Application of Pulse Plating and Pulse Reverse Plating techniques in Nickel electrodeposition – a review

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An overview of nickel and nickel alloy pulse and pulse reverse plating literature in recent years is given.

From the papers cited it was concluded that implementation of pulse current reduces defects, influences the grain size, influences the surface morphology, improves the corrosion resistance, improves the hardness, influences crystal lattice defects, influences the current efficiency and reduces peeling and burning. Further to that, pulse reverse current electro deposition of nickel is shown to reduce deposit stress, improve throwing power, improve deposit appearance and influence the crystallographic structure. It is stressed however that pulse or pulse reverse electro deposition of nickel is significantly different from copper electro deposition.

The literature cited on nickel alloy plating using pulse and pulse reverse current concerned improving corrosion resistance, wear resistance, electrical and magnetic properties. Both alloys and (alloy) multi layer compounds were reported.

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Introduction

The nickel electroplating industry is responsible for a significant part of the annual nickel consumption. The world nickel production in 2000 is estimated to be 1.230.000 metric tons [1]. Of this production, approximately 10% is used in electroplating and electroforming [2]. Combined this amounts to 14.000 m^3 of electrodeposited nickel annually.

In general, metals are deposited electrochemically using DC current. Recently however pulse and pulse reverse current deposition methods have gained more attention for various reasons. The power supplies for pulse and pulse reverse current plating became available for high currents. The reliability of these power supplies was improved significantly enabling industrial implementation. The engineering requirements for materials have changed. Environmental requirements have resulted in an attention for new and a renewed attention for existing materials and production methods. And economic considerations led to an increased attention for the precise, reliable and relatively cheap production method electroplating is.

In this review, a summary is presented of the research into nickel and nickel alloy electro deposition during recent years, illustrating the possibilities of pulse and pulse reverse deposition.

Nickel plating: a short history

Cronstedt in Sweden discovered nickel in 1751. It took until the 1830's, when the then recently discovered galvanic cells were put to the test, for e.g. silver to be deposited electrochemically and copper and nickel were to follow soon. In 1840, Shore filed a patent for electrochemical nickel deposition, followed in 1842 by Böttger who actually plated nickel from a nickel ammonium sulphate solution. Around 1870, chloride and boric acid additions are described.

From an electroplating point of view, the years between 1870 and 1940 were rather tame. One improvement is however worth mentioning. In 1916 Watts developed his formulation, still known as the Watts bath. This increased current densities tenfold, from 0.5 to 5 Adm^{-2}.

In the 1950's, new acid baths started replacing the cyanide formulations thus improving safety. However, only with the worldwide introduction of wastewater regulations in the 1970's large efforts were employed and high progress was realized in the entire field of electroplating. More recently, the electronics industry seems the major driving force for progress. In the years to come, the introduction of micro and even nano-structured devices will challenge all production methods involved, including electroplating and electroforming.

Pulse plating is already described by the end of the 19th century, but received its first real wave of attention through the work of Jernstedt in the late 1940's dealing with pulse and pulse reverse deposition. From a modern perspective, these experiments are hardly designated as pulsed, since the forward current time should be "at least 45 seconds" and the "deplating time should not be less than 30 % of the plating time" [3]. The results however were worthwhile.

From the 1970's, the subject received increasing attention, possibly because the limits of electro deposition baths and additives were recognized or simply because the quality of power supplies was vastly improved with respect to pulse shape, pulse frequency an power output.

In recent years, the printed circuit board industry has adopted the pulse reverse current electroplating method as the preferred method for copper plating through-holes and micro-vias. Following this success, other implementations of the technique are being investigated. Nowadays however the industrial translations of academic studies are no longer hampered by the absence of adequate equipment.

Nickel electrochemistry

Nickel in electro deposition solutions is present as the bivalent ion, mostly complexated by its counter ion(s). The reduction reaction rate is believed to be governed by the rate of formation of the $Ni(OH)^+$ ion in the cathode boundary layer. The reduction rate is strongly determined by the boundary layer pH. Nickel reduction is a strongly inhibited process, in which the inhibiting species determine the deposit texture to a large degree. The cathode current efficiency is rather high, in general well over 95%. In general the anodic current efficiency supersedes the cathode efficiency slightly.

