particles could increase the brightness of nickel deposits by perturbing the process of crystal nucleation and polishing the cathode surface during electrodepositing [6].

At Košice, Slovakia and Brno, Czehch Republic, electrodeposition of nickel on a paraffin impregnated electrode (PIGE) has been studied by cyclic voltammetry (CV) and chronoamperometry from chloride and sulphate electrolytes. The differences in mechanism of nickel deposition from these solutions have been observed. The experimental results obtained from cyclic voltammetry were evaluated by elimination voltammetry with linear scan (EVLS). The results indicated two basic differences between the nickel deposition process in both electrolytes: (i) in chloride electrolyte the initial stage is Ni^{2+} reduction, while in sulphate electrolyte it is the proton reduction; (ii) in choride electrolyte the charge carrying species is $NiCl^+$, while in sulphate solutions it is $NiOH^+$ [7].

At Sao Paolo University (Brasil) the electrodeposition of nickel on to platinum substrate in a Watts bath in the presence of glycerol, mannitol or sorbitol has been studied. The presence of polyalcohols in the electrolytic solution proved to be significant since deterioration of the bath contents during operation was not observed [8].

In Denmark, at Lyngby, the influence of current density and the temperature on the microstructure and hardness of nickel layers electrodeposited from an additive-free sulphamate bath were investigated [9].

2. Actual directions about establishing nickel electroplating mechanism

A group of researchers from *Košice-Slovakia* and *Leics, Great Britain* have studied ternary alloys of nickel with copper and cobalt. Special attention was given to the mechanism of electrodeposition process [10]. The mechanism is the following one:

$$Ni^{2+} + X^- \rightarrow NiX^+ \quad (1)$$

$$NiX^+ + e^- \rightarrow NiX_{ads} \quad (2)$$

$$NiX_{ads} + e^- \rightarrow Ni + X^- \quad (3)$$

The anion X^- has been variously assumed to be OH^-, SO_4^{2-} or Cl^-. By comparing the experimentally determined kinetic parameters to those calculated for the various rate-determining steps and ranges of coverage, they deduced that if a reaction mechanism of the general type (1)-(3) is applied in a Watts bath (consisting of $NiSO_4 + NaCl + H_3BO_3$): (i) the anion X^- must be the chloride and (ii) the rate-determining step was the reaction (2), what means the first-electron transfer step [10].

Some studies on the electrochemical deposition of nickel have indicated that the nickel monohydroxide ion, $NiOH^+$, is an important species in the charge transfer steps in aqueous non-buffered solutions:

$$Ni^{2+} + H_2O \leftrightarrow Ni(OH)^+ + H^+ \quad (4)$$

$$Ni(OH)^+ + e^+ \rightarrow Ni(OH)_{ads} \quad (5)$$

$$Ni(OH)_{ads} + Ni^{2+} + 2e^- \rightarrow Ni + Ni(OH)_{ads} \quad (6)$$

$$Ni(OH)_{ads} + e^- \rightarrow Ni + OH \qquad (7)$$

where $Ni(OH)_{ads}$ represents the active intermediate, which may also be a chloride containing complex. Two one-electron metal reduction reactions take place in succession, giving rise to two clearly identifiable peaks in the cyclic voltammograms. The hydrogen evolution also occurred under different extents in the same potential region.

The electrolytic deposition of nickel from a Watts bath onto a paraffin impregnated graphite electrode (PIGE) at pH 2, 3 and 4 was studied, also from the chloride electrolyte. Cyclic voltammetry and elimination voltammetry with a linear scan were applied. The results indicated three steps in the deposition mechanism from the Watts electrolyte solution: (i) a chemical reaction preceding an electrochemical reaction, (ii) the occurrence of surface reactions with the adsorption of intermediates onto the PIGE and (iii) a reaction of the electro active substance transported to the electrode by diffusion. Taking these results into account the reaction mechanism proposed was:

$$Ni^{2+} + H_2O \leftrightarrow Ni(OH)_{aq}^{+} + H^+ \quad (8)$$

$$Ni(OH)_{aq}^{+} \leftrightarrow Ni(OH)_{ads}^{+} \quad (9)$$

$$Ni(OH)_{ads}^{+} + e^- \rightarrow NiOH \quad (10)$$

$$NiOH + H^+ + e^- \rightarrow Ni + H_2O \quad (11)$$

The adsorption of chloride anions on PIGE was detected from the chloride electrolyte. The elimination voltammetry indicated the importance of a kinetically controlled adsorption/ desorption process in the nickel deposition mechanism. Following the distribution diagram, the particle most likely to be electro active at the start of electro reduction is $NiCl^+$ [10].

