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# Investigating The Corrosion Behavior of Electrodeposited Nickel-Nano Diamond Composite Coating On Porous Materials by The Cyclic Voltammetry Method


Tutku Saatcı[1*], Elmas Salamci[1], Rahmi Unal[1], Neli Gidikova[2], Radoslav Valov[2], and Vladimir Petkov[2]

[1] *Mechanical Engineering Department, Engineering Faculty, Gazi University, Turkey*

[2] *Institute of Metal Science, Equipment and Technologies, Bulgarian Academy of Sciences, Bulgaria*

[*] *(saatcitutku@gmail.com)*



***Abstract* –** In this work, Intralube E with 0.38 % C press-ready mix powders were pressed with 550 MPa pressure and sintered 25 min at 1120 °C. Samples were coated electrochemically with nano diamond (ND) reinforced nickel to study the effect of nano composite coating on corrosion behavior by cyclic voltammetry method. The corrosion properties of uncoated, nickel-plated and samples coated with ND reinforcement at seven (0, 1, 1.5, 2.5, 5, 7.5, 10, 20 g/l) different concentrations were investigated. Corrosion resistance of these samples improved with the coating and with increasing ND content. The pitting formation decreased with the presence of ND. Breakdown potential increased from -210 mV to 30 mV, protection potential increased from -430 mV to 10 mV, passivation range increased from 0.97 mV to 1.25 mV, the current peaks on the anodic branches decreased from 53.89 mA to 0.42 mA, and lastly the difference between $E_b$ and $E_p$ decreased from 220 mV to 20 mV from uncoated to 20 g/l nano-diamond reinforced nickel coating. The less the difference, the less the susceptibility to corrosion. Decreasing current means increased corrosion resistance and improved passivation increases the corrosion resistance. Finally, $Cl^-$ ions were observed on the corroded surfaces with the EDS and SEM analyses.



*Keywords* – nano composite, electrochemical coating, cyclic voltammetry, corrosion resistance, EDS (energy dispersive X-ray spectroscopy), SEM (scanning electron microscope)


## I. INTRODUCTION

Powder metallurgy (PM) deals with pressing the metal powders and then sintering them to enhance strength. PM is preferred because of its sensitive and uniform final shape control, tolerance, lightweight, and not needing machining for production [1, 2]. However, they are susceptible against wear and corrosion. Porosities in the PM parts increase the pitting corrosion susceptibility [3]. At this point, solving the corrosion problems of PM products will extend the possible application areas of PM. Cathodic and anodic protection, coating, and alloying are the methods used to improve the corrosion resistance of PM parts. Researchers studied with these techniques to improve the corrosion behavior of PM products [4-17]. The method used for coating in the present study is electrodeposition, a technique used for producing nanocomposites by using deposition of dispersed nano particles to perform the uniformity of the external layer of a part [3, 14, 16]. Rather than the micro particles, nano particles used as reinforcement in the matrix is a new field needed to be investigated more.

Awasthi et al. [13] reported the effect of different concentrations of diamond particles (2.5-10.g/l) on the wear mechanism of electrophoretic Ni. They observed that ND addition improved the wear resistance. Etaat et al. [1] investigated the corrosion behavior of nickel coated iron compacts produced by powder metallurgy. They performed three different secondary operations to specimens: steam-treatment, resin impregnation, and copper infiltration before electroplating with nickel. They reported that steam treated specimens showed better corrosion behavior. Vaezi et al.[18] studied on Ni-SiC nano-composite electrodeposited coatings with different contents of SiC nano particulates to evaluate corrosion resistance. They reported that corrosion resistance increased with increasing content of the SiC. Hou et al. [14] researched composite coatings obtained by electrodeposition from a Ni-W plating bath containing suspended diamond particles similar with the present study. Nevertheless, they investigated wear behavior and obtained improvement with increasing ND. Sui et al. [15] reported that they produced diamond-like carbon films on NiTi substrate by plasma immersion ion implantation and deposition. They found that increasing diamond reduced the corrosion attack. Mazaheri and Allahkaram [19] investigated the corrosion resistance of Ni-P/nano-diamond composite. They reported that adding ND to coating improved the corrosion resistance compared with Ni-P only. However, they observed an optimum concentration of ND by the linear polarization and electrochemical impedance spectroscopy.