Current densities of up to 35 Adm^{-2} can be achieved in specific electrolytes (highly concentrated nickel sulphamate). In general, the current density is determined by required deposit properties (stress, roughness) and anode passivation.

The nickel morphology highly depends on the plating circumstances. Electrolyte composition (both base electrolyte and additives), bath temperature, current density and also pulse pattern determine the deposition properties.

Applied anode materials are pure nickel (Watt’s, chloride and mixed electrolytes), sulphur-depolarized nickel (for high current density applications in chloride-free electrolyte) or, in specific cases dimensionally stable anodes like titanium or platinum. In the latter cases, nickel will have to be dissolved externally to make up for metal ion depletion during deposition.

Pulse and Pulse Reverse current in electro deposition of nickel

Various authors have studied the effect pulse and pulse reverse current has on nickel electrodeposits. This chapter is probably far from complete, but intends to address some of the subjects touched by various authors in recent years.

El-Sherik et al. state that previous investigations already showed that grain size, surface morphology and preferred orientation of thick nickel deposits depend on electrolysis conditions and electrolyte composition [4]. The texture development itself is shown to depend on interfacial inhibitors (atomic hydrogen, molecular hydrogen, nickel hydroxide). Ultra-fine-grained deposits can be obtained from an organic-free Watts bath. The difficulty however is that experimental circumstances vary throughout various papers. Pulsed current deposition was studied, and the experiments show that short on-times render smallest number of pit defects in the deposit layer, probably caused by hydrogen gas evolution. Longer on-times presumably lead to higher cathode overpotentials and a pH shift in the boundary layer. These effects influence crystal growth and orientation. Longer off-times also reduce hydrogen pits. Also, nickel adatoms have more time to migrate and thus form larger crystals. Previous work showed the necessity for grain refiners (saccharin) to go to nanometer size crystals since the surface mobility of nickel adatoms is not rate limiting. This is confirmed in this paper: crystals down to approx. 100 nm were produced in this work.

Tang et al. studied Watts baths in different compositions as well as a sulphamate bath [5]. Throwing power, hardness, elongation, yield stress, tensile strength, current efficiency, corrosion resistance and internal stress were tested as a function of pulse and pulse reverse parameters. Their experiments show that pulsing the current improves corrosion resistance. Pulse reverse deposition reduces internal stress, especially in the Watts baths. Pulse current does not affect throwing power, whereas pulse reverse deposition in a modified Watts bath with chloride addition to prevent anode passivation during the reverse pulse improves the throwing power by approximately 23% and as a bonus improves the deposit appearance. The hardness of the deposit is significantly improved by pulse current deposition using high frequency pulses but the author doubts the industrial implementation of these schemes due to the necessity of high frequency, high current pulses.

Toth-Kadar et al. deposited pulse plated nano-crystalline nickel (10-100 nm grains) following previous DC work [6]. The pulse plating induces grain refinement and decreases surface roughness. At least the temperature coefficient of resistivity, α, and the room temperature thermo power, S, depend on pulse plating parameters. Not only grain size but also crystal lattice defect density is influenced by pulse plating parameters.

Qu et al. derived a model and performed experiments investigating the quality of surface finishes (surface roughening) in pulse and pulse reverse current deposition of nickel [7]. Their aim was to render post-machining obsolete since micro-electroforming generally does not allow for this. It was shown that pulse deposition produced significantly better deposits in terms of surface roughening. Approximately 15% improvement was again observed comparing pulse current deposition to pulse reverse deposition.

Chan et al. performed crystallographic texture analysis on samples of nickel deposited from a sulphamate bath for improvement of magnetic and mechanical properties [8]. The specific crystal orientation depends on electro crystallisation circumstances. It was shown pulse reverse current deposition significantly influences these circumstances. Especially the [100] texture was studied; this orientation is known to be related to the amount of absorbed inhibiting species (nickel hydroxide, hydrogen) and the overall nickel deposition rate. The orientation density can be varied by a factor of 3.5 through varying the pulse parameters.

Hadian et al. performed a comparative study of DC and pulse current deposition in Watts electrolyte [9]. It was shown that pulsing the current lowered the mean stress, increased the micro hardness, increased the current efficiency, greatly reduced burning and peeling in high current density areas of the samples and improved deposit distribution.