Similar results were obtained by *Ji and Cooper* [11]. They determined the nickel speciation in aqueous chloride solutions over a broad range of concentration and pH, and clarified the role of boric acid in nickel electrodeposition. They found that in concentrated $NiCl_2$ solution the predominant nickel species in the acidic region were Ni^{2+} and $NiCl^+$ and in a concentrated mixed sulphate-containing, Ni^{2+}, $NiCl^-$ and $NiSO_4$ were important. The concentration of the $NiOH^+$ species was negligible until the $NiCl_2$ concentration was lowered to 10^{-3} mol/dm^3.

The reduction of $Ni(II)$ was one of the first steps in the mechanism proposed for nickel deposition by *Gomez* et al.[12]:

$$Ni(II)+e^- \rightarrow Ni(I) \qquad (12)$$

followed by one more steps that lead to the deposition. This simple scheme may apply to potentials close to those just after the start of the deposition (until the maximum potential of the reduction peak) and may explain the compact, uniform deposits obtained. At more negative potentials, the first step was maintained but was followed by a possible disproportion reaction of $Ni(I)$:

$$Ni(I)+Ni(I) \rightarrow Ni(0)+Ni(II) \qquad (13)$$

Moreover, under these conditions a simultaneous reaction may occur between $Ni(I)$ and H_2O:

$$Ni(I)+H_2O \rightarrow NiOH(I)+H \qquad (14)$$

The reaction (14) explains the production of hydrogen during the nickel deposition.

Using voltammetric and potentiostatic methods, *Gomez et al.* [12] studied the initial stages of the deposition of nickel onto vitreous carbon from an aqueous chloride solution. The morphology of the deposit was observed by scanning electron and optical microscopy.

The mechanism of the Ni^{2+} reduction from acid sulphate, chloride and Watts electrolytes has also been extensively studied by *Epelboin, Wiart et al.*[13]. In an impedance study of nickel deposition, they observed that the electrode kinetics were dependent on the type of anion. In chloride electrolytes, slow electrode activation with cathodic polarization was predominant. In sulphate solutions, the low-frequency capacitive feature, favoured by a pH decrease, appeared to result from interactions between the nickel and hydrogen discharges. An interpretation was proposed in which the ad-ion Ni_{ads}^{+} acts as both a reaction intermediate and a catalyst, associated with a propagating kink site, and where the adsorbed species $H_{ads}*$, generated by the presence of Ni_{ads}^{+}, inhibited the hydrogen evolution. It was concluded that the active area is closely connected to the extent of coverage by adsorbates. Further impedance measurements showed that the electrolyte composition influenced the kinetics of nickel electro crystallization. The following mechanism was suggested for electrolytes of pH 2-4.

$$2\,(H^{+} + e^{-}) \rightarrow H_2 \quad (15)$$

$$Ni^{2+} + e^{-} \rightarrow Ni_{ads}^{+} \quad (16)$$

$$Ni_{ads}^{+} + e^{-} \rightarrow Ni \quad (17)$$

$$Ni_{ads}^{+} + H^{+} + e^{-} \rightarrow Ni_{ads}^{+} + H_{ads}* \quad (18)$$

$$2H_{ads}* \rightarrow H_2 \quad (19)$$

$$Ni_{ads}^{+} + H_{ads}* + e^{-} \rightarrow Ni + H_{incl} \quad (20)$$

An electrochemical impedance spectroscopic (EIS) study of metal deposition by *Wiart* [14] showed that the inhibition of the charge transfer was caused by adsorbates (hydrogen, anions and additive molecules) or by an interfacial layer. Various examples (*Cu, Ag, Ni, Zn*) illustrated these situations.

