

STUDY ON CORROSION BEHAVIOR OF COBALT NANO COMPOSITE COATINGS

Z. Shahri and S. R. Allahkaram

* akaram@ut.ac.ir

Received: May 2013

Accepted: October 2013

School of Metallurgy and Materials Engineering, University College of Engineering, University of Tehran, Tehran, Iran.

Abstract: Metal matrix nano composite coatings possess enhanced properties such as corrosion and wear resistance. This paper aims to study the corrosion behavior of pure Co and Co-BN nano composite coatings deposited with different particles concentration (5-20 g L⁻¹) on copper substrates using electroplating technique. Morphology and elemental compositions of the coatings were investigated by means of scanning electron microscope (SEM) equipped with an energy dispersive spectroscopy (EDS). The corrosion behavior was analyzed in a 3.5 wt% NaCl via polarization and impedance techniques. The results obtained in this study indicate that the co-deposition of BN nano particles improved corrosion resistance of electrodeposited cobalt coatings.

Keyword: Corrosion; Electroplating; Polarization; Impedance.

1. INTRODUCTION

Metal matrix composite coatings (MMCs) have excellent properties such as desired electrical or magnetic properties as well as good wear or corrosion resistance [1-4]. Since, corrosion and wear are almost the most significant reasons of various industrial parts degradation, comprehensive investigations have been conducted to develop the methods for reducing wear and corrosion costs [1, 5]. The introduction of ceramic nano particles in to the metal matrix leads to increase in the mechanical and physical properties such as wear and corrosion resistance [6]. Despite numerous information on the nickel composite coatings electrodeposited, there have been very few reports on electrodeposition of the cobalt matrix composite coatings in the literature. Cobalt-base coatings can present comparable or even better properties than nickel metal matrix [7-14]. For cobalt matrix electrodeposits, the incorporated inert particles including: ZrO₂ [15], LaCrO₂ [16] and Y₂O₃ [17] have been used for either enhancing the corrosion or wear resistance. There are reports on the corrosion properties of Co-ZrO₂ composite coatings [15]. The results obtained by polarization and EIS methods in these reports indicate that the obtained Co-ZrO₂ composite coatings, compared with the traditional polycrystalline Co film, exhibit the

enhanced corrosion resistance in SBF solution.

Due to desirable characteristics of BN such as high temperature stability, electrical resistivity, extreme pressure performance and inertness in a wide variety of chemical environments [18-20], it has been selected as the nano constituents in the cobalt matrix in this research.

In the present study, Co-BN nano composite coatings and pure Co were fabricated from a chloride solution by electrodeposition and subsequently the corrosion behavior of deposits was investigated. The BN inclusion to the Co metal matrix also improved the wear behavior of the coating. However the results for that part will be reported in a separate paper, elsewhere.

2. EXPERIMENTAL PROCEDURES

Co coatings used in this study were fabricated by pulse current electrodeposition method from chloride solutions containing different concentrations of BN particles (0-20 g L⁻¹). The detailed plating conditions have been shown in Table 1. Copper plates and pure cobalt plates were used as cathode and anode, respectively. Before each experiment, the cathodes were ground (with emery papers of the following grades: 120, 400, 600, 800, 1000, 1500, 2000 and 2500), degreased in Uniclean 675 solution (an acidic commercial product containing sodium hydrogen sulfate and sodium fluoride) and then

Table 1. Bath composition and deposition parameters.

Cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$)	210 g L^{-1}
Boric acid (H_3BO_3)	20 g L^{-1}
BN (h) concentration	0-20 g L^{-1}
Saccharine	0.25 g L^{-1}
pH	3
Temperature	45°C
Current density	100 mA cm^{-2}
Duty cycle	10%
Pulse frequency	50 HZ

chemically cleaned in acetone for 3 min followed by distilled water for 1 min. Finally, it was activated in chloride acid for 30 s. In order to keep the particles in suspension, the electrolyte was under ultrasonic waves for 30 min prior to the process, and during electroplating it was magnetically stirred with the aid of a 300 rpm magnetic stirrer placed at the cell bottom to avoid sedimentation of particles.

