Electrodeposition of Ni–Co / nano Al₂O₃ composite coating on low carbon steel and its characterization

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Ni–Co / nano-Al₂O₃ composite coat was electrodeposited from environmentally friendly citrate tub. The electrodeposition was established from agitated solutions, containing disparate amounts of nano-Al₂O₃ particles. The addition of nano-Al₂O₃ to the plating solution decreases the polarization for Ni–Co alloy plating. The quantity of Al₂O₃ in the composite rises with concentration of Al₂O₃ in the coating solution, current density and decreasing temperature. Composites were examined by scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy dispersive X – ray (EDX) techniques. The obtained composites were crystalline and had face-centered cubic (FCC) structure. The thickness of composite diminishes with increasing the amount of Al₂O₃ in the composite however, the microhardness increases. The resistance of Ni–Co / nano-Al₂O₃ composite against corrosion in 3.5 % salt water was tested by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Ni–Co / nano-Al₂O₃ composites had a good corrosion resistance.

Keywords: electrodeposition; citrate bath; Ni–Co / nano-Al₂O₃; microhardness

1. INTRODUCTION

Electrodeposited metallic composites may be single metal or alloy. These composites are harder to be applied in severe environments, which are subjected to both chemical and mechanical wear attack. As a result, there was an exigent necessity to create novel classes of wear- and corrosion-resistant coating materials [1].
There is a growing demand to ameliorate Metal Matrix Composites (MMCs). Advances in technology need materials with particular properties. In general, composites possess topnotch characteristics such as eminent hardness, acceptable resistance to corrosion at higher temperatures, surpass wear and oxidation resistances. In addition to electrical and magnetic properties, self-lubrication, tensile and breakage strength, high thermal stability, chemical and biological compatibility relative to conventional pure metal or metallic alloy composites [1–3].

Nano-particles show various specific physical & chemical properties due to quantum size and quantum tunnel effects. Nano-composites plating technique, in which nanoparticles are inserted into to metallic composites, to enhance their physical & mechanical properties, illustrates how nanotechnology can be utilized for plating of composites.

Composites can be obtained by a variety of techniques such as thermal spraying, plasma spraying, chemical vapor deposition (CVD), physical vapor deposition (PVD), electroless deposition and electrodeposition [4–6]. Among these techniques electrodeposition technique has proved itself to be a promising technique to produce metal matrix composites in a single step. It produces harder and smoother surfaces. This enhances bonding among codeposited molecules and metal and allows fine control for the coating thickness [7 & 8].

Electrodeposited MMCs fundamentally composed of elastic metal / alloy matrix in which another fine indissoluble inert phase with a diversified particle size, ranges from micrometric and sub-micrometric to nano-metric one, is distributed [9 &10]. The particle size has a pronounced effect on the properties of the coating. In chief, the properties of the coat were improved greatly as the particle size of codeposited particles decreases [11]. In the last few years, a variety of nano-sized particles ranging from 4 - 800 nanometers have been incorporated successfully into metallic composites. Currently, there is a growing trend to use particles less than 100 nanometers to obtain a new innovative of advanced materials [12 &13].

The particles that used in composites were categorized into 2 important categories: soft & hard particles. Soft particles act as self-lubricant substances to minify friction between sliding surfaces. On the other hand, hard particles such as SiO₂, Al₂O₃, SiC, and Si₃N₄ amend the mechanical properties and microhardness of deposited metals and alloys [14–17].

Ceramics in the form of oxides are inorganic compounds of metallic (Al, Ti, Cr) or metalloid (Si) elements with oxygen. They have the ability form a variety of composites with different metallic matrixes. They are utilized to increase the oxidation resistance, hardness and wear improvement over conventional composites. Several oxides such as alumina (Al₂O₃), silica (SiO₂), chromia (Cr₂O₃), ferric oxide (Fe₂O₃), zirconia (ZrO₂), ceria (CeO₂), titania (TiO₂), yttria (Y₂O₃), Dysprosium oxide (Dy₂O₃) and lanthana (La₂O₃) form different composites with various metallic matrixes [17– 24].

