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Influence of Bath Composition on the Structure and Properties of Nickel Coatings Produced by Electrodeposition Technique

Işıl BİRLİK*[1], N. Funda AK AZEM[1]

[1]Dokuz Eylül Üniversitesi, Mühendislik Fakültesi, Metalurji ve Malzeme Mühendisliği Bölümü, 35390, Buca-İzmir
(ORCID: 0000-0003-3098-2001; ORCID: 0000-0002-4446-1437)

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Abstract: Electrodeposited nickel coatings are extensively used in engineering applications due to their excellent corrosion and wear resistance and easy mechanical operation. The structural characteristics, corrosion and mechanical properties of nickel coatings are related to the deposition parameters; such as bath component, composition, current density, pH, deposition time and additives. Electrodeposition technique is one of the most technologically feasible and economical techniques for producing metallic coatings. Watts bath is the most commonly applied nickel electrodeposition bath. Aim of this study is to optimize Watts bath composition by changing nickel chloride concentration and to investigate structural, morphological, corrosion and mechanical properties of produced coatings. It was found that coatings prepared with 0.17M nickel chloride concentration in Watts bath present the better corrosion resistance and mechanical property.

Banyo Kompozisyonunun Elektroçöktürme Yöntemi ile Üretilen Nikel Kaplamaların Yapısı ve Özelliklerine Etkisi

Anahtar Kelimeler
Nikel kaplama,
Watts banyosu,
Elektroçöktürme,
Yüzey özellikleri,
Korozyon

Özet: Elektroçöktürülmüş nikel kaplamalar mükemmel korozyon ve aşınma dayanımları ve mekanik olarak kolay işlenebilirlikleri sebebi ile mühendislik uygulamalarında yaygın olarak kullanılmaktadır. Nikel kaplamaların yapısal karakteristikleri, korozyon ve mekanik özellikleri banyo bileşenleri, kompozisyonları, akım yoğunluğu, pH, kaplama süresi ve katkılar gibi kaplama parametrelerine bağlıdır. Elektroçöktürme tekniği metalik kaplamaların üretiminde kullanılan teknolojik olarak en uygulanabilir ve ekonomik yöntemlerden birisidir. Watts banyosu nikelin elektroçöktürülmesinde en yaygın olarak kullanılan banyodur. Bu çalışmanın amacı nikel klorür konsantrasyonunun değiştirilmesi ile Watts banyo kompozisyonunu optimize edilmesi ve üretilen kaplamaların yapısal, morfolojik, korozyon ve mekanik özelliklerinin incelenmesidir. 0,17M nikel klorür konsantrasyonuna sahip Watts banyosu ile hazırlanmış olan kaplamaların daha iyi korozyon direncine ve mekanik özelliğe sahip olduğu bulunmuştur.

**Corresponding author: isil.kayatekin@deu.edu.tr*

1. Introduction

Nickel is one of the most important metals applied by electrodeposition. It is used extensively in many engineering applications [1, 2]. Nickel deposits improve the appearance, extend the life and the performance of materials and products in different applications [3]. It is driven by numerous actual industrial or potential applications, such as deposition of protective, functional and decorative coatings, magnetic structures, micro-electromechanical systems, substrates for hydrogen evolution, codeposition of alloys or composite layers [4, 5].

Nickel and nickel alloy coatings are commonly deposited by electrodeposition, electroless plating, thermal spraying, weld surfacing, pulsed-current plating, and chemical vapour deposition (CVD) techniques [6]. Electrochemical methods of coating metallic layers are attractive due to: (a) low cost, as it involves minor modification of conventional electrodeposition technologies, (b) easy of control, as the electrodeposition parameters can be easily controlled to produce the required crystal grain size, alloy chemistry and texture, and (c) versatility, as the codeposition technology can produce a variety of novel materials such as nanocomposites [7].

Nickel coating is the electrolytic deposition of a layer of nickel on a substrate. The process involves the dissolution of one electrode (the anode) and the deposition of metallic nickel on the other electrode (the cathode). Direct current is applied between the anode (positive) and the cathode (negative). The aqueous solution of the nickel salts gives the conductivity between the electrodes. The length of time that the substrate is immersed in the electrolyte is the major factor in determining the thickness of the resulting deposit. The thermal, electrical and chemical characteristics of the electrolyte bath also influence the deposition process [6].