The electrodeposition from a low concentration of nickel onto vitreous carbon at pH 3 and 5 with different anions has been studied by *Proud and Műller* using EIS. They observed an adsorption process starting at potentials far removed from the potential corresponding to the deposition process. This process occurred more rapidly in chloride systems at pH 5 and more slowly in sulphate systems at pH 3 indicating that the adsorbing species was dependent primarily upon the pH of the system and secondly upon the anion. An overall mechanism was proposed based on the work of Wiart. Reaction:

$$Ni(OH)_{aq}^{+} \leftrightarrow Ni(OH)_{ads}^{+} \quad (21)$$

was the predominant step for the initiation of deposition at pH 5. The next step was:

$$Ni(OH)_{ads}^{+} + e^{-} \rightarrow Ni(OH)_{ads} \quad (22)$$

In the pH 3 system, the first step was the direct discharge of the hydroxylated complex:

$$Ni(OH)^{+} + e^{-} \rightarrow Ni(OH)_{ads} \quad (23)$$

Nickel deposition then took place via the steps:

$$Ni(OH)_{ads} + Ni^{2+} + 2e^{-} \rightarrow Ni + Ni(OH)_{ads} \quad 24)$$

$$Ni(OH)_{ads} + e^{-} \rightarrow Ni + OH^{-} \quad (25)$$

Protons were discharged simultaneously with nickel deposition:

$$H^{+} + e^{-} \rightarrow H_{ads} \quad (26)$$

$$2H_{ads} \rightarrow H_2 \quad (27)$$

$$Ni(OH)_{ads} + H_{ads} + e^{-} \rightarrow Ni + H_{incl} + OH^{-} \quad (28)$$

The adsorbed hydrogen (H_{ads}) was responsible for the passivation observed at the lower potentials at pH 5. At higher potentials this intermediate tended to evolve gaseous hydrogen or produce hydrogen-containing forms of nickel.

The second passivation process occurred through the precipitation of a passivating coverage of the hydroxylated nickel species:

$$Ni^{2+} + 2OH^{-} \rightarrow Ni(OH)_2 \quad (29)$$

This passivation was eventually broken by the relative acceleration of other processes or the potential dependence of the reaction:

$$Ni(OH)_2 + 2e^{-} \rightarrow Ni + 2OH^{-} \quad (30)$$

EIS was used by *Holm* and *O'Keefe* [15] to characterize the deposition of nickel onto stainless steel cathodes from non-buffered acid sulphate electrolytes at pH from 2 to 3,5. The impedance spectra showed features, which were related to both the quality of the deposit and possible shifts in the deposition mechanism. The spectra for good quality nickel deposits consisted of a single, high frequency loop. As the deposit quality worsened, a second loop appeared at lower frequencies. The characteristics of this loop indicated the formation of a passivating nickel hydroxide layer, possibly resulting from the onset of diffusion control. The second loop was related to the presence of an oxidized nickel film which can form if the hydrogen ion concentration is low. From the kinetic measurements during the electrodeposition of nickel, it was found that the rate of this discharge reaction was controlled by ion transport through the double layer. It had also been established experimentally that the rate-determining stage of the overall reaction was the single electron discharge of $NiOH^+$ to $NiOH_{ads}$. This offered the possibility of studying the time dependence of the current or potential during the transitional processes of nickel nucleation and growth.

Nickel nucleation onto glassy carbon substrates has been extensively studied. *Bozhkov et al.* [16] determined the concentration of nickel ad-atoms at the surface during the initial stages of nickel deposition onto glassy carbon substrates from the Watts electrolyte using both galvanostatic and potentiostatic pulse methods. They found that nickel ad-atoms carried a partial positive charge corresponding to about 25% of the total charge of the ion in the bulk of the solution.

3. Recent studies about establishing models for nickel electrodeposition processes

Abyaneh and co-workers [17] proposed a model for the electro crystallisation processes, following the application of a pre-pulse method. The transient equations derived on this basis were shown to closely fit the behaviour of the recorded pre-pulse transients for the electro crystallisation of nickel onto a vitreous carbon electrode from Watts-type baths. The kinetic information about the initial nucleation and growth of the nickel deposit was obtained by analyzing the experimental current-time transients. Nucleation rate constants were obtained over a range of deposition potentials [18].

Trevisan-Souteyrand et al. [19] also their stepwise computer model to be applicable to the potentiostatic current-time transient response of the nucleation of hemispherical centres and the radial growth mechanism. Particular attention was devoted to the effects of the ohm drop on the transient responses and on the number of growing centres. Computed values were compared to experimental transient curves and to transmission electron microscopy (TEM) micrographs obtained in the case of nickel electro crystallization onto vitreous carbon.

Jensen et al. [20] investigated the process of nickel electrochemical deposition from Watts-type electrolytes under the influence of high frequency ultrasound. An improvement in the distribution of the deposited nickel in millimetre-sized groove-features on the cathode surface was observed.

Lemaire et al. [21] focused their work on nickel electrodeposition from an eutectic *LiCl-KCl* melt, which is the most frequently used molten salt in industrial processes. A discrete Fourier transform (DFT) analysis was carried out of the interfacial processes which occurred in the first steps of electrodeposition. By means of molecular modelling techniques, the most stable complexes were determined, and their interaction with the nickel cathode during electrodeposition process was studied. The results showed that complexes with more than four chlorine atoms were not stable.

A computational model for nickel electrodeposition from acid solutions (pH 1) was presented by *Lantelme et al.* [22].

The growth of the nickel film prepared by electrodeposition was described by *Saitou et al.* [23]. Two kinds of growth rate were measured using columnar photo-resists formed on indium-tin glass plates. The nickel film surface was analysed by atomic force microscopy. The ratio of the mean growth rate at the edge to that of the nickel layer indicated the presence of anisotropy between the up and down steps of the incorporation probabilities of the ad-atoms. Experimental results suggested that the nickel growth process had a dynamic scaling property.

4. Actual studies about nucleation, growth and structure of electrodeposits

The structural and magnetic properties of nickel films growth by electrodeposition from sulphate solutions onto GaAs surfaces have been studied by *Evans et al.* [24]. In-plane X-ray diffractometry was used to study the nickel growth. The results showed that both the preferred growth relationship of growing film and the magnetic properties were strongly dependent on the substrate orientation.

According to *Amblard et al.* [25], the structure of the Ni electrodeposits grown on oriented substrates resulted in a competition between an epitaxial growth process and a non-epitaxial growth initiated by a substrate-independent nucleation. This independent nucleation was a necessary step prior to the progressive development of a definite fibre texture in thicker deposits. Both processes were investigated separately on two kinds of cathodic substrates: single crystals and amorphous carbon. For an amorphous substrate, multi-twinned particles with a roughly hemispherical shape were generated by independent nucleation. Several competitive growth processes contributed to the whole current when the substrate was a low-index plane of a single crystal (Cu or Ni). Models were also proposed which accounted for the experimental current-time transients.

The same group discussed the quantitative X-ray diffraction analysis of the fibre texture exhibited by the nickel electrodeposits obtained from a Watts bath. They investigated the preferred orientations exhibited by the nickel samples, which had been characterized by well-defined conditions of both preparation and X-ray diffraction analysis. Experimental results described the quantitative modification of four different orientations – namely [110], [211], [100] and [210] – vs two relevant parameters; the pH of bulk solution and [100] orientation exhibited the character of a rather free growth, unlike the three other orientations. These were found to be associated with a definite chemical species $Ni(OH)_2$, H_{ads} or gaseous H_2 which disturbed Ni electro crystallization.

Correia et al. [26] used chronoamperommetry to study the Ni and Co electro crystallization onto carbon vitreous substrate and onto gold substrate from diluted chloride baths. Scanning electronic microscopy and atomic force microscopy were used to view the surface morphology and particularly growth centres.

5. Actual researches regarding influence of additives in the electrolyte solution

Previous research showed that the addition of a modifier, such as boric acid, enhanced the electro winning from high quality nickel deposits under a broad range of electrolyte parameters. Inorganic additives showed little influence on the current efficiency. Increasing either the nickel concentration or the electrolyte temperature improved the current efficiency, while decreasing the pH significantly reduced the current efficiency. The additives and operating parameters had a complex relationship in terms of their influence on the deposition mechanism.

Mockute and *Bernotiene* [27] examined the interaction of additives with the cathode during nickel electrodeposition in the Watts electrolyte. The interplay of saccharin, 2-butyne-1,4-diol and phthalimide, were studied by the determination of the consumption rates of cathodic reaction products, and the incorporation of sulphur and carbon in the electrodeposits. A synergistic effect of the additives was observed. The aromatic compounds increased additive adsorption by carbonyl group, and 2-butyne-1,4-diol increased the adsorption of saccharin by sulphonyl group.