The aim of this study is to evaluate the corrosion behavior of ND reinforced nickel coating on the PM samples by the cyclic voltammetry. There are no studies on corrosion behavior of ND reinforced nickel coating on the PM substrate in the literature. The use of cyclic voltammetry method for the corrosion test of ND reinforced nickel coating on the PM substrate has not yet been found in the literature.

## II. MATERIALS AND METHOD

The chemical composition of Intralube E press-ready mix powders was given in Table 1. The metal powders were pressed at 550 MPa in a floating biaxial mold into 31.7×12.7×10.0 mm dimensions and sintered for 25 min in 0.6 % carbon potential atmosphere at 1120 °C. Before the nickel and nickel-ND coating processes, the surface oxide layer of the samples was cleared through degreasing with ethanol and activated for 10 min. The electrochemical coating bath composition were 240 g/l $NiSO_4.7H_2O$, 150 g/l $Na_2SO_4.10H_2O$, 66 g/l $Na_2SO_4$, 15 g/l NaCl, 20 g/l $HBO_3$, 0, 1, 1.5, 2.5, 5, 7.5, 10, 20 g/l of ND concentration. The working conditions were 3 A/dm$^2$ current density, 25 – 28 °C temperature, 15 min coating duration, 120 rpm stirring rate, 5.0-5.5 pH, 6 nm average ND particles size, nickel as anode and a 20-30 mm distance between the anode and the cathode.

Archimedes principle was used to calculate the densities of the sintered samples. In the calculation of the average theoretical porosity percentage, theoretical density and calculated density were used. Besides, the experimental porosity percentage was calculated using Image J computer program by taking the average of 10 microphotographs. Samples were ground with SiC papers (grit 240,400,600,1000, and 1200). Then they were polished with 3 µm and 1 µm polishing suspension for characterization with optical microscope. Coating thickness of the samples were investigated by taking the average of 10 different regions.

The corrosion behavior of electrodeposited nickel-ND composite coatings were investigated by cyclic voltammetry method (CV). Three-electrode corrosion cell system (reference, working, and counter) were utilized for the experiments. CV tests were performed between -1.8 V and 0.2 V with 50 mV/s scan rate in 3.5-weight percent NaCl solution with two cycles at room temperature. EDS and SEM analyses were conducted for the corroded surfaces.

Table 1 Chemical composition of the investigated powders (wt.%)

| Components | C | Cu | MnS | Lube E | Fe |
|---|---|---|---|---|---|
| wt.% | 0.38 | 1.56 | 0.50 | 0.78 | Balance |

## III. RESULTS

Theoretical and calculated densities of the sintered samples were 7.807 and 6.901 g/cm$^3$, respectively. Theoretical and experimental porosities of the sintered samples were found to be 11.604 % and 10.87 %, respectively. Coating thickness were determined as 26.72, 30.11, 29.09, 28.86, 18.84, 28.73, 20.33, 23.49 µm for the 0, 1, 1.5, 2.5, 5, 7.5, 10, 20 g/l of ND concentrated samples, respectively. Figure 1 shows the surface porosities of the sintered samples. Figure 2 shows an example for the coating thickness view.

