Effects of Deposition Time on Surface Properties of Co-Ni-Fe Alloy Synthesised on Hex Bolts

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Abstract*: *Electrodeposition is one of the methods used to perform a protective coating. It is commonly used in the industry because it capable to produce coating with good properties. The objective of this study is to perform the electrodeposition process of cobalt-nickel-iron (Co-Ni-Fe) alloy coatings onto the mild steel hex bolt (M12 x 50). This study also investigated the effect of deposition time on thickness, hardness, surface roughness and the corrosion rate of the electrodeposited Co-Ni-Fe alloy coating. The electrodeposition was performed on the substrate with four different deposition times: 15, 30, 60 and 120 minutes. The working temperature of the sulphate solution was 60ºC and the current supplied was 1.5 A. All the samples undergone surface properties analysis. For the corrosion rate, it was conducted using the potentiodynamic polarization (PDP) test. There were three types of solution used for PDP; hydrochloric acid (HCL), distilled water and sodium hydroxide (NaOH) with pH 3, pH 7 and pH 9 respectively. Scanning electron microscope (SEM) image showed the thinnest coating was 4.74 µm for deposition time of 15 minutes and the thickest coating with 102.77 µm. The coating hardness decreased as deposition time increased and the lowest hardness obtained was 349.6 HV at 120 minutes deposition time. The surface roughness decreased until 60 minutes of deposition time (1.0279 µm) and started to increase at 120 minutes of deposition time (4.0655 µm). The sample with 60 minutes of deposition time had the lowest corrosion rate in all solution; pH 3 = 0.1311 mmpy, pH 7 = 0.0393 mmpy and pH 9 = 0.0512 mmpy. Therefore, it is proven that deposition time is an important plating parameters that determine the surface properties and subsequently the corrosion resistance of electrodeposited Co-Ni-Fe alloy.

Keywords* : *Co-Ni-Fe, corrosion, deposition time, hex bolts, surface properties.

I. INTRODUCTION

Corrosion is one of the biggest problems faced by the industries in the world. It is an on-going issue because it may shorten the life span of the product. Besides, corrosion may causes incidents at the industrial area and also harm the environment as well. Recently Martin Fenker *et al.* [1] stated that the loss because of corrosion is around $2,151,100 - $2,868,000 worldwide. If the corrosion problem is not solved wisely, serious issues including negative social impact, loss of life, and water resources and environmental pollution may occur [2]. Therefore, coatings are solution for this issue. It is known that, coatings play a big role to avoid the corrosion because it can prevent steel surface from directly exposed to the air or environment. There are varieties of coating processes and technologies had been created and all of them have the same goal to prevent corrosion.

Metal likes mild steel is commonly used in the industries. Being low corrosion resistance, it requires intricate storage to prevent it from corrode. Several factors influence the corrosion behavior of steel like nature of metal, environment, concentration of electrolyte, temperature, electrode potential and hydrogen over voltage. A reaction between ferrous ions and hydroxyl ion is called anodic reaction which can result from the hydrated oxide which called "rust".

Electrodeposition is one of the method commonly used in the industries as a surface treatment because it is easy to handle and most importantly is low-cost [3], [4]. Electrodeposition is the process where base metal is coated with a thin layer of other metal to improve properties of materials. Materials from polymers, metals, alloys and composites can use this method as well. Usually, nanocrystallines formed with grain size less than 100nm in diameter [5], [6]. So, it will affect the physical, chemical and mechanical properties of the materials. Smaller grain size may improve the protection of the corrosion materials towards the materials. Based on previous study, cobalt-nickel-alloy (Co-Ni-Fe) alloy coating has good strength and wear properties [4], [7]. It also can protect any substrate from atmospheric corrosion. This will improve the existing surface properties of mild steel hex bolt if it is coated with Co-Ni-Fe alloy.

Previously, coating was synthesised using different deposition times on flat metal sheet instead of hex bolts. Another study conducted by N. A. Resali *et al.* tested Co-Ni-Fe coating in solutions with different pH value using one set of parameter only [8]. So, the corrosion behavior of sample synthesised using different plating parameters were unknown.

The objective of this study was to investigate the various surface properties of nanocrystallines Co-Ni-Fe alloy coating synthesised using different deposition time. Then, the corrosion rate was analysed too because different deposition times give different surface properties and subsequently, the corrosion resistance will also differ.

Therefore, the approach begun by electrodeposit Co-Ni-Fe onto hex bolts with different deposition time in the same bath condition. Scanning electron microscope (SEM) was used to measure thickness of coating.