In another study, the same authors examined the reaction mechanism of some benzenesulphobamide and saccharin derivatives during nickel electrodeposition in the Watts electrolyte. It was found that the methyl group of *o-* and *p-*toluenesulphonamides and *N*-methyl-saccharin increased the rates of the consumption of additives, mainly by the acceleration of desulphurization reactions. The triple bond in the *N*-(2-butyn-4-ol) saccharin derivative complicated the reaction mechanism.

The effect of Cd^{2+} ions on the current efficiency, surface morphology and crystallographic orientation of the electrodeposited nickel from sulphate solutions has been studied by *Mohanty et al.* [28]. Their results indicated that Cd^{2+} ions did not have a significant effect on the current efficiency but caused a noticeable change in the surface morphology and deposit quality. X-ray diffractometry was used to study the crystallographic orientation of the electrodeposited nickel. They also examined the effect of pyridine and its derivatives on the electrodeposition of nickel from aqueous sulphate solutions onto nickel and stainless steel substrates. The results indicated that the presence of additives did not have a significant effect on current efficiency, but changed the surface morphology of the deposits. The electrochemical reactions occurring during the deposition of nickel were examined by cyclic and linear sweep voltammetry techniques. Kinetic parameters, such as Tafel slope, transfer coefficient and exchange current density, were determined.

Froment and *Wiart* [14] also studied the effect of different organic inhibitors, especially *2-butyne-1,4-diol* on nickel deposits from a Watts electrolyte on the basis of differential interferometry. The inhibiting action of an organic additive was characterized by a movement of the current density/cathode potential curve towards more negative potentials. The maximum amplitude was determined of the micro-relief of a deposit. Using impedance measurements, the process was also investigated in strongly acidic chloride and sulphate electrolytes and in electrolytes containing two additives: *2-butyne-1,4-diol* and sodium benzenesulphonate. The additives had a more pronounced inhibiting effect in chloride than in sulphate solutions. In chloride electrolytes, the inductive low-frequency effect was observed at more negative potentials than in additive-free electrolytes. With the addition of sodium benzenesulphonate in Watts or in chloride electrolytes, both an inductive and a capacitive low-frequency feature were present. These observations were interpreted on the basis of the specific effects of the anions. In sulphate electrolytes, the model involved the interaction between adsorbed hydrogen strongly bonded to the surface and the intermediate ad-ions Ni_{ads}^{+}. In chloride electrolytes, the model were based on the slow desorption of an adsorbed anionic species.

Kuzeci et al. [29] studied the effect of organic commercial extractors *LIX841,* *Cyanex272, D2EHPA, Versatic10* and *TBP* with or without Mg^{2+} ions, through different parameters of nickel electrodeposition on stainless steel substrate from aqueous sulphate solutions. There were not significant modification in current efficiency in presence of these additives, but there were observed changes in deposits morphology and in crystal orientation even when deposits were brightly, smooth and coherent. The changes also were observed in cathodic polarization behaviour in presence of these additives.

Nickel is often recovered by hydrogen reduction and electrodeposition from industrial waste and wastewaters. The quality of produced metal is strongly influenced by metallic and organic impurities, even at trace level. The impurities come from initial materials or are introduced in recuperation process. It was detected the effect of impurities in nickel electrodeposition process. Organic reagents used for extraction from solvents are the major contamination source. These are adsorbed usually in active coal or other solid materials. The presence of LIX64N in bath, even in low concentration, produces petting, fissures and deposits black coloured. Also the authors noted a decreasing in current efficiency with increasing in LIX64N concentration. Also, bright and smooth nickel deposits were obtained in presence of D2EHPA, at high values of current efficiency (96%), but concentration has not exceeded 50 mg/L.

Lin and co-workers [30] examined the influence of ammonium ions on the texture and structure of Ni deposits plated from a sulphamate bath onto a copper plate. The detailed microstructure of the nickel deposits was characterized using plane-view and cross-sectional TEM. The results indicated that the presence of ammonium ions in the bath created harder nickel deposits. The internal stress of the deposits also increased markedly when 100 ppm of ammonium ions was added.

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