



## Surface activation pretreatment for cobalt alloys electroplating

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KEYWORDS	ABSTRACT
Activator Coating Nitric acid Cobalt alloy Steel	A protective coating is a common solution applied in industry to resist the steel from rusting. The coating must be homogeneous and smooth to ensure strong adhesion with the steel. A crucial step for this to be achieved is the activation pretreatment. The aim of this study is to investigate the effect of the activation step on the cobalt alloy coating performance. This was done by acid dipping low carbon steel into nitric acid solution at different concentrations (3 vol%, 5.5 vol%, and 10 vol%) and dipping time (35 s and 45 s). The steel was then deposited with a cobalt alloy coating using the electroplating process. The final product was characterized using XRD, SEM, EDX, surface roughness and Vickers hardness tester. It was observed that the coated product achieved the lowest surface roughness of 0.528 $\mu\text{m}$ and the highest Vickers hardness of 346.7 HV when the concentration of activator was at 10 vol% and dipping duration of 45 s. It is concluded that a well-designed activation pretreatment process is crucial before the electroplating process is conducted to produce notable coating protection.

### 1.0 INTRODUCTION

Steel is one of the most versatile materials in the world. Steels containing iron are used to build structures, tools, and machine parts. However, most of the steel (without heat treatment) has a major disadvantage. They are prone to corrosion, particularly rust. This is unavoidable for steel

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structures that are exposed to the outdoor environment such as marine, climate change and agriculture conditions (Maraveas, 2020). Seawater, sulphur dioxide and carbon dioxide will hasten the corrosion of the steel.

A possible option to overcome this problem is to make use of coating. Coating plays a huge function in the machine parts because it can increase the lifespan of a part and shield it from corrosion. One of the techniques to form a coating is electrodeposition or electroplating. There are many metals compatible with the mild steel and facile to form a coating layer. Cobalt is a common and non-toxic metal coating plated on mild steel (Zhang et al., 2020). Cobalt, particularly cobalt alloys such as cobalt-molybdenum (Co-Mo) (Santos et al., 2020), nickel-cobalt (Ni-Co) (Radadi and Ibrahim, 2021), and cobalt-iron (Co-Fe) (Denisova et al., 2020) are among favourite coatings due to their special ability to provide extra resistance to corrosion (Quan and He, 2015).

The condition of a coating is the essential first place to be considered to have a durable coating. Defects such as cracks or pores should be avoided in the protective coating. One of the important factors to ensure a proper coating formation is the pretreatment step on the substrate. A suitable pretreatment should be concerned to clean and activate the surface of the steel. Then, a defect-free coating can be deposited on the steel to gain a noteworthy improvement in corrosion resistance and other mechanical performance (Tsai et al., 2015). The plasma treatment inhibited oxygen absorption and removed the oxide layer from the surface of the metal substrate (Wu et al., 2020). In fact, the most economical activation pretreatment that could be done for surface preparation is acid dipping.

Surface preparation is important to ensure a substrate is clean and provides a proper condition for the adhesion in the electroplating process (Wang et al., 2021). For the best result of the final coating, the substrate surface is needed to have the best wettability. The coating adhesion increases if the substrate has homogeneous wetting. Previous work (Uhlman and Jackowski, 2018) has shown that activation using acid dipping leads to better coating adhesion. Acid activation, in particular, is important to electroplating because it removes the oxide layer, neutralizes alkaline film, eliminates impurities, and activates the modal surface that is prone from the oxide layer on the substrate (Wang et al., 2016). However, the acid can corrode the surface of the substrate if the acid dipping is too long or the concentration is too high, and this will affect the adhesion process, especially at a high current density.

This shows that optimizing the concentration and the duration of the acid dipping process is important to ensure better coating quality. Besides, the textured surface quality improvement using either mechanical or chemical processes greatly enhances the surface properties (Husna et al., 2020). Thus, the objective of this study was to investigate the optimum activation pretreatment for a cobalt alloy electroplated on a low carbon steel substrate. The activator used in the pretreatment was nitric acid.

## 2.0 EXPERIMENTAL PROCEDURE

The experiment in this study used an AISI 1018 low carbon steel sheet as a specimen substrate. The sheet was cut into a plate having a dimension of 50 mm x 20 mm x 1 mm. The low carbon steel had Vickers hardness of 131 HV and tensile strength of 440 MPa.