Alumina particles are one of the most studied ceramic materials [25-38]. It has many unique properties such as great chemical stability, utmost elastic modulus, large thermal stability, high hardness and corrosion resistance [25–27]. Moreover, it is an electrically nonconducting substance [28]. Wu and coworkers [26] prepared Ni–Co/Al₂O₃ composites using codeposition of alloys and Al₂O₃ from sulfamate tub. They studied the effect of plating conditions on the amount of Al₂O₃ particles in Ni–Co alloys. Chang and his team [29] deposited Ni–Co/Al₂O₃ composite coating using
pulse reverse current under ultrasonic conditions. The effect of ultrasonic power on composition, appearance, microhardness microstructure & residual macrostress of composite coating was studied.

The given work aims to electrodeposit Ni–Co / nano-Al₂O₃ composites coating at low carbon steel cathode. The deposition was established from conventional citrate bath by electrodeposition technique. The study was carried out under different experimental conditions and comprises the evaluation of microstructure of the prepared composites by (SEM), (EDX) & (XRD) techniques. The corrosion resistance of composites is tested in 3.5 % salt water by potentiodynamic measurements and impedance technique.

2. EXPERIMENTAL

2.1. Electrodeposition procedure

Electrodeposition was established from solutions contain 0.08 M nickel sulphate e, 0.12 M cobalt sulphate, 0.2 M anhydrous sodium sulphate, 0.3 M tri – sodium citrate and different amounts of nano-sized Al₂O₃ powder with average size of 16.4 nm. Agglomeration of Al₂O₃ was minified by ultrasonic dispersion for 20 minutes. The pH was measured using digital Fisher pH-meter.

The experimental setup was mentioned formerly [39]. It composed of a Perspex trough, in the form of rectangle, equipped with a sheet of low carbon steel cathode and a stainless steel (type – 304) sheet anode. Every sheet had a total area of 9 cm². The working sheet was burnished mechanically with progressively fine grades of emery papers, cleaned with bi-distilled water, rinsed with acetone and weighed. The plating was completed from agitated solutions. The deposition time was 20 minutes, after which the coated steel was washed with bi-distilled water, dried & weighed. The alloy composition was ascertained by atomic absorption spectrophotometer (type Solaar S4). It was found that the proportion of Al₂O₃ nano particles in the composites ranging from 2.5 to 4.4%.

2.2. Potentiodynamic polarization measurements

Corrosion of composite coating in 3.5 wt. % salt water was examined by potentiodynamic polarization. This is carried out by the aid of an electrochemical analyzer (Iviumstat Electrochemical Interface) supplied by IVIUM technologies. The electrochemical analyzer is linked to a personal computer for potential control and data acquisition and a classical three-electrode cell with a steel working electrode of exposed area of 1 cm². All potentials measured referred to saturated calomel electrode (SCE). Pt gauze acted at counter electrode. Before starting run, steel electrode was immersed in the test solution for 30 minutes to achieve steady state. The potentials were scanned from −0.5V below OCP to a final potential of +0.5 V, at a sweep rate of 1 mV s⁻¹. Three experiments were made for each sample to ensure reliability. The corrosion potential (E_corr) and corrosion current density (I_corr) obtained from the intersection of the cathodic and anodic polarization curves constructed by Tafel extrapolation methods are listed in Tables 3. The corrosion current density (i_corr) was measured using the following equation:

\[
I_{\text{corr}} = \frac{B}{R_p}
\]  (1)
Where: \( R_p \) is the polarization resistance & \( B \) is the Stern–Geary constant, calculated by the following equation:

\[
B = \frac{\beta_a \beta_c}{2.303(\beta a + \beta c)}
\]  

(2)

Where: \( \beta_a \) and \( \beta_c \) are the anodic and cathodic Tafel slopes, respectively.

The corrosion current density \( (I_{corr}) \) can be converted to corrosion rates (mm/year) based on the following Faraday’s law:

\[
\text{Corrosion rate} = 3.15 \times 10^5 \times \left(\frac{M}{nFD} \right) \times I_{corr}
\]

(3)

Where \( M \) is atomic mass, \( n \) is the number of electrons involved in the corrosion reaction in mole \((n = 2)\), \( F \) is Faraday’s constant in coulombs/mole \((F = 96500)\), and \( d \) is the density of alloy in g/cm\(^3\) \((d = 9.55)\).

