

Electrodeposition of Co-Ni-Fe on Railway Fastener

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Abstract

Electrodeposition is known as a simple and low-cost method to synthesize good-quality coating with excellent hardness. Co-Ni-Fe is one of the new coating elements and has greater properties in terms of aesthetic and physical properties. The objectives of this project are to carry out electrodeposition of Co-Ni-Fe towards railway clip and to investigate the corrosion formed, thickness of coating layer and hardness of the electrodeposited Cobalt-Nickel-Iron (Co-Ni-Fe) alloy coating of the railway clip. The railway clip is made of high carbon steel. The electrodeposition of Co-Ni-Fe on the railway clip plays important role in enhancing the mechanical behaviour of the coating. Due to its large size, half of the clip was electrodeposited while the other half was left uncoated. The railway clip was electrodeposited at duration of 15 minutes. The pH and working temperature of the sulphate solution were pH 2 and 50°C with tolerance $\pm 5^\circ\text{C}$, respectively. The whole clip was then cut into two halves; the electrodeposited and uncoated. The electrodeposited half was then cut into five pieces. One piece was used for hardness test and the other four pieces were used for corrosion properties. The four pieces were soaked into four types of solution; sulphuric acid (H₂SO₄), alkali (NaOH), salt water and distilled water with initial pH 4.8, 11.5, 7.0 and 6.0 respectively. The four pieces were left soaked in the solution for seven days. After seven days, the formation of rust on each piece was observed. FESEM and EDX tests were conducted and two regions of the cross-section of the sample were analysed. The regions analysed had different thickness of coating layer and the average thickness of the coating layer on region 1 and region 2 were 413 μm 141.6 μm respectively. In the hardness test, it was recorded the non-coated fastener had higher average hardness (498.3 Hv) compared to the Co-Ni-Fe coated fastener (339.9 Hv).

Keywords: Coating; Corrosion; Co-Ni-Fe; Electrodeposition; Railway fastener

1. Introduction

Coating is a protecting layer applied to the outer surface of an object [1,2]. In other words, it is a thin layer that is applied or deposited chemically, with purpose to enhance its properties and build protection of the surface against deterioration of the surface due to its reaction with surroundings. Coating is not only about metallic coating; paint is also considered as coating. Corrosion resistant coatings can increase the lifespan of a part, as well as reduce maintenance and replacement costs, but in order to select the appropriate coating it is important to identify what kind of corrosion a part is prone to. Other examples are also inorganic lining like glass and porcelain lining, organic covering such as polymeric material, varnish and optical film covering and etched or printed covering.

Electrodeposition is one of the coating processes where base metal is coated with thin layer of other metal to improve or modify its properties. The process takes place in a plating solution where the base metal is the cathode and the coating metal is the anode. In the process, reduction occurs from the coating metal where it releases cations in the solution while oxidation occurs at the base metal where it received the cations in the solutions to be coated. However, the transfer of cations does not occur by merely submerging the base metal and coating metal in the solution. The transfer of cation is caused by the salt bridge. Salt bridge is a solution of salt that allows the movement of metal ions to go from anode to cathode. As a result, electrodeposition helps improve corrosion resistance,

resistance against general wear, erosion, pitting and cavitation and improved physical appearance [3]. This study focuses on the effect of pH solution by corrosion, uniformity of coating layer and hardness of the clip after electrodeposited.

2. Methodology

2.1. Preparation of Substrate

The project started with preparation of substrate. Since the substrate is a rusted railway clip, the rust has to be removed. The clip was immersed in acetic acid (vinegar) for 12 hours to ease the removal of rust as shown in Fig. 1. After 12 hours the rust falloff inside the vinegar. The clip then brushed with copper brush to remove the remaining oxides on the surface. The cleaned substrate is shown in Fig. 2.



Fig. 1: Immersed clip in acetic acid



Fig. 2: After brushed with copper brush

2.2. Preparation of Electrolyte Solution

There were 6 chemicals required to make the electrolyte solution. 2 Litre of solution is made base on the mass of each chemical compound as in the Table 1. The mixture then poured into distilled water. The distilled water heated by water until $\pm 50^{\circ}\text{C}$ heater for 15 minutes while the stirrer rotates to stir the solution [4,5].