The main parameters in this study were the concentration and dipping time of the activator. The pretreatment was done by submerging the steel plate in nitric acid (HNO<sub>3</sub>) activator. The original nitric acid batch had a concentration of 65 vol%. The batch was diluted with 500 ml of distilled water to yield the concentration of 3.0 vol%, 5.5 vol%, and 10 vol%. The submergence

was done in room temperature under a fume hood for two different time duration: 35 s and 45 s. The low carbon steel was usually surface treated by hydrochloride or sulfuric acid. Sulfuric acid was more common to be used because it was cheaper than hydrochloride acid. Previous work investigated the precleaning of Ni-Co alloy using 12.5% of sulfuric acid from 35 s to 55 s (Kirubaharan and Begum, 2017). It is known that nitric acid is stronger than hydrochloride and sulfuric acid. Thus, this study explored the acid cleaning and activation of the steel using nitric acid at the processing time from 35 s to 45 s.

After the activation pretreatment, the steel plate was sent to the electroplating process. The electroplating process used an electrolyte solution from a combination of cobalt (II) sulfate ( $\text{CoSO}_4$ ), nickel (II) sulfate ( $\text{NiSO}_4$ ), (II) sulfate ( $\text{FeSO}_4$ ), boric acid ( $\text{H}_3\text{BO}_3$ ), and saccharin additive. The concentration of the solution was given in details in the previous study (Hyie et al., 2016). The solution was kept at 51 °C and a maximum pH of 2.99. The current density applied during the process was less than 0.1 A/cm<sup>2</sup>. The electroplating process used a platinum mesh as the anode. The electroplating process was allocated in 10 minutes to obtain a thin single layer of cobalt-nickel-iron (Co-Ni-Fe) coating. Figure 1 shows a schematic diagram of the electroplating process set up.

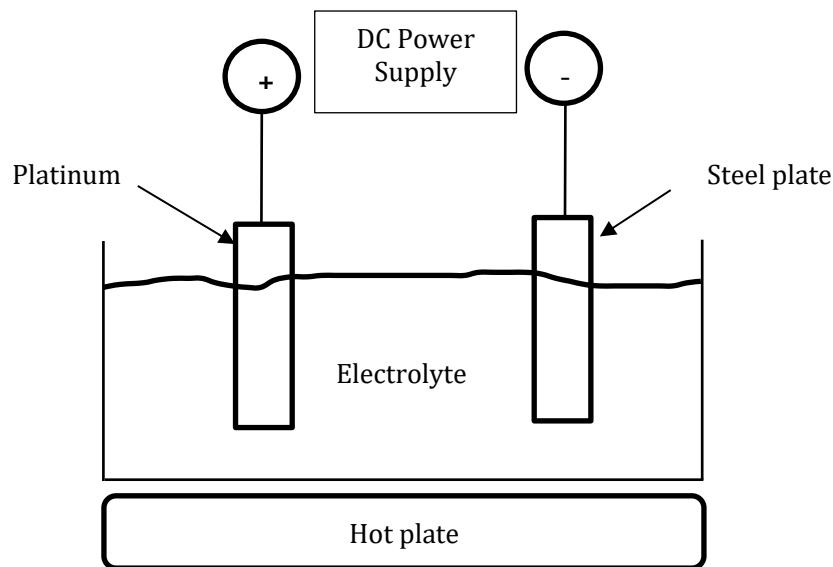


Figure 1: Electroplating setup diagram.

Once the electroplating was done, the coated specimen was tested for its surface coating quality. The existence of the cobalt alloy coating and steel substrate were verified by the Rigaku model X-ray Diffractometer (XRD). The scanning electron microscope (SEM) test was used to visually inspect the coating surface. SEM allowed any small crack and pits in the coating to be detected. The energy dispersive X-ray analysis (EDX) on the other hand, was used to examine the elements of the coated specimen as well as impurities detection on the base substrate. Both SEM and EDX tests were done by a single machine, Hitachi TM3030 PLUS model.