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Vickers microhardness indenter was used to measure the microhardness of each sample. Surface roughness was measured using Alicona 3-D measurement system. These samples were then immersed in different pH solution to conduct electrochemical tests which were potentiodynamic polarization (PDP).

II. METHODOLOGY

A. Materials

Material used for the experiment was M12 x 50 hex bolt made of AISI 1018 Steel is shown in Fig. 1. Mild steel contains approximately 0.05% – 0.25% of carbon which make it more ductile and malleable. Firstly, the oil residue from manufacturing process was removed from the surface by using thinner. Brush was used to ensure the threads of bolt were free from oil residue. Then, the bolts were immersed in diluted hydrochloric acid for about 30 minutes to remove the rust. Next, bolts were put into ultrasonic cleaner filled with distilled water and cleaned for 5 minutes to remove contaminants and impurities.

Fig. 1: Hex bolt

B. Bath Preparation

Bath preparation was needed before electrodeposition process. The composition of the chemical substances used is shown in the Table I. All the chemical substances were weighed using the digital scale and mixed with 2 liter of distilled water.

Table I: Composition of electrolyte

Chemical Substances	Weight (g)
Volume of distilled water	2L
Cobalt (II) Sulphate	28.12
Nickel (II) Sulphate	70.08
Iron (II) Sulphate	11.12
Boric Acid	32.96
Ascorbic Acid	23.48
Saccharin	2.72

C. Electrodeposition Process

The mixture solution was stirred and heated until the temperature 60ºC using hotplate stirrer prior to electrodeposition. Then, the electrolyte was poured into a glass aquarium. The bolt was immersed in the electrolyte and placed between two pieces of platinized titanium mesh to ensure uniform deposit distribution on the bolt. The platinized titanium connected with positive terminal (anode) while the bolt was connected with the negative terminal (cathode). Current was supplied at fixed value of 1.5A. The processes were done at four deposition times which were 15, 30, 60 and 120 minutes and different bolts were used for every deposition time. Next, the bolts were rinsed with distilled water and dried with laboratory tissues paper before proceeding with the tests to investigate their properties and corrosion behaviour.

D. SEM Analysis

A cross-section of the bolt was required to determine the coating thickness of each sample thickness. The bolts heads were separated from the threads using grinder and the hex head pieces were cut in half. Scanning electron microscope (SEM) images was used to measure the thickness of Co-Ni-Fe coating. SEM images were taken using 15 kV of energy and 100x magnification.

E. Vickers Microhardness

Mitutoyo MVK-H1 Hardness Testing machine with a diamond intender was used to obtain the microhardness of the Co-Ni-Fe alloy coating. The test was conducted on the side of head because a flat surface has lower uncertainty readings. The specimens placed perpendicular to the spindle or the diamond intender. A load of 1kg was applied on the flat surface for 10 seconds. The test was conducted at three different spots and the data were calculated to get the average microhardness.

F. Surface Roughness

Surface roughness of the Co-Ni-Fe alloy coating was measured using Alicona 3-D Surface Measurement. It is a high resolution equipment which able to measure the surface roughness (Ra) of the sample. 5x magnification lens was used on sample with 120 minutes deposition time and 10x lens was used for the rest of the samples to get clear images with suitable vertical resolution. The mapping process took 20 minutes to scan each sample's surface to produce high resolution 3D image. The value of Ra was recorded and compared.

G. Potentiodynamic Polarization

In order to obtain the corrosion rate of the coating, potentiodynamic polarization (PDP) method were employed. Three solutions with different pH values were prepared for the test. Acidic solution was made from hydrochloric acid (HCL) diluted with distilled water until the pH value dropped to 3. Distilled water was used as the neutral medium with pH 7. The alkaline solution with pH 9 was the mixture between sodium hydroxide (NaOH) and distilled water. Graphite rod (counter electrode), saturated calomel electrode (reference electrode), and coated sample (working electrode) were immersed in beaker containing 300 ml solution and connected to the potentiostat of a computer.

The sample surface area, weight and density were keyed into the input value of GAMRY Framework software. The test begun with the open circuit potential (OCP) for 60 minutes to make sure the reference electrode reach a steady state [9]. Then, PDP was conducted for 5 minutes with a scan rate of 0.5 mV/s. Tafel fit was used to calculate the corrosion rate in the presence of value E_{corr} and I_{corr} to replicate the technique used by N. A. Resali *et al.* [10]. The test was repeated using three types of solution which were acidic (pH 3), distilled water (pH 7) and alkaline (pH 9).