Table 1: List of chemical compound

Volume (L)	1L	2L	3L
Chemicals	Mass (g)		
Cobalt sulphate	14.06	27.12	42.18
Nickel sulphate	35.04	70.08	105.12
Iron (II) sulphate	5.56	11.12	16.68
Boric acid	16.43	32.96	49.44
Ascorbic acid	11.74	23.48	35.22
Saccharine	1.36	2.72	4.08

2.3. Immersion test

Immersion test is one of the methods to observe the corrosion formed on the samples with different solutions. Immersion tests measure the progress of corrosion damage obtained from the immersion length within a corrosive environment, as well as other factors that can accelerate the corrosion process [6]. Immersion corrosion test was conducted in this research to observe the condition of the electrodeposited railway clip in four (4) different solutions as shown in Fig. 3, Fig. 4, Fig. 5 and Fig. 6. The specimens were let immersed in the solutions for seven (7) days. The purpose of this period is to observe the corrosion developed and its change during the period. By the end of this test, the specimen was then cleaned and the corrosion rate of the surface was observed. Due to the large size of the clip, then the clip was cut into a few fragments in order to fit inside the small beaker. The specimens were immersed in the small beaker with four (4) different solutions for seven (7) days. After seven (7) days, the specimens taken out to observe the corrosion on the Co-Ni-Fe surface coating. The effect of pH values of each solution also observed.

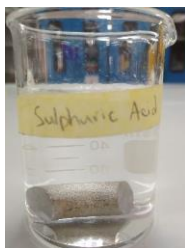


Fig. 3: Immersed in acid (H_2SO_4)



Fig. 4: Immersed in salt water

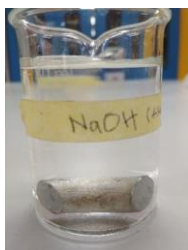


Fig. 5: Immersed in alkali (NaOH)



Fig. 6: Immersed in distilled water

2.4. SEM and EDX tests

Scanning electron microscope images is a sample surface by faster scanning over it with a high-energy beam of electrons [7]. In this study, SEM analysis was used to determine the thickness of the electrodeposition of Co-Ni-Fe on the clip's surface. Small fraction of the clips was placed on the platform in the SEM. When the specimens were placed, the SEM was closed. The parameters including magnification and zoom were all set in the computer. Fig. 7 shows the SEM Hitachi machine that was used for the SEM

and EDX test. Field emission scanning electron microscope (SEM) and energy-dispersive x-ray (EDX) were conducted on the small fragment of the clip. These tests were conducted to observe the thickness layer of the coating and the element contained in the coating. As for EDX, the same specimens were also be analysed. In EDX analysis, three spots were dotted on the surface of the specimens. The analysis was to determine the element contained in the specimens including the Co-Ni-Fe coating layer.



Fig. 7: Samples on the SEM Hitachi

2.5. Hardness test

Hardness is a characteristic of a material, not a fundamental physical property. It is defined as the resistance to indentation and it is determined by measuring the permanent depth of the indentation. Hardness test is one of the methods that are used to determine the hardness of a material. It is a mechanical test for material properties which are mostly applied in analysis and engineering design, structures, and material properties [8]. In this test, Vickers hardness test was used. It is also referred as micro-hardness test because it requires for small part of specimens. The sample was placed on the shiny metallic platform as in Fig. 8 and the platform can be adjusted to the left or right and also its height to ensure the diamond indenter touches the sample. Then the load was applied on the sample for 10 to 15 seconds. After the material has dented mark, the dented image was displayed on a computer display as well as setting the d1 and d2. The average was then calculated automatically after setting the d1 and d2.



Fig. 8: Mitutoyo Vickers Hardness machine

3. Result and Discussion

3.1. Immersion test

The pH values obtained were then converted into a graphical figure to see the pattern of its variation as shown in Fig. 9. It shows the line pattern of variation of each solution used for immersion test. From the graph, it can be seen that the corrosion of the sample in salt water has risen until day 6 and remained constant at 8.3

pH value until day 7. For alkali solution, the pH values has dropped from 11.5 to 9.2 on day 1 until day 4, but remained constant at 9.2 pH value until day 6 and rose back to 9.4. As for acid, the acidity of the solution has decreased as the lower the pH value, the higher the acidity. Distilled water is usually known to have pH 6. It is neither acidic nor alkaline. For this research, the pH of distilled water has risen from 6 to 9 and dropped a little bit at the end of the day. On day 7, all the specimens in the respective solution were taken out to observe the surface of the specimens. Each specimen was cleaned thoroughly and the rust formation was completely removed.

