We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

4,800
Open access books available

122,000
International authors and editors

135M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

BOOK CITATION INDEX INDEXED
CLARIVATE ANALYTICS

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Effects of Electroplating Characteristics on the Coating Properties

Ebru Saraloğlu Güler

Abstract

Electroplating parameters that can be listed as bath temperature, pH of the bath, current density, surfactant addition or type, coating thickness must be controlled during the deposition process since they determine the properties of the coating. However, it is difficult to manage the effects of this high number of parameters including their interaction effects. At this point, fractional factorial design that is a statistical method steps in that have the advantage of evaluating the influences and the complex variable interactions of parameters with a plausible number of experiments. In the design low and high values must be attributed to the parameters before the experiments and these values are selected according to the solution used. There are suitable plating conditions (written in handbooks) for each bath without particle addition and low – high values can be chosen between these ranges or just below or above them. For instance, the temperature range is 40-60°C, current density range is 2-7 A/dm^2 and pH range is 3.5-4.0 for nickel electroplating [36]. Besides the coating property, the electroplating parameters influence the hydrogen evolution reaction that is a side reaction that takes place at the cathode and may lead to morphological problems on the coated surface. The aim of this chapter is to provide information about how the parameters affect the amount of particles in the deposit. Because the reason of adding the particles to the bath is to improve the matrix properties by the particles emerged. So the more particles present and disperse in the coating, the more they will contribute to the coating property. Another important effect is the internal stress that led to departure of the deposit.

Keywords: Electroplating parameters, coating properties, composite deposition, electrocodeposition, particle concentration

1. Introduction

The electroplating method can be used to produce composite coatings by adding particles in the metal plating bath. The particles are trapped in the coating during deposition. Composite

coatings are composed of an electrodeposited metal matrix and dispersed solid particles. The metal powders, metal alloy powders and metal oxide powders of Al, Co, Cu, In, Mg, Ni, Si, Sn, V, Zn and nitrides of Al, B, Si and C (graphite or diamond) and carbides of B, Bi, Si, W and MoS_2 and organic materials such as polytetrafluoroethylene (PTFE) and polymer spheres are used as the particles [40].

The main application areas of the composite deposition are electronic, biomedical, telecommunication, automotive, space and consumer applications where high strength, equiaxed micro-components are required.

The electroplating parameters must be controlled during electrodeposition since they have significant effect on the coating properties, deposition efficiency and hydrogen evolution. Besides the current density, pH of the bath, bath temperature that places among the main electroplating parameters [36], there are more parameters including the type, the size, the concentration of the particles [37] and the addition of surfactants and their types [20]. The main properties of the coating can be listed as the corrosion resistance in TiO_2 – nickel coating [38], tribological properties in MoS_2 – nickel coating [4], mechanical properties in TiO_2 – nickel coating [38], internal stress in MoS_2 – nickel coating [9], texture in chromium – carbon deposit [39], particle content of the deposit [24] are severely affected by the electroplating parameters.

The aim of this chapter is to emphasize on the electroplating parameters, their effects and interaction effect on the coating properties. Particle incorporation in the deposit is an important property that must be analysed since composite electroplating aroused in order to improve the matrix properties with particle addition. Another important property is the internal stress that must kept at minimum levels not to disrupt the deposit.

2. Electroplating parameters

2.1. Current density

Electrodeposition process consists of two steps that are nucleation, growth mechanisms and thickening of the primary layer. The nucleation is enhanced by high current density unlike the growth process [1]. Thus, smaller grain sizes are observed at higher current densities due to the increase in the nucleation rate [2]. On the other hand, high current density increases pH in the vicinity of the electrode during the reduction process that creates a competition between metal deposition and hydrogen gas [6] [3]. Hydrogen evolution contributes to the internal stress in the deposit [4][5]. Therefore, it is important to figure out the current density values at which hydrogen evolution does not occur together with metal deposition [4].