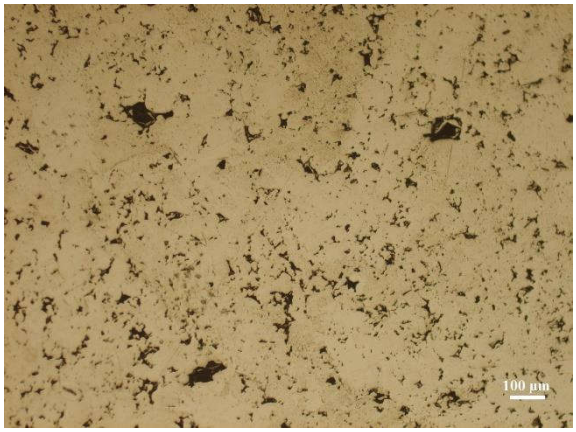



Fig. 1 Surface porosities of the sintered sample

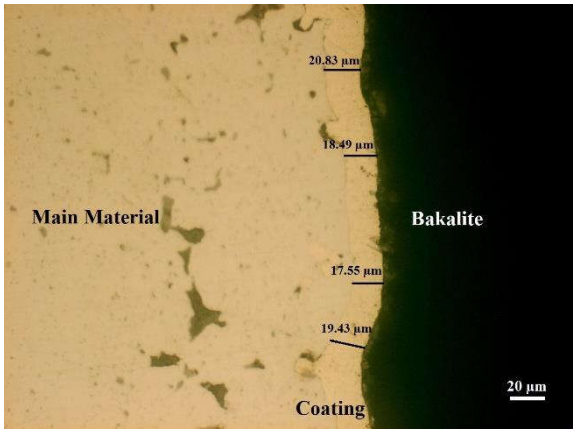



Fig. 2 Coating thickness view

The CV graphs were depicted in between Figures 3-11. The black and green cycles represent the first and the second cycles, respectively. As coding, INT. Ni/NE. 5.0-3-15 means that Intralube E base coated at 3 A/dm$^2$, 15 min with 5 g/l ND reinforced nickel. Quantitative results of the CV graphs were given in Table 2. EDS and SEM images for the corroded surfaces were given in Figures 12-15.