2.3. Electrochemical impedance spectroscopy measurements

(EIS) measurements were carried out in the frequency range of 60 kHz - 10 MHz with a 5 mV sine wave as excitation signal. The corrosive medium was a solution of 3.5 wt. % salt water. The experiments were carried out at a fixed temperature \((\pm 1 \, ^\circ \text{C})\). For investigational data, the parameters as a proportional factor \((Y_o)\), phase shift \((n)\), \( R_s \), and \( R_{ct} \) were evaluated using the ZSimpWin program. The fitted impedance parameters are given in Table 4. The CPE type impedance, \( Z_{CPE} \), was calculated from the subsequent equation:

\[
Z_{CPE} = \frac{1}{Y_o(j\omega)^n}
\]

(4)

Where the exponent \( n \) is the phase shift; provides information about the degree of non-ideality in capacitive behavior, \( J^2 = -1, \omega = 2\pi f \). For \( n = 0 \), \( Z_{CPE} \) represents a resistance with \( R = Y_o^{-1} \), for \( n = 1 \) a capacitance with \( C = Y_o \), for \( n = 0.5 \) a Warburg impedance with \( W = Y_o \) and for \( n = -1 \) an inductive with \( L = Y_o^{-1} \).

2.4. Coating characterization

The morphology of composites was checked by (SEM) (QUATNTA FEG 250) engaged with energy dispersive spectrometer (EDX – FEI – QUATNTA FEG 250). The latter was utilized to identify the components of the composites. Microstructure of the composite coating was analyzed by X-ray diffractometer (X’pert Pro P analytical operated at 45 KV & 40 mA with Cu-K\(\alpha \) radiation \( \lambda = 0.154 \) nm). The thickness of the composites was determined by coating thickness gauge (model TT210). The thickness of the composites ranged from 6.5 to 11 \( \mu \)m. Microhardness was measured by microhardness tester with a load force of 100 g for 5 seconds. The microhardness was found to be ranged from 140 to 330 Hv.
3. RESULTS AND DISCUSSION

3.1. Cathodic polarization measurements

To expound the influence of nano-sized Al₂O₃ inert particles on the electrodeposition process of Ni–Co alloy, cathodic polarization experiments were carried out [40]. Polarization methods involve changing the working electrode potential and measured the corresponding current that is produced [41].

![Cathodic polarization curves](image)

**Figure 1.** Cathodic polarization curves for Ni-Co / Al₂O₃ composite on steel at pH = 10, temperature = 25 °C and stirring speed = 500 rpm from solutions with 0.08 M NiSO₄·6H₂O, 0.12 M CoSO₄·7H₂O, 0.3 M Na₃C₆H₅O₇·2H₂O, 0.2 M Na₂SO₄ and different concentrations of nano sized Al₂O₃: (a) 0, (b) 1, (c) 2 and (d) 4 g/l. Scan rate = 20 mV/s.

The impact of concentration of nano-sized Al₂O₃ particles in the coating tub, upon the cathodic polarization of Ni–Co alloy is illustrated in figure (1). Increasing the content of Al₂O₃ particles in the plating tub reduces polarization for Ni–Co alloy plating. Al₂O₃ particles facilitate alloy deposition [42]. This behavior was reported for conducting particles such as Cr particles and semi-conducting particles like SiC [43]. The noble shift for deposition potential of Ni–Co alloy ascribed to improvement in the rate of transfer of depositing ions by Al₂O₃ nano particles. This increases the metal nuclei on the steel sheet and thusly encouraging its deposition [44]. In addition, Al₂O₃ nanoparticles can facilitate the adsorption of the alloying ions and hence increment the current density [45& 46].

3.2. Composition of composites

The content of particles and their dispersion in electrodeposited composites mainly depend on numerous parameters such as concentration and size of inert particles, the utilized current density, and
the deposition temperature, pH of the bath, agitation and deposition time [47]. The effects of some variables on the electrodeposition process are shown in Figs (2 – 4).