The morphology and elemental compositions were evaluated by scanning electron microscopy (SEM) equipped with energy dispersive spectroscope (EDS). Polarization and electrochemical impedance spectroscopy (EIS)

techniques were used to study the corrosion behavior of pure Co and Co-BN nano composite coatings in a 3.5 wt. % NaCl solution. Electrochemical behaviors of coatings were examined using potentiodynamic polarization technique (EG&G Potentiostat/Galvanostat Model 273 A) at room temperature. Ag/AgCl electrode and platinum plate were used as reference and counter electrodes, respectively. The potentiodynamic polarization curves were obtained by scanning from +400 mV to -900 mV with respect to open circuit potential (OCP) at a scan rate of 1mVs^{-1} . The EIS measurements were also acquired at OCP in a frequency range from 0.01Hz to 100 kHz. The equivalent circuit simulation program (ZView2) was used for data analysis, synthesis of the equivalent circuit and fitting of the experimental data.

3. RESULTS AND DISCUSSION

3. 1. Surface Morphology-BN Particles Dispersion

Fig. 1 displays secondary scanning electron micrograph (SESEM) and (EDS) elemental

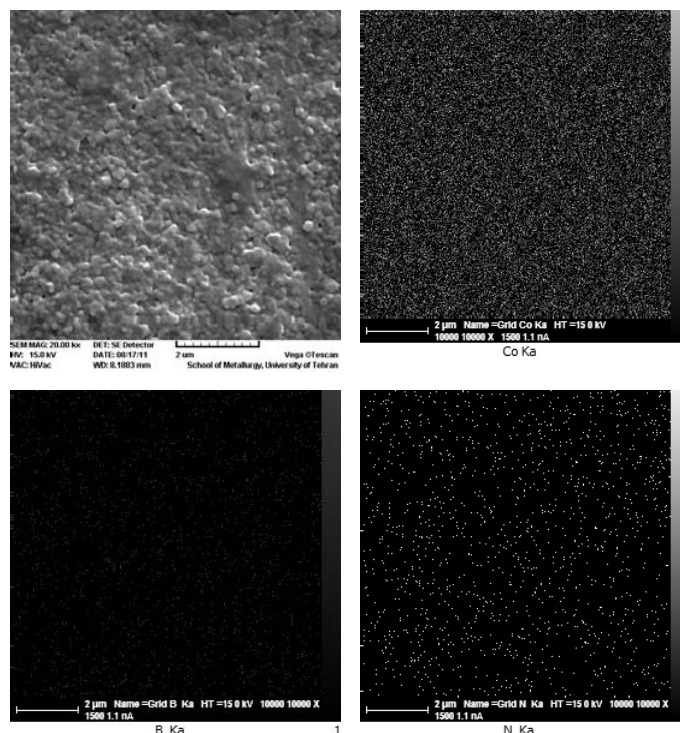


Fig. 1. SEM and EDS analysis of Co-BN (4 wt%) nano composite coatings.

Table 2. Particles content in the coatings as a function of BN particles concentration.

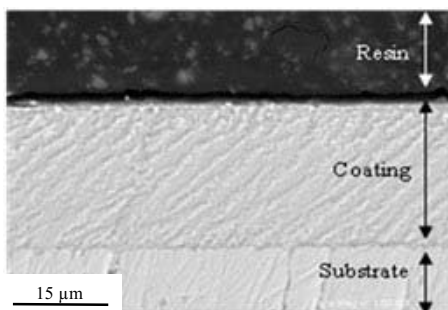
BN concentrations in the solution.	0 g L ⁻¹	5 g L ⁻¹	10g L ⁻¹	15 g L ⁻¹	20 g L ⁻¹
Particles content in the coatings.	0 wt%	4.1 wt%	4.9 wt%	5.1 wt%	5.2 wt%

mapping images (Co, B, N map) of the selected Co-BN nano composite coatings with approximately 4 wt% BN. The thickness of as-deposited coatings without any inter layer was about 23 μm (Fig. 2). Morphological analyses of the coatings confirmed the possibility of homogeneity, compactness and smoothness, free of deflection deposition with no obvious cracks, holes, and so on obtained by electroplating method. The micrograph depicted in Fig. 1 was also typical of electrodeposited nano coatings obtained under these deposition parameters. Moreover, the EDS analysis revealed uniform

distribution of the BN nano particles throughout the matrix of cobalt that was electroplated by virtue of mechanical stirring and no particle agglomerations at 5 g L⁻¹ concentration could be distinguished within the coatings, which was an important factor to gain an appropriate composite coating [21]. Table 2 shows particles content (wt%) in the coatings as a function of BN nano particles concentration (0-20 g L⁻¹) in the solution. As this table shows, particles incorporation increased somewhat under powder addition to the bath.