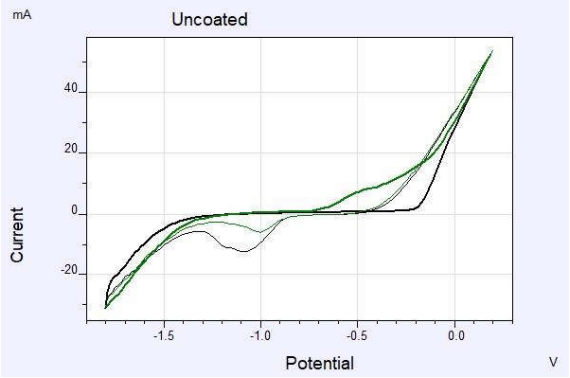



Fig. 3 CV Graph of uncoated specimen

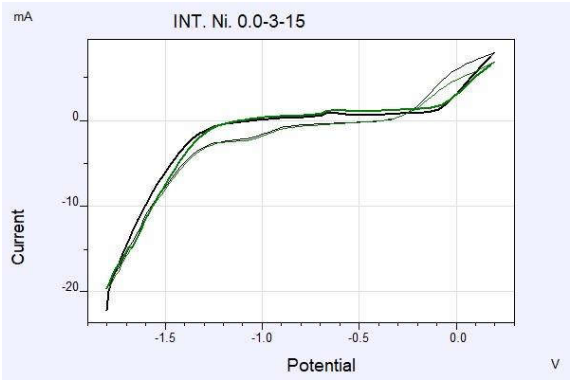



Fig. 4 CV Graph of INT. Ni. 0.0-3-15

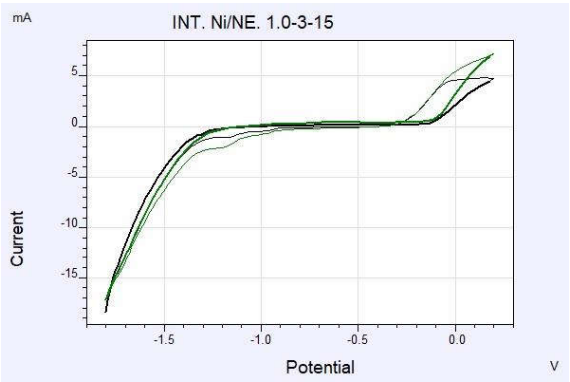



Fig. 5 CV Graph of INT. Ni/NE. 1.0-3-15

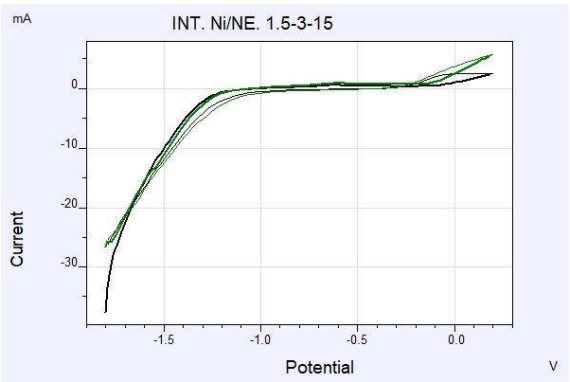



Fig. 6 CV Graph of INT. Ni/NE. 1.5-3-15

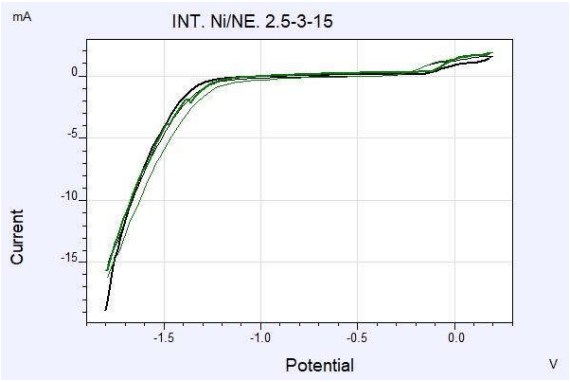



Fig. 7 CV Graph of INT. Ni/NE. 2.5-3-15

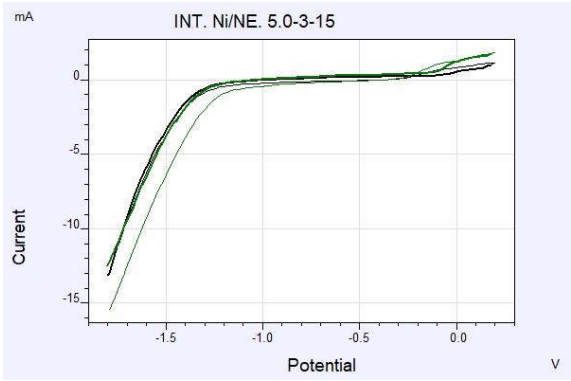



Fig. 8 CV Graph of INT. Ni/NE. 5.0-3-15

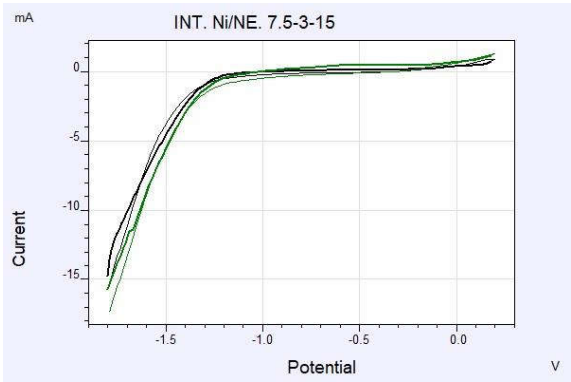



Fig. 9 CV Graph of INT. Ni/NE. 7.5-3-15

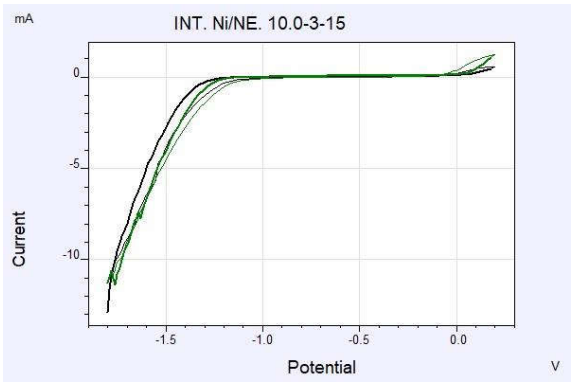



Fig. 10 CV Graph of INT. Ni/NE. 10.0-3-15

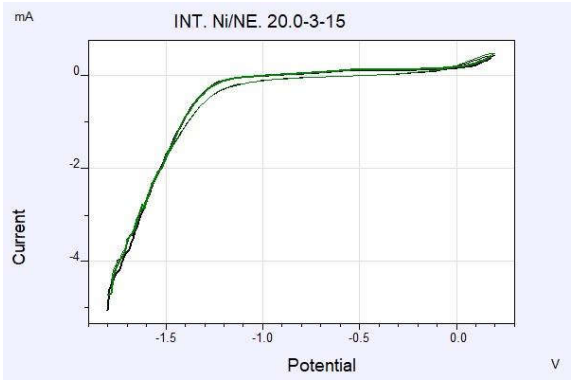



Fig. 11 CV Graph of INT. Ni/NE. 20.0-3-15

Table 2 Quantitative results for the CV graphs

| Specimen | First Cycle Peak (mA) | Second Cycle Peak (mA) | $E_b$ (Breakdown Potential) Pitting Starting Volts (mV) | $E_p$ (Protection Potential) Repassivation (mV) | $E_b - E_p$ (mV) | Passivation Range (mV) |