Wong et al. published a series of papers dealing with theoretical and experimental work on the optimum wave shape for nickel deposition [10-13]. The waveform influence on the electro deposit surface finish using pulse current deposition was studied in a Watts electrolyte with added chloride [10]. The studied pulse shapes included a standard rectangular pulse, a ramp followed by a relaxation period relaxation, a ramp, a triangular pulse with a relaxation period and a triangular pulse. The ramp with relaxation or triangle with relaxation gave best surface finishes. A theory supporting these findings was presented. In [11] the ramp down pulse was introduced. The surface roughness influence order was established to be ramp down > triangle > ramp up > rectangle. The finer grain resulting from the initial high growth rate at step-up and the decrease of crystal growth during the ramp down period explained this. The relaxation period is believed to influence the diffusion layer conditions. In [12] the pulse schemes were extended to comprise “pulse on pulse” through the introduction of ramp-down spikes. A total surface roughness reduction by at least a factor of 3 was reported. Best results were obtained from ramp-down spike in ramp-down waveform (with relaxation time). In [13], a mathematical model for growth of nickel as a function of waveform applied is derived. The model parameters include 3D nucleation, 3D step growth through surface diffusion and 3D step growth through direct transfer. The nucleation rate is shown to be highest at the ramp-down waveform, whereas the highest growth rate occurs with rectangular waveforms. The finest grain structure is found at the highest nucleation rate. The model compares well with all results previously obtained.

Aroyo et al. presented comparative data of DC, pulse current and pulse reverse current deposition of nickel [14]. Although the text is not fully compliant to the accompanying picture, the pulse current levelling power is claimed to exceed the DC levelling power by 100%. The reverse pulse current levelling power even exceeds the DC levelling power by 180%, which is rather impressive.

Alting et al. present pulse reverse current electroforming of thick nickel pieces, using patented technology to minimize stress. The resulting work piece had a thickness of 2-4 mm where no hardness or tensile strength variation throughout the piece was observed.

Fritz et al. studied the nickel structure dependence on plating parameters and the influence of the initial substrate on texture and structure [15]. Copper and gold were used as substrates and DC was compared to pulse current deposition. Experiments were performed in a sulphamate electrolyte using bromide as anode activator. The gold substrate had a strong {111} orientation whereas the copper had no preferred orientation. As the mean current density was increased, the orientation of electrodeposited nickel changed from {110} to {100} texture, which is consistent with other literature in other electrolytes. The {110} orientation is associated with "hydrogen inhibited growth", the {100} orientation with "free growth": hydrogen inhibits the {110} growth direction to a lesser extent than other directions. Copper and nickel possess high lattice similarities, gold and nickel have a high mismatch: Au {111} produces Ni{110}. At high current densities the substrate influence is lost as the growth progresses.

Rasmussen studied pulse current deposition of nickel and concluded that copper and nickel have a completely different deposition mechanism [16]. The pulse patterns for copper cannot be used to improve nickel deposition quality.

Nickel alloy deposition

Nickel alloy deposition in combination with pulse or pulse reverse current was studied for various alloys and for even more reasons. A selection of the materials deposited and properties studied is summarized in this chapter.

Nickel-copper alloys were studied in [17-20]. Bakonyi et al. studied nano-scale nickel-copper/copper multilayers that were produced by pulse plating [17]. These multilayer materials are known to exhibit Giant Magneto Resistance, and are of interest to magnetic data storage devices. The electrical resistivity and Curie temperature of these materials were investigated. Ghosh et al. optimised pulse parameters for pulse current deposition of copper-nickel alloys from a citrate bath [18]. Coherent, smooth and bright coatings were obtained. The deposits are nano-crystalline in nature, as opposed to DC coatings. The internal stress of the deposit is lowered as compared to DC deposition. The measured corrosion resistance exceeds DC plated material and commercial Monel alloy. Kazeminezhad et al. took the multilayer deposition method to it's extreme for copper-nickel alloy films and multilayers produced by fast pulse plating, where the deposition thicknesses were down to sub-monolayer thicknesses of copper and nickel quantities in alternation [19]. Nickel clustering during electro deposition was concluded from magnetic dipole measurements. The preparation of protective coatings based on the ternary nickel-copper-molybdenum system was studied by Beltowska-Lehman et al. [20]. This study is also theoretically of interest since nickel and molybdenum are known to be an induced codeposition system whereas nickel and copper behave as a regular system. Pulse plating is shown to allow control of both composition and current efficiency. Larger copper and molybdenum contents can be obtained. Metallic, bright and compact layers were produced.

