

Electrochemical Characterization of Electrodeposited Ni-titanium Dioxide Deposits on Copper and their Corrosion Study

Khadidja BERARMA^{1,2}, Amina RAGHDI³ and Ghania BENAICHE^{4*}

¹Department of Chemistry, Faculty of Sciences, Mohamed Boudiaf- M'sila University, M'sila, 28000, Algeria

²Laboratory of Inorganic Materials, Department of Chemistry, Faculty of Sciences, Mohamed Boudiaf- M'sila University, M'sila, 28000, Algeria

³Department of Physics, Faculty of Sciences, Mohamed Boudiaf- M'sila University, M'sila, 28000, Algeria

⁴Department of Nature and Life Sciences, Faculty of Sciences, Mohamed Boudiaf- M'sila University, Algeria

*CORRESPONDING AUTHOR:

Ghania BENAICHE

Email: ghania.benaiche@univ-msila.dz

**ISSN : 2382-5359(Online),
1994-1412(Print)**

DOI:

<https://doi.org/10.3126/njst.v20i1.43347>

ACCESS THE ARTICLE ONLINE



CONFLICT OF INTEREST: None

Copyright: The Author(s) 2021. This is an open access article under the [CC BY](https://creativecommons.org/licenses/by-nc/4.0/) license.



ABSTRACT

This work aimed to produce and characterize composite coatings of nickel incorporating TiO₂ nanoparticles on a copper substrate. These deposits were obtained from watts bath. In the study, the cyclic voltammetry technique was employed to provide a better understanding of the cathodic behavior of nickel deposition. The effects of the potential scanning rate and the effect of cathodic limits on cyclic voltammograms deposition of Ni in Primitive Watts Bath (BWP) were determined. The composite coatings of nickel incorporating TiO₂ nanoparticles were characterized using various electrochemical techniques such as open circuit potential (OCP) and potentiodynamic polarization measurements, and electrochemical impedance spectroscopic methods. The current density values for the Ni-TiO₂ in the case of 5 g/L and 10 g/L of TiO₂ determined from the polarization curves recorded in 3.5% NaCl indicate that the corrosion process on nickel incorporating the TiO₂ nanoparticle composite surface is slower than on pure nickel. The TiO₂ particles embedded in the electroplated nickel, increase the polarization resistance and decrease the corrosion rates as compared with electrodeposited pure nickel. Electrochemical impedance spectra obtained at the open-circuit potential (OCP) in 3.5% NaCl showed an increase of polarization resistance with time in all cases.

Keywords: Corrosion, Electrolytic co-deposition, Nickel composite

1. INTRODUCTION

The study of corrosion phenomena is a field of materials science that appeals to concepts of chemistry as well as physics. Corrosion is a critical global problem that strongly affects natural and industrial environments (Bhattarai *et al.* 2021; Subedi *et al.* 2019). Today, it is generally accepted that corrosion and pollution are interrelated harmful processes, as many pollutants accelerate corrosion, and corrosion products such as rust also pollute water bodies (Dahal *et al.* 2021; Gautam & Bhattarai 2013). Both are pernicious processes that undermine the quality of the environment, the efficiency of industry, and the sustainability of infrastructure assets (Devarakonda & Koka 2018; Valdez *et al.* 2012). Therefore, the study of corrosion phenomena and the means of protection which at least reduce its effects if not being able to eliminate it represent a certain interest for industrialists as well from the point of view of safety industrial than economic.

Among the means which are frequently used to combat the phenomena of corrosive, we can cite the coatings of the parts to be protected. Composite coatings are the most effective. Indeed, composite coatings are experiencing a development growing industrial thanks to the particular properties conferred on them by the incorporation of solid particles (Kumar *et al.* 2017; Lopez *et al.* 2007; Paunovic & Schlesinger 2010; Kumar *et al.* 2020; Stoytcheva *et al.* 2010).

Metal matrix composites are attractive materials due to their properties such as increased hardness and wear resistance, low coefficients of thermal expansion, dry lubrication properties, and better corrosion resistance as compared with pure metallic coatings (Cotell *et al.* 1999; Gomes *et al.* 2010; Musiani 2000; Prashantha & Park 2005; Sachin *et al.* 2007; Shibli *et al.* 2006).

There is a large number of useful metal/particles combinations, including metals like copper (Bund & Thiemig 2007), nickel (Devarakonda & Koka 2018; Szczygieł & Kołodziej 2005) zinc (Tuaweri & Wilcox 2006), and inert materials such as oxides (Chen *et al.* 2006), carbides (Nowak *et al.* 2000) graphite (Yang *et al.* 2006) etc. which are

successfully used in many practical applications such as advanced surface finishing, electronic industry, etc.

The incorporation of such electro active metals in particulate form within composite coatings represents a natural extension of conventional metallurgical approaches, potentially minimizing the amount of metal deployed to inhibit corrosion, permitting the development of ultra-thin coatings, and allowing for additional functionality.

Co and TiO₂ are in great demand for the generation of particles and composite coatings on steel and alloys with other metals (Basavanna & Naik 2012; Dikici *et al.* 2010). Zn–Co coatings are reported to have attracted greater interest due to their corrosion protection than Zn coatings; they also have characteristics similar to those of Zn–Ni. Subsequently, the potential advantage of Co addition in bath has been recognized to give resistance to abrasion and improved coating properties (Dikici *et al.* 2010). Titanium dioxide (TiO₂) with a metallic coating significantly contributes to wear and corrosion resistance, better hardness (Fustes *et al.* 2008; Gomes *et al.* 2010; Prashantha & Park 2005; Praveen, Venkatesha, Naik & Prashantha 2007; Vasilyeva *et al.* 2012).

The need for improved coatings with better properties has developed the requirement for the use of composite electrodeposits, by embedding solid particles in the structure of nickel, such as titanium oxide (TiO₂) which is a hard compound, chemically stable, and irreducible. In this context, the objective of this work is the electrochemical characterization of the composite coatings nickel-titanium oxide (TiO₂), to improve the corrosion resistance of the deposits. These coatings are obtained by electro deposition technique from a bath of sulfate nickel on a copper substrate. The characterization has been carried out by corrosion.

2. MATERIALS AND METHODS

The electrochemical experiments were performed in a three-electrode cell with a capacity of 100 mL and which are connected directly to a VOLTALAB PGZ 402 type potentiostat/galvanostat, controlled

by a microcomputer (voltmaster software) for recording the data. The working electrode was a copper disc, the reference electrode was a Hg/Hg₂Cl₂/KCl electrode, and the counter electrode

was a platinum foil. The Ni and Ni-TiO₂ films were galvanostatically deposited on the copper substrate. The basic composition of electrolyte and deposition parameters is given in (Table 1).

Table 1. Electrolyte composition and deposition conditions

Electrolyte	Primitive Watts Bath (BWP) (Watts, 1916)
Acidic nickel sulfate-bath	300g/L NiSO₄ .6H₂O , 64g/L;NiCl₂. .6H₂O and 48g/L H₃BO₄Acide.
Current density	1.5 mA/cm ²
Temperature	57°C
Plating time	20 min
Dispersion	TiO ₂ : 5g/L, 10g/L, 15g/L

Cyclic voltammetry (CV) was used to define potential regions and to characterize the Ni deposition process. The scanning rate effect on the deposition process was investigated, and the effects of cathodic limits on cyclic voltammograms deposition of Ni were investigated in a primitive watts bath (BWP).

Corrosion test was carried out in 3.5% aerated NaCl solution, at room temperature. Open-circuit potential (OCP) measurements were performed as a function of time. Anodic and cathodic polarization curves were recorded in a potential range of $E = E_{corr} \pm 200$ mV for kinetic studies, with a scan rate of 5 mV/s. Electrochemical impedance spectroscopy measurement was performed at the OCP. The impedance spectra were acquired in the frequency range 100 kHz to 10 MHz at 5 points per hertz decade with AC voltage amplitude of ± 10 mV.

3. RESULTS AND DISCUSSION

A weakly ionized boric acid acts as a buffer in nickel plating electrolytes. It works by regulating the pH in the cathode film and preventing precipitation of nickel hydroxide there; its effect is maximum around pH 4 ± 1 (Vasilyeva *et al.* 2012; Yang *et al.* 2006). A preliminary study carried out by cyclic voltammetry is devoted to the electrochemical behavior of boric acid on an inert platinum electrode in a potential range of -1.5V to 1.5V / ECS at a scanning speed (vb) of 5 mV/s.

Reading the curve (Figure 1) shows that the redox of the acid is practically inactive in the potential range explored. It is clear that in this area of

potential, the release of hydrogen is not a problem, which justifies the use of boric acid in industrial electrolysis.

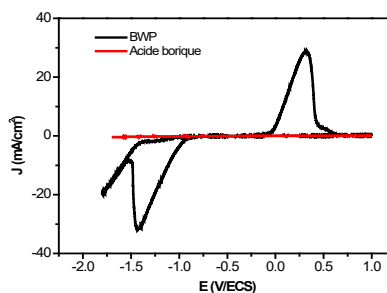
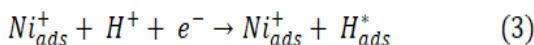
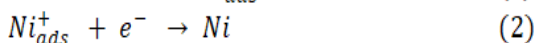
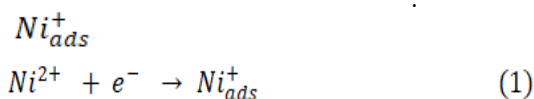


Fig.1. Cyclic voltammograms of an inert platinum electrode in an electrolyte containing boric acid and in the primitive watt bath at vb = 5 mV/s

The mechanism of electrolytic deposition of nickel from a Watts electrolyte solution was studied by Epelboin and Wiart (Chassaing *et al.* 1983; Epelboin, Jousselein & Wiart 1979 1981; Epelboin & Wiart 1971; Froment & Wiart 1963; Wiart 1990). The following mechanisms have been suggested for electrolytes of pH 2 to 4 where the intermediate adion acts both as a reaction intermediate and as a catalyst, associated with a propagation folding site, and where the adsorbed species, generated by the presence of



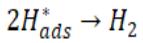
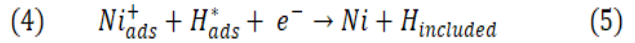


Figure 2 shows typical voltammograms for deposition of Ni at different scan rates. All voltammograms displayed a single reduced peak of N^{2+} which is transferred to higher currents and more cathodic potentials with



increasing scan rate. Similarly, in the anodic zone where the anodic peak current increases with increasing scan rate and the peak position shifted towards more positive potentials.

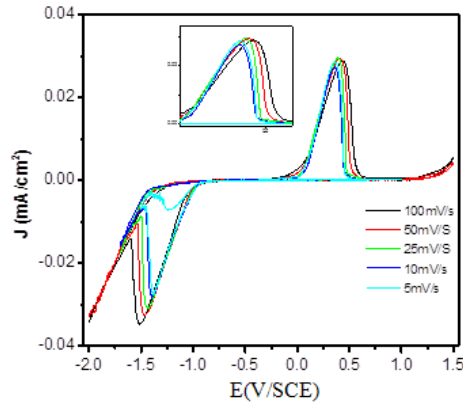


Fig. 2. Cyclic voltammograms for deposits of Ni on Pt at different scanning rates: 100 mV/s; 50 mV/s; 25 mV/s; 10 mV/s and 5 mV/s

The variations in the intensity of the cathode peak and its potential represented, respectively, as a function of $(v^{1/2})$ and of $(\log v)$ for the reduction of N^{2+} are given in (Figure 3).

We observe, also, that the relation between the current of the cathodic peak and the

square root since the scanning speed is linear this linearity is expected for processes that occur under diffusion control. However, the line, not going through the origin, indicates that another additional process other than diffusion is occurring (Fuentes *et al.* 2015; Zhang & Hua 2014; Zhang *et al.* 2012).

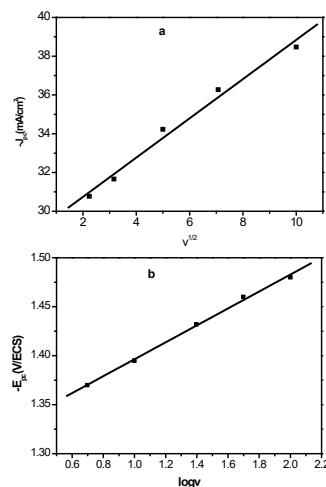


Fig. 3. A variation of the intensity of the cathode peak (IP) as a function of the square root of scanning speed $(v^{1/2})$ (a), and the potential of the cathode peak (E_{pC}) as a function of the logarithm of the scanning speed $\log(v)$ (b) for electroplating Ni on platinum.

Figure 4 shows the effect of cathodic limits on cyclic voltammograms deposition of Ni at a potential scanning rate of 10 mV / s in the primitive watts bath. All cyclic voltammograms demonstrate almost a similar pattern as in (Figure 1), which indicates that for the different cathodic limits the deposition process follows the same trend. During the cathodic scan, a peak appeared at -1.4 V which corresponds to the reduction of N^{2+} into nickel metal. This is followed by a further increase in current due to a reduction of H^+ . During the reversed scan, a single anodic peak at around 0.35 V was noticed which correspond to the oxidation of nickel metal into N^{2+} . The oxidation peak current increased when the limit was rendered more negative, demonstrating that there is a correlation between the cathodic and anodic processes.

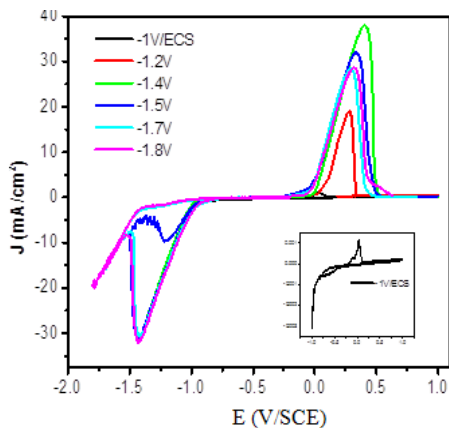


Fig. 4. Effect of cathodic limits on cyclic voltammograms

Corrosion experiments were carried out in 3.5% aerated NaCl solution, at room temperature. The open-circuit potentials (OCP) evolution in time for nickel coating in BWP and composite coatings nickel-titanium oxide (Ni-TiO₂) recorded after their immersion in 3.5% NaCl solution is presented in (Figure 5). For all electrodes, a shift of the OCP towards more positive potentials is observed during the first minutes to reach a stationary state, suggesting a more noble character of the Ni-TiO₂ coating, associated with an inhibition of the anodic reaction and, consequently, with stronger corrosion resistance.

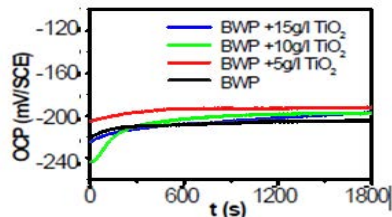


Fig. 5. Evolution of OCP of the nickel coating in BWP in the absence and the presence of TiO₂ tested in 3.5% NaCl solution.

The behavior and performance of metals or alloy films depended on their chemical composition and surface morphology. The interpretation of the polarization curves in the logarithmic form by nonlinear regression allowed us to obtain the kinetic parameters of the corrosion process such as the corrosion current (I_{cor}), Tafel slopes of the anodic (β_a) and cathodic (β_b) reactions, and the corrosion potential (E_{corr}) (Flitt & Schweinsberg 2005) which are given by the Stern-Geary equation, as given in equation (6) (Stern 1958; Stern & Geary 1957)

$$I_{cor} = \frac{\beta_a \beta_b}{2.203 R_p (\beta_a + \beta_b)} \quad (6)$$

The corrosion of nickel coating in PBW in the absence and presence of TiO₂ tested in 3.5% NaCl solution was evaluated using linear polarization. The E_{corr} and I_{cor} correlation for the Ni coatings can be seen in (Figure 5).

Figure 6 shows E_{corr} shifting to more positive potentials and the I_{cor} shifting to lower current values for Ni-TiO₂ in the case of 5g/L and 10g/L of TiO₂. Kinetic parameters of the corrosion process obtained from the Tafel straight lines of deposits tested in 3.5% NaCl solution at 25°C are given in Table 1. As can be seen from (Table 2), the values of the Tafel coefficients in the presence of TiO₂ change in comparison with pure Ni coatings, which indicate that the TiO₂ particles influence the kinetics of both the cathodic and anodic processes. The poor results obtained in the case of 15 g/L TiO₂ in the bath can be explained by the formation of defects and dislocations or in the metal matrix, at high concentrations of the particles (Chen *et al.* 2006) or by non-uniform incorporation of the particles due to the formation of agglomerates.

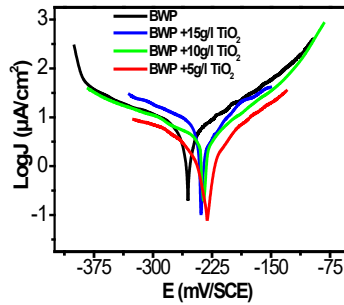


Fig. 6. Polarization curves of nickel coating in BWP in the absence and the presence of TiO_2 tested at 3.5% NaCl solution

Table 2. The kinetic parameters of the corrosion process obtained from the Tafel lines in 3.5% NaCl solution.