3. 2. Tafel Measurements

Corrosion behavior of the pulse plated coatings was investigated in a 3.5wt% NaCl solution. Fig. 3 (a) and (b) presents the polarization curves (E vs. I plots) obtained for as-deposited pure Co and Co-BN nano composite coatings in the potential range of -900 mV to +400 mV. Table 3 lists the corrosion potential (E_{corr}) and corrosion current density (i_{corr}) extracted from E vs. I plot (Tafel plot extrapolation) as well as polarization resistance (R_p) and porosity density (P.D.) values. Polarization resistance of pulse plated coatings was calculated by linear polarization relationship (1):

**Fig. 2.** The cross-section of nano composite coating (4 wt%).**Table 3.** Electrochemical parameters of the coatings derived from polarization plots.

	$i_{\text{corr}}/\mu\text{A cm}^{-2}$	$E_{\text{corr}}/\text{mV vs Ag/AgCl}$	$R_p/\Omega\text{ cm}^2$	Porosity/%
Pure Co	6.8	-510.81	1713.4	0.24
Co-BN (5 g L ⁻¹)	3.1	-549.36	3324.7	0.21
Co-BN (10 g L ⁻¹)	2.3	-490.31	4407.7	0.11
Co-BN (15 g L ⁻¹)	1.4	-474.71	4411.7	0.075
Co-BN (20 g L ⁻¹)	1.2	-458.19	4493.3	0.039

