Synthesizing the Nanocrystalline Cobalt-Iron Coating Through The Electrodeposition Process With Different Time Deposition

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Abstract. In the engineering world, electrodeposition or electroplating has become the most popular method of surface coating in improving corrosion behavior and mechanical properties of material. Therefore in this study, CoFe nanoparticle protective coating has been synthesized on the mild steel washer using electrodeposition method. The electrodeposition was conducted in the acidic environment with the pH value range from 1 to 2 with the controlled temperature of 50°C. The influence of deposition time (30, 60, 90 minutes) towards characteristic and properties such as particle size, surface morphology, corrosion behavior, and microhardness were studied in this investigation. Several results can be obtained by doing this experiment and testing. First, the surface morphology of Cobalt Iron (CoFe) on the electrodeposited mild steel washer are obtained. In addition, the microhardness of the mild steel washer due to the different deposition time are determined. Next, the observation on the difference in the grain size of CoFe that has been electrodeposited on the mild steel plate is made. Last but not least, the corrosion behavior was investigated. CoFe nanoparticles deposited for 30 minutes produced the smallest particle size and the highest microhardness of 86.17 and 236.84 HV respectively. The CoFe nanoparticles also exhibit the slowest corrosion rate at 30 minutes as compared to others. The crystalline size also increases when the time deposition is increased. The sample with 30 minute deposition time indicate the smallest crystalline size which is 15nm. The decrement of deposition time plays an important role in synthesizing CoFe nanoparticles with good corrosion resistance and microhardness. CoFe nanoparticles obtained at 30 minutes shows high corrosion resistance compared to others. In a nutshell, it was observed that the decrement of deposition time improved mechanical and corrosion properties of CoFe nanoparticles.

Keywords— Corrosion, time deposition, electrodeposition, CoFe, mild steel

1.Introduction

Surface and coating technology is a technology that has been used in many engineering applications. The surface coating is used to modify and improve the surface properties of materials for protection in demanding contact conditions or in aggressive environment or for enhanced functional performance. In other words, the surface coating is used to increase the lifetime of components exposed to corrosive conditions. High mechanical and corrosion protective properties of nanoparticle alloy coating
are needed for the design and operation of devices, machine, and structural systems in extreme environments [1].

Electrodeposition is exceptionally versatile and the valuable application keeps being invented. The added value of this method is cost-effective and less time-consuming if compared to physical methods such as sputtering or evaporating. Moreover, by controlling deposition parameters such as deposition time, it is possible to achieve a remarkable change in the chemical composition, mechanical and corrosion properties of electrodeposited materials [2].

In this investigation, the effect of the time deposition on the corrosion behavior and microhardness of CoFe deposited mild steel washer were investigated.

2. Literature Review

A. Factors that Influenced The Rate of Corrosion

The influencing factors of the corrosion can be categorized into two types of factors which are the external factor and internal factor. The external factor is more likely related to the properties of the environment, for instance, temperature, pressure, chemical and the concentration, flow rate, the presence of the stray electric current and the presence of the dissimilar metals. Those are the parameters that can influence the rate of the corrosion. Meanwhile for the internal factor, it is commonly related to the metal properties itself. The examples of the properties are, chemical content, imperfections, structure, presence of stress and heat treatment. Therefore to combat this particular problem, surface modification of the metal material is necessary to protect them against various types of degradation [3].

B. The Effect of The Time Deposition on The Electrodeposited Material’s

The previous study was done by using different time deposition (30mins, 90mins, 120mins,) in order to investigate the effect of the Cobalt-Nickel-Iron nanoparticles coated on stainless steel substrate. The crystallite sizes of Co-Ni-Fe nanoparticles were slightly increased when the deposition time was longer. One of the purposes of the electrodeposition process is to prevent the corrosion. In term of the corrosion rate, it can be observed that the increment of the deposition time will increase the rate of corrosion. In this case, Co-Ni-Fe prepared at 30 mins deposition time showed the lowest corrosion rate compared to the 60 mins and 90 mins of deposition time [4]. It can be concluded that the smaller the particle size the higher the corrosion resistance of the material. If we look into the microhardness properties, it was found that the microhardness for the 90 mins deposition time is lower compared to those of 30mins and 60mins. Hence, the lower the deposition time, the higher the microhardness. If we relate this phenomenon to the particle size, we can say that smaller particle size will create a greater number of particle boundaries. These particles boundaries actually act as the barrier to stop the dislocation motion. In term of surface roughness, it was found that surface roughness is increased if the deposition time is increased [4].
C. Nanoparticle Materials

Nanoparticle materials are the material that have extremely small particle in their microstructure. The size of nanoparticle material could range from 1 to 100 nanometers in size. In order to enhance the mechanical and physical behavior of nanoparticle material, we need to change the particle into nano size. In term of the corrosion rate, the corrosion rate will decrease with the decrement of the particle size. Small particle size has a high volume friction fraction of particle boundaries. High volume boundaries will result in better physical and mechanical properties. Other than that, the hardness also has similar relation to the particle size. The material is said to be harder if it has smaller particle size. When we talk about the hardness, the parameter that influence the level of hardness of a certain material is the density of particle boundaries. Smaller particle size has high density of the particle boundaries which is good to disrupt the propagation of dislocations [5].

3. Methodology

In this experiment, the specimen used was a mild steel washer with a dimension of approximately 2.5 cm in diameter. The sulphate bath was prepared in order to conduct the electrodeposition process of the CoFe nanoparticles on the mild steel washer. Figure 1 shows the mild steel bolt that is used in this investigation.

![Fig. 1. Mild steel washer used in this experiment](image)

The experiment begins with the preparation of the electrolyte bath before electrodeposition process takes place. The bath is a mixture of cobalt sulphate, iron sulphate, boric acid, saccharine and also sodium chloride. Table 1 shows the mass of the compound in the bath composition. According to the previous study, boric acid and saccharine were added in the electrolyte as a pH buffer and also functioning as grain refinement agent [5]. All the substances are mixed together to form a solid chemical compound. The mixing agent used in this experiment is the distilled water and the mixing process is conducted in the beaker and the volume of distilled water is 500ml. Then, the plating bath was constantly stirred using a magnetic stirrer to ensure proper mixing of the electrolyte solution. The temperature was controlled at 50°C while the current density was maintained at 1.1 A/cm². The electrodeposition process starts with the immersing the prepared mild steel washer (cathode) into the bath parallel with the graphite rod electrode (anode).

Each experiment was carried out with a freshly prepared solution. In this experiment, the manipulated parameter is the time deposition while others parameters were kept constant. The time deposition used were 30, 60, 90 minutes. After completing the electrodeposition process, the specimen was rinsed with distilled water and then dried room temperature. The characteristic test and corrosion behavior study were made after the electrodeposition process is done.

The equipments used to investigate the characterization of CoFe coating were ULTIMA IV FD 3668N, X-ray diffractometer (XRD), and the microstructure of the CoFe coating is synthesized by Scanning Electron Microscope (SEM). The hardness of the coating sample was measured with a MITUTOYO
MVK-H1, Vickers microhardness tester. Meanwhile, to study the corrosion behavior, Salt Spray (fog) Test was conducted according to ASTM B117.

TABLE 1. Bath composition of CoFe deposition

| Bath composition | Mass of compound (g) |
|------------------|----------------------|
| Cobalt Sulphate  | 7.027                |
| Iron Sulphate    | 2.78                 |
| Sodium Chloride  | 8.244                |
| Boric Acid       | 2.0                  |
| Saccharine       | 0.6836               |

4. Results and Discussion

D. Morphology and Microstructure

The morphology and microstructural characterizations were observed by using Scanning Electron Microscope (SEM). Figure 2 shows the grain structure of the CoFe nanoparticles at different time deposition. From the finding, it can be observed that all the three samples of electrodeposited mild steel washer produced the dendritic structure, but still has the differences observed between samples. Based from the microstructure, it can be observed that the CoFe coating prepared at 30 minutes produced a compact and full structure. The coating prepared at 30 minutes also presents smaller size and lower in agglomeration [6]. It also shows no obvious voids existing on this microstructure. Next in the CoFe coating prepared at 60 minutes, the structure is also almost compact and full but there were some voids existed and it can be seen on the microstructure. It is also noted that the particle size was larger and almost combined with each other to form agglomerates [5]. The previous study clarified that the longer the deposition time, the larger the particle size [2]. Lastly, for the CoFe prepared at 90 minutes, the presence of the voids increases. It also can be noted that the particle size of this sample was larger. The presence of the voids on the microstructure of the sample is believed to come from the uncoated CoFe nanoparticle. It can be indicated that the coating is not fully covered during the electrodeposition process. The formation of the voids might be due to the existence of the oxide in the space between grains and also may be due to the agglomeration process covering the sample surface. By relating the microstructure and the corrosion resistance, it can be concluded that the presence of voids and the larger the particle size that contribute to the formation of the agglomeration will decrease the corrosion resistance [4].

The particles size for CoFe coating is determined from the measurement of the particles was taken by measuring the average grain size of at least 5 grains. The particle size of CoFe coating for 30mins, 60mins, and 90mins are 3.29μm, 6.72μm, and 7.68μm respectively. Based on the observation, the smallest grain size was found in the sample with 30 mins of deposition time. Meanwhile, the largest grain size is obtained from the sample with 90 mins of deposition time. Based on previous study [6], coating with nanocrystalline grain size often demonstrated excellent chemical, mechanical and physical properties. These characteristics are resulted from the reduction in its grain size in addition to the existence of a huge numbers of grain boundaries in the microstructure. To summarize this finding, the grain size is increased when the time of deposition increase.
Fig. 2. SEM micrograph of CoFe at (a) 30mins (b) 60mins (c) 90min

E. Microhardness

Microhardness test was conducted by taking the average measurement by using Vickers microhardness. Five measurements were performed on the different spots on the sample and the average measurement was calculated. Figure 3 shows the effect of the microhardness of the CoFe coating based on different deposition time. From figure 3, it can be seen that the highest value of microhardness was showed by the sample with deposition time of 30mins. Meanwhile, the average microhardness of CoFe nanoparticles prepared at 90 minutes was found to be the lowest than the samples prepared on 30 and 60 minutes.

![Graph showing the relationship between time deposition and microhardness](image)

Fig. 3. The relationship between time deposition and microhardness
By referring to the finding above, it can be concluded that the microhardness of the CoFe nanoparticle decreased with the increment of the deposition’s time. As we can see, the final value of the microhardness of the CoFe nanoparticles at 30, 60, 90 minutes are 236.84 HV, 166.74 HV, and 118.64 HV respectively. The increment and decrement in the nanoparticles hardness are related to the particle size of nanocrystalline material itself. Particles size plays a major role that contributed to the microhardness behavior of the CoFe coated mild steel washer. Figure 4 shows the correlation between the microhardness and particle size of the CoFe nanoparticles prepared at different deposition time. The microhardness of the CoFe nanoparticles prepared at 30 minutes seems to be higher compared those with 60 mins and 90 mins of deposition time. The highest microhardness of the CoFe nanoparticles deposited at 30 minutes is believed to be affected by the formation of the numerous grain boundaries in the microstructure. The formation of the grain boundaries has caused the reduction of particle size [7]. Previous study clarified that the decreasing in the particle size will result in the increasing of the microhardness of the nanocrystalline material [8]. In addition, the stoppage of dislocation motion or the changing dislocation direction occurs with the formation of grain boundaries as it acts as hindrance. This will result in the hardening of the material and the plastic deformation in the material can be prevented due to the restricted motion of dislocation in the nanoparticles. As the conclusion, the CoFe nanoparticles coated prepared at 30 minutes of deposition time has the greatest value of hardness compared to the other samples.