Electrolyte	$E_{(corr)}$ (mV/SCE)	R_p Kohm.cm ²	J_{corr} (µA/cm ²)	β_a mV	β_b mV
B.W.P	-254.4	1.61	4.07	90.3	-122
BWP+TiO ₂ (5g/L)	-230.9	16.36	2.18	83.8	-81.4
BWP+TiO ₂ (10g/L)	-233.2	3.7	3.86	86.7	-90.8
BWP+TiO ₂ (15g/L)	-239.1	0.73	6.2	104.3	-127.8

Nyquist plots (Figure 7) of pure Ni and Ni-TiO₂ composite coatings after 30 min immersion in 3.5% NaCl at 25°C showed the diameter of the depressed uncompleted semicircles is larger in the case of Ni-TiO₂ compared to pure Ni deposit. The addition of TiO₂ in the electroplating bath does not change the appearance of the Nyquist plots, we observe the presence of a single loop reflecting the capacitance of the double layer in parallel with a charge transfer resistance (Scully *et al.* 1993). Note that the diameters of these capacitive loops which represent the charge transfer resistance increase with the presence of TiO₂. The increase in the resistance R_t with the increase in the TiO₂ content shows less and less active surfaces and an increasingly difficult charge transfer at the metal-solution interface, indicating that the corrosion resistance in the NaCl medium of composite deposits increases and which displays increased stability of the passive film in the case of Ni-TiO₂.

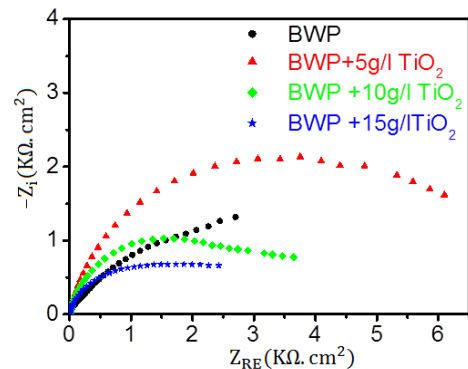


Fig.7. Nyquist diagrams of nickel coating in BWP in the absence and the presence of TiO_2 tested in 3.5% NaCl solution

4. CONCLUSION

In the present study, Ni-TiO₂ nano-composite coatings were developed successfully by using an electro-deposition process on the copper substrate from a nickel sulfate bath. The addition of TiO₂ nanoparticles in the nickel bath with

different concentrations improves the electrochemical characteristics of the nickel deposit on copper such as resistance to corrosion. Corrosion tests in an aggressive 3.5% NaCl solution indicate a reduced electrochemical activity and lower corrosion rate in the case of composite deposits compared to the deposition of pure Ni, being confirmed the beneficial effect of the incorporation of TiO₂ into the Ni matrix. The best results are obtained for a concentration of 5 g/L of TiO₂. The deposits obtained at this concentration showed improvements concerning the corrosion resistance which is greater in comparison with other concentrations. The results of the impedances are in agreement with the results of corrosion current densities and the resistance of polarization which indicates the best resistance to corrosion in the case of the deposition of Ni obtained from the bath in the presence of 5 g/L TiO₂.

ACKNOWLEDGEMENT

Authors are grateful to the assistance of the department of chemistry, faculty of science, university of Mohamed BOUDIAF (M'sila Algeria). Thanks for technical support and laboratory facilities.