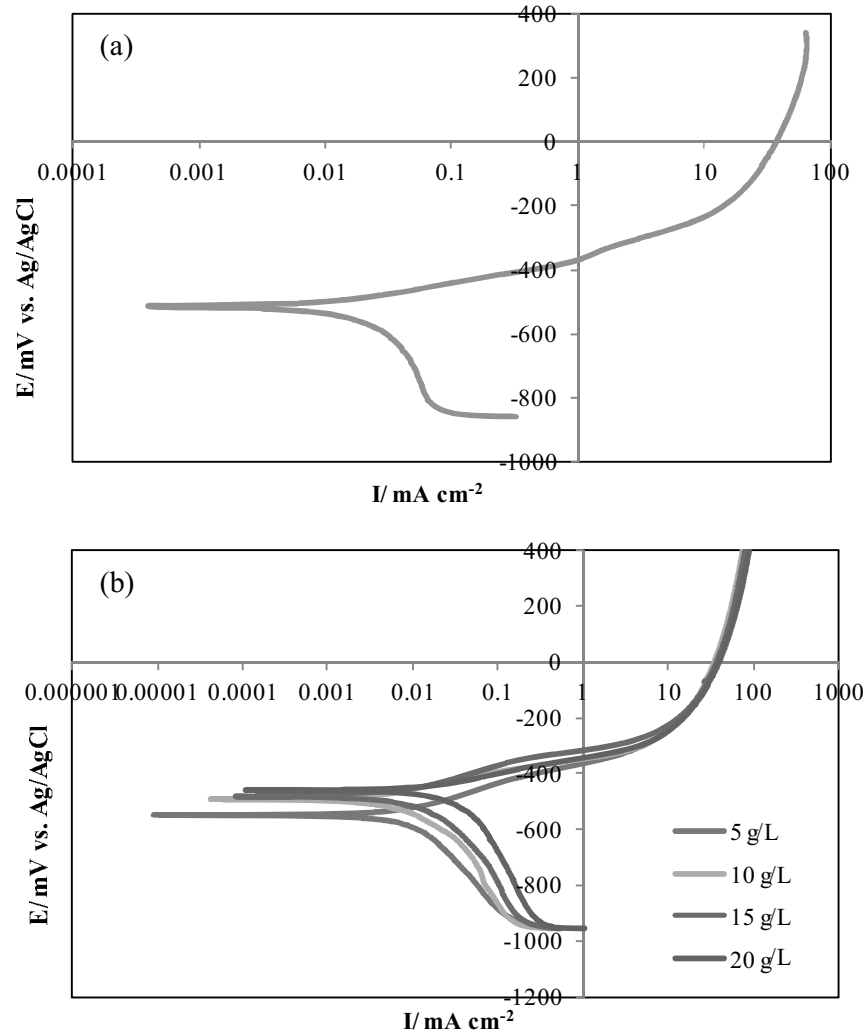


Fig. 3. Potentiodynamic polarization curves of (a) pure Co and (b) Co-BN nano composite coatings with different particles concentration (5-20 g L⁻¹).

$$I_{corr} = \frac{\beta}{R_p} \quad (1)$$

β is a constant calculated by the following equation,

$$\beta = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)} \quad (2)$$

where β_a and β_c is anodic and cathodic Tafel slopes, respectively [22-24].

Moreover, the porosity density (P.D.) values was measured by,

$$P.D. = R_{ps} / R_p \times 10^{-(\Delta E / \beta_a)} \quad (3)$$

Where R_{ps} is the copper substrate polarization resistance, R_p polarization resistance of the coatings, ΔE the difference of corrosion potential of the coatings and substrate and β_a is the anodic Tafel extrapolation slope for the substrate [25].

As the results of polarization experiments show, the presence of BN particles into the cobalt

coating caused a decrease in the corrosion current density (i_{corr}) as well as porosity and an increase in the polarization resistance (R_p), indicating a better corrosion behavior of the composite coating. However, no significant differences were found in the shape of polarization curves for investigated coatings. The polarization resistance of the Co-BN nano composite coating was about 3 times higher than that of the as-plated Co coating. The lowest current density and porosity was measured to be approximately 0.04% and $1 \times 10^{-6} \text{ A cm}^{-2}$, respectively which were obtained from the composite coatings. In general, the composite coatings had lower i_{corr} and higher R_p and hence possessed better corrosion resistance than that of pure cobalt coating. It meant that incorporation of BN nano particles into the cobalt coating improved corrosion behavior and resistance of deposition by filling surface defects such as micro or nano holes, porosities and crevices with particles and acted as a barrier to corrosive ions diffusion to the electrode surface [25-26].

3. 3. EIS Measurements

Electrochemical impedance spectroscopy (EIS) measurements were performed in order to gain a better understanding of the anticorrosive ability of deposits. The Nyquist and Bode plots of

EIS for as-plated pure Co and Co-BN nano composite coatings obtained in the test media at their respective open circuit potentials (OCPs) are shown in Figs. 4 and 5. As it can be seen from Fig. 4, the Nyquist curves of all coatings appear to be similar, consisting of a single semicircle arc (capacitive loop) in the investigated frequency region. The occurrence of a single semicircle in the Nyquist plots signifies that all the coatings follow the same electrochemical process (the charge controlled reaction across the electrode surface which appears as a capacitive loop) [22, 25, 27]. Similar impedance patterns are seen for coatings such as Ni-Zn-P/nano TiO_2 [22] and Ni-P-CNT coatings [1]. It should be noted that in spite of similar shape, the impedance arc of composite coatings increased significantly in diameter compared to that of pure Co and their diameters increased by increasing the particles content. The increased radius of impedance arc was indicative of the better anticorrosive property of the deposits [22, 28]. This meant that the corrosion resistance was increased by BN particles incorporation. Thus, the results of the EIS studies confirmed the results obtained from the polarization curves, which showed that the co-deposition of the BN particles into cobalt matrix improved the anticorrosion properties. In the Bode plots (Fig. 5), the as-plated coating showed a single inflection point and only one