The current density also affects the particle content in the deposit. The particle (WC) content of the coating increases linearly with an increase in the current density from 0.1 to 0.5 A/dm^2 regardless of the particle diameters [7]. On the other hand, Kuo [6] claims that the particle (MoS_2) content in the deposit decreases when the current density increases from 4 to 8 A/dm^2. According to the results of Hu and Bai [41], increasing current density generally increased the particle content but the effect of current density depends on pH. Figure 1 shows that when

the current density (B) is increased, the particle content is increasedwhen pH (C) is 1 and decreased when pH is 5 [41].
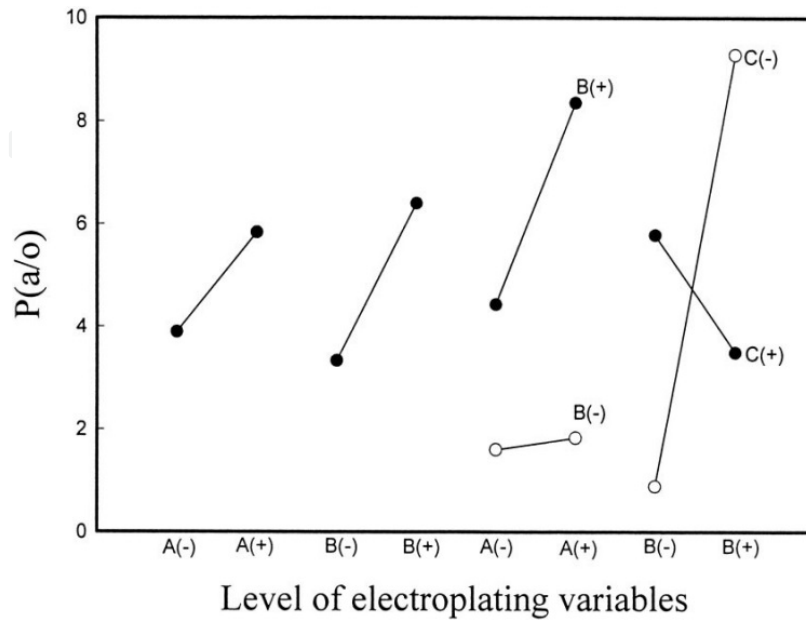

Figure 1. The effects and interaction effects of parameters on the atomic percent of phosphorus in the deposit. A: main effect of temperature, B: main effect of current density, BxC: current density – pH interaction effect, AxB: temperature – current density interaction effect [41]
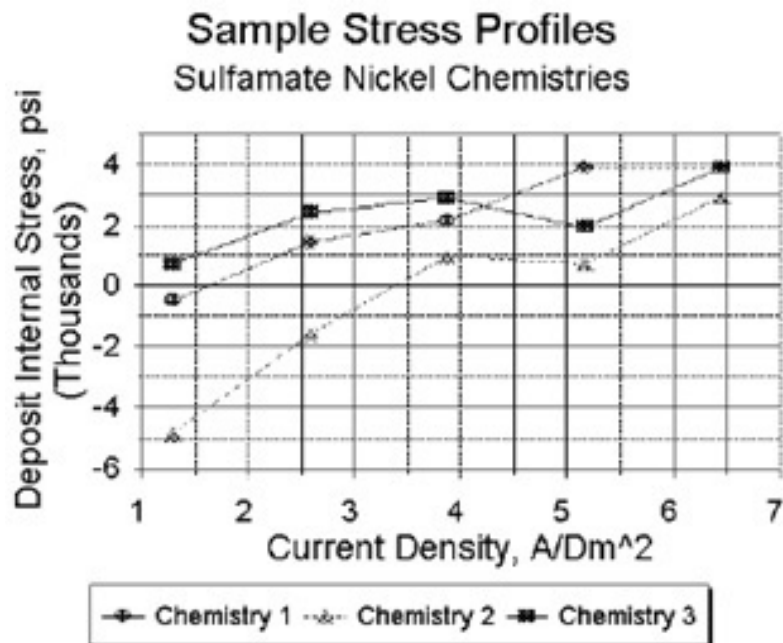