![Fig. 4. The correlation between microhardness and particles size.](image)

**F. Phase and Crystallographic Structure**

XRD measurements of as-synthesized Co-Fe coatings were carried out from 2θ angle of 10° to 90° angle using Cu radiation. Figure 5 to 7 shows the XRD patterns of the electrodeposited Co-Fe coatings at different deposition times of 30, 60, and 90 minutes.
The XRD spectrum for the Co-Fe phase reveals the characteristic peaks at angles of 45°, 65°, and 82°. The Co-Fe phase is identified as the BCC crystal structure with JCPDF No. 030657519 [4,14]. From the figures above, it can be seen that there are differences between the peaks or the relative intensity. Based on the previous study, it clarifies that the difference between the XRD peaks intensity is related to the morphology. Morphology is fundamentally different among the samples due to the difference of crystal face. This study also stated that, crystal morphology changes based on the reaction conditions such as pH, additives and reaction time [9]. The calculation of the crystalline size is made by using the Debye Scherrers’ equation. Theoretically, the crystallite size can be calculated using Debye Scherrers’s equation assuming that there is no crystal defect and voids [10, 11]. Based on the calculation, the values obtained for 30, 60, 90 minutes of the deposition time are 15nm, 22nm, and 22.3nm respectively. Table 2 summarized the value of crystalline size of the CoFe nanoparticles regard to its deposition times. From the result, it can be concluded that the increment of the crystalline size is occurred with the increment of the time deposition [12].
TABLE 2. Crystallite size of CoFe nanoparticles.

| Time deposition (minutes) | Crystallite size (nm) |
|---------------------------|-----------------------|
| 30                        | 15                    |
| 60                        | 22                    |
| 90                        | 22.3                  |

G. Salt Spray (Fog) Test

The Salt Spray (fog) Test is an accelerated corrosion test. All the specimens were placed in enclosed salt spray chamber and being exposed to a continuous indirect spray of salt water solution. This corrosion test was conducted according to the ASTM B117 standard by dissolving 265g sodium chloride (NaCl) into 5000 ml of distilled water. The sample is placed in the chamber for 24 hours before the samples were taken out. Figure 8 shows the result of the corrosion formation after 24 hours of the salt spray (fog) test. The first sample, which is the 30 minute of deposition time, demonstrates a small area of corrosion. The light brown color corrosion only takes place at the side part of the washer. The center part of the washer shows no obvious corrosion takes place and the coating is still intact with the sample. For the second sample, which is 60 minutes of deposition time, the sample shows several light reddish brown areas of corrosion. The corrosion formation did not covered all the surface of the sample as there certain small area on the sample is still intact with the coating. Meanwhile, for the third sample which is 90 minutes of deposition time, it can clearly be seen that the washer demonstrates a large reddish brown area of corrosion compared to the other two samples. The corrosion fully forms on the surface of the sample. Based on this result, after these three samples undergo the salt spray (fog) test, the 30 minutes deposited washer shows the best corrosion resistance compared to others samples. Light brown area of corrosion is barely found on the surface of the sample. The CoFe coating also still remains after 24 hours of the salt spray (fog) test. Therefore it can be concluded that, the area of the corrosion increase with the increment of deposition times [13]. Other than that, it can also be concluded that the corrosion resistance is increased as the time deposition decreases [14].
Table 1: Sample and after salt spray (fog) test

| Sample | After Salt Spray (fog) Test |
|--------|-----------------------------|
| CoFe (30 minutes) | ![Image] |
| CoFe (60 minutes) | ![Image] |
| CoFe (90 minutes) | ![Image] |

![Image] Fig. 8. Sample after the salt spray (fog) test

5. Conclusion
The synthesizing of nanocrystalline Cobalt-Iron (CoFe) coating through the electrodeposition process with the different deposition time is successfully done. The various deposition times (30-90 minutes) have a huge effect on the surface morphology, corrosion behaviour and microhardness of the CoFe nanoparticles. It can be seen that from the result, has influenced the microhardness of CoFe nanoparticles. The sample with the lowest deposition time which is 30 minutes showed the highest average of microhardness (236.84 HV) and lowest particles size (3.29μm). In addition, the crystallite size of the CoFe coating for the sample prepared on 30 minutes of deposition time gives the smallest size (15nm). Meanwhile, the corrosion behavior of the CoFe nanoparticle was accelerated with the increment of the deposition time. From this study, it can be concluded that the deposition time plays a major role in the synthesizing process of the CoFe nanoparticles. From this study also, it can be said that the most efficient deposition time in order to produce the CoFe nanoparticles with magnificent corrosion resistance and microhardness is 30 minutes. Therefore, it is important to synthesize the CoFe nanoparticles at a shorter time in order to obtain a remarkable corrosion behavior and hardness.

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