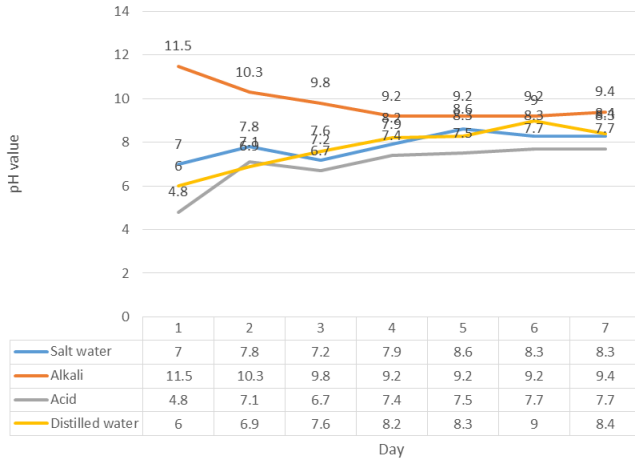
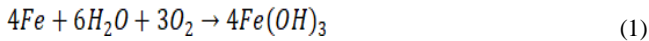
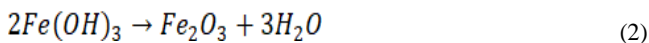


Fig. 9: Graph of pH vs. day of respective solution

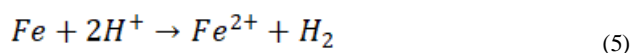
Rust is ferric hydroxide compound layer that commonly forms on mild steel due to atmospheric corrosion. The formation of brown rust is shown in the equation below. Generally, corrosion of metals can occur in fresh water, salty water, acid and alkali solution. In equation (1), iron combines with water and oxygen to produce an insoluble reddish-brown corrosion product that falls out of the solution.



If the corrosion is formed in the atmosphere, the ferrite hydroxide dehydrates and forms red-brown ferric oxide which is rust as stated in equation 2 below.



For samples immersed in salt water and alkali, both had slightly oxides formed on the surface and the Co-Ni-Fe layer was still intact on the surface. This is a uniform and general attack, in which the entire metal surface area exposed to the corrosive environment is converted into its oxide form [3]. It is the uniform thinning of a metal without any localized attack since corrosion does not penetrate very deep inside, and the most familiar example is the rusting of steel in air. Uniform corrosion is assumed to be the most common form of corrosion and particularly responsible for most of the materials loss. However, with the Co-Ni-Fe coating, it reduces the severity of the corrosion.. Equation (3) shows that iron took part in the reaction with every solution in a valence of 2. The valence of 2 then ionized with hydrogen ion to produce H_2 as in equation 4.



3.2 SEM test

Scanning electron microscopy (SEM) was achieved through the use of a field emission gun of SEM Hitachi [7]. At region 1, resolution of $500 \mu m$ was achieved under 15kV with magnification of 70. In Fig. 10, it shows the general image of the coated sample under the SEM. Meanwhile in Fig. 11, it was the same as Fig. 10 but the thickness of Co-Ni-Fe layer was dimensioned. The following thickness recorded was $459 \mu m$, $411 \mu m$ and $369 \mu m$. The average thickness of Co-Ni-Fe layer was $413 \mu m$. At this region, it can be observed that the thickness was almost constant and uniform. However, the line pattern of the Co-Ni-Fe layer was parallel.

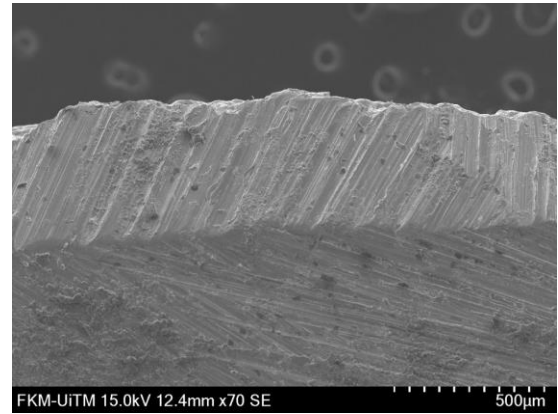


Fig. 10: Cross-section of Co-Ni-Fe coating layer

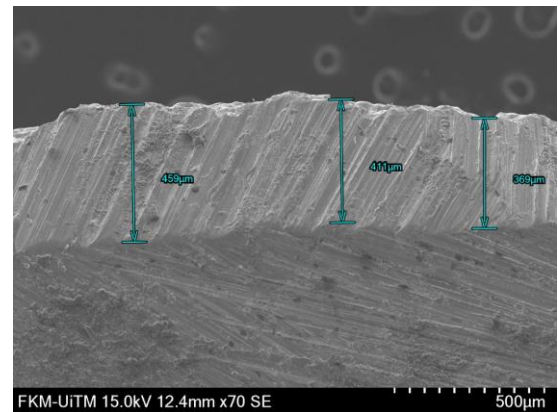


Fig. 11: Thickness of the Co-Ni-Fe coating layer

In the electrodeposition process, the uniform coating of specimen depends upon the current distribution parameter [9]. In general, the ions in the solution were attached to the cathode (railway clip) at certain region. This was due to the position or the way the railway clip was hanging while electrodeposited could affect the attachment of ions onto the surface of the railway clip. The railway clip was actually left hanging vertically during the electrodeposition process. Due to its irregular shape, the ions might be unable to reach at certain region on the surface of the railway clip.