Figure 2. Stress behaviour for sulfamate nickel electrolytes with three different chemistries [42]

Another effect of increasing current density from 0.15 to 5 A/dm^2 is increasing the internal stress [8] since the stress stems from the residual stresses. However significant effect cannot be detected when the current density increased from 1.2 to 4.8 A/dm^2 [9] because the effect of current density on the internal stress depends on the electroplating solution composition. Figure 2 shows the effect of changing only one component amount of the solution on the current density dependence of the internal stress [42]. Moreover the effect of the current density depends on pH.

2.2. pH of the bath

The effect of pH on particle incorporation is dependent on the nature of the particles. For instance, when MoS_2 particles are used as the incorporate particles, the effect of pH value on the particle content in deposit was insignificant. Nevertheless it can be concluded that increasing pH decreased the amount of particles present in the coating [6]. However, incorporated particles are significantly decreased when pH is below 2 in Al_2O_3-Ni coating pair [11]. In addition, decreasing pH is preferred to manage the internal stress. Low pH values, less than 5, are selected to obtain acceptable stress levels [10]. Increase in pH of the solution may lead to discharge of hydroxyl ions instead of nickel dissolution and oxygen evolution [10] resulted in high internal stresses. It is also concluded that the internal stress was increased when the pH was increased from 2 to 4 in MoS_2 – Ni system [12].

3. Bath temperature

The effect of the temperature on the particle content in the deposit depends on the type of the particle. There is a small increase in the particle (MoS_2) content in coating with increasing the temperature 30, 40, 50 respectively [6]. It was mentioned that the temperature has an insignificant effect. For instance, no effect of temperature was detected in $BaCr_2O_4$-Ni [13] and Al_2O_3-Ni [14] coating couples. Because, the applied voltage is the main parameter that directly affects the activity of the reaction. In addition, Ni deposits more efficiently with increase in temperature. On the other hand, the influence of the temperature was reported as positive up to certain point. After that point, the amount of particles decreases with increasing the temperature.

General trend on the effect of the bath temperature on the internal stress is positive, meaning that increasing temperature decreases the internal stress. On the other hand, according to some of the studies the stress is more influenced by the current density regardless of the temperature [10].

Another advantage of the high temperature is the polarization effect. It is known that concentration polarization is the component of the polarization which is due to the change in the electrolyte concentration that stems from the current flow through the electrode – solution interface. So, the electrochemical cell potential difference deviates from its equilibrium value. Concentration polarization is decreased by increasing temperature because diffusion layer thickness gets smaller and ionic diffusion increases.

On the other hand, high temperature values increases energy consumption and supply heat for bath evaporation. Furthermore, thermal stresses will arrive at high processing tempera‐ tures and can become a serious problem especially when the coating and substrate have different thermal expansion coefficients. Therefore, an optimum plating temperature must be preferred to satisfy energy consumption and the coating quality.

4. Particle type

It is a common fact that if the amount of the particles in the solution is increased, the particle content in the deposit will also increase up to a certain point. However the type of the particle also acts as an important parameter. Both of the conductive and non-conductive particles have their own advantages against each other. Because conducting particles (molybdenum disul‐ fide, chromium carbide, zirconium diboride, graphite) attracted to the cathode then act as depositing sites which resulted in dendritic growth [15]. Despite the advantage of easily attraction of conducting particles to the cathode, selective deposition on the conducting sites led to increased surface roughness.
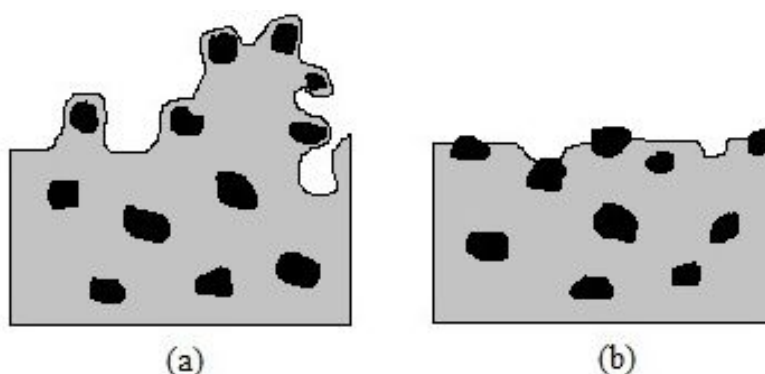