III. RESULTS AND DISCUSSION

A. Thickness

The image of cross-section of coated sample taken using SEM shown in Fig. 2 with thickness measurement at three different spot. There is a horizontal interface that separates the coating from the substrate. The average of three measurement for each sample are plotted in Fig. 3.

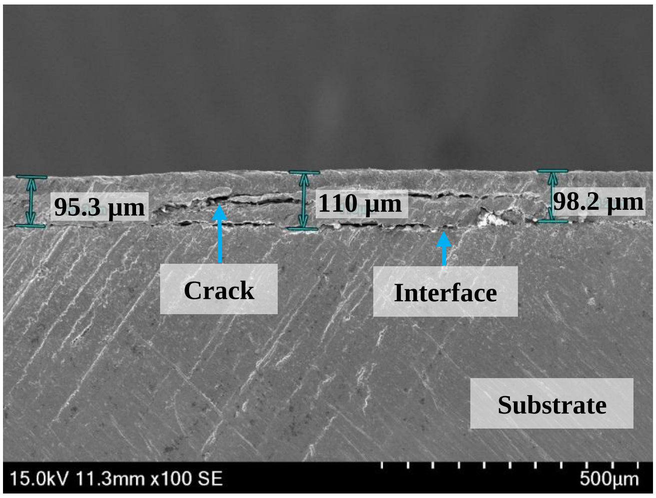

Fig. 2: Thickness dimension of the Co-Ni-Fe alloy coating for 120 minutes of deposition time.

The thickness varies across four deposition times. For 15 minutes deposition time, coating had thickness of 4.74 ± 1.16 μm whereas the coating with 102.77 ± 7.35 μm thickness was synthesised for 120 minutes. Theoretically, the values are acceptable since the longer the deposition time, higher the thickness value. The thickness increased linearly from 15 minutes until 60 minutes in Fig. 3 and then a change at 120 minutes. This surge of thickness change is also observed by K. M. Hyie *et al.* [11] albeit occurred at different deposition time.

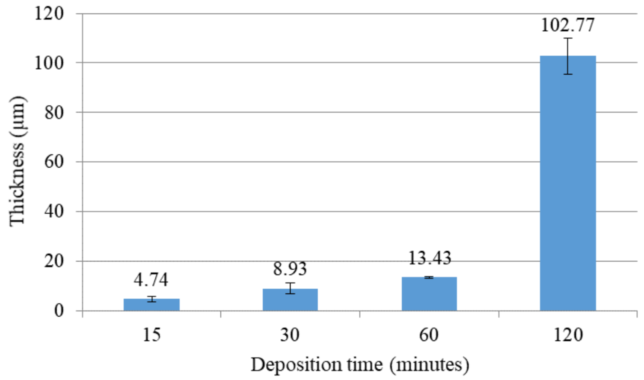

Fig. 3: Graph of thickness of Co-Ni-Fe against deposition time.

Based on Fig. 3, the high thickness value increment was influenced by the presence of major cracks formed in the middle of coating, also known as median cracks which induced by voids. The high number of voids also found in sample with the longest deposition time which reported by N. A. Resali *et al.* [12]. The voids created weak spots where the grain able to slides freely along the median plane [13]. The cracks propagated along the plane when it reached its limit of tensile stress. It may be solved by using the right amount of saccharin as additives to reduce residual stress. Besides, the gap at substrate-coating interface is an indicator that the coating lost the adhesion strength.

B. Microhardness

Based on the result shown in Fig. 4, the microhardness value declines as the deposition time gets longer. This similar trend was observed by N. A. Resali *et al.* [10] where 90 minutes of deposition time had lower hardness compared to 60 minutes and 30 minutes of deposition time. The highest value of hardness in Fig. 4 is 442.4 ± 2.6 HV but decreased 17% when deposited for 120 minutes. A study by N. R. N. M. Masdek *et al.* [14] stated that the microhardness of coating attributed by the grain size and iron content. At 15 minutes of deposition times, the particles were larger and able to create smaller number of particles boundaries compared to other sample. These particles boundaries acted as the barriers that can prevent the dislocation of motion and control direction of motion.