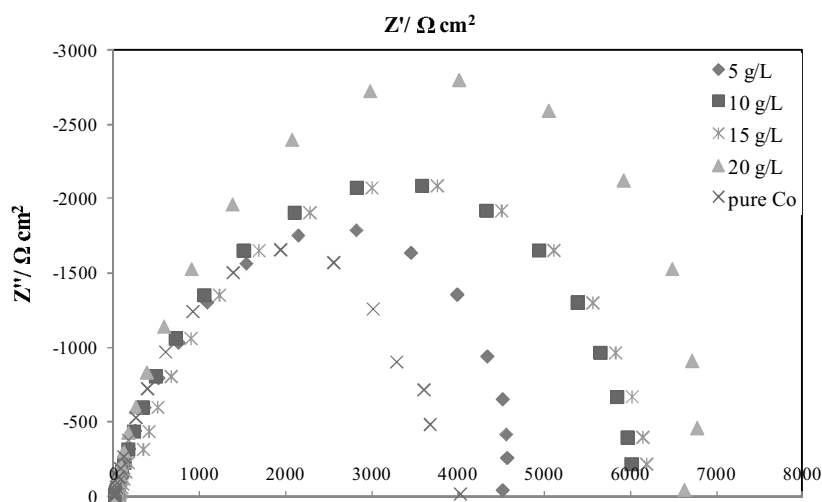


Fig. 4. Nyquist plot of electrochemical impedance spectroscopy of pure Co and Co-BN nano composite coatings at different particles concentration.

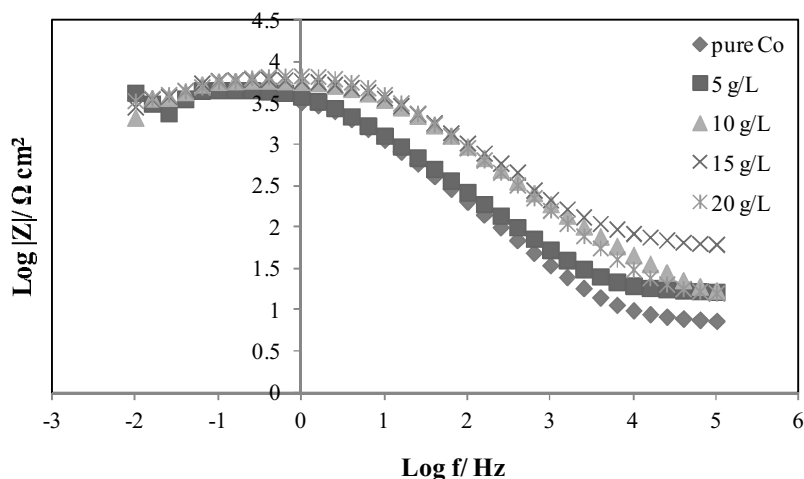


Fig. 5. Bode plot (Log|Z| vs. Logf) for as-plated coatings.

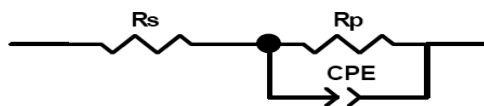


Fig. 6. Equivalent circuit model for the corrosion behavior of the as-plated coatings in 3.5 wt%NaCl solution.

maximum was observed in the phase angle versus frequency plot, indicating the process involved only a single time constant (a capacitive behavior) [22]. Moreover, in this figure, the whole curve related to pure cobalt was below that of composite coatings, which represented that the composite coating brought a higher $|Z|$ in comparison with as-plated pure Co coating. This higher $|Z|$ demonstrated that the composite coatings had a better anticorrosion property in corrosive medium [29].

The most suitable equivalent electrical circuit model (Fig. 6), which consisted of solution resistance between the reference electrode and the working electrode (R_s), polarization resistance (R_p) and constant phase element (CPE), were employed to characterize the corrosion kinetic parameters and analyze the EIS data of the coatings via Zview2 software. This figure consisted of one time constant (OTC) model, where the solution resistance was in series with a parallel combination of the constant phase

element and the polarization resistance (i.e., the value of the real part impedance when $f \rightarrow 0$).

A constant phase angle element (CPE) is the double layer capacitance depending on frequency (not pure capacitor), as a result of microscopic inhomogeneity in surfaces and introduced for impedance data fitting by replacing with all the capacitance components in the equivalent circuit [5, 15]. It is a modified Randles circuit and has the following equation:

$$Z = \frac{1}{Y_0(j\omega)^n} \quad (4)$$

Where $Z(\omega)$ is impedance of the CPE ($Z=Z'+jZ''$), (Ω); j imaginary number ($j^2 = -1$); ω angular frequency (rad); n CPE power ($n=\alpha/(\pi/2)$); α constant phase angle of the CPE (rad) and Y_0 is part of the CPE independent of the frequency (Ω^{-1}) [23, 30-32]. In general, for a CPE, the exponent n is less than one, but the exponent n is one for the pure capacitor [31].