Next, the uniformity of the Co-Ni-Fe coating was also influenced by the temperature of the solution. Increase in bath temperature increases solubility and thereby the transport number, which in turn leads to increased conductivity of the solution [9,10]. Increasing the bath temperature also decreases the viscosity of the solution. It could replenish the coating layer faster. However, for the solution used for the railway clip, the temperature sometimes drops below the required temperature. This low temperature of bath could have affected the uniformity of the coating layer.

The inconsistency of the coating layer thickness might also be affected by the electrodeposition time. In general, the plating

thickness increases directly proportionately to the plating time and current [10]. During the electrodeposition process, sometimes the substrate electrodeposited with inconsistent time. There was a time when the electrodeposition time dragged until 30 minutes from 15 minutes because there were some regions that did not fully electrodeposit. The reason was to increase the thickness of the coating because theoretically the longer the electrodeposition time, the higher the thickness is.

3.3. EDX test

Fig. 12 until Fig. 15 shows the EDX spectra of Co-Ni-Fe coating layer [11]. In this test, three spots were taken. Spot 1 was observed on the Co-Ni-Fe layer to determine the elements in the coating layer as shown in Fig. 12. From Fig. 13, the coating layer showed the presence of Cobalt (Co), Nickel (Ni) and Iron (Fe). The presence of Cobalt (Co) peaked at about 7.00 keV, Nickel (Ni) at about 7.50 keV and Iron (Fe) at 6.40 keV which could be observed in the spectra. However, there was also the presence of other elements such as carbon and oxide. It can be observed that Spot 1 had high concentration of Oxide (O_2).

Meanwhile on Spot 2 in Fig. 14, the spot was selected in between the base metal and Co-Ni-Fe coating layer. Compared to Spot 1, this area had the highest presence of Iron (Fe). There was also the presence of Cobalt (Co), Oxygen (O) and Carbon (C).

In Fig. 15, the spot selected was at the base metal itself. The spectrum showed that the base metal had the highest concentration of Oxygen (O).