Figure 3. Schematic view of the composite coating including a) conducting and b)non-conducting particles

On the other hand, non-conductive particles end up with smoother deposit surfaces with low porosity [15].

Mechanical properties can be changed by the type of the incorporated particles. For instance, PTFE in Ni matrix increases wear resistance [16], MoS_2 incorporated with Ni decreased the coefficient of friction [9], Al_2O_3 and SiC dispersed in Cu increased the microhardness of the coatings [17]. Moreover, wear and corrosion resistance can be improved by the addition of silicon carbide nano-particles [18] [19].

5. Particle size

Small particle sizes can be agitated easily and led to an increase in the particle concentration in the deposit during composite electroplating. For example, the amount of particles is

increased by decreasing the particle size in Ni/SiC system [21]. Furthermore, the effect of particles in decreasing the friction coefficient is more effective when the particle size is decreased in Ni-MoS$_2$ system [9].

6. Particle concentration

Generally, increasing the particle concentration in the bath increases the weight percentage of particles in the deposit up to a certain point [9] [22] [23]. That point can be thought like the saturation point. There is a rapid increase in the particle amount in the low particle concentration regions whereas a slight increase occurs in the high concentration regions. The collisions between particles and cathode determine the codeposition of the particles and they are diminished in the high MoS$_2$ concentration region resulting in slight increase or decreased particle amount in the growing metal deposit [6].

7. Surfactant addition / type

Coating performance can be developed by the addition of the surfactants like (cetyltrimethylammonium bromide (CTAB), sodyumdodecyl sulfate (SDS), and saccharine [20]. The advantage of adding surfactants is their dispersing effect of particles. Thus the property of the particles will be uniform on the surface. Surfactants adsorb on the particles and favor the distribution of the particles [24].

Surfactants are indispensable especially for the hydrophobic particles (fluorographite, MoS$_2$) to be dispersed in the electroplating solution. Surfactants like sodium lauryl sulphate enhanced the electrostatic adsorption of suspended particles on cathode surface by increasing their positive charges [25]. Similarly, azobenzene (AZTAB) promoted particle deposition into the nickel matrix by their more positive reduction potential than that of nickel [26]. Another surfactant, cetyl trimethyl ammonium bromide (CTAB) has an advantage of increasing the volume percentage of SiC in the deposit besides homogeneous and non-agglomerated distribution of particles in SiC-nickel composite coatings [27].

Further advantage of the surfactants is suppressing the hydrogen evolution reaction. For example, saccharin which is an anionic surfactant is an effective way to overcome the hydrogen evolution problem [34].

The surfactants can be grouped under two main headings which are anionic and cationic surfactants according to their charges. Cationic surfactants increased the particle incorporation in the coating [28] [29] [30] [31]. Anionic surfactants may have positive or negative effect on the codeposition efficiency of the particles depending on the particle type and bath solution. For instance, SDS which is an anionic surfactant did not affect the codepositon of particles [31]. On the other hand, cationic surfactants have the advantage of adsorbing

on the particles that have negative surface charge [29]. Therefore, a net positive charge was formed by the adsorption of cationic surfactants that inhibited the formation of particle clusters and led to more stable particle suspension in the bath. Moreover, this positive charge improved the tendency of particles to move towards cathode and increased the amount of particles in the deposit [29] [30]. For instance, addition of cationic surfactant benzyl ammonium salts (BAS), increased the amount of MoS_2 codeposition [32]. In addition, BAS adsorbed on MoS_2 particles decreased the conductivity of the particles and resulted in homogeneous deposition of nickel and MoS_2 particles [32] [15]. On the other hand, it was stated that anionic surfactants in the electrolyte can give particles a negative charge and make them to move towards the substrate [35].