The variations of fit parameters values that are derived from equivalent electrical circuit model and impedance data using Zview2 software are listed in Tables 4. The solution resistance (R_s) is very small and negligible in comparison to the polarization resistance (R_p) of the coatings. The admittance Y_0 is proportional to the area involved

Table 4. Electrochemical impedance analysis data.

	$R_p / \Omega \text{ cm}^2$	n	$Y_0 / \Omega^{-1} \text{ cm}^{-2} \text{ s}^n$
Pure Co	4010	0.74528	2.9879×10^{-5}
Co-BN (5 g L ⁻¹)	4589	0.75891	1.9239×10^{-5}
Co-BN (10 g L ⁻¹)	5950	0.79521	6.6349×10^{-6}
Co-BN (15 g L ⁻¹)	5972	0.79871	8.6379×10^{-6}
Co-BN (20 g L ⁻¹)	6889	0.81806	6.2855×10^{-6}

in the electrochemical reaction, i.e. a surface area of coating in contact with the solution [28]. The exponent (n) of the constant phase element (CPE) can be used to evaluate the inhomogeneity (roughness, porosity, microcrack) of coatings, and the coating inhomogeneity was decreased with the increase of the n value [32]. As seen from Table 4, the polarization resistance of pure Co coating ($4010 \Omega \text{ cm}^2$) is smallest and the higher values of R_p ($6889 \Omega \text{ cm}^2$) obtained for the composite coatings. It implies that composite coating has more protection ability against corrosion and corrosion resistance improves by adding ceramic particles into the coating due to decreasing the density of micro or nano porosities of the deposits [25] and less tendency of corrosion creates by compositing the cobalt matrix with BN nano particles. Incorporation of BN particles causes a decrease in the coatings admittance and the admittance Y_0 of the composite coatings capacitance reduces with increased particles content. Therefore, the decrease in the admittance Y_0 of coatings indicates that the effective metallic area prone to corrosion is decreased considerably in the case of composite coating, even though the apparent area remains the same. Moreover, the value of less than 1 for n1 indicates that the corroded surface for all tested samples was not homogeneous [31]. This could be ascribed to the surface porosity, though the differences are quite negligible.

4. CONCLUSION

BN nano particles had been successfully co-deposited with Co matrix to generate Co-BN nano composite coatings. Incorporation of BN particles affected the corrosion behavior of the deposit and higher corrosion resistance was obtained for Co-BN nano composite coatings with different particles content in comparison with pure Co coating.

REFERENCES

1. Alishahi, M., Monirvaghefi, S. M., Saatchi, A., and Hosseini, S. M., "The Effect of Carbon Nanotubes on the Corrosion and Tribological Behavior of Electroless Ni-P-CNT Composite Coating," *Applied Surface Science*, Vol. 258, No. 7, 2012, pp. 2439–2446.
2. Eslami Rad, N., Dehghanian, Ch., "Effects of Co-deposition of Cr_2O_3 and MoS_2 on Corrosion Properties of Nanocomposite Electroless Nickel Coating", *Iranian Journal of Materials Science and Engineering*, Vol. 7, No. 4, 2010, pp. 1-7.
3. Samadi, P., Afshar, M. R., Aboutalebi, M. R., Seyedain, S. H., "An Investigation on the Effect of Electromagnetic Force on the Characteristics of Electrodeposited Ni/ Al_2O_3 Composite Coatings", *Iranian Journal of Materials Science and Engineering* Vol. 9, No. 1, 2012, pp. 21-28.
4. Allahkaram, S. R., Faezi Alivand, R., Bakhsh, M. S., "Corrosion Behavior of Electroless Ni-P/NanoZnO Coating", *Iranian Journal of Materials Science and Engineering* Vol. 10, No. 1, 2013, pp. 10-17.