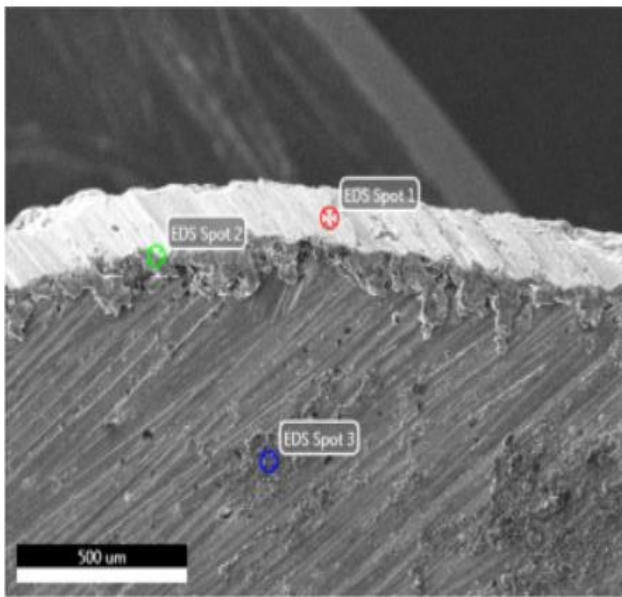


Fig. 12: EDS spot on coating region

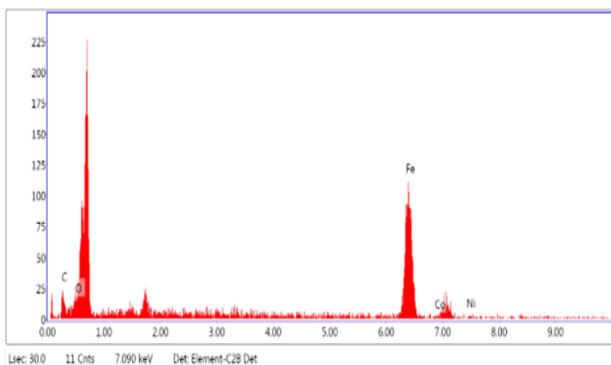


Fig. 13: EDS Spot 1

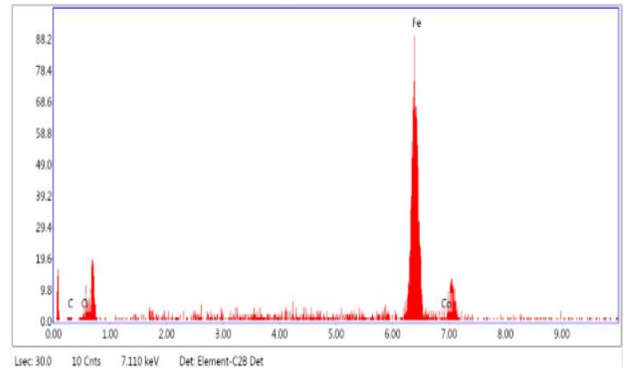


Fig. 14: EDS Spot 2

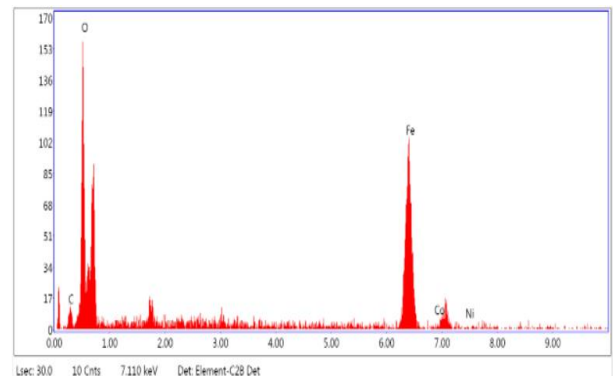


Fig. 15: EDS spot 3

3.4 Hardness test

In this test, all specimens had 500g of force applied on them. For each of the fragment, the hardness reading was taken from three different spots. From each reading, the average hardness was calculated and tabulated in Table 2. From Table 2, it was found that the non-coated specimen had a higher average hardness than the Co-Ni-Fe coated which were 498.3 Hv and 338.9 Hv respectively. What makes a big difference here was the 2nd reading of non-coated that reached until 638.8 Hv while the highest coated sample reached 409.5 Hv. There was possibility that Co-Ni-Fe coated had some errors while the hardness test was carried out when d1 and d2 were determined.

Table 2: Hardness reading of coated and non-coated railway clip

Specimen	Reading (Hv)			Average hardness (Hv)
	1	2	3	
Co-Ni-Fe coated	225.4	351.7	409.5	338.9
Non-coated	389.7	638.8	466.5	498.3

Fig. 16 shows the average Vickers hardness of coated sample and non-coated sample in graphical image. It can be observed that Co-Ni-Fe coated has less hardness compared to non-coated sample.

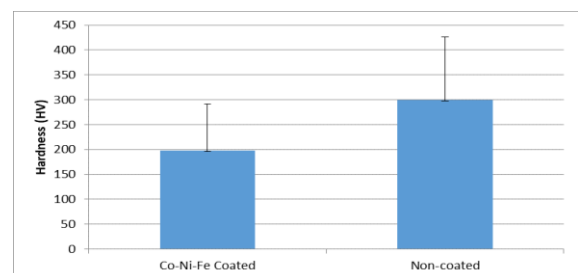


Fig. 16: Average Vickers hardness of coated sample and non-coated sample

4. Conclusion

In conclusion, electrodeposition of railway fastener was successfully achieved. This study investigated the electrodeposition of Co-Ni-Fe on railway fastener including the immersion test, SEM and EDX and hardness test. The results showed that electrodeposition Co-Ni-Fe has reduced the corrosion rate towards the specimen in immersion test. The corrosion occurred in both conditions; during immersing and post-immersing (cleaned). However, the corrosion of the specimens affected the pH value of the solution. Each of the solution has varied result along the day the specimen was immersed. In hardness test, the hardness of the coated specimens was supposed to be higher than the non-coated but somehow the non-coated had higher hardness. As in SEM test, it showed the electrodeposition uniformly coated the surface of the specimen. The following points are concluded from the study:

- i. The result from the immersion test shows that the coated sample immersed in sulphuric acid has a greater corrosion. The least corrosion occurred on the sample immersed in alkali solution.
- ii. The result obtained from SEM analysis concluded that the uniformity of the coating layer is inconsistent.
- iii. For the EDX analysis, it can be concluded that all the elements (Cobalt Nickel Iron) at Co-Ni-Fe coating layer were in presence.
- iv. Hardness of the samples was successfully obtained. However, the results obtained showed the hardness of non-coated was greater than the coated one.

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