The disadvantage of the surfactants may occur if there are unabsorbed free surfactants, because they could lead to stress development and brittleness in the deposit [33]. Since the amount of incorporated surfactant is generally very small, their undesirable effects may be ignored [33]. However, increasing surfactant (CTAB) amount caused an increase in the internal stress due to the high possibilty of embedded CTAB in the nickel matrix [32].

8. Fractional factorial design

2^{n-1} fractional factorial design is a statistical design that can be used to identify the effects of n electrodeposition variables on the coating properties with the reasonable number of experiments. In addition, the interaction effects of the parameters can be analyzed by the help of fractional factorial. The property of the coating in other words the response value in the program is generally taken as the amount of particles in the deposit during composite coatings. For instance, in the study of Hu and Bai [41], phosphorus content in the deposit was taken as the response value and temperature, current density pH, NaH_2PO_2 H_2O concentration of the solution and agitation rate were taken as the electroplating parameters. Another most commonly used response value during composite coating is internal stress. Electroplating parameters were MoS_2 particle concentration, temperature, pH, current density and coating thickness where the response value is the internal stress in the study of Saraloglu Guler et. al. [9]. Other response values can be listed as friction coefficient, corrosion resistance, wear resistance, hardness which are the properties obtained by particle addition so increased amount of particle content in the deposit will have a positive effect on these values. The hydrogen evolution reaction must also be considered during this selection. The effects of the electroplating parameters on hydrogen evolution reaction can be studied before the composite deposition in order to determine the current density range where H_2 is not simultaneously discharged with Ni plating [12].

Fixed limit values that are said to be low (-1) and high (1) levels are selected for the electroplating parameters in fractional factorial design. Table 1 shows the parameters and their low and high fixed limit values for levels of fractional factorial design.

Electroplating Characteristics	Properties of the Coating
Current density	The coefficient of friction
pH of the bath	Wear resistance
Bath temperature	Corrosion resistance
Particle concentration of the bath	Mechanical Properties
Particle size	Internal Stress
Particle type	Texture formation
Surfactant addition/ type	Particle content of the deposit
	Grain size
	Electrodeposition/ particle uniformity

Table 1. The electroplating parameters and the properties of the deposit

Author details

Ebru Saraloğlu Güler

Address all correspondence to: esaraloglu@gmail.com

Baskent University, Ankara, Turkey

References

[1] Pletcher D.. Industrial Electrochemistry. Springer Netherlands; 1984. 325 p.

[2] Bockris J.O'M., Conway B.E., White R.E., editors. Modern Aspects of Electrochemistry. New York: Springer; 1992. 551 p.

[3] Schlesinger M., Paunovic M., editors. Modern Electroplating. 5th ed. John Wiley & Sons; 2010. 736 p.

[4] SaralogluGulerE..Electrocodeposition of molibdenum disulfide particles in nickel [thesis]. Turkey: Middle East Technical University; 2013. 94 p.

[5] Mizushima I., Tang P.T., Hansen H.N., Somers M.A.J.. Residual stress in Ni - W electrodeposits. Electrochim. Acta. 2006;51(27):6128.

[6] Kuo S.L.. The Influence of Process Parameters on the MoS2 Content of Ni-MoS2 Composite Coating by the Robust Design Method. Journal of the Chinese Institute of Engineers. 2004;27(2):243-251.

[7]   Nunez M., editor. Metal Electrodeposition. New York: Nova Science; 2005.