5. Ramesh1, D., and Vasudevan, T., "Evaluation of Corrosion Stability of Water Soluble Epoxy-Ester Primer through Electrochemical Studies," *Materials Sciences and Applications*, Vol. 3, No. 6, 2012, pp. 333-347.
6. Dong, D., Chen, X. H., Xiao, W. T., Yang, G. B., and Zhang, P. Y., "Preparation and Properties of Electroless Ni-P-SiO₂ Composite Coatings," *Applied Surface Science*, Vol. 255, No. 15, 2009, pp. 7051-7055.
7. Guo, C., Zuo, Y., Zhao, X., Zhao, J. and Xiong, J., "The Effects of Pulse-Reverse Parameters on the Properties of Ni-Carbon Nanotubes Composite Coatings," *Surface and Coatings Technology*, Vol. 201, No. 24, 2007, pp. 9491-9496.
8. Low, C. T. J., Wills, R. G. A. and Walsh, F. C., "Electrodeposition of Composite Coatings Containing Nanoparticles in a Metal Deposit," *Surface and Coatings Technology*, Vol. 201, No. 1-2, 2006, pp. 371-383.
9. Thiemig, D., Lange, R. and Bund, A., "Influence of Pulse Plating Parameters on the Electrodeposition of Matrix Metal Nanocomposites," *Electrochimica Acta*, Vol. 52, No. 25, 2007, pp. 7362-7371.
10. Kan, J. X., Zhao, W. Z. and Zhang, G. F., "Influence of Electrodeposition Parameters on the Deposition Rate and Microhardness of Nanocrystalline Ni Coatings," *Surface and Coatings Technology*, Vol. 203, No. 13, 2009, pp. 1815-1818.
11. Borkar, T. and Harimkar, S. P., "Effect of Electrodeposition Conditions and Reinforcement Content on Microstructure and Tribological Properties of Nickel Composite Coatings," *Surface and Coatings Technology*, Vol. 205, No. 17-18, 2011, pp. 4124-4134.
12. León, O. A., Staia, M. H. and Hintermann, H. E., "High Temperature Wear of an Electroless Ni-P-BN (h) Composite Coating," *Surface and Coatings Technology*, Vol. 163-164, 2003, pp. 578-584.
13. Weston, D. P., Shipway, P. H., Harris, S. J. and Cheng, M. K., "Friction and Sliding Wear Behaviour of Electrodeposited Cobalt and Cobalt-Tungsten Alloy Coatings for Replacement of Electrodeposited Chromium," *Wear*, Vol. 267, No. 5, 2009, pp. 934-943.
14. Kim, S. H., Aust, K. T., Erb, U., Gonzalez, F. and Palumbo, G., "A Comparison of the Corrosion Behavior of Polycrystalline and Nanocrystalline Cobalt," *Scripta Materialia*, Vol. 48, No. 9, 2003, pp. 1379-1384.
15. Benea, L., Ponthiaux, P. and Wenger, F., "Co-ZrO₂ Electrodeposited Composite Coatings Exhibiting Improved Micro Hardness and Corrosion Behavior in Simulating Body Fluid Solution," *Surface and Coatings Technology*, Vol. 205, No. 23-24, 2011, pp. 5379-5386.
16. Shaigan, N., Ivey, D. G. and Chen, W., "Co/LaCrO₃ Composite Coatings for AISI 430 Stainless Steel Solid Oxide Fuel Cell Interconnects," *Journal of Power Sources*, Vol. 185, No. 1, 2008, pp. 331-337.
17. Sivaraman, K. M., Ergeneman, O., Pané, S., Pellicer, E., Sort, J., Shou, K., Suriñach, S., Baró, M. D. and Nelson, B. J., "Electrodeposition of Cobalt-Yttrium Hydroxide/Oxide Nanocomposite Films From Particle-Free Aqueous Baths Containing Chloride Salts," *Electrochimica Acta*, Vol. 56, No. 14, 2011, pp. 5142-5150.
18. Chen, B., Bi, Q., Yang, J., Xia, Y. and Hao, J., "Tribological Properties of Solid Lubricants (graphite, h-BN) for Cu-Based P/M Friction Composites," *Tribology International*, Vol. 41, No. 12, 2008, pp. 1145-1152.
19. Salles, V., Bernard, S., Chiriac, R. and Miele, P., "Structural and Thermal Properties of Boron Nitride Nanoparticles," *Journal of European Ceramic Society*, Vol. 32, No. 9, 2011, pp. 1867-1871.
20. Pawlak, Z., Kaldonski, T., Pai, R., Bayraktar, E. and Oloyede, A., "A Comparative Study on the Tribological Behaviour of Hexagonal Boron Nitride (h-BN) as Lubricating Micro-Particles—An Additive in Porous Sliding Bearings for a Car Clutch," *Wear*, Vol. 267, No. 5-8, 2009, pp. 1198-1202.
21. Wang, W., Hou, F. Y., Wang, H. and Guo, H. T., "Fabrication and Characterization of Ni-ZrO₂ Composite Nano-Coatings by Pulse Electrodeposition," *Scripta Materialia*, Vol. 53, No. 5, 2005, pp. 613-618.
22. Ranganatha, S., Venkatesha, T. V. and Vathsala, K., "Development of Electroless Ni-Zn-P/nano-TiO₂ Composite Coatings and Their Properties," *Applied Surface Science*, Vol. 256, No. 24, 2010, pp. 7377-7383.

23. Tomachuk, C. R., Sarli, A. R. D. and Elsner, C. I., "Anti-Corrosion Performance of Cr⁺⁶-Free Passivating Layers Applied on Electrogalvanized," *Materials Sciences and Applications*, Vol. 1, No. 4, 2010, pp. 202-209.
24. Fu, L., Yang, J., Bi, Q. and Liu, W., "Electrochemical Behavior of Nanocrystalline Fe₈₈Si₁₂ Alloy in 3.5 wt% NaCl Solution," *Materials Sciences and Applications*, Vol. 2, No. 5, 2011, pp. 435-438.
25. Mazaheri, H. and Allahkaram, S. R., "Deposition, Characterization and Electrochemical Evaluation of Ni-P-Nano Diamond Composite Coatings," *Applied Surface Science*, Vol. 258, No. 10, 2012, pp. 4574-4580.
26. Kim, S. K. and OH, T. S., "Electrodeposition Behavior and Characteristics of Ni-Carbon Nanotube Composite Coatings," *Transactions of Nonferrous Metals Society of China*, Vol. 21, No. 1, 2011, pp. 68-72.
27. Mafi, I. R. and Dehghanian, C., "Comparison of the Coating Properties and Corrosion Rates in Electroless Ni-P/PTFE Composites Prepared by Different Types of Surfactants," *Applied Surface Science*, Vol. 257, No. 20, 2011, pp. 8653- 8658.
28. Cho, K. W., Rao, V. S. and Kwon, H. S., "Microstructure and Electrochemical Characterization of Trivalent Chromium Based Conversion Coating on Zinc," *Electrochimica Acta*, Vol. 52, No. 13, 2007, pp. 4449-4456.
29. Mu, S., Li, N., Li, D. and Xu, L., "Corrosion Behavior and Composition Analysis of Chromate Passive Film on Electroless Ni-P Coating," *Applied Surface Science*, Vol. 256, No. 13, 2010, pp. 4089-4094.
30. Farzaneh, M. A., Zamanzad-Ghavidel, M. R., Raeissi, K., Golozar, M. A., Saatchi, A. and Kabi, S., "Effects of Co and W Alloying Elements on the Electrodeposition Aspects and Properties of Nanocrystalline Ni Alloy Coatings," *Applied Surface Science*, Vol. 257, No. 13, 2011, pp. 5919-5926.
31. Jung, H. and Alfantazi, A., "An Electrochemical Impedance Spectroscopy and Polarization Study of Nanocrystalline Co and Co-P Alloy in 0.1M H₂SO₄ Solution," *Electrochimica Acta*, Vol. 51, No. 8-9, 2006, pp. 1806-1814.
32. Yao, Z., Jiang, Z. and Wang, F., "Study on Corrosion Resistance and Roughness of Micro-Plasma Oxidation Ceramic Coatings on Ti Alloy by EIS Technique," *Electrochimica Acta*, Vol. 52, No. 13, 2007, pp. 4539-4546.