|---|---|---|---|---|---|---|
| Uncoated | 53.890 | 53.770 | -210 | -430 | 220 | 0.97 |
| INT. Ni. 0,0-3-15 | 6.780 | 7.870 | -130 | -260 | 130 | 1.07 |
| INT. Ni/NE. 1,0-3-15 | 4.739 | 7.168 | -130 | -280 | 150 | 1.11 |
| INT. Ni/NE. 1,5-3-15 | 2.472 | 2.472 | -90 | -220 | 130 | 1.11 |
| INT. Ni/NE. 2,5-3-15 | 1.531 | 1.875 | -130 | -220 | 90 | 1.07 |
| INT. Ni/NE. 5,0-3-15 | 1.079 | 1.807 | -80 | -200 | 120 | 1.12 |
| INT. Ni/NE. 7,5-3-15 | 0.843 | 1.275 | 40 | 20 | 20 | 1.24 |
| INT. Ni/NE. 10,0-3-15 | 0.535 | 1.201 | 20 | -10 | 30 | 1.23 |
| INT. Ni/NE. 20,0-3-15 | 0.417 | 0.465 | 30 | 10 | 20 | 1.25 |

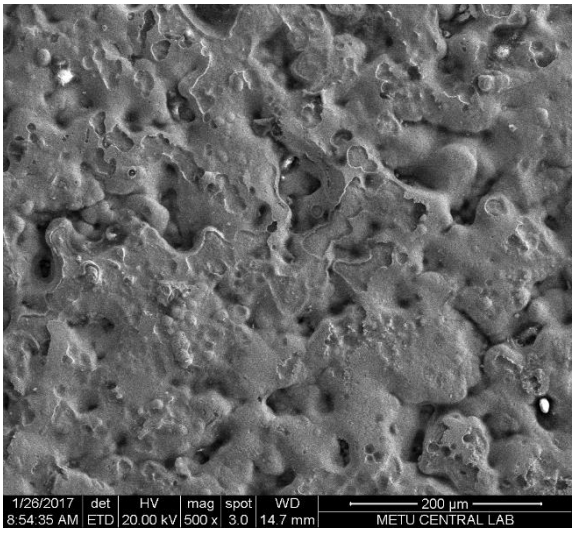



Fig. 12 Corrosion surface of INT. Ni. 0.0-3-15 (500X)

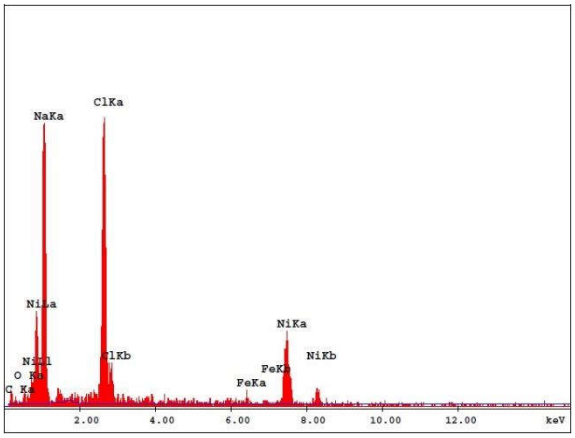



Fig. 13 $Cl^-$ ion on corrosion surface by EDS analyses

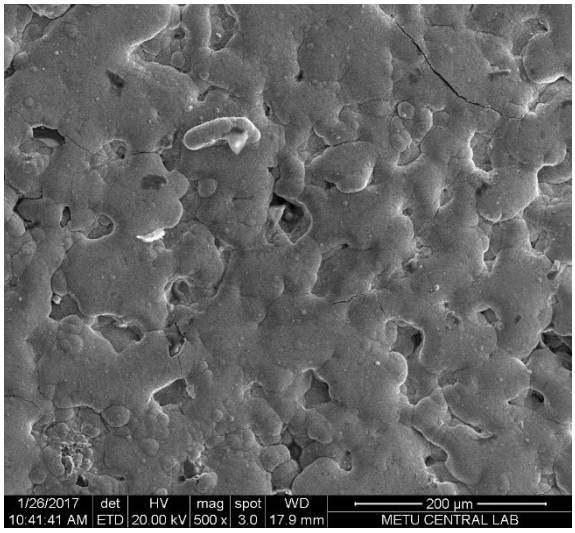



Fig. 14 Corrosion surface of INT. Ni. 10.0-3-15 (500X)