**Figure 2.** The impact of concentration of nano Al$_2$O$_3$ particles on the composition of Ni-Co / Al$_2$O$_3$ composite on steel from a bath with 0.08 M NiSO$_4$.6H$_2$O, 0.12 M CoSO$_4$.7H$_2$O, 0.3 M Na$_3$C$_6$H$_5$O$_7$.2H$_2$O, 0.2 M Na$_2$SO$_4$ and different concentrations of nano Al$_2$O$_3$ at time = 20 min., pH = 10, current density = 55.55 mA cm$^{-2}$, temperature = 25 °C and stirring speed = 500 rpm.

**Figure 3.** The impact of current density on the composition of Ni-Co / Al$_2$O$_3$ composite on steel from a bath with 0.08 M NiSO$_4$.6H$_2$O, 0.2 M Na$_2$SO$_4$ 0.12 M CoSO$_4$.7H$_2$O, 0.3 M Na$_3$C$_6$H$_5$O$_7$.2H$_2$O and 4 g/l of nano-sized Al$_2$O$_3$ at time = 20 min., pH = 10, temperature = 25 °C and stirring speed = 500 rpm.
Figure 4. The effect of tub temperature on the composition of Ni-Co / Al₂O₃ composites on steel from a bath with 0.08 M NiSO₄.6H₂O, 0.12 M CoSO₄.7H₂O, 0.3 M Na₃C₆H₅O₇.2H₂O, 0.2 M Na₂SO₄ and 4 g/l of nano-sized Al₂O₃ at time = 20 min., pH = 10, current density = 66.66 mA cm⁻² and stirring speed = 500 rpm.

The amount of embedded particles in the metallic coatings is based on their amounts in the coating solution. Figure (2) demonstrates the effect of rising nano-sized Al₂O₃ amount in the plating tub on its percentage in the composites. The amount of Al₂O₃ particles in the composite gradually increases with increasing its quantity in the tub and then tends to level off at 5 g/l. The obtained graph is analogous to Langmuir adsorption isotherm [48–51]. This behavior can be explained by adsorption model of Guglielmi [52]. As the quantity of inactive nanoparticles in the solution increases, the number of particles that transfer from the bulk of solution to cathode surface layer increases. Thus, the possibility of striking and adsorption to the electrode surface is enhanced. Consequently, the adsorption speed is accelerated, leading to a higher weight percent of the codeposited Al₂O₃ particles in the metallic matrix. However, the limiting content could be assigned to a steady state of equilibrium. At this state, the number of codepositing particles equals the number attaining the cathode surface [53 & 54].

Current density is the most crucial factors that affecting the codeposition process of inactive particles with metallic matrix from a suspended solution [55]. Figure (3) exhibits the impact of practical current density on the weight percentage of nano-sized Al₂O₃ particles in the deposited Co–Ni alloy. Low current density has no remarked influence on the content of Al₂O₃ in the deposit. Nevertheless, high current densities raise the proportion of Al₂O₃ in the deposit. At low current density and due to the difference in energy of activation demand for deposition, the freely solvated metal ions need small energy for deposition. Consequently, the free Ni²⁺ and Co²⁺ ions will be deposited preferentially on the steel cathode at the expense of Al₂O₃ inert particles. On increasing the current density, the energy difference becomes little important as there is sufficient energy to intensify the
diffusion and convection rates of the particles. This increases both the co-deposition of metallic ions and the unreactive particles [56].

The impact of bath temperature on the amount of nanosized Al₂O₃ particles in Ni–Co coating is shown in Fig. (4). Rising the tub temperature from 10 to 65 °C causes a two-fold effect on deposition of Al₂O₃ particles. As the temperature rises, the kinetic activity of the particles increases, which is helpful for the codeposition of Al₂O₃ particles. In addition, on increasing temperature, the mass transfer of metallic ions is markedly increases by diffusion, convection and migration. This leads to an increase of both kinetic energy and deposition rate. According to Langmuir, the adsorption of adsorbate (inactive particles) diminishes with temperature. This minimizes the chance for Al₂O₃ particles to be instilled in the coat and therefore reduces its percent in the composite [57].

3.3. Morphology and microstructure of composites

The morphological study was investigated to relate characteristics of the composites to electrochemical response during the electrodeposition process. SEM was used for the analysis of composites, obtained under varied experimental conditions. Generally, electrodeposited Ni–Co alloy composites containing Al₂O₃ nanoparticles are orderly, smooth, compact and acquire a dull gray color. The coat brightness increases as the Al₂O₃ proportion increases in the coating. But on the contrary, the darkness of the composites increases with current density.

![Figure 5](image)

**Figure 5.** Scanning electron photographs of electrodeposited Ni-Co alloy with: (a) 2.52 and (b) 4.29 wt. % of nano-sized Al₂O₃, obtained from baths with 0.08 M NiSO₄.6H₂O, 0.12 M CoSO₄.7H₂O, 0.3 M Na₃C₆H₅O₇.2H₂O and 0.2 M Na₂SO₄ at current density = 55.55 mA cm⁻², pH = 10, time = 20 min., temp. = 25 °C, stirring speed = 500 rpm.
Figure (5) illustrates the influence of nano-sized Al₂O₃ content in the plating tub on the appearance of electrodeposited Ni–Co composites. The addition of 1 g/l Al₂O₃ particles to the coating tub changes the morphology of the deposit from irregular and dendritic shapes into regular and dense form with small size, Fig. (5a). Further addition of Al₂O₃ changes the morphology of electrodeposited composites to compact agglomerates. Composites contain some pores due to hydrogen evolution. The decrease in size of Ni–Co matrix could be ascribed to the addition of inactive particles to the plating coating tub. During growing of electrodeposited layer, there is a competition between crystal growth and nucleation mechanisms. The unreactive particles adsorbed on a growing lattice and thus, inhibit its growing. This enables more nucleation sites, resulting in small size crystals [58 & 59].

The phase and microstructure of electrodeposited Ni–Co / nano Al₂O₃ composites were tested using XRD measurements. X-ray patterns evidenced that the total composites are crystallized, Fig. 6. The peaks are acute and good – characterized, indicating good crystallization. The structure of the electrodeposited Ni–Co / nano Al₂O₃ composites is a solid solution. It has a face centered cubic (FCC) structure. The electrodeposited alloys showing three – well defined diffraction peaks, (111), (200) and (220), respectively [58 & 59].

**Figure 6.** X-ray diffraction of electrodeposited Ni-Co alloy with: (a) 2.52 and (b) 4.29 wt. % of nano-sized Al₂O₃, obtained from baths with 0.08 M NiSO₄ 6H₂O, 0.12 M CoSO₄ 7H₂O, 0.3 M Na₃C₆H₅O₇ 2H₂O and 0.2 M Na₂SO₄ at current density = 55.55 mA cm⁻², pH = 10, time = 20 min., temp. = 25 °C, stirring speed = 500 rpm.
Figure 7. EDX analysis patterns of electrodeposited Ni-Co alloy with: 4.29 wt. % of nano-sized Al₂O₃, obtained from baths with 0.08 M NiSO₄.6H₂O, 0.12 M CoSO₄.7H₂O, 0.3 M Na₅C₆H₅O₇.2H₂O and 0.2 M Na₂SO₄ at current density = 55.55 mA cm⁻², pH = 10, time = 20 min., temp. = 25 °C, stirring speed = 500 rpm.

The plane (111) is a predominant one. There are no peaks for Al₂O₃ particles because their proportions in the coating are less than 5 %. EDX analysis confirmed the presence of Al₂O₃, Fig. (7).

3.4. Coating thickness

The coat thickness mainly depends on the imposed current density, the deposition time. Additionally, the amount of dispersed particles in the electrolyte has a noticeable effect on the thickness of the coating [60]. The variation of thickness of electrodeposited Ni–Co / nano Al₂O₃ composites coating with the quantity of incorporated nano Al₂O₃ in the deposit is shown in Table 1. Thickness of Ni–Co / nano Al₂O₃ composite linearly decreases with increasing the percent of Al₂O₃ in the deposit. The reinforced Al₂O₃ particles in the composites behave as barriers which retard the growing of grain. Also, they provide many nucleation positions for the growing of new grains and thence, thinner composites are obtained [61]. The presence of a diffraction apex for steel substrate in XRD patterns confirmed this result.