The surface roughness of the coated specimen was measured using the Mitutoyo SURFTEST SJ-210 machine. The hardness test was performed on the coated specimen using the Mitutoyo HM-200 Vickers hardness testing machine. The indented loading used in the test was 0.1 kg, 0.5 kg, and 1.0 kg.

### 3.0 RESULTS AND DISCUSSION

#### 3.1 XRD Patterns

Figure 2 demonstrates the XRD patterns for cobalt alloy coating and the low carbon steel substrate after the acid activation pretreatment. Figure 2 (a) shows that only Fe peaks are found on the base metal substrate at the angle of  $45^\circ$  (100),  $64^\circ$  (200), and  $83^\circ$  (211). This finding is similar to the previous finding reported on the carbon steel without corrosion attacked (Paul et al., 2014). The presence of Co-Ni-Fe coating is clearly indicated by the XRD peak intensities as shown in Figure 2 (b). The Co-Ni peaks are evident at  $45^\circ$  (111),  $51^\circ$  (200),  $76^\circ$  (220) and  $93^\circ$  (311). As for NiFe, the peaks are mapped with reference to  $52^\circ$  (200),  $77^\circ$  (220) and  $94^\circ$  (311). The crystallize size of Co-Ni-Fe was determined using the line width found in the XRD peaks and Scherrer formula (Cullity, 1978). It is found that the average crystallize size was less than 30 nm.

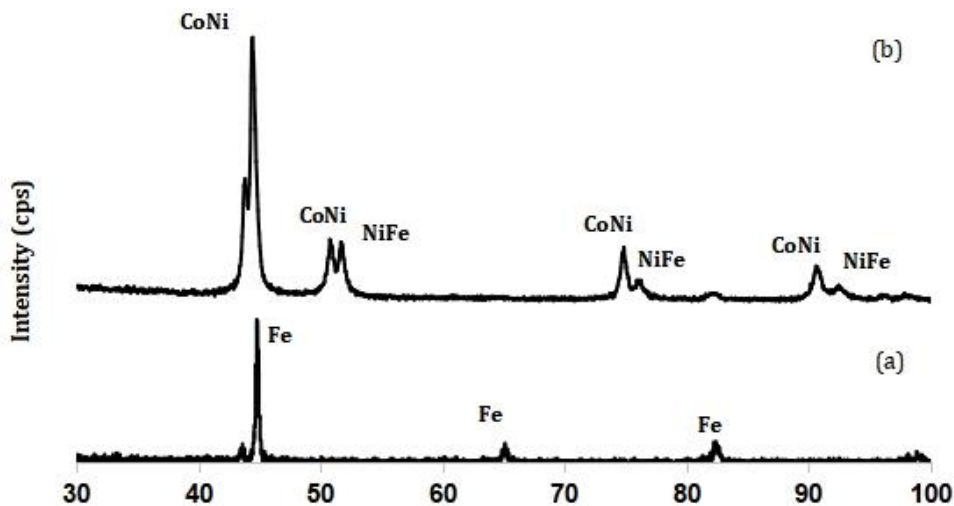


Figure 2: XRD patterns for (a) base substrate (b) cobalt alloy coated specimen.

The XRD pattern was similar to all the specimens regardless the effect of activator concentration and submergence time. There was no impurity observed in the steel substrate and coated specimen. The acid activation helped appreciably to remove the impurities from the steel surface before a smooth coating layer was deposited on the steel.

#### 3.2 Surface Roughness

The surface roughness was determined by taking the reading on the same specimen at three different points to minimize the error. Table 1 shows the average surface roughness of the coated specimen prepared at different submerged times and activator concentrations. It can be seen that

the surface roughness for the coated specimen without pretreatment is 1.584  $\mu\text{m}$ . By adding the activation pretreatment step before the coating process, the surface coating has been improved significantly. The surface roughness decreased gradually when the activation concentration was increased. On the other hand, the roughness was declined when the submergence time was increased. This is due to the removal of small granules or impurities on the base metal during the activation process. The evidence shown by Liu and his co-workers further supports the statement (Liu et al., 2016). A compact and smoother surface coating were produced after the pretreatment. The coating had low porosity, which resulted in better adhesive strength.

Table 1: The average surface roughness of coated specimens at different activator concentrations and submergence time.

Activation Concentration (vol%)	Surface Roughness, Ra ( $\mu\text{m}$ )	
	35s submergence time	45s submergence time
0	1.584	1.584
3	0.919	0.770
5.5	0.737	0.700
10	0.680	0.528

### 3.3 Hardness Results

The average hardness is tabulated in Table 2 and Table 3 after three (3) readings were collected from each specimen. A higher concentration of the activator produced greater hardness. The hardness was reduced as the resistance of the specimen to the deformation became weaker when the applied indented load was increased. The results also show an increased hardness with the increased submergence time. The highest hardness was obtained by the coated specimen prepared at 10 vol% activator concentration and 45 s submergence time. This observation correlates well with the surface roughness. A small surface roughness correlates to higher surface hardness. The smooth surface of the substrate after pretreatment enhanced the adhesion of the coating to the substrate during the electroplating process. As a result, better resistance of the coated specimen was performed when an external loading was applied.

Besides that, the acid activator pretreatment conducted at 10 vol% and 45 s was sufficient to remove the impurities, dirt and oxide layer on the surface of the steel without excessively corroding the steel. Thus, the surface roughness and the hardness were improved in this study.

Table 2: Hardness finding for cobalt alloy coated steel at 35 s submergence time.

Load Applied (kg)	Vickers Hardness (HV)			
	Activator concentration (vol %)			
	0	3	5.5	10
0.1	329.1	330.8	335.7	339.6
0.5	178.5	177.6	180.3	185.0
1.0	140.1	140.2	141.3	150.8

Table 3: Hardness finding for cobalt alloy coated steel at 45 s submergence time.

Load Applied (kg)	Vickers Hardness (HV)			
	Activator concentration (vol%)			
	0	3	5.5	10
0.1	329.1	329.8	345	346.7
0.5	178.5	179.7	187.8	190.6
1.0	140.1	141.0	148.0	152.9

It is found that selective corrosion could happen along the grain boundary of the substrate if the pretreatment parameter was not optimized (Zhou et al., 2016). If the concentration was higher or the submergence time was longer than a certain limit, the substrate could be destroyed and corroded.

The nitric acid reacted with many metals. Iron, cobalt and nickel were passivated by nitric acid depending on the concentration of the acid. The mild steel tank which stored the hydrofluoric acid was continuously corroded by nitric acid until failure occurred by perforation (Dai et al., 2021). Hence, the concentration and submergence time of nitric acid as the activator must be carefully monitored.

### 3.4 Surface Morphology of Coating

A visual inspection of the coating was carried out using SEM examination. Figure 3 displays the images from the SEM analysis for the steel plates before the coating process. Figure 3(a) shows that the surface of the specimen without pretreatment was rough and filled with granules. The granules were contaminated from the steel machining process as well as the oxide layer formed on the surface of the specimen. The oxide layer inhibited the coating to form and adhering to the surface of the specimen. After pretreated with 5.5 vol% activator concentration for 45 s, it can be observed in Figure 3(b) that some rougher features on the steel surface were removed, and the surface appeared to be smoother. When the steel was pretreated with 10 vol% activator concentration for 45 s as shown in Figure 3(c), the surface roughness of the steel was further reduced. A clear and smooth surface of the substrate facilitated a better overall coating quality that had a low surface roughness and high surface hardness.

The surface images of the specimens after being coated with cobalt alloys are depicted in Figure 4. The coating surface without activation was rough and uneven associated with the highest surface roughness of 1.584  $\mu\text{m}$ , as reported in Table 1. The dirt and small granules attached to the substrate surface were trapped in the surface coating. Besides, oils or unwanted gases may trap in the pores on the steel surface (Zhou et al., 2016), which also induced poor adhesion between the coating and the steel substrate.

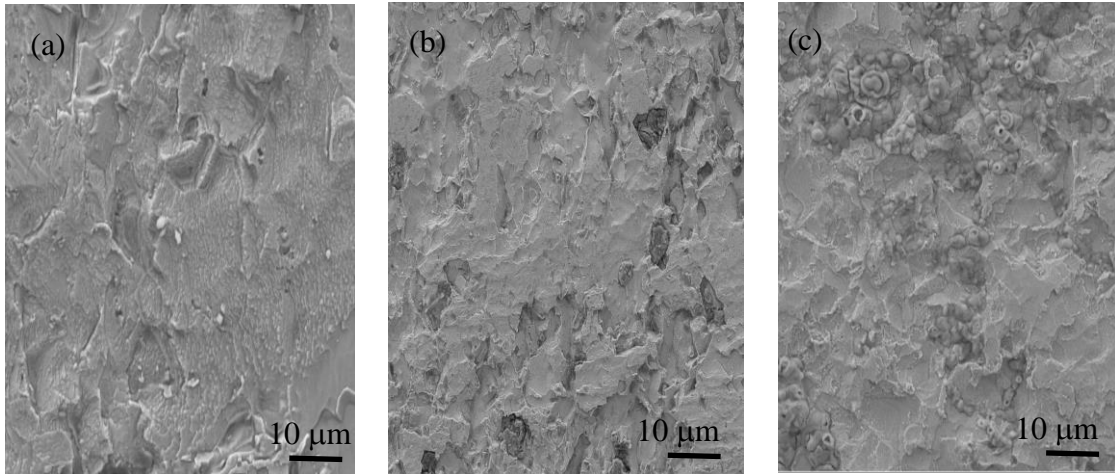


Figure 3: SEM images of steel surfaces (a) without activation (b) after activation at 5.5 vol% (c) after activation at 10 vol%.

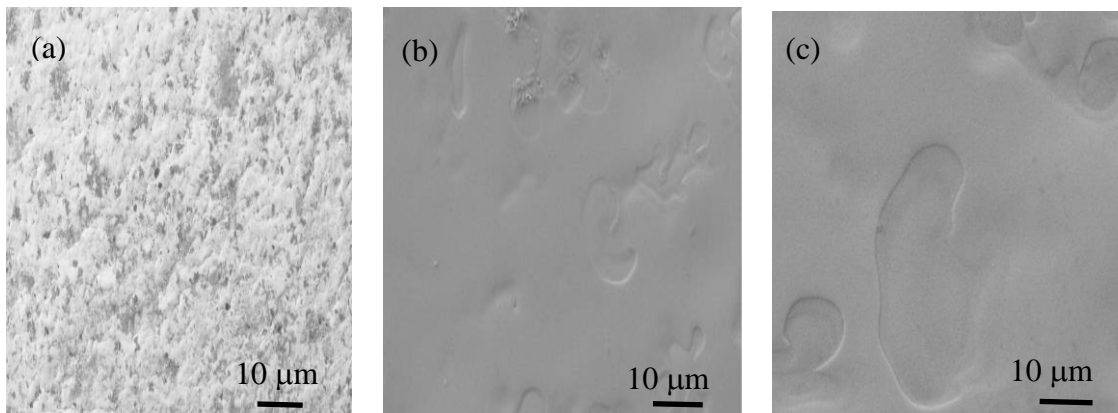


Figure 4: SEM images of cobalt alloy coated specimens (a) without activation (b) after activation at 5.5 vol% (c) after activation at 10 vol% for 45 s submergence time.

In contrast, the coating surface after activation was smooth and cleaned thus producing a smooth and uniform coating. It is validated by the result reported in Table 1, that the coated product prepared at 10 vol% acid concentration achieved the lowest surface roughness of 0.528  $\mu\text{m}$ . The effect of activation pretreatment was indeed proven in SEM images that removal of impurities and dirt from the substrate surface enhanced the quality of the coating. A thin layer of less than 10  $\mu\text{m}$  coating was successfully formed at a minimum of 10 minutes of electroplating time with a high current density. It is believed that a prolonged electroplating process could cause thicker coating and grain growth (Hyie et al., 2016). Moreover, the electrolyte solution containing boric acid helped to attract the active sites for hydrogen evolution reactions. Hence, the gas evolution was minimized and gas bubble formation was suppressed from the electroplating process (Graham, 2014).

### 3.5 Element Composition

Figure 5 compares the EDX results for the specimens before and after coating. Both specimens were detected to have a small amount of carbon. This may be due to the carbon tape used to fit the specimen on the test holder. It was not considered as part of the actual composition for the specimen itself. The EDX result in Figure 5(a) reveals that the main element of the un-coated specimen is only iron after the activation pretreatment. There is no other significant element. This is similar to the finding as shown in Figure 2 (a). In Figure 5(b), nickel, cobalt, and iron are noticed. The finding indicates that the cobalt alloy coating without other impurities was electroplated on the steel substrate, as proven in XRD results.

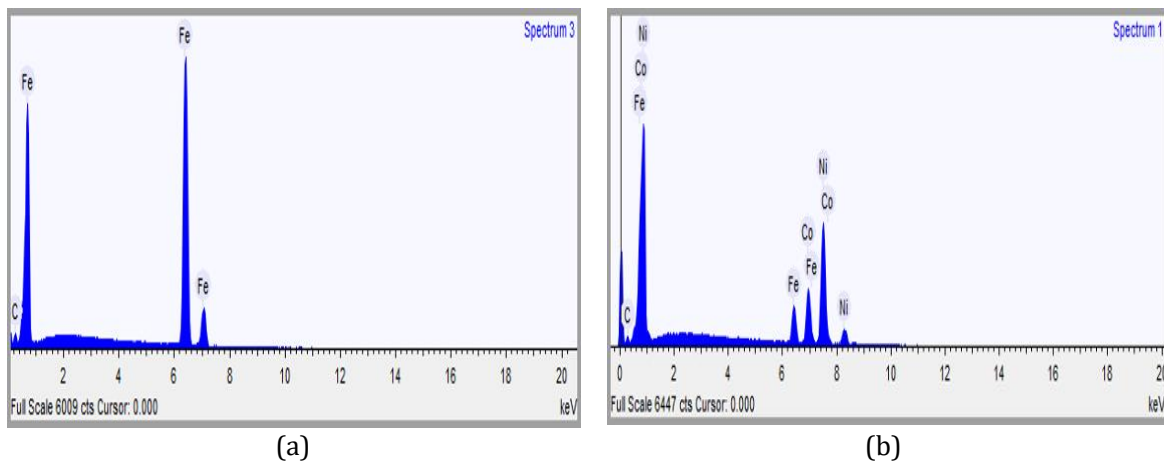


Figure 5: EDX results for specimen (a) before coating (b) after coating.

The weight percentage of the elements found in the EDX test can be seen in Table 4. As for the uncoated specimen, the main elements were iron with 93.719 wt.%, carbon at 6.282 weight% and no trace of cobalt or nickel. However, it can be observed that nickel became the main element with 63.535 weight% in the coated specimen, followed by cobalt, iron, and carbon. It shows that the coating had fully covered the steel specimen and the Co-Ni-Fe coating was observed on the specimen.

Table 4: Element composition for uncoated and coated specimen.

Element	Weight %	
	Un-coated specimen	Cobalt alloy coated specimen
Carbon	6.282	4.526
Iron	93.719	9.990
Cobalt	Not found	21.948
Nickel	Not found	63.535



## CONCLUSIONS

The formation of Co-Ni-Fe coating was performed on the low carbon steel as a single thin layer having less than 10  $\mu\text{m}$  thickness. The coating did not contain other oxide or impurities. The use of nitric acid in the activation pretreatment prior to the cobalt alloy electroplating process greatly improved the surface roughness and Vickers hardness of the coated products. The impurities and dirt were removed from the steel substrate after the activation pretreatment. The surface coating became smooth, uniform and had less porosity after being activated with nitric acid. The specimen which experienced the activation pretreatment achieved higher reading (346.7 HV) compared to the one without pretreatment. It is concluded that the hardness was increased when higher concentration and longer submergence time of activator were applied.

As for the surface roughness, the coating surface became smoother without granules when a higher concentration of activator and prolonged submergence time was implemented. The surface roughness reduced drastically by about 66% after the steel substrate was submerged in acid nitric of 10 vol% concentration for 45 s, if compared to the one without pretreatment. The future work will extend the concentration and submergence time of nitric acid until a maximum limit where the activator may corrode and deteriorate the quality of the substrate surface.

In fact, the chemical process is the fastest and the most economical pretreatment favored by industrial users. The minimal cost but the enhanced coating performance is the key factor in the electroplating industry. Thus, a pretreatment to the substrate surface to be coated is highly recommended to obtain a better coating performance.

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