[8]   Pathak S., Guinard M., Vernooij M.G.C., Cousin B., Wang Z., Michler J., Philippe V.. Influence of lower current densities on the residual stress and structure of thick nickel electrodeposits. Surface Coating Technology. 2011;205(12):3651.

[9]   SaralogluGuler E., Karakayaİ., KoncaE.. Effects of current density, coating thickness,temperature, pH and particle concentration on internal stress during Ni–MoS2 electrocodeposition. SurfaceEngineering. 2014;30(2):109-114.

[10]   Lowenheim F. A., editor. Modern Electroplating. 3rd ed. NewYork: Wiley; 1974. 801 p.

[11]   Alkire R.C., Kolb D. M., editors. Advances in Electrochemical Science and Engineering. Germany: Wiley; 2002.

[12]   Saraloglu Guler E., Konca E., Karakaya İ.. Effect of Electrodeposition Parameters on the Current Density of Hydrogen Evolution Reaction in Ni and Ni-MoS2 Composite Coatings. International Journal of Electrochemical Science. 2013;8:5496 - 5505.

[13]   Quyang J.H., Liang X.S., Wen J., Liu Z.G., Yang Z. L.. Electrodeposition and Tribological Properties of Self-lubricating Ni–BaCr2O4 Composite Coatings. Wear. 2011;271(9-10)

[14]   Alkire R.C., Kolb D.M., editors. Advances in Electrochemical Science and Engineering. 7th ed. Verlag: Wiley; 2001. 193-223 p.

[15]   Abi-Akar H., Riley C.. Electrocodeposition of Nickel-Diamond and Cobalt-Chromium Carbide in Low Gravity. Chemistry of Materials. 1996;8(11):2601–2610.

[16]   You Y., Gu C., Wang X., Tu J.. Electrochemical Preparation and Characterization of Ni–PTFE Composite Coatings from a Non-Aqueous Solution Without Additives. Int. J. Electrochem. Sci.. 2012;7:12440 - 12455.

[17]   Stankovic V.D., Gojo M.. Electrodeposited composite coatings of copper with inert, semiconductive and conductive particles. Surface and Coatings Technology. 1996;81(2-3):225–232.

[18]   Shi L., Sun C., Gao P., Zhou F., Liu W.. Mechanical properties and wear and corrosion resistance of electrodeposited Ni–Co/SiC nanocomposite coating. Applied Surface Science. 2006;252(10):3591–3599.

[19]   Yao Y., Yao S., Zhang L., Wang H.. Electrodeposition and mechanical and corrosion resistance properties of Ni–W/SiC nanocomposite coatings. Materials Letters. 2007;61(1):67–70.

[20]   Fahami A., Nasiri-Tabrizi B, Rostami M., Ebrahimi-Kahrizsangi R.. Influence of Surfactants on the Characteristics of Nickel Matrix Nanocomposite Coatings. ISRN Electrochemistry. 2013;2013

[21] Garcia I., Fransaer J., Celis J.P.. "Electrodeposition and sliding wear resistance of nickel composite coatings containing micron and submicron SiC particles. Surface and Coatings Technology. 2001;148(2-3):171–178.

[22] Chang Y.C., Chang Y.Y, Lin C.I.. Process Aspects of the Electrolytic Codeposition of Molybdenum Disulfide with Nickel. Electrochimicia Acta. 1998;43(3-4):315-324.

[23] Huang Z.J., Xiong D.J.. MoS2 Coated with Al2O3 for Ni-MoS2 / Al2O3 Composite Coatings by Pulse Electrodeposition. Surface Coatings Technology. 2008;202(14): 3208–3214.

[24] Walsh F.C., Ponce de Leon C.. A review of the electrodeposition of metal matrix composite coatings by inclusion of particles in a metal layer: an established and diversifying technology. Transactions of the IMF. 2014;92(2):83-98.