The structural characteristics and properties of nickel deposits are closely related to the plating parameters, such as bath component, composition, pH, bath temperature, current density, stirring and addition of organic compounds [8, 9]. The selection of electroplating bath depends mainly on the characteristics of the nickel deposit required [6]. Various baths such as Watts or sulphamate are used for obtaining uniform electrodeposits with required quality and morphology [5, 10]. Nickel deposit by using sulfamate bath has low stress and good mechanical properties, on the other hand it is considerably expensive [6]. Watts baths are used mainly for electrodeposition of coatings [5, 10]. The Watts electrolyte composed of nickel sulphate, nickel chloride, and boric acid is widely applied for nickel electrodeposition [11]. Nickel sulphate is the principal ingredient; it is used as the main source of nickel ions because it is readily soluble (570g/l 50^{o}C), relatively cheap, commercially available and is a source of uncomplexed nickel ions. In nickel plating solutions the activity of nickel ions is governed by the concentration of nickel salts in solution, their degree of dissociation and the nature and concentration of other components of the solution. If the concentration of Ni^{2+} available for deposition is low, burnt deposits will be produced at a relatively low current density, and in addition the limiting current density will be low. For these reasons the concentration of nickel sulphate must be high [12]. The presence of chloride has two main effects: it assists anode corrosion and increases the diffusion coefficient of nickel ions thus permitting a higher limiting current density. A small amount of nickel chloride is usually enough to minimize anode passivity especially at high current densities [6, 12]. Boric acid is used as a buffering agent in Watts nickel solution in order to maintain the pH of the cathode at a predetermined value. Boric acid solutions of the strength used in Watts nickel solutions have a pH of about 4.0 due to the nickel ions. From this, it would appear that boric acid should be most suitable as a buffer at about pH 4, which is rather convenient, since most nickel solutions are operated near this value [12]. Experimentally typical Watts bath composition is 240-340 g/l $NiSO_4.7H_2O$, 30-60 g/l $NiCI_2$. $6H_2O$ and 20-40 g/l H_3BO_3 [8]. There are many studies in the field of nickel electrodeposition but there is still need to develop electrolytes to obtain deposits at reduced concentration of precursor salts. Therefore, it is also important for decreasing nickel plating costs and electroplating sewage. Aim of this study is to optimize Watts bath composition by changing nickel chloride concentration and to investigate structural, morphological, corrosion and mechanical properties of produced coatings.

2. Material and Method

Nickel coatings on steel substrates were electrodeposited by using a standard nickel Watts bath with varying nickel chloride concentrations of 0.08-0.25 M (composition is given in Table 1).

Table 1. Composition of the deposition bath.

Chemicals	Amount of constituents [M]
Nickel (II) Sulfate Hexahydrate ($NiSO_4.6H_2O$)	0.91
Nickel (III) Chloride Hexahydrate ($NiCl_2.6H_2O$)	0.08-0.25
Boric Acid (H_3BO_3)	0.49

All process parameters are given in Table 2. Distance between the nickel anode and steel cathode was 3 cm. Nomenclature of Nickel coatings are given in Table 3.

Table 2. Deposition parameters of coatings.

Electrodeposition Parameters	
Current Density (A/dm^2)	3
Time (min.)	15
Temperature (̊C)	45
pH	3.94-4.03

Table 3. Nomenclature of the coatings.

$NiCl_2.6H_2O$ (M)	Nomenclature
0.08	C1
0.13	C2
0.17	C3
0.21	C4
0.25	C5

The phase analysis of the deposited films was analyzed by X-ray diffractometer (XRD, Rigaku D/max-2200/PC) with grazing incident of 1° at 40 kV and 36 mA using CuK_α radiation. The crystalline size of Ni coating was calculated through the Scherrer equation. The surface morphology and elemental composition of the obtained coatings were examined using a scanning electron microscope (SEM). The surface roughness of coatings was measured by Surface Roughness Tester Mitutoyo SJ301. The corrosion measurements were carried out using a Gamry potentiostat/galvanostat system controlled by the Gamry Framework software and Echem Analyst software, for the acquisition and analysis of electrochemical data, respectively. A conventional three-electrode cell was used for the corrosion experiments. Graphite electrode, Ag/AgCl, and prepared coatings were used as counter electrode, reference electrode, and working electrode, respectively. Measurement of the open circuit potentials (OCP) were performed in the test solution for 30 min. The potentiodynamic curves were obtained sweeping potential, starting at OCP, from -0.25V vs OCP to 0.6 V vs Ag/AgCl at a scan rate of 1 mV/s. The Vickers hardness was measured by a Shimadzu HMV-2 model microhardness tester with a load of 50 g for 10 s.

3. Results

X-ray diffractometer patterns of coatings produced by using different concentrations of nickel chloride are shown in Figure 1. The XRD pattern is characterized by (111), (200), and (220) diffraction peaks of Ni phase (JCPDS 70-1849). That implies nickel coatings are successfully deposited on the steel substrates. According to the pattern, (111) and (200) planes are the main diffractions. As shown in the figure, with the increase of nickel chloride in the electrolyte, the intensity of (200) peaks is slightly increased and act as the main diffraction plane. The results indicate that the crystallographic orientation was not randomly oriented, but grew at a specific orientation and influenced by nickel chloride concentration. The crystalline sizes of Nickel coatings are tabulated in Table 4. Crystalline sizes are 20 nm and do not change for different coatings.

The surface morphology of the electrodeposited nickel coatings are shown in Figure 2. It shows from Figure 2 that the all deposits are crack free and exhibit nodular morphology regardless of the concentration of Watts bath at which they were deposited. It is obvious that surface morphology consist of pyramidal-shaped crystallites surrounded by finer grains and nodular structures and does not significantly influenced by the concentration of nickel chloride in the bath. Additionally, there is a slight amount of increase at the nodular structure and denser surface for the coating prepared from bath containing 0.25M nickel chloride.

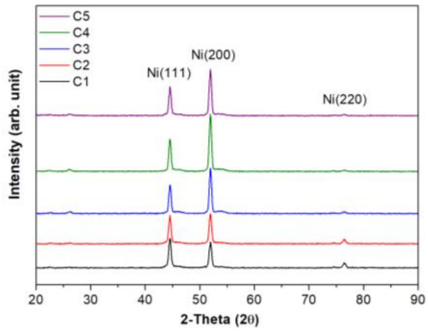

Figure 1. X-ray diffraction patterns of Ni coatings produced at different concentrations of nickel chloride.

Table 4. Crystalline sizes (nm) of coatings.

	C1	C2	C3	C4	C5
Ni (111)	20	19	20	20	20
Ni (200)	18	19	21	20	20

The main surface roughness parameters R_a (arithmetical mean roughness), R_z (mean roughness depth), rms (R_q-root mean square), R_{sk} (skewness) and R_{ku} (kurtosis) are listed in Table 5. The results showed that the change in the roughness values was not so significant. Ra values measured below 1 and close to each other for the nickel coatings prepared from baths containing nickel chloride concentration below 0.25M and increased to 1.43 for the coating prepared at 0.25 M concentration. This was in agreement with the surface morphology investigations.

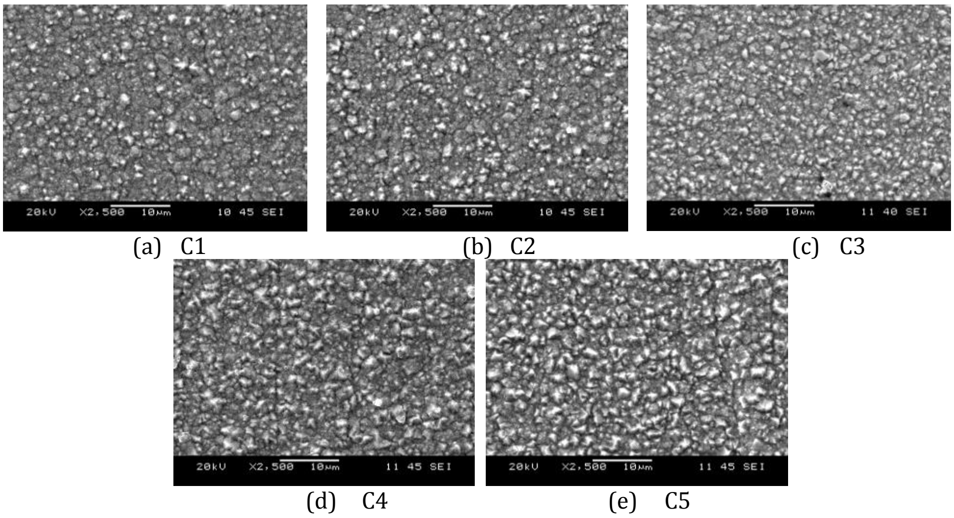

Figure 2. Surface morphology of nickel coatings with different concentrations of Nickel chloride in the bath.

Skewness is a measure of the asymmetry of the profile about the mean line. A symmetrical height distribution, i.e. with as many peaks as valleys, has zero skewness. Profiles with peaks removed or deep scratches have negative skewness. Profiles with valleys filled in or high peaks have positive skewness. Kurtosis describes the sharpness of the probability of the profile if $R_{ku}<3$ the distribution curve is said to be platykurtoic and has relatively few high peaks and low valleys. If $R_{ku}>3$ the distribution curve is said to be leptokurtoic and has relatively many high peaks and low valleys [13]. In our case, the coating with 0.25M nickel chloride concentration has a negative skewness, indicating a lot of valleys, probably due to presence of more nodular structures of the coating. If the skewness has positive values, the surfaces consisted in few valleys and a lot of peaks. The other coatings addition exhibited a positive skewness and this result is consistent with surface morphology investigation. A good corrosion resistance was found when the skewness has more positive values, while negative skewness indicates the pitting corrosion [14]. Rougher surfaces with deeper groves have lower openness (ratio of width to depth at opening of the grooves) which limit the diffusion of the corrosive ions out of the formed grooves, hence have a higher possibility to grow larger. On smooth surfaces however the formation of stable passive film is more possible to occur which will result in less corrosion [15]. In our case, coatings with nickel chloride concentration lower than 0.25M proved to have positive skewness, expected to have superior corrosion resistance than others.

Coating with 0.13M nickel chloride concentration revealed a kurtosis value higher than 3 indicating relatively many high peaks and low valleys. All other coatings revealed a kurtosis value lower than 3.

Table 5. Surface roughness parameters of the coatings.

	R_a	R_z	R_q	R_{sk}	R_{ku}
C1	0,88	4,58	1,29	0,05	-1,10
C2	0,57	2,62	1,11	2,61	7,14
C3	0,97	3,56	1,00	0,46	-1,37
C4	0,32	1,58	0,37	0,99	1,28
C5	1,43	7,73	1,65	-1,20	2,25

The evolution of the open circuit potential in %3.5wt NaCl solution is presented in Figure 3. In the studies of Mansfeld [16] and Hack et al. [17] reported that the open circuit potential (E_{oc}) is the parameter which describes the nobility of a material at contact with a corrosive solution. A higher corrosion resistance is commonly associated to a higher E_{oc} value [16, 17]. After approximately 20 min, the E_{oc} potential exhibited a stable value for all the coatings, until the end of the test. It can be observed that there is an increase of the E_{oc} potential with the decreasing nickel chloride concentration of the coatings.

Various criteria have been proposed to evaluate the behavior of the materials at corrosive attack. First one is referred to the corrosion potential ($E_{i=0}$). A more positive value of $E_{i=0}$ indicates a better corrosion resistance [16, 18]. Potentiodynamic polarization curves of nickel coatings are presented in Figure 4. Electrochemical parameters of the corrosion potential ($E_{i=0}$) and corrosion current density (i_{cor}) results are summarized in Table 6. The corrosion potential of the coating with 0.17M nickel chloride concentration is higher than other coatings. It can be concluded that $E_{i=0}$ value of this coating shifted to noble direction compared to other coatings, thus suggesting the improved corrosion resistance of the coating. The coating with 0.25M nickel chloride concentration presented the most electronegative $E_{i=0}$ value indicating a poor resistance in NaCl solution.

Electroplated nickel coatings provide ductility, excellent corrosion resistance and good wear resistance, which primarily depends on the hardness ranging from 150 to 700 HV. The typical mechanical properties result from the electroplating bath operation (Watts nickel bath or a nickel sulfamate bath) and solution composition variables.

However, the electroplating variables which enhance hardness and wear resistance likewise increase undesirable residual stress values [19]. The hardness of the coatings prepared with different concentrations of Nickel chloride in the bath are presented in Figure 5.

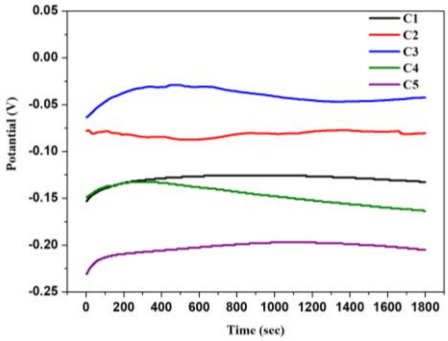

Figure 3. Evolution of open circuit potential (E_{OC}) vs. time.

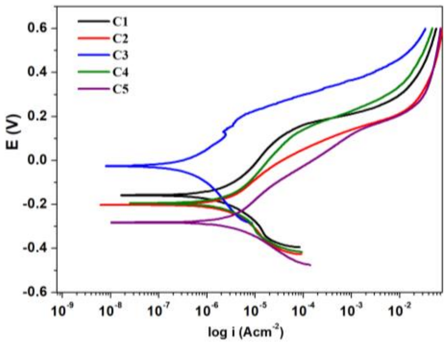

Figure 4. Potentiodynamic polarization curves of the investigated coatings.

Table 6. Electrochemical parameters of nickel coatings prepared with different concentrations of Nickel chloride in the bath.

	C1	C2	C3	C4	C5
i_{cor} (nA/cm^2)	284	448	114	446	597
$E_{i=0}$ (mV)	-157	-196	-29	-197	-281
Corrosion rate (10^{-3} mpy)	64,80	102,5	26,09	101,9	136,4

Hardness values of the deposited coatings are in the range of 231-262 HV. Hardness of the coating with 0.17M nickel chloride concentration is higher compared to other coatings. It can be found that the hardness values of coatings until 0.25M nickel chloride concentration slightly differs from each other but there is noticeable decrease at hardness at 0.25M nickel chloride concentration. This result is consistent with the corrosion behavior of coatings.

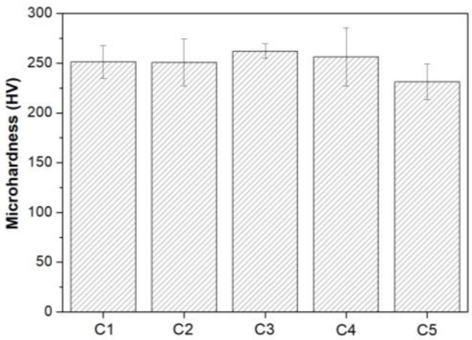

Figure 5. The hardness of the coatings prepared with different concentrations of Nickel chloride in the bath

4. Discussion and Conclusion

In this study, nickel coatings were deposited on steel substrates by electrodeposition technique, structural, corrosion and mechanical behavior of the coatings were investigated. The results can be summarized as follows:

- According to the XRD results, coatings are characterized by (111), (200), and (220) diffraction peaks of Ni phase.
- All coatings are successfully deposited on the steel substrates and surface morphology of the coatings consist of pyramidal-shaped crystallites surrounded by finer grains and nodular structures.
- Coating with 0.17M nickel chloride concentration has improved corrosion resistance in NaCl solution.
- Hardness of the coating with 0.17M nickel chloride concentration is higher compared to other coatings.

As a conclusion, coatings prepared from a Watts bath containing 0.17M nickel chloride concentration revealed the highest corrosion resistance and better mechanical property.

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