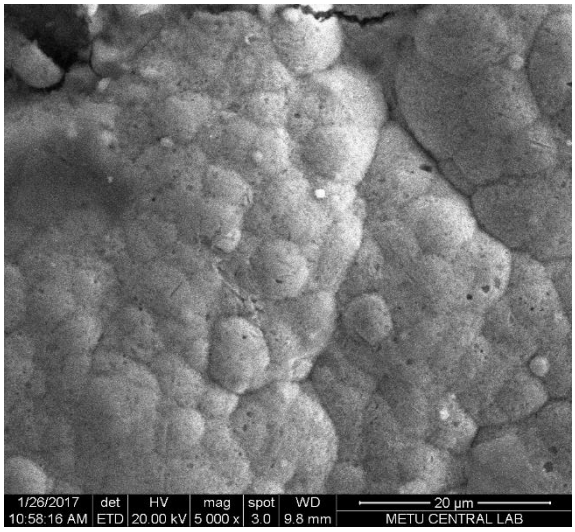



Fig. 15 Corrosion surface of INT. Ni. 10.0-3-15 (5000X)

## IV. DISCUSSION

Coating thickness changed non-uniformly with the increasing ND content. Porosities affect the homogeneous current density distribution for the coating process and

decrease the sensibility of controlling the coating thickness. In short, corrosion behavior improved with increasing ND concentration. Cyclic voltammetry graphs mainly include five important variables which are breakdown potential ($E_b$), protection potential ($E_p$), passivation range, current peaks, and difference between $E_b$ and $E_p$.

$E_b$ is the starting potential of the pitting on forward scan (the lowest potential at which pitting occurs), so the increase in $E_b$ means that there is more pitting resistance. In the present study, $E_b$ increased with increasing ND content. As can be seen from Table 2, $E_b$ increased from -210 mV to 30 mV. As the potential decreases on the reverse scan, a decrease in current with a hysteresis occurs. $E_p$ is the potential where the reverse scan crosses forward scan. The repassivation starts at $E_p$ and it occurs always at a lower potential than $E_b$. $E_p$ increased from -430 mV to 10 mV as shown in Table 2. The difference between $E_b$ and $E_p$ is associated to susceptibility to corrosion; the less the hysteresis in the CV curve, the less the corrosion susceptibility. The difference between $E_b$ and $E_p$ decreased from 220 mV to 20 mV with increasing ND content as indicated in Table 2 so that corrosion resistance improved. Passivation (the wide, straight plateau on the polarization curve at about 0 mA which is known as protection layer) range increased from 0.97 mV to 1.25 mV with increasing ND content as given in Table 2. Passivation can be defined as the removal of a metal from the surface of a metal and mixing with oxygen instead of mixing into a solution, depositing on the surface and cutting off the connection between the metal and the environment to prevent further corrosion. Improved passivation increases the corrosion resistance. Additionally, the passivation of the uncoated sample fluctuated prominently as shown in Figure 3, the line is not going on its straight path meaning that some material broken off suddenly. The magnitude of the current peak on anodic branch is related to the tendency to pitting corrosion; the greater the current in the CV curve, the greater the pitting corrosion tendency. The current peaks on the anodic branches decreased from 53.89 mA to 0.42 mA from uncoated to 20 g/l nano-diamond reinforced nickel coating as shown in Table 2. Decreasing current peaks means increased corrosion resistance. Comparing the Figures 12-15, pitting corrosion regions reduced with the increase in ND content. In Figure 14, the magnification is not enough to see the pitting corrosion but they are visible with larger magnification in Figure 15. Finally, $Cl^-$ ions were observed on the corroded surfaces by the EDS and SEM analyses as indicated in Figure 13.

There are very few studies on nickel coating with various reinforcements and base material for different examinations [1-20]. There are no investigation with ND reinforced nickel coating on PM samples to study the corrosion behavior in the literature. Exactly the cyclic voltammetry method has not been used for analyzing the corrosion behavior of ND reinforced nickel coating on PM samples. Therefore, there is no exact research to compare in the literature. Researchers reported that increasing ND increased corrosion resistance by using some other methods rather than the cyclic voltammetry method for corrosion behavior in line with the present study. There are studies [21-26] that cyclic voltammetry method was used with various materials and coatings.

## V. CONCLUSION

Increasing ND content increased the corrosion resistance. In all samples INT. Ni/NE. 20.0-3-15 exhibited the best corrosion behavior. The coating significantly increased the corrosion resistance as indicated in Table 2 compared with the uncoated sample. The Ni ND nano-composite coating has better corrosion resistance than the nickel coating. Pitting corrosion zones occurred on the corroded surfaces reduced with an increase in ND content. The passivation and breakdown potential increased, the current peak decreased with an increase in ND content.

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