REFERENCES

1. Basavanna, S. and Y.A. Naik. (2012). Electrochemical and reflectance studies of bright Zn-Co alloy coatings. *Indian Journal of Chemical Technology*, 19 (2), 91-95.
2. Bhattarai, J., M. Somai, N. Acharya, A. Giri, A. Roka and N.R. Phulara. (2021). Study on the effects of green-based plant extracts and water-proofers as anti-corrosion agents for steel-reinforced concrete slabs. *E3S Web of Conferences*, 302, 1-10. <https://doi.org/10.1051/e3sconf/202130202018>
3. Bund, A. and D. Thiemig. (2007). Influence of bath composition and pH on the electro-deposition of alumina nanoparticles and copper. *Journal of Applied Electrochemistry*, 37, 345-351.
4. Chassaing, E., M. Jousselein and R. Wiart. (1983). The kinetics of nickel electrodeposition: Inhibition by adsorbed hydrogen and anions. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, 157, 75-88.
5. Chen, L., L. Wang, Z. Zeng and T. Xu. (2006). Influence of pulse frequency on the microstructure and wear resistance of electrodeposited Ni-Al₂O₃ composite coatings. *Surface and Coatings Technology*, 201, 599-605.
6. Cotell, C., J. Sprague and F. Smidt. (1999). ASM Metals Handbook. Surf. Eng, 5, 804.
7. Dahal, K.P., J.N. Timilsena, M. Gautam and J. Bhattarai. (2021). Investigation on a probabilistic model for corrosion failure level of buried pipelines in Kirtipur urban areas (Nepal). *Journal of Failure Analysis and Prevention*, 21 (3), 914-926.
8. Devarakonda, S. K. and N.S.S. Koka. (2018). Estimation of high cycle fatigue life of AZ91E-Ni coated Al₂O₃ particulate nanocomposites using reliability-based approach. *Journal of The Institution of Engineers (India): Series D*, 99, 201-208.
9. Dikici, T., O. Culha and M. Toparli. (2010). Study of the mechanical and structural properties of Zn-Ni-Co ternary alloy electroplating. *Journal of Coatings Technology and Research*, 7, 787-792.
10. Epelboin, I., M. Jousselein and R. Wiart. (1979). Impedance of nickel deposition from sulfate and chloride electrolytes. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, 101, 281-284.
11. Epelboin, I., M. Jousselein and R. Wiart. (1981). Impedance measurements for nickel deposition in sulfate and chloride electrolytes. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, 119, 61-71.
12. Epelboin, I. and R. Wiart. (1971). Mechanism of the electrocrystallization of nickel and cobalt in acidic solution. *Journal of the Electrochemical Society*, 118, 1577-1582.
13. Flitt, H. J. and D.P. Schweinsberg. (2005). Evaluation of corrosion rate from polarisation curves not exhibiting a Tafel region. *Corrosion Science*, 47, 3034-3052.

14. Froment, M. and R. Wiart. (1963). Quelques recents progres dans les methodes d'etude du depot electrolytique du nickel. *Electrochimica Acta*, 8, 481-488.
15. Fuentes, A. S., A. Filippin and M.d.C Aguirre. (2015). Pd nucleation and growth mechanism deposited on different substrates. *Procedia Materials Science*, 8, 541-550.
16. Fustes, J., A. Gomes and M. da Silva Pereira. (2008). Electrodeposition of Zn-TiO₂ nanocomposite films-effect of bath composition. *Journal of Solid State Electrochemistry*, 12, 1435-1443.
17. Gautam, M., and J. Bhattarai. (2013). Study on the soil corrosivity towards the buried-structures in soil environment of Tanglaphant-Tribhuvan University Campus-Balkhu areas of Kirtipur. *Nepal Journal of Science and Technology*, 14 (2), 65-72.
18. Gomes, A., I. Almeida, T. Frade and A.C. Tavares. (2010). Zn-TiO₂ and ZnNi-TiO₂ nanocomposite coatings: corrosion behavior. In *Materials Science Forum* (Vol. 636, pp. 1079-1083): Trans Tech Publ.
19. Kumar, D. S., K. Suman and P. Poddar. (2017). Effect of particle morphology of Ni on the mechanical behavior of AZ91E-Ni coated nano Al₂O₃ composites. *Materials Research Express*, 4, 066505.
20. Lopez, B., S. Valdez, K. Zlatev, P. Flores, B. Carrillo and W. Schorr. (2007). Corrosion of metals at indoor conditions in the electronics manufacturing industry. *Anti-Corrosion Methods and Materials*.
21. Musiani, M. (2000). Electrodeposition of composites: an expanding subject in electrochemical materials science. *Electrochimica Acta*, 45, 3397-3402.
22. Nowak, P., R. Socha, M. Kaisheva, J. Fransaer, J-P, Celis and Z. Stoinov. (2000). Electrochemical investigation of the co-deposition of SiC and SiO₂ particles with nickel. *Journal of Applied Electrochemistry*, 30, 429-437.
23. Paunovic, M. and M. Schlesinger. (2006). *Fundamentals of Electrochemical Deposition* (2nd edition). Hoboken, New Jersey, USA: John Wiley & Sons, Inc., pp. 373.
24. Prashantha, K. and S. Park. (2005). Nanosized TiO₂-filled sulfonated polyethersulfone proton conducting membranes for direct methanol fuel cells. *Journal of Applied Polymer Science*, 98, 1875-1878.
25. Praveen, B. M., T.V. Venkatesha, Y.A. Naik and K. Prashantha. (2007). Corrosion behavior of Zn-TiO₂ composite coating. *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*, 37, 461-465.
26. Sachin, H., G. Achary, Y.A. Naik and T. Venkatesha. (2007). Polynitroaniline as brightener for zinc-nickel alloy plating from non-cyanide sulfate bath. *Bulletin of Materials Science*, 30, 57-63.
27. Sameer Kumar, D., K. Suman and P. Poddar. (2020). A study on the impact and fatigue failure of AZ91E-Ni coated alumina composites. *Canadian Metallurgical Quarterly*, 59, 316-323.
28. Scully, J. R., D.C. Silverman and M.W. Kendig. (1993). Electrochemical impedance: analysis and interpretation. In: *ASTM Philadelphia*.
29. Shibli, S., V. Dilimon, S.P. Antony and R. Manu. (2006). Incorporation of TiO₂ in hot-dip zinc coating for efficient resistance to bio-growth. *Surface and Coatings Technology*, 200, 4791-4796.
30. Stern, M. (1958). A method for determining corrosion rates from linear polarization data. *Corrosion*, 14, 60-64.
31. Stern, M. and A. Geary. (1957). A theoretical analysis of the shape of polarization curves. *Journal Electrochemical Society*, 104, 56-63.
32. Stoytcheva, M., B. Valdez, R. Zlatev, M. Schorr, M. Carrillo and Z. Velkova. (2010). Microbially Induced Corrosion in the Mineral Processing Industry. In *Advanced Materials*

- Research* (Vol. 95, pp. 73-76): Trans Tech Publ.
33. Subedi, B. N., K. Amgain, S. Joshi and J. Bhattarai. (2019). Green approach to corrosion inhibition effect of Vitex negundo leaf extract on aluminum and copper metals in biodiesel and its blend. *International Journal of Corrosion and Scale Inhibition*, 8 (3), 744-759.
34. Szczygieł, B. and M. Kołodziej. (2005). Composite Ni/Al₂O₃ coatings and their corrosion resistance. *Electrochimica Acta*, 50, 4188-4195.
35. Tuaweri, T. J. and G. Wilcox. (2006). Behavior of Zn-SiO₂ electrodeposition in the presence of N, N-dimethyldodecylamine. *Surface and Coatings Technology*, 200, 5921-5930.
36. Valdez, B., M. Schorr, R. Zlatev, M. Carrillo, M. Stoytcheva, L. Alvarez, A. Eliezer and N. Rosas. (2012). Corrosion control in industry. Environment and Industrial Corrosion, *Practical and Theoretical Aspects*.
37. Vasilyeva, M., V. Rudnev, I. Korotenko and P. Nedorozov. (2012). Producing and studying oxide coatings containing manganese and nickel compounds on titanium from electrolyte suspensions. *Protection of Metals and Physical Chemistry of Surfaces*, 48, 106-115.
38. Watts, O. P. (1916). Rapid nickel plating. Transactions of the American. *Electrochemical Society*, 29, 395-403
39. Wiart, R. (1990). Elementary steps of electro-deposition analyzed by means of impedance spectroscopy. *Electrochimica Acta*, 35, 1587-1593.
40. Yang, X.-H., Y.-B., Liu, Q.-F. Song and J. An. (2006). Microstructures and properties of graphite and Al₂O₃ short fibers reinforced Mg-Al-Zn alloy hybrid composites. *Journal of Transactions of Nonferrous Metals Society of China*, 16, 1-5.
41. Zhang, Q. and Y. Hua. (2014). Electrochemical synthesis of copper nanoparticles using cuprous oxide as a precursor in choline chloride-urea deep eutectic solvent: nucleation and growth mechanism. *Physical Chemistry Chemical Physics*, 16, 27088-27095.
42. Zheng, Y., S. Zhang, L. Xingmei, W. Qian, Z. Yong, and L. Lian. (2012). Low-temperature electrodeposition of aluminum from Lewis acidic 1-allyl-3-methylimidazolium chloroaluminate ionic liquids. *Chinese Journal of Chemical Engineering*, 20, 130-139.