Table 1. Variation of thickness of composites with Al₂O₃ %

<table>
<thead>
<tr>
<th>Al₂O₃ content in composites (wt. %)</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10.9</td>
</tr>
<tr>
<td>1.1</td>
<td>9.1</td>
</tr>
<tr>
<td>2.5</td>
<td>7.5</td>
</tr>
<tr>
<td>3.1</td>
<td>7.1</td>
</tr>
<tr>
<td>3.9</td>
<td>6.6</td>
</tr>
<tr>
<td>4.3</td>
<td>6.4</td>
</tr>
</tbody>
</table>
3.5. Microhardness

Hardness is considered as important property that characterizes the material because ample practical applications mainly depend on the hardness. Table 2 reveals that there is a detectable elevation in microhardness of Ni–Co / nano Al₂O₃ composite as the percentage of Al₂O₃ increases in the composite.

Table 2. Variation of hardness of composites with Al₂O₃ %

<table>
<thead>
<tr>
<th>Al₂O₃ content in composites (wt. %)</th>
<th>Hardness (Hv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>145</td>
</tr>
<tr>
<td>1.1</td>
<td>199</td>
</tr>
<tr>
<td>2.5</td>
<td>248</td>
</tr>
<tr>
<td>3.1</td>
<td>261</td>
</tr>
<tr>
<td>3.9</td>
<td>283</td>
</tr>
<tr>
<td>4.3</td>
<td>330</td>
</tr>
</tbody>
</table>

The presence of inactive particles in metal matrix disorders the regular crystalline structure and turns it into a fine crystal structure. The existence of inert particles in the coating influences two competitive processes: formation of metal nuclei and growth of crystals. The addition of particles facilitates greater nucleation sites available for metal ions. This causes higher nucleation rate but low growth rate as it reduces the growing of crystal grains. Accordingly, more uniform surface with a microcrystalline grain is obtained and consequently the microhardness increases.

Furthermore, a section of microhardness improvement in the Ni–Co composite containing Al₂O₃ particles is attributed to the greater microhardness of the Ni–Co alloy, due to formation of substitution type - solid solution [10]. The presence of the latter improves the microhardness of the composites via solid solution hardening mechanism [62].

3.6. Corrosion resistance studies

3.6.1. Potentiodynamic polarization measurements

Anodic and cathodic polarization curves for Ni – Co / nano Al₂O₃ composite in 3.5 % salt water are exhibited in Fig.8. As the % of Al₂O₃ nano – particles increases in the coatings, the rate of corrosion decreases. The values of corrosion potentials, the corrosion current density and other electrochemical parameters were calculated and given in Table 3. The data show that the corrosion current density diminishes with increasing the embedded of Al₂O₃ in the composite.
Table 3. Electrochemical parameters of Ni-Co / nano-Al2O3 composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\beta_a$ (mV dec$^{-1}$)</th>
<th>$\beta_c$ (mV dec$^{-1}$)</th>
<th>$I_{corr}$ (µA cm$^{-2}$)</th>
<th>$R_p$ (Ω)</th>
<th>$-E_{corr}$ (mV/SCE)</th>
<th>$CR$ (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Co / 0 wt. % Al2O3</td>
<td>237</td>
<td>82</td>
<td>28</td>
<td>933</td>
<td>792</td>
<td>$3.7 \times 10^{-4}$</td>
</tr>
<tr>
<td>Ni-Co / 3.3 wt. % Al2O3</td>
<td>226</td>
<td>60</td>
<td>20</td>
<td>1041</td>
<td>761</td>
<td>$2.6 \times 10^{-4}$</td>
</tr>
<tr>
<td>Ni-Co / 3.9 wt. % Al2O3</td>
<td>90</td>
<td>10</td>
<td>1.4</td>
<td>2816</td>
<td>722</td>
<td>$1.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>Ni-Co / 4.3 wt. % Al2O3</td>
<td>171</td>
<td>347</td>
<td>0.8</td>
<td>62821</td>
<td>562</td>
<td>$1.1 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

Figure 8. Potentiodynamic polarization for Ni-Co / nano Al2O3 composites in 3.5 % salt water at scan rate of 1 mVs$^{-1}$.