Nickel-iron alloys were studied in [21-27]. Amongst others, nickel-iron microstructures were deposited as magnetically actuated components for micro-systems using the pulse current deposition method in [21]. Pulse current and pulse reverse current deposition methods for the deposition of nickel-iron alloys were used in [22, 23]. Nickel-iron plating is known to be an anomalous system, since nickel deposition is inhibited and iron deposition is enhanced in the codeposition process. In this study, boric acid, which is shown to act not just as a buffer since it alters the deposit composition, the pulse frequency, which showed the average partial nickel current density to decrease on increasing pulse frequency or decreasing pulse time, the pH, where both nickel and iron deposition rates increase on increasing pH, and the temperature, where the partial iron current density was shown to increase on increasing temperature, were studied. Pulse current was shown to influence both composition and morphology of the deposits, but these effects are interrelated with mass transfer and solution composition. Hadian et al. studied the influence of pulse current on various nickel-iron deposits [24]. It was shown pulse current generally lowers mean stress, increases micro-hardness and increases cathode efficiency for all compositions. Tang reports pulse reverse current experiments in baths without wetting agents or sulphur-codepositing additives since sulphur codeposition influences the corrosion resistance and the magnetic properties of materials [25]. The accent in this study was on internal stress and material distribution. Pulse reverse current deposited coatings showed better material distribution, less pores, almost mirror finishes (depending however on base electrolyte) and lowered residual stress. The deposition rates are fairly low, mainly due to the risk of passivation. Rasmussen et al. reported on cobalt-nickel-iron alloy electroplated using pulse reverse current [26]. This alloy is a promising material for magnetic micro-systems since it exhibits a high magnetic saturation flux density and a low magnetic coercivity. Pulse reverse current deposition is used to minimize residual stress levels in the deposited material at high (96%) current efficiency. Donten et al. produced nickel-iron-tungsten ternary alloys, which can be applied as magnetic materials with increased durability, hardness and resistance to high temperatures as compared to the binary nickel-iron alloy [27]. The material also can be used as replacement for hard chromium coatings. Nickel-iron-tungsten is less brittle than nickel-tungsten and exhibits vastly reduced tensile stress. The pulse deposition method refines the texture of the alloy bulk and increases its surface smoothness. Pulse deposition allows for higher tungsten contents to be obtained. The current efficiency however lowers using pulse current.

Nickel-zinc electrodeposits are studied in [28-31]. Potentially these materials can replace zinc for corrosion protection. The materials show a significant improvement of corrosion resistance, up to a factor of 6. This allows for significantly thinner protective layers. Alfantazi et al. show pulse plating produces harder deposits by 20% as compared to DC literature data due to the finer grain structure [28]. The micro structured alloys are thermally stable up to 200 °C for 24 hours. In [29] he shows copper or steel substrates to be irrelevant since no compositional differences and no phase distribution or texture differences are found. Pagotto et al. studied nickel-zinc alloys, where they compared DC plating to pulse current plating [30]. Pulse current is shown to produce finer grained deposits, with the finest grains at the smallest on-times. Pulse current deposited alloys also exhibit the best corrosion resistance. Ashassi-Zorkhabi et al. showed the nickel content in nickel-zinc alloys increases with the use of pulse current as compared to DC. The hardness of the deposit is shown to increase with increasing pulse frequency.

Nickel-tungsten-phosphorous alloys were studied in [32]. Multilayered high and low tungsten content alloy layers of varying thicknesses were produced, using pulse currents to vary the tungsten content. The thermal properties of these coatings were studied in [33].

Although not an alloy, the composite material composed of nickel and silicon carbide particles described in [34] is worth mentioning. The coatings exhibit ductile and high wear-resistance properties. Pulse current deposition resulted in the lowest silicon-carbide content, the lowest hardness and the worst oxidation resistance. Pulse reverse current deposition on the other hand gave the hardest, most ductile deposits exhibiting the lowest internal stress and the best corrosion resistance.