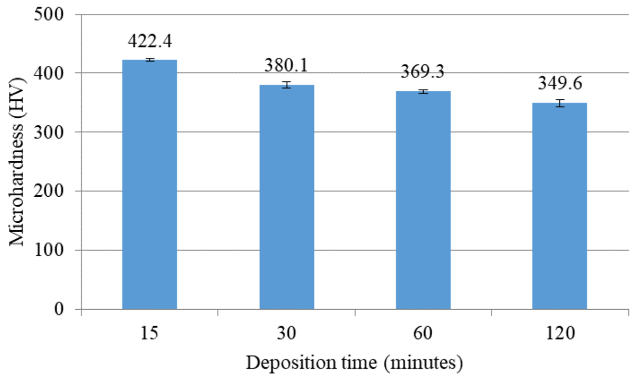

Fig. 4: Graph of hardness of Co-Ni-Fe against deposition time.

C. Surface Roughness

Surface roughness was analysed based on the number of peaks per unit length, scribe undercutting resistance and has a measurable impact on adhesive [15]. Fig. 5 shows the average value of surface roughness of each samples. Surface roughness decreased until 60 minutes of deposition times. At this point, the surface became smoother along with deposition time. However, the Ra value of 120 minutes deposition time increases up to 4.07 ± 0.24 μm compared to 60 minutes sample which only has 1.03 ± 0.02 μm.

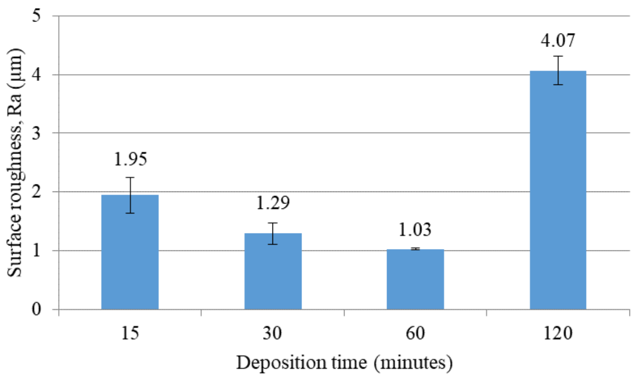

Fig. 5: Graph of roughness of Co-Ni-Fe against deposition time.

The increment happened due to the presence of voids during electrodeposition process in sulphate bath [10]. The voids also plagued the thickness reading as discussed in previous section. Besides, the stability of the temperature during the electrodeposition process affects the surface roughness of coating [16]. So, the longer deposition time introduced another issue: temperature inconsistency. The unstable temperature changed the Co-Ni-Fe crystal size and grain size [17].

D. Corrosion Rate

Fig. 6 shows the results for the potentiodynamic polarization curves of electrodeposition Co-Ni-Fe coating for all four type of specimens at different pH (3, 7 and 9) solutions.