The little rate of corrosion of Ni–Co / nano Al2O3 composite could be attributed to contribution of high positive potential Al2O3 nanoparticles in the composites. Also the formation of more homogenous structure with small grains reduces the corrosion rate. This may exhibit a high activation barrier, which prevents anodic dissolution. The sum of cathodic and anodic Tafel slopes, $\beta_c$ and $\beta_a$, does not attain unity because both the anodic and cathodic curves asymmetrical about E$_{corr}$ [63].

3.6.2. Electrochemical impedance spectroscopy studies

Impedance studies for Ni–Co / nano-Al2O3 composites in 3.5 wt. % salt water at their OCPs are shown in Fig 9. The compensating circuit that illustrated in Fig. 10 is used to simulate the metal / solution interface, in addition to analyze the Nyquist plots. It composes of a constant phase element (CPE) that is connected in parallel way to the charge transfer resistance (R$_{ct}$). Both adjoin in series
with the solution resistance \( (R_s) \). The constant phase element like a capacitor, but the phase angle does not attain 90°. This is commonly utilized to explicate the inhomogeneity of the system.

**Figure 9.** Plots of Nyquist for Ni-Co / nano Al\(_2\)O\(_3\) composites in 3.5 % salt water.

**Figure 10.** Electrical circuit utilized to fit the practical data of EIS plots.

\( R_s, R_{ct} \) & CPE values are listed in Table 4. Nyquist plots obtained for Ni–Co / nano-Al\(_2\)O\(_3\) composites exhibited depressed semicircles that differ in width. The width of semicircle reflects the corrosion resistance of the composite. As the semicircle diameter increases, the corrosion resistance increases. The corrosion resistance of the composites increases as the percentage of Al\(_2\)O\(_3\) nano – particles increases. The high values of \( R_{ct} \) obtained in the present work imply a good corrosion
protective ability for Ni–Co / nano-Al₂O₃ composites. These results are in good agreement with the results of potentiodynamic polarization measurements.

The (CPE) values were evaluated using Brug and others [64] equation. Its value related to the porosity of the coating. The low (CPE) values indicate that the Ni–Co / nano-Al₂O₃ composites are less porous in nature.

Table 4. Electrochemical impedance analysis data for Ni-Co / nano-Al₂O₃ composites in 3.5 % salt water.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rₛ (Ω cm⁻²)</th>
<th>Rᶜ (Ω cm⁻²)</th>
<th>CPE (µF cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Co / 0 wt. % Al₂O₃</td>
<td>36</td>
<td>600</td>
<td>3710</td>
</tr>
<tr>
<td>Ni-Co / 3.3 wt. % Al₂O₃</td>
<td>99</td>
<td>3530</td>
<td>343</td>
</tr>
<tr>
<td>Ni-Co / 3.9 wt. % Al₂O₃</td>
<td>138</td>
<td>4160</td>
<td>311</td>
</tr>
<tr>
<td>Ni-Co / 4.3 wt. % Al₂O₃</td>
<td>189</td>
<td>11150</td>
<td>183</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS

Application of Ni–Co / nano-Al₂O₃ composite onto low carbon steel cathode was successfully established using electrodeposition technique. Ni–Co / Al₂O₃ nano composites can be prepared by incorporating Al₂O₃ nano-particles to the Ni–Co plating tub. EDX spectroscopy confirmed the existence of nano-scale Al₂O₃ in composites, which increases with increasing its concentration of Al₂O₃ in the plating tub, current density and decreasing temperature. The thickness of Ni–Co / nano-Al₂O₃ coating decreases with increasing the percentage of nano-scale Al₂O₃ in the coating, however the microhardness of the coating increases. Different electrochemical measurements evidenced that Ni–Co / nano-Al₂O₃ composite coatings possess acceptable corrosion resistance in 3.5 % salt water.

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