Conclusions

From the literature cited it is concluded that pulse and pulse reverse electro deposition methods of nickel significantly extend the possibilities of the DC electro deposition method.

The literature reviewed on nickel alloy deposition reflects an implementation of pulse and pulse reverse production methods in the search for new and improved materials.

Not only better and improved materials and processes are discussed, but also new materials are produced using the pulse and pulse reverse techniques. These new and high-tech applications might revive the electro deposition altogether.

References

[1] US Geological Survey, "*Mineral Commodities Survey 2001*", US Government Printing Office, Washington, 2001.
[2] Parkinson, Hart, "*Electroplating on Plastics*", The Nickel Development Institute, 1995.
[3] Jernstedt, Patrick, "*Process of electrodeposition of metals by periodic reverse current*", US patent 2678909, 1954.
[4] El-Sherik, Erb, Page, *Surface and Coatings Technology*, 88(1996)70
[5] Tang, Leisner, Moller, *Sur/Fin 1993*, AESF, 1993
[6] Toth-Kadar, Bakonyi, Pogany, Cziraki, *Surface and Coatings Technology*, 88(1996)57
[7] Qu, Chan, Zhu, *Surface and Coatings Technology*, 91(1997)220
[8] Chan, Qu, Zhu, *Surface and Coatings Technology*, 99(1998)69
[9] Hadian, Gabe, *Surface and Coatings Technology*, 122(1999)118
[10] Wong, Chan, Yue, *Surface and Coatings Technology*, 115(1999)132
[11] Wong, Chan, Yue, *Surface and Coatings Technology*, 135(2000)91
[12] Wong, Chan, Yue, *Surface and Coatings Technology*, 140(2001)284

[13] Wong, Chan, Yue, *Applied Surface Science,* 178(2001)178
[14] Aroyo, Tzonev, *Sur/Fin 2000*, AESF, 2000
[15] Fritz, Mokwa, Schnakenberg, *Electrochimica Acta*, 47(2001)55
[16] Rasmussen, *Sur/Fin 2001*, AESF, 2001
[17] Bakonyi, Toth-Kadar, Toth, Becsei, Tarnoczi, Kamasa, *Journal of Physics: Condensed Matter*, 11(1999)963
[18] Ghosh, Grover, Dey, Totlani, *Surface and Coatings Technology*, 126(2000)48
[19] Kazeminezhad, Schwarzacher, *Journal of Magnetism and Magnetic Materials*, 226-230(2001)1650
[20] Beltowska-Lehman, Ozga, Chassaing, *Surface and Coatings Technology*, 78(1996)233
[21] Lochel, Maciossek, Quenzer, Wagner, Engelmann, *Sensors and Actuators A*, 46-47(1995)98
[22] Yin, Jan, Lee, *Surface and Coatings Technology*, 88(1996)219
[23] Yin, Jan, *Surface and Coatings Technology*, 79(1996)252
[24] Hadian, Gabe, *Surface and Coatings Technology*, 122(1999)118
[25] Tang, *Electrochimica Acta*, 47(2001)61
[26] Rasmussen, Ravnkilde, Tang, Hansen, Bouwstra, *Sensors and Actuators A*, 92(2001)242
[27] Donten, Cesiulis, Stojek, *Electrochimica Acta*, 45(2000)3389
[28] Alfantazi, Erb, *Materials Science and Engineering*, A212(1996)123
[29] Alfantazi, Brehaut, Erb, *Surface and Coatings Technology*, 89(1997)239
[30] Pagotto Jr., de Alvarenga Freire, Ballester, *Surface and Coatings Technology*, 122(1999)10
[31] Ashassi-Zorkhabi, Hagrah, Pavini-Ahmadi, Manzoori, *Surface and Coatings Technology*, 140(2001)278
[32] Panagopoulos, Papachristos, Christoffersen, *Thin Solid Films*, 366(2000)155
[33] Papachristos, Panagopoulos, Wahlstrom, Christoffersen, Leisner, *Materials Science and Engineering*, A297(2000)217
[34] Orlovskaja, Periene, Kurtinaitiene, Surviliene, *Surface and Coatings Technology*, 111(1999)234