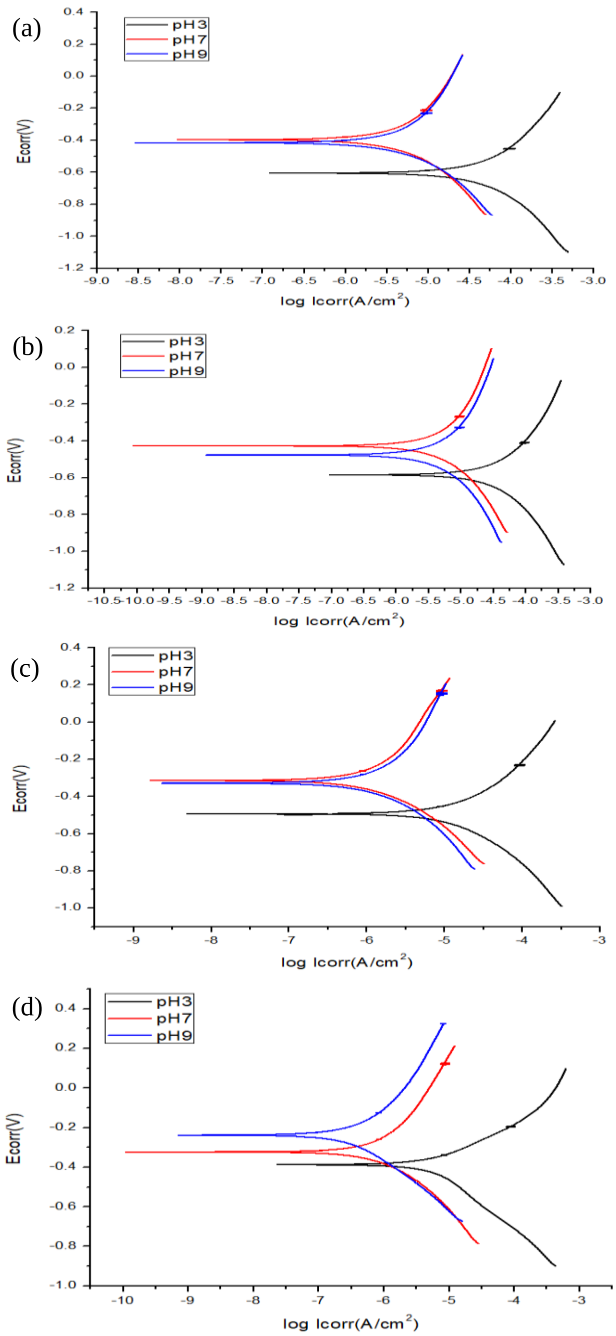

Fig. 6: Potentiodynamic polarization curves of Co-Ni-Fe electrodeposited substrates for four different deposition times: (a) 15 minutes, (b) 30 minutes, (c) 60 minutes, and (d) 120 minutes.

All curves exhibited an active behaviour. Sample with 60 minutes of deposition time had the lowest corrosion rate in all pH solutions compared to other deposition times. Meanwhile, the highest corrosion rate were recorded by sample with 15 minutes deposition time in all pH solutions. Grain size and the compactness of the microstructure played an important role that influence the corrosion rate [16], [17].

Based on the Table II, the lowest corrosion rate recorded is 0.0393 mmpy for 60 minutes sample at pH 7 solution and the highest corrosion rate is 8.3480 mmpy on 15 minutes sample in pH 3 solution. Using relative scale for corrosion of metal outlined by R. Revie *et al.* [20], corrosion rate less than 0.125 mmpy is the best. The moderate corrosion rate is between 0.125 mmpy to 1.25 mmpy. Lastly, the corrosion rate can be considered worst when the rate is more than 1.25 mmpy. Therefore, in terms of deposition time parameters, sample with 60 minutes deposition time has the best corrosion resistance because the other deposition times can be categorised as worst corrosion rate. Based on the value of surface roughness (Ra), sample with 60 minutes of deposition time had the smoothest surface. Therefore, it able to minimize the corrosion rate because pitting corrosion is less likely to occur on smooth and uniform surface.

In terms of pH value, the range of corrosion rate in the alkaline environment (pH 9) is between 0.2308 mmpy to 0.0512 mmpy for all samples, while the range of corrosion rate in acidic environment (pH 3) is between 8.348 mmpy to 0.1311 mmpy for all samples. The coating exhibited the lowest corrosion rate in alkaline solution (pH 9) while the highest corrosion rate occurred in acidic solution (pH 3). Therefore, this study agrees with N. A. Resali [8] that Co-Ni-Fe suffered from corrosion more in acidic solution than alkaline. While for alkaline solution, K. M. Hyie *et al.* stated the refinement mixed morphologies of spherical and dendritic structure which exhibits less percentage of oxygen elements for the smallest particle size which provides higher resistance towards corrosion [6]. Thus, the mechanical properties especially surface roughness of the alloy is important in order to control the corrosion behaviour.

Table II: Corrosion rate of sample synthesized using different deposition times in three types of solution.

Deposition time (minutes)	pH value	Corrosion rate (mmpy)
15	3	8.3480
	7	0.2671
	9	0.2308
30	3	2.1000
	7	0.2122
	9	0.1916
60	3	0.1311
	7	0.0393
	9	0.0512
120	3	0.2375
	7	0.2562
	9	0.1279

IV. CONCLUSION

Electrodeposition of nanocrystallines Co-Ni-Fe alloy coating on mild steel bolt was successfully achieved. This study analyses the surface properties of Co-Ni-Fe on mild steel bolt including the hardness, thickness and surface roughness. All the mechanical properties affects the characteristics of the corrosion of the coating. Samples with different deposition time showed different surface properties. From the potentiodynamic polarization test, the corrosion rate of samples had been analysed. The following points are concluded in the study:

- The deposition time has direct relationship with the thickness of coating.
- Vickers hardness test showed that the longer the deposition time, the lower the hardness of the coating.
- The result obtained from Alicona 3-D Surface Measurement concluded that surface roughness becomes smoother within 60 minutes of deposition time. However, the surface becomes rougher when the coating process is longer than that.

Sample with 60 minutes of deposition time had the lowest corrosion rate in all solutions (acid, neutral and alkali) because corrosion is less likely to occur on low roughness surface area.

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