[25] Sharma G., Yadava Y.K., Sharma V.K.. Characteristics of Electrocodeposited Ni–Co–SiC Composite Coating. Bulletin of Materials Science. 2006;29(5):491-496.

[26] Shrestha N.K., Kawai M., Saji T.. Co-deposition of B4C particles and nickel under the influence of a redox-active surfactant and anti-wear property of the coatings. Surface & Coatings Technology. 2005;200:2414–2419.

[27] Hou K.H., Ger M.D., Wang L.M, Ke S.T.. The wear behaviour of electro-codeposited Ni–SiC composites. Wear. 2002;253(9-10):994–1003.

[28] Ouyang J., Liang X., Wen J., Liu Z., Yang Z.. Electrodeposition and tribological properties of self-lubricating Ni—BaCr2O4 composite coatings. Wear. 2011;271(9-10): 2037–2045.

[29] Shrestha N.K., Sakurada K., Masuko M., Saji T.. Composite coatings of nickel and ceramic particles prepared in two steps. N. K. Shrestha, K. Sakurada, M. Masuko and T. Saji,. 2001;140(2):175–181.

[30] Shrestha N.K., Masukob M., Saji T.. Composite Plating of Ni/SiC Using Azo-cationic Surfactants and Wear Resistance of Coatings. Wear. 2003;254(5-6):555–564.

[31] García-Lecina E., García-Urrutia C., Díez J.A., Fornell J., Pellicer E., Sort J.. Codeposition of inorganic fullerene-like WS2 nanoparticles in an electrodeposited nickel matrix under the influence of ultrasonic agitation. Electrochimica Acta. 2013;114:859–867.

[32] Wang L.M.. Journal of Applied Electrochemistry. Effect of surfactant BAS on MoS2 codeposition behaviour. 2008;38(2):245-249.

[33] Hovestad A., Jansen L.J.J.. Electrochemical codeposition of inert particles in a metallic matrix. Journal of Applied Electrochemistry. 1995;25(6):519-527.

[34] Popov B.N., Yin K., White R.E.. Galvanostatic Pulse and Pulse Reverse Plating of Nickel-Iron Alloys from Electrolytes Containing Organic Compounds on a Rotating Disk Electrode. Journal of The Electrochemical Society. 1993;140(5): 1321-1330.

[35] Wünsche F., Bund A., Plieth W.. Investigations on the electrochemical preparation of gold-nanoparticle composites. J. Solid State Electrochem. 2004;8:209-213

[36] Nickel Institute. http://www.nickelinstitute.org/ [Internet]. 2013. Available from: http://www.nickelinstitute.org/~/Media/Files/TechnicalLiterature/NPH_141015.pdf

[37] Ahmad Y H., Mohamed M.A.. Electrodeposition of Nanostructured Nickel-Ceramic Composite Coatings: A review. Int. J. Electrochem. Sci.. 2014;9:1942 - 1963.

[38] Shao W., Nabb D., Renevier N., Sherrington I., Luo J.K.. Materials Science and Engineering. Mechanical and corrosion resistance properties of TiO2 nanoparticles reinforced Ni coating by. 2012;40

[39] Yar-Mukhamedova G.S.. Investigation of the Texture of Composite Electrodeposited Chromium–Carbon Coatings. Materials Science. 2000;36(5):752-754.

[40] Palumbo G., Brooks I., Mccrea J., Hibbard G.D., Gonzales F., Tomantschger K.. Process for Electroplating Metallic and Metal MAtrix Composite Foils, Coatings and Microcomponents. European PAtent Specification. 2008;EP 1 516 076 B1

[41] Hu C., Bai A.. Composition control of electroplated nickel]phosphorus. Surface and Coatings Technology. 2001;137:181]187.

[42] Stein B.. A Practical Guide to Understanding, Measuring and Controlling Stress in Electroformed Metals. In: ESF Electroforming Symposium; Las Vegas. Las Vegas: 1996.