

Short Communication

Corrosion Behavior of Electrodeposited Ni-B Coatings Modified with SiO₂ Particles

R. A. Shakoor^{1,*}, Umesh S. Waware¹, Ramazan Kahraman^{2,*}, Anton Popelka¹,
Moinuddin M. Yusuf¹

¹ Center for Advanced Materials, Qatar University, P. O. Box 2713, Doha, Qatar

² Department of Chemical Engineering, College of Engineering, Qatar University, P. O. Box 2713, Doha, Qatar

*E-mail: shakoor@qu.edu.qa, ramazank@qu.edu.qa

Received: 2 February 2017 / Accepted: 25 March 2017 / Published: 12 April 2017

The need for coatings with improved operation is vital to insure safety and high output of industrial plants. Electrodeposition is a valuable surface modification technology that can be used to develop various kinds of coatings. Although, Ni-B coatings have good mechanical properties (hardness and wear) but are suffering from inferior corrosion resistance. The development of Ni-B composite coatings by incorporating insoluble hard particles such as metal oxides (Al₂O₃, TiO₂) through electrodeposition process has generated a great interest among the research community because of auspicious improvement in properties. The main purpose of this research work was to study the influence of addition of SiO₂ particles on corrosion performance of Ni-B coated surfaces which has not been reported so far. Coatings of Ni-B and Ni-B-SiO₂ were deposited on steel through electrodeposition process. The microstructural (SEM) analysis confirms the formation of uniform, dense nodular structure in coatings of Ni-B and Ni-B-SiO₂. Surface examination (AFM) discloses that the addition of SiO₂ increases surface smoothness. Electrochemical characterization of the synthesized coatings indicates that Ni-B-SiO₂ composite coatings demonstrate better anticorrosion properties when compared to Ni-B. Enhanced corrosion performance may be ascribed to reduction in the active surface area and grain size refinement which reduces the porosity by the addition of inactive SiO₂ particles.

Keywords: Coating, composite, electrodeposition, crystal structure, corrosion

1. INTRODUCTION

Ni-B coatings demonstrate good characteristics such as wear resistance, hardness, uniform thickness, low cost, low porosity and good ductility. Owing to these properties, Ni-B coatings are attractive for automobile, aerospace, petrochemical and many other related industries [1]. However, it

is worth mentioning to note that Ni-B coatings have inferior anticorrosion properties as compared to Ni-P coatings which limits their application in more demanding applications [2]. In order to extend their utilization to more aggressive and harsh environment further improvement in properties is required. A satisfactory work has already been started along this front and some reports showing modification/upgradation in characteristics of Ni-B coatings through the addition of some alloying elements, including Co[3] and Zn[4] or insoluble, hard second phase particles like CeO₂[5], Al₂O₃[1], ZrO₂[6], TiO₂ [7], SiC[8] and Si₃N₄ [9] etc can be found in the literature.

Electrodeposition (ED) is a promising process, enabling us to deposit coatings on a large variety of substrates which comprised of metals, ceramics and polymers, etc. The electrodeposition process provides many other advantages as well, which broadly includes; good economy, less porosity, good phase purity, mass productivity, ease of shapes handling, ability to process different materials, good compositional control and ability to produce unique compositions that cannot be achieved by other methods. Furthermore, during the electrochemical deposition process, since the layer is developed on an atomic level, thus this method can also be suitable to develop nanocomposite coatings. Besides, these attractive features, this method has not been fully adopted for the synthesis of Ni-B coatings [1, 5, 6]. A variety of reducing agents which also act as the source of boron have been employed to develop different Ni-B coatings using electrodeposition technique. The most commonly used reducing agents are sodium borohydride [10], dimethylamine borane [2, 5, 9, 11], trimethylamine borane [12], sodium decahydrodecaborate [13, 14] and carborane ion [13].

The effect of SiO₂ incorporation on the performance of Zn-Ni coatings have been reported in an early report [15]. The purpose of this study was co-deposition of nano-SiO₂ particles into Zn-Ni matrix to enhance surface properties. The effect of addition of SiO₂ on composition, surface features, structure and anticorrosion properties of developed coatings were studied. However, our study focuses on mainly on the electrochemical behavior of coatings of Ni-B and Ni-B-SiO₂ in an aqueous solution of 3.5% NaCl (wt.%) which is entirely a different coating system. The coatings of Ni-B and Ni-B-SiO₂ were deposited on steel, employing electrodeposition technique. Furthermore, the structural and electrochemical characteristics of Ni-B and Ni-B-SiO₂ were compared to determine the effects of SiO₂ particles addition to the matrix. Our electrochemical tests performed on the developed coatings indicate that Ni-B-SiO₂ has better anticorrosion properties as compared to Ni-B. This work is useful and interesting because the resulting effect of SiO₂ addition to Ni-B has not been fully investigated yet.

2. EXPERIMENTAL

Coatings of Ni-B and Ni-B-SiO₂ were developed on steel surfaces (30 x 30 x 1.5 mm) employing electrodeposition process. The substrate steel specimens were polished using silicon carbide abrasive papers at various grit sizes (220 to 1200) and were then cleaned with alkaline solution. As a next step, the prepared substrates were applied sonication in acetone for 30 minutes to remove last traces of any surface contamination followed by water rinsing. Finally, the substrates were prior to starting the electrodeposition. The compositional and operational information about coating

synthesis are given in Table 1. Two separate coating baths were used for synthesis of Ni-B and Ni-B-SiO₂. A high purity nickel sheet (anode), mild steel substrate (cathode) was used to carry out the electrodeposition process (45 ±2°C, 60 minutes). The coating baths were continually agitated at a speed of 500 RPM using a hot plate and magnetic stirrer. The compositional analysis of developed coatings was studied through Energy Dispersive X-Ray Spectroscopy (EDX) and -Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS). Boron and nickel contents were determined by using ICP. However, SiO₂ was analyzed with EDX technique. Additional structural analysis (grain size, shape, morphology, porosity, etc.) of coatings was studied through field emission scanning electron microscope (FE-SEM). Surfaces were analyzed through atomic force microscopy (AFM). The details are available in our published work [1, 5].

Corrosion performance of the coatings of Ni-B and Ni-B-SiO₂ was studied by Potentiodynamic polarization technique. The tests were conducted in a solution of 3.5 NaCl (wt.%) at 25°C employing triple electrode cell. The triple electrode cell consisted of the working electrode (coated sample), reference electrode (saturated calomel) and a counter electrode (graphite). A fixed exposed area of 0.785 cm² of all coated samples was used. All the test specimens were scanned at a rate of 0.167 mV Sec⁻¹.

Table 1. Compositional analysis of coating bath and processing parameters.

No	Chemicals	Bath 1(Ni-B)	Bath 2 (Ni-B-SiO ₂)
1	Nickel sulphate hexa hydrate	240g/l	240g/l
2	Nickel chloride hexa hydrate	45g/l	45g/l
3	Boric acid	30g/l	30g/l
4	Dimethylamine borane complex	3g/l	3g/l
5	SiO ₂ powder particles	-	15 g/l
Operating conditions			
1	pH	4±0.2	4±0.2
2	Temperature	45±2°C	45±2°C
3	Time for deposition	60 minutes	60 minutes
4	Current density	50 mA/cm ²	50 mA/cm ²
5	Bath agitation	500 RPM	500 RPM

3. RESULTS AND DISCUSSION

EDX analyses of Ni-B binary and Ni-B-SiO₂ composite coatings in synthesized form are illustrated in Figure 1. It can be detected that both boron (B) and silica (SiO₂) are co-deposited with nickel leading to the building of coatings of Ni-B and Ni-B-SiO₂. Furthermore, compositional and metallic luster alterations have also been noticed by SiO₂ particles incorporation to Ni-B. These

observations are in agreement with the previous studies [2, 4, 5,9, 11]. Although, co-deposition of “B” in “Ni” through the electrodeposition process has not so far been well understood, the boron co-deposition into Ni is thought to take place because of adsorption of Dimethylamine Borane Complex [1, 2, 4, 5, 6,11]. SiO₂ incorporation into Ni-B is presumed to happen, firstly due to nickel ions adsorption on SiO₂ particle surfaces. Next, these particles move in the direction of cathode through a diffusion layer leading SiO₂ particles to loosely adhere to the cathode. Later on, discharging of nickel ions at the cathode results in embedment of SiO₂ particles into the matrix, Ni-B. Similar co-deposition mechanism of boron and nickel has also been suggested in the earlier reports [1, 5, 9, 11].

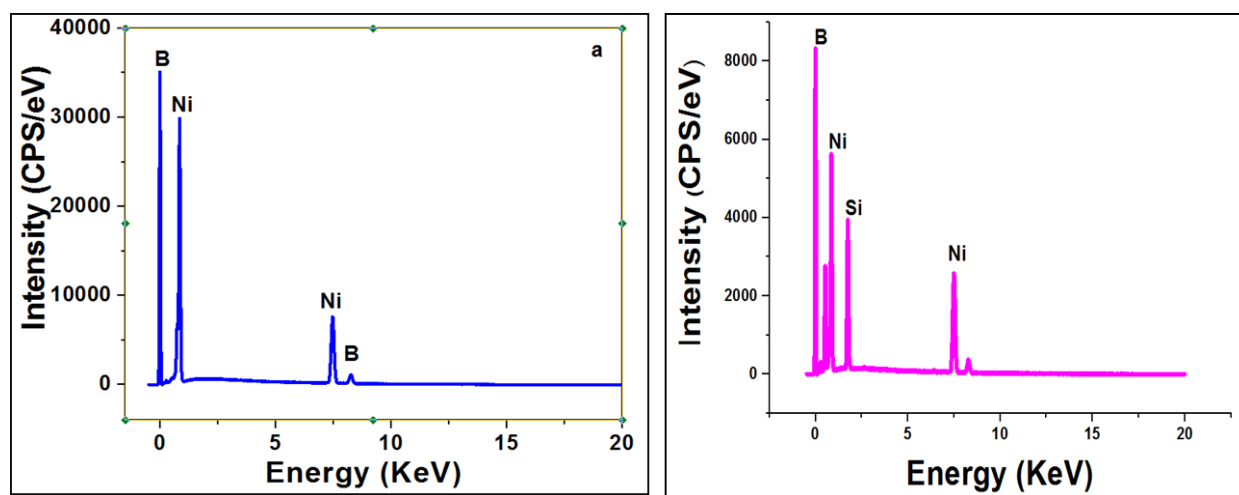


Figure 1. EDX analysis of Ni-B and Ni-B-SiO₂ coatings.

Structural analysis of coatings of Ni-B and Ni-B-SiO₂ is shown in Figure 2. A comparison reveals the dense, uniform and nodular structure of Ni-B and Ni-B-SiO₂. Presence of SiO₂ is also clearly visible in the Ni-B-SiO₂ composite coatings and this is consistent with our EDX compositional analysis (Figure 1). As also seen Ni-B-SiO₂ coatings are fine grained relative to the Ni-B coatings. The formation of fine grained structure in Ni-B-SiO₂ composite coatings can be explained on the basis of increase in electrocrystalline potential and retardation of grain size due to the presence of insoluble SiO₂ particles. Actually, during the electrodeposition technique, insoluble particles such as SiO₂ adsorb cations in the coating solution under sufficient high potential gradient. These particles are then taken away to the cathode surface by electrophoresis process and then adsorbed on the surface of cathode surface. This phenomenon leads to an increase in electrocrystalline potential. The increase in electrocrystalline potential can be ascribed to the decrease in the active area of cathode surface due to the presence of adsorbed inactive particles (SiO₂). Moreover, the presence of new nuclei due to adsorbed particles (SiO₂) can also restrict the grain growth. The formation of fine grained structure due to the incorporation of insoluble particles has also been previously reported [16,17].

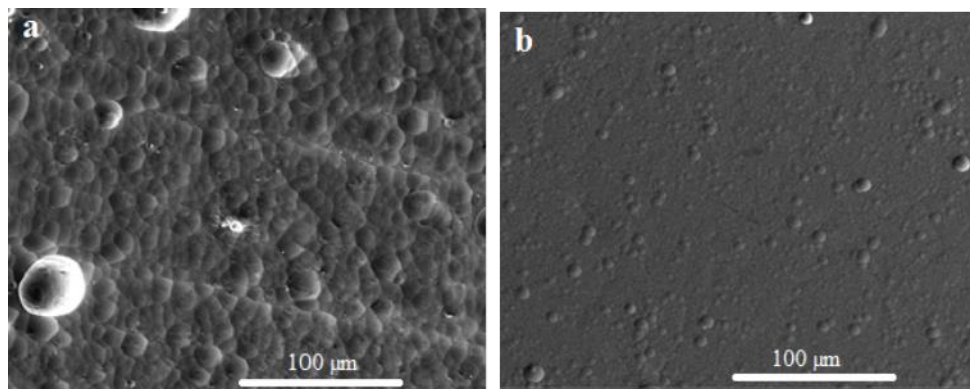


Figure 2. Surface morphology of developed coatings (a) Ni-B and (b) Ni-B-SiO₂.

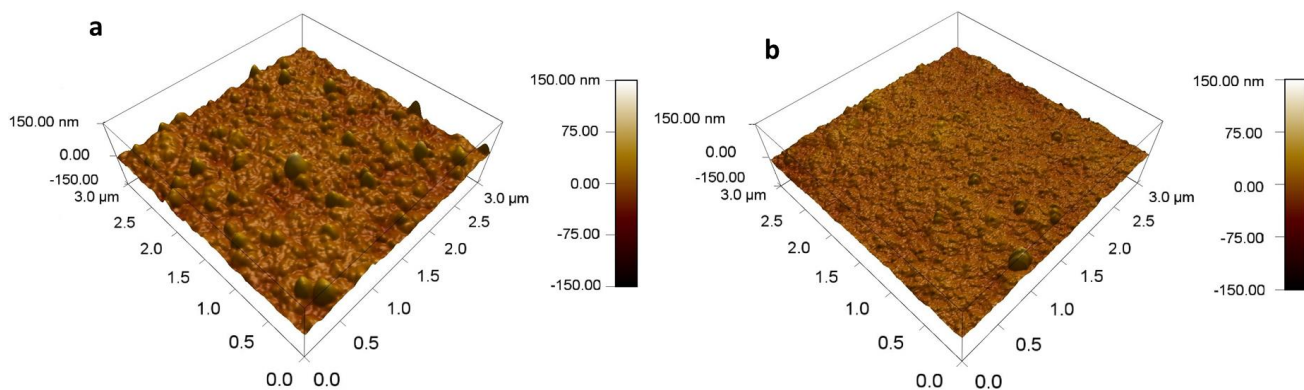


Figure 3. Atomic force microscopic images coatings (a) Ni-B and (b) Ni-B-SiO₂.

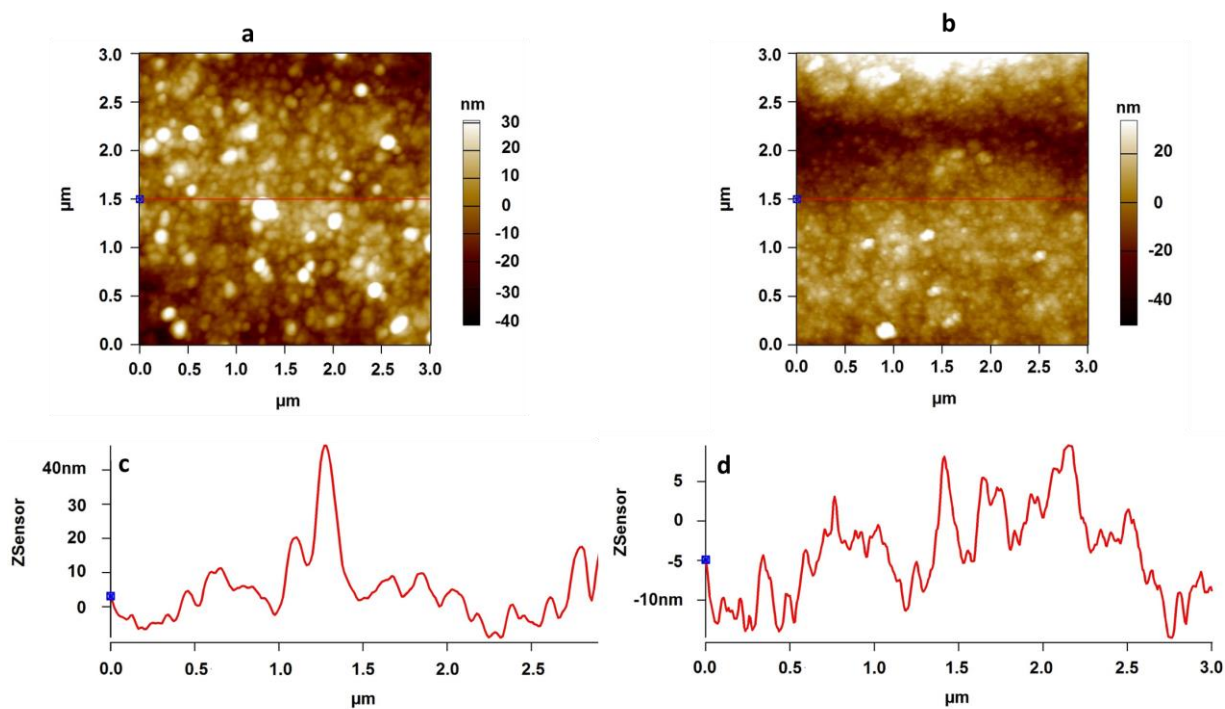


Figure 4. AFM images and roughness results of coatings: Ni-B (a, c) and Ni-B-SiO₂ (b, d).

3D figures of Ni-B and Ni-B-SiO₂ coatings as studied by AFM are shown in Figure 3. A very smooth surface of the coatings of Ni-B-SiO₂ is seen as compared to the surface of Ni-B which is in agreement with our SEM analysis.

Surface roughness profiles of coatings of Ni-B and Ni-B-SiO₂ are displayed in Figure 4. As the comparison shows the surface of the coatings of Ni-B-SiO₂ are smoother than Ni-B and this is again consistent with our SEM and AFM analyses. This observation again confirms that SiO₂ particles incorporation into Ni-B has led to reduce surface roughness. This can be attributed to the heterogeneous nucleation, which hindered the grain growth during the formation of the coating. The low roughness of Ni-B-SiO₂ composite coatings is essentially because of their small grains, which are uniformly packed together to reduce the surface roughness.

The corrosion performance of developed coatings in an aqueous solution of 3.5 % NaCl was investigated as summarized in Figure 5 and Table 2. Comparison of corrosion current densities (*i*_{corr}) and corrosion rate (mpy) for the mild steel substrate, Ni-B and Ni-B-SiO₂ suggests that SiO₂ particles addition to Ni-B has led to improvement in its corrosion resistance. The corrosion current density of Ni-B-SiO₂ composite coatings (15.5 μA/cm²) is 15% less as compared to the Ni-B coatings (18.20 μA/cm²). However, the value of *i*_{corr} of Ni-B-SiO₂ is found to be higher when compared to Ni-B-TiO₂ (5.53μA/cm²) [7], Ni-B-ZrO₂-Al₂O₃ (9.70μA/cm²) [18] and Ni-B-Si₃N₄ (10.92 μA/cm²) [2] composite coatings which indicate its relatively inferior corrosion protection and suggests its further improvement.

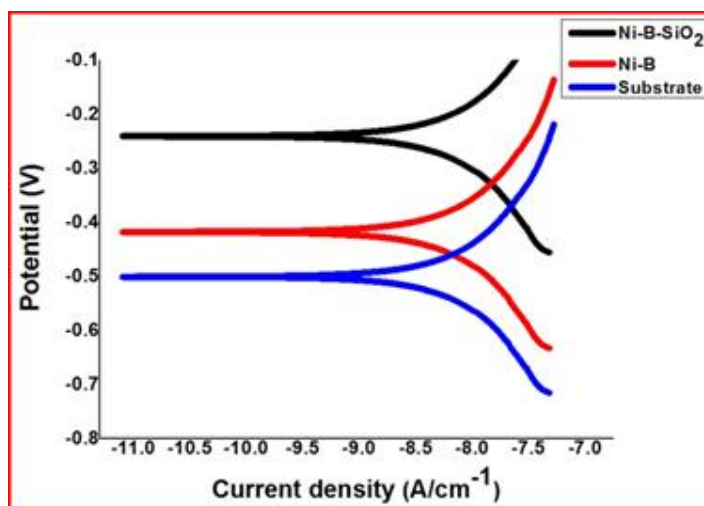


Figure 5. Potentiodynamic polarization curves of coatings in 3.5% NaCl (wt. %) at room temperature.

Table 2. Summarized corrosion data of the coatings of Ni-B and Ni-B-SiO₂.

Sample Name	<i>E</i> _{corr} (mV)	<i>i</i> _{corr} (μA/cm ²)	β _a (mV/decade)	β _c (mV/decade)	Corrosion rate (mpy)
Substrate	-0.53	33.20	119.6	667.0	39.86
Ni-B	-0.42	18.20	329.0	505.0	21.83
Ni-B-SiO ₂	-0.24	15.50	455.5	434.7	18.39

The corrosion protection efficiency (η) of the coatings was calculated using the following formula [19].

$$\eta = 1 - \frac{i_2}{i_1} \times 100\%$$

Where i_1 and i_2 correspond to the corrosion current densities of the substrate and the coated samples respectively. The corrosion protection efficiency of Ni-B coatings is ~45%, whereas for Ni-B-SiO₂ coatings is ~53%. The improved corrosion performance of Ni-B by SiO₂ particles incorporation might be explained by lessening of active area of Ni-B by inactive SiO₂ particles and the fine grained structure formation which may have resulted in less porosity in the structure. The presence of SiO₂ particles in the Ni-B matrix may also have led to the filling of the some of the active pores and thus reduces the porosity and the associated corrosion rate. However, we think the larger particle size of SiO₂ particles may have rendered Ni-B-SiO₂ composite coatings to effectively block its pores to attain a comparative performance as compared to other reported composite coatings. This finding is also consistent with the previous studies [2]. It is, therefore, recommended to use nanoparticles of SiO₂ to further improve the electrochemical performance of Ni-B-SiO₂ composite coatings. Further corrosion analysis using electrochemical Impedance Spectroscopy (EIS) will be useful to have more insight to the corrosion behavior of such developed coatings and to understand the corrosion mechanism.

4. CONCLUSIONS

1. Coatings of Ni-B and Ni-B-SiO₂ were successfully formed by electrodeposition on steel substrate surfaces.
2. Structural analysis confirms the formation of dense, uniform, nodular structure in both types of developed coatings.
3. The addition of SiO₂ particles into Ni-B matrix refines grain size and improves surface smoothness. This might be because of increased electro crystalline potential and grain growth retardation as a result of the presence of insoluble hard ceramic particles.
4. Ni-B-SiO₂ composite coatings demonstrate relatively superior anticorrosion properties when compared to Ni-B. This might be a result of refinement in grain size, decreasing porosity and lessening of active Ni-B matrix area by SiO₂ particles which are insoluble and inactive.

ACKNOWLEDGEMENTS

This publication was made possible by NPRP Grant NPRP-9-080-2-039 from Qatar National Research Fund (a member of the Qatar Foundation). Statements made herein are solely the responsibility of the authors.

References

1. R.A. Shakoor, R.K. Umesh, S. Waware, Y. Wang and W. Gao, *Mater. Des.*, 64 (2014) 1271.
2. K. Krishnaveni, T.S.N.S. Narayanan and S.K. Seshadri, *J. Alloys Compd.*, 480 (2009) 765.
3. S. Narayanan, A. Stephan, and S. Guruskanthan, *Surf. Coat. Technol.*, 179 (2004) 56.

4. R.A. Shakoor, R.K. Umesh, S.Waware, Y. Wang and W. Gao, *Int. J. Electrochem. Sci.*, 9 (2014) 520.
5. R.A. Shakoor, R.K. Umesh, S. Waware, Y. Wang and W. Gao, *Mater. Des.*, 59 (2014) 421.
6. R.A. Shakoor, R. Kahraman, U.S. Waware, Y. Wang and W. Gao, *Int. J. Electrochem. Sci.*, 10 (2015) 2110.
7. Y.S. Wang, W. Gao, W. Lu and B. Yan, *J. Alloys Compd.*, 617 (2014) 472.
8. H. Ogihara, H. Wang and T. Saji, *Appl. Surf. Sci.*, 296 (2014) 108.
9. K. Krishnaveni, T.S.N.S Narayanan and S.K. Seshadri, *J. Alloys Compd.*, 466 (2008) 412.
10. C.R. Pichard, Z. Bouhala, A.J Tosser, A. Rashid and J. Fechon, *J. Mater. Sci.*, 20 (1985) 3305.
11. K. Krishnaveni, T.S.N.S. Narayanan and S.K. Seshadri, *Mater. Chem. Phys.*, 99 (2006) