

Effects of Current Density and Deposition Time on Corrosion Behaviour of Nickel-based Alloy Coatings

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DOI: <https://doi.org/10.30880/ijie.2022.14.05.025>

Received 26 June 2022; Accepted 15 August 2022; Available online 25 August 2022

Abstract: Corrosion of fasteners is an on-going issue and stainless steel 304 (SS304) is prone to this destructive process. One method to mitigate corrosion is electrodeposition of Co-Ni-Fe nanoparticles. This paper studied the effects of deposition time and current density on corrosion behaviour of Co-Ni-Fe coated SS304 bolt. Co-Ni-Fe ternary alloys were electrodeposited onto SS304 bolt in 15, 30, or 45 minutes by using current density of 28, 35, 42 mA/cm². Combinations of these parameters produced 9 samples. These samples were electrochemically tested by a potentiostat using open circuit potential (OCP) and potentiodynamic polarization (PDP). The samples were also characterised in terms of surface roughness and thickness of the coatings by using 3D surface metrology system. The OCP value decreased when deposition time was increased. All sample synthesised in 30 minutes had a more stable OCP curve. PDP curves exhibited active behaviour without passivation region. The corrosion potential (E_{corr}) of T15 samples was more anodic than T30 and T45 samples. The corrosion current density (I_{corr}) of all samples fluctuated. Sample synthesised in 30 minutes using 42 mA/cm² had the lowest corrosion rate. It was found that the surface roughness influences the corrosion behaviour in which a lower surface roughness tends to produce coating with better corrosion performance. Current density had small effect on the thickness of coating, whereas the tendency of a thickness to increase was obvious for deposition time.

Keywords: Bolt, Co-Ni-Fe, corrosion behaviour, current density, deposition time

1. Introduction

Corrosion is an important topic in engineering field and the study on corrosion will never stop because it is a law of nature. Disaster will occur when one overlooks corrosion management in a project. Corrosion can cause mechanical, chemical, and electrical properties of materials to deteriorate. Fastening components such as bolt are regularly inspected for any sign of corrosion because they are of essential connectors between structural members. Stainless steel 304 (SS304), being one of the widely used materials for its resistant to corrosion, could not avoid the corrosion itself at all.

A lot of protective methods have been introduced to cope with corrosion matter and one of them is electrodeposition. It is a flexible coating synthesis technique that is able to enhance a lot of properties [1]. Different types and shapes of metals have been successfully plated with this method and yet it is rather a simple and economical

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setup. Based on previous study, Co-Ni-Fe coating was more resistant to corrosion compared to its singular (Co) and binary (Co-Fe) counterparts [2].

Electroplating parameters are the variables that influence the outcome of the process such as surface properties which will also affect the corrosion performance of the coating. Previous study concluded that an increase of deposition time and current density has improved the mechanical and corrosion properties of Co-Ni-Fe coatings [3]. Thus, optimization of deposition time and current density will ensure that the synthesised coating is of the highest quality.

The purpose of this study is to analyse the effects of deposition time and current density on corrosion behaviour of Co-Ni-Fe coated SS304 bolt. The selected deposition times were 15, 30 and 45 minutes whereas current densities were 28, 35 and 42 mA/cm². Electrochemical measurements such as open circuit potential (OCP) and potentiodynamic polarisation (PDP) provide an in-depth understanding on corrosion mechanism of this coating. The corrosion behaviour was then associated with surface roughness. Besides, the thickness of the coating was investigated too. Both surface roughness and thickness were measured by using 3D surface metrology system.

2. Methodology

2.1 Materials

The materials used were SS304 hex bolts. The bolts were fully-threaded heavy duty hex bolt with a dimension of 1/2"-13 x 2" UNC.

2.2 Preparation of Substrate

The surface treatment method used to clean the surface of the substrates was ultrasonic cleaning. The substrate was placed in distilled water tank of an ultrasonic cleaner. During cleaning process, the water was heated to 40°C and transducer vibrated at 42 kHz ultrasonic frequency to remove small contaminants such as grain of dirt on the surface of the substrate. The cleaning duration was 5 minutes. Then, the substrate was taken out from the cleaner and let to dry.

2.3 Preparation of Electrolyte

The electrolyte used was sulfate solution made up of reagent grade compounds. Cobalt (II) sulfate-7-hydrate, nickel (II) sulfate-7-hydrate, and iron (II) sulfate-7-hydrate supplied metal ions whereas boric acid, ascorbic acid and saccharin were used as additives. Two litres of distilled water were mixed with the compounds to dissolve them. The solution was stirred and heated to 50°C by using hotplate stirrer. The solution was ready to be used when it became dark and crystal clear with no powder remnants.

2.4 Electrodeposition Process

Two pieces of 10 cm x 10 cm platinized titanium mesh (anode) were connected in parallel to the positive terminal of a DC power supply. The substrate was connected to negative terminal to become cathode. A glass tank was filled with the electrolyte and placed on top of a hotplate stirrer that heated the solution at 60 ± 5 °C. The selected deposition times were 15, 30 and 45 minutes and the current densities were 28, 35 and 42 mA/cm². By combining both parameters, nine samples were synthesised as shown in Table 1. Each sample had different properties. Samples were labelled using T_{XX}-CD_{YY} where T is deposition time and CD is current density. For example, sample T15-CD28 was synthesised for 15 minutes using current density of 28 mA/cm².

Table 1 - Designation code for different combination of deposition time and current density

Designation code	Deposition time (minutes)	Current density (mA/cm ²)
T15-CD28	15	28
T15-CD35		35
T15-CD42		42
T30-CD28	30	28
T30-CD35		35
T30-CD42		42
T45-CD28	45	28
T45-CD35		35
T45-CD42		42

2.5 Corrosion Behaviour of the Coatings

All electrochemical measurements were carried out using Gamry Series-G 300 Potentiostat and the interface was provided by Gamry Framework software. The samples were evaluated by open circuit potential (OCP) and potentiodynamic polarization (PDP) to monitor corrosion behaviour of the samples. Three-electrode cell assembly was used, and the arrangement included Co-Ni-Fe coated sample as working electrode (WE), graphite as counter electrode (CE), and Hanna Instruments HI4000 saturated calomel electrode as reference electrode (RE). The working electrodes consisted of Co-Ni-Fe coatings with active surface area of 29.81 cm^2 having different surface finish due to different plating parameters. The electrolytes used were 250 ml of 0.1M NaOH to obtain pH value of 12. The OCP was monitored for 3600 seconds (one hour). Next, PDP was conducted to obtain polarisation curve. The scan rate of PDP was 1 mV/s with a potential range of -500 mV to 500 mV . Both OCP and PDP were performed at room temperature. All recorded electrochemical measurements were further analysed using Gamry Echem Analyst. Tafel extrapolation was employed on the polarisation curve to calculate the corrosion rate.

2.6 Surface Roughness

As a result of synthesis using different deposition time and current density, the surface roughness varied [4]. A 3D surface map of the head of the bolt was generated by using Alicona 3D surface metrology system. Before being placed on the measuring platform, the bolt was mated with a nut acting as a support; so, the axis was perpendicular to the surface of the platform. The measurement of the bolt was taken on the surface of the top of the head. The output parameters for this test were arithmetical mean height, S_a which complemented the analysis of corrosion behaviour.

2.7 Thickness of the Coatings

Stainless steel has smooth surface which makes surface roughness reading has lesser noise and does not influence the local thickness of coating relatively. The substrate was weighed before and after electrodeposition to calculate the weight of the coating. A portion of the surface was covered with Kaptan tape to create a masking. Coating could not form on the masking because its surface was non-conductive. So, a step was formed once the masking was removed. Using Alicona 3D surface metrology system, it can pick up the height difference of two discontinuous planes that comprised of substrate surface and Co-Ni-Fe coating surface. The desired parameter was total height of the roughness profile, R_t . It is a difference between height of the highest peak, R_p and depth of the deepest valley, R_v within the evaluation length, l_n .

3. Results and Discussion

3.1 Open Circuit Potential

The open circuit potential (OCP) of samples immersed in NaOH was measured for 3600 seconds. OCP gave the information about thermodynamic stability of the coating in the electrolyte. Fig. 1 shows the plot of OCP curves of samples synthesised using different deposition times and current densities varied with time. In the beginning, the values of OCP were between -405.9 mV to -264.2 mV . The potentials moved steadily in nobler (less negative value) direction until they reached a steady state due to the formation of a passive layers that inhibited corrosion [5]. The variation of open circuit potential (OCP) was influenced by the oxidation tendency on the surface [6]. Generally, the potential value decreased in the following order of deposition time (regardless of current density): 15 minutes, 30 minutes, and 45 minutes. However, all T30 samples exhibited more stable curves compared to the curves of T15 and T45, which had minor zig-zag patterns.

The influence of current density on the OCP was strong for samples synthesised in 15 and 45 minutes. As current density was increased, the OCP decreased. On the other hand, 30 minutes of deposition time produced an interesting result. The OCP values of T30-CD28 and T30-CD42 were close and both curves overlapped each other. The highest current density gave the highest potential. The possible explanation of this contrasting behaviour is due to the surface roughness of T30-CD42 being the lowest of all samples as shown in Table 2. Besides, the curve of T30-CD42 was the most stable which agreed to previous study that stable oxide film formed faster on a smoother surface [7]. Thus, a more stable potential can be achieved using 30 minutes of deposition time and 42 mA/cm^2 of current density because the native oxide formed after synthesis is thermodynamically resistant to chemical dissolution in the alkaline electrolytes [8].

3.2 Potentiodynamic Polarisation

A PDP curve represents the polarisation domains of the surface of Co-Ni-Fe coating in 0.1M NaOH electrolyte. Fig. 2 shows the PDP curves of all samples after 3600 seconds of stabilisation. These curves were fitted using Gamry Echem Analyst while the calculated corrosion potentials (E_{corr}) and corrosion current densities (I_{corr}) were tabulated in Table 3. Stern-Geary equation was used to calculate E_{corr} and I_{corr} , on Tafel slopes of PDP curve. When a PDP curve has high corrosion potential or low corrosion current density, it typically has good corrosion resistance and thus, low

corrosion rate [9]. Based on Fig. 2, the shape of all curves is typically similar to each other, which is an indication that the samples had similar mechanism of electrochemical corrosion. All of the curves had active behaviour with no sign of passivation region. Passivation did not occur because the oxide/hydroxide became unstable and dissolved in the electrolyte [10].

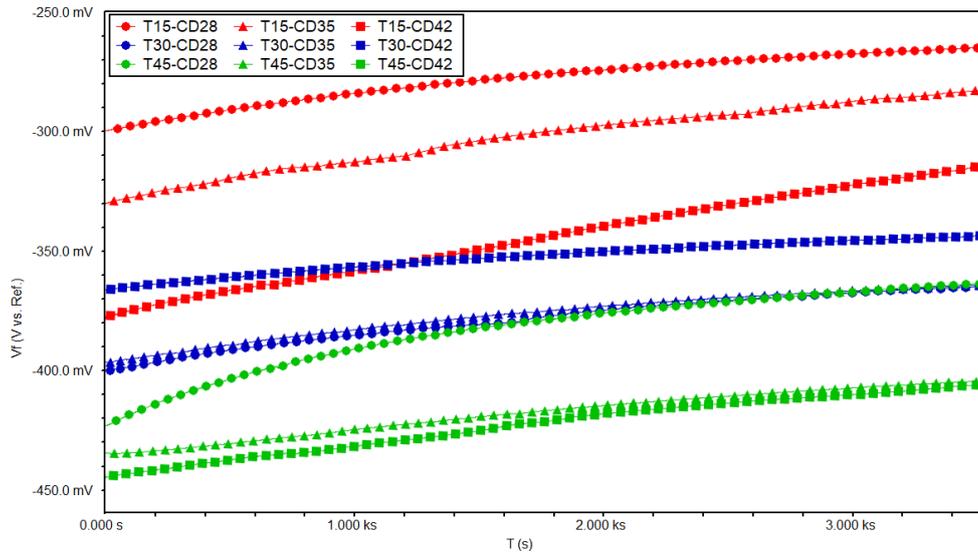


Fig. 1 - OCP curves of Co-Ni-Fe synthesised using different deposition times and current densities

Table 2 - Open circuit potential and surface roughness of Co-Ni-Fe coatings

Designation code	OCP (mV)	Surface roughness, Sa (µm)
T15-CD28	-264.2	0.75812
T15-CD35	-281.9	0.95701
T15-CD42	-313.4	0.53573
T30-CD28	-364.4	0.53851
T30-CD35	-364.6	0.77206
T30-CD42	-343.7	0.39498
T45-CD28	-377.6	0.43841
T45-CD35	-404.5	0.61067
T45-CD42	-405.9	0.41512

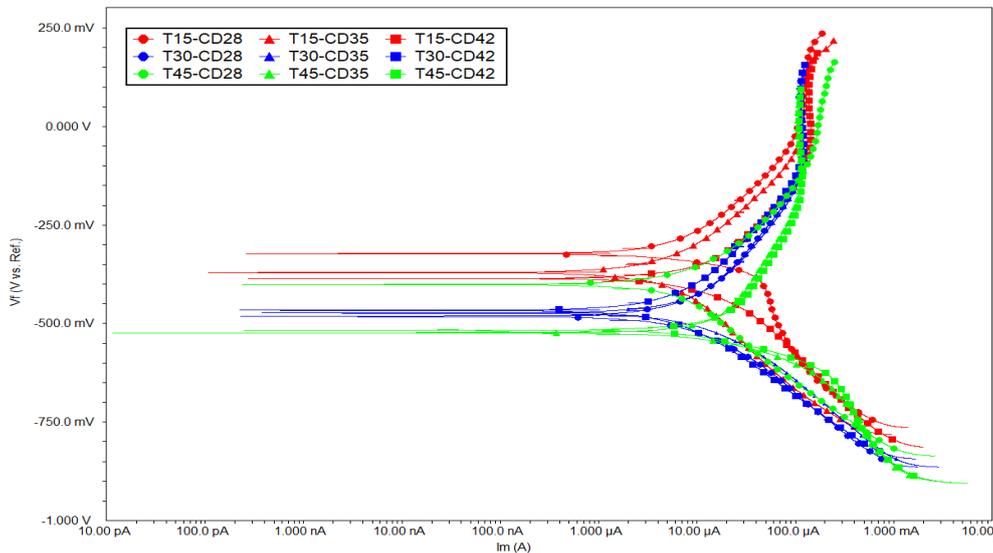


Fig. 2 - PDP curves of Co-Ni-Fe synthesised using different deposition times and current densities

Table 3 shows that the E_{corr} of T15 samples were more anodic than T30 and T45 samples. When the sample was synthesised using 15 minutes of deposition time and 28 mA/cm^2 of current density, the E_{corr} was -322 mV , I_{corr} was $610 \times 10^{-9} \text{ A/cm}^2$ and its corrosion rate was the third lowest. As current density increased and deposition time fixed, the E_{corr} increased. However, such phenomena did not occur for T30 and T45 samples. The I_{corr} of all samples did not have a recognizable pattern because the values fluctuated. Sample T30-CD42 demonstrated the lowest tendency of metal oxidation; thus, a lower corrosion occurred rate when compared to other sample. Although T30-CD42 did not have the smallest I_{corr} value, the Tafel slope on its PDP curve contributed to the lowest corrosion rate. The corrosion resistance of most CD28 samples was worse than CD45 samples which had lower I_{corr} .

Table 2 - Open circuit potential and surface roughness of Co-Ni-Fe coatings

Designation code	E_{corr} (mV)	I_{corr} (A/cm^2)	Corrosion rate (mppy)
T15-CD28	-322	610×10^{-9}	24.993×10^{-3}
T15-CD35	-370	256×10^{-9}	11.236×10^{-3}
T15-CD42	-386	$2,590 \times 10^{-9}$	5.911×10^{-3}
T30-CD28	-481	384×10^{-9}	15.168×10^{-3}
T30-CD35	-473	476×10^{-9}	6.629×10^{-3}
T30-CD42	-466	262×10^{-9}	3.758×10^{-3}
T45-CD28	-401	381×10^{-9}	7.6205×10^{-3}
T45-CD35	-523	$1,250 \times 10^{-9}$	6.466×10^{-3}
T45-CD42	-517	595×10^{-9}	5.529×10^{-3}

The corrosion rate of all samples synthesised at various parameters is shown in Fig. 3. The highest and lowest corrosion rates were $24.993 \times 10^{-3} \text{ mppy}$ and $3.758 \times 10^{-3} \text{ mppy}$ respectively. In terms of deposition time, there was a clear relationship between corrosion rate and surface roughness. Sample with the lowest roughness had the least corrosion rate of $3.758 \times 10^{-3} \text{ mppy}$. Nickel is an active-passive metal and this relationship agrees with the theory that lower surface roughness of active-passive metal leads to lower corrosion rate [11]. Similar behaviour on nickel-based materials was also reported on another study [12]. Based on Fig. 3, as the deposition time increased, the corrosion rates did not necessarily decrease but the deposition times at 30 minutes gave the lower corrosion rate when combined with current density of 35 and 42 mA/cm^2 . On the other hand, the higher the current density, the lower the corrosion rate.

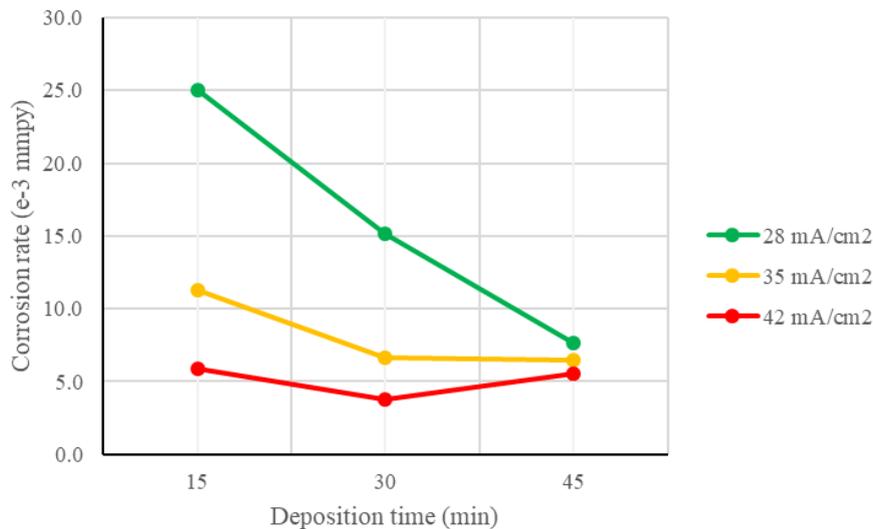


Fig. 3 - Effects of deposition time and current density on corrosion rate of Co-Ni-Fe coatings

3.3 Thickness of the Coatings

Fig. 4 illustrates the 3D surface with a clear interface between coating and substrate. The edge of coating with bright green colour was slightly thicker because the current density was higher around the masked area. Using profile form measurement as shown in Fig. 4, ΔZ between coating and substrate was calculated. This value represents approximation of coating thickness. Fig. 5 shows a rising trend for all three lines. The thickest coating was $30.1 \mu\text{m}$ and the thinnest was $5.8 \mu\text{m}$. Typically, zinc plating produced a coating thickness of $39 \mu\text{m}$ [13]. Since it is commonly applied to fasteners, the coating of Co-Ni-Fe in this study was lower than the value of zinc coating. So, all plating

parameters in this study were able to produce a coating thickness that was viable for industrial uses. All samples had thicker coating when deposited for longer time or at higher current density. The reason for the rate change is that as the current density increased, the deposition rate increased; thus, the thickness increased too. It is similar for deposition time in which more metals are deposited, the build-up increases the thickness. This phenomenon agrees to Faraday’s Law of Electrolysis.

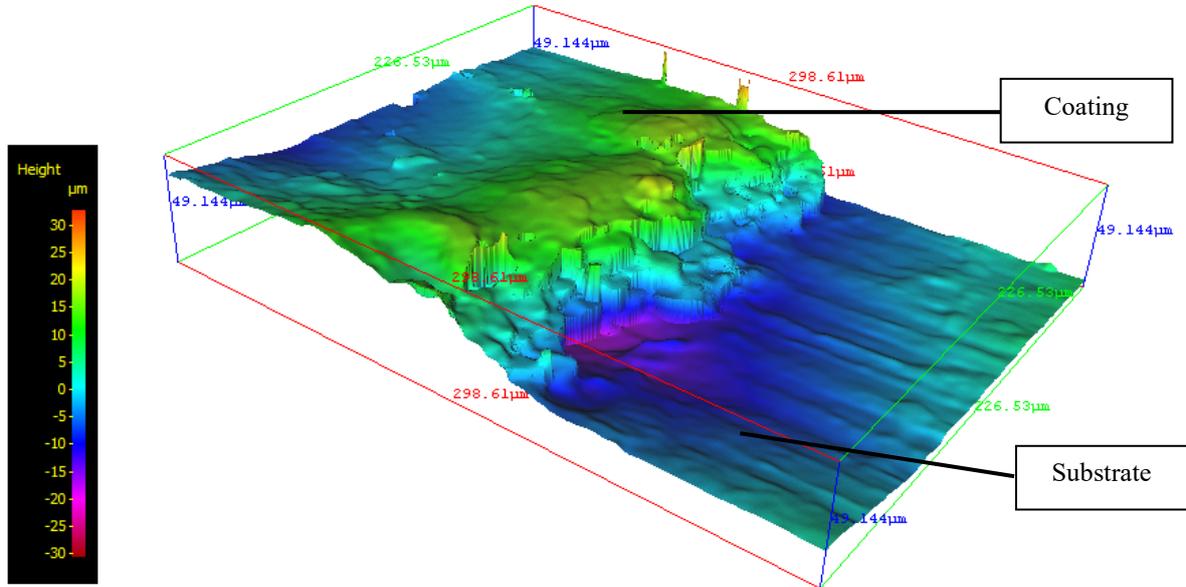


Fig. 4 - 3D Surface with pseudo colour of sample prepared at 42 mA/cm² for 45 minutes

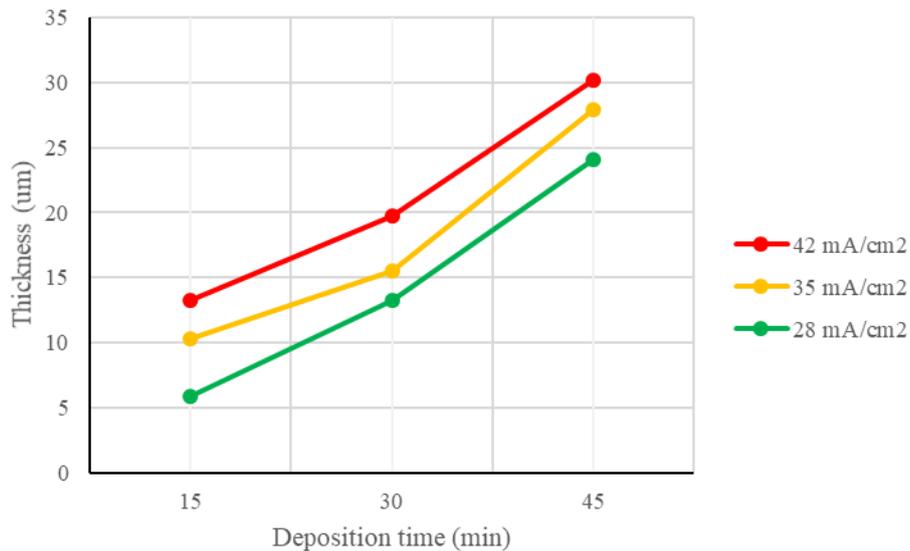


Fig. 5 - Effects of deposition times and current densities on the thickness of coating

4. Conclusion

The deposition time and current density affected the corrosion behaviour and surface properties of Co-Ni-Fe coating. T30 samples had the most stable OCP curve. PDP curves exhibited active behaviour with no sign of passivation region. The E_{corr} of T15 samples were more anodic than T30 and T45 samples. I_{corr} of all samples did not have a recognizable pattern because the values fluctuated. The lowest corrosion rate was achieved by sample synthesised in 30 minutes using 42 mA/cm². It can be deduced that the lower surface roughness contributes to the improvement of corrosion resistance. As deposition time and current density increased, the thickness of the coating increased. However, current density had lesser impact on the thickness of coating, whereas the thickness increase was largely influenced by deposition time. Thus, a shorter deposition time will save the cost as lesser metal deposit is required. Besides, the desired coating properties can be fine-tuned by changing the current density. The bolts will be used as fasteners for granite dust filled glass fibre pipe in the future.

Acknowledgement

The authors gratefully acknowledge College of Engineering, Universiti Teknologi MARA for providing equipment and other support. This research was funded by 100-RMC 5/3/SRP PRI (038/2020) grant. It was also conducted in collaboration with AANS Technical and Services Sdn Bhd with financial aid by Ministry of International Trade and Industry (MITI) Malaysia through Research and Commercialization Grant (GPPV) [Ref no.: APP/GPV/A/01A/1] and also under support of TECHKNOWHOW-(001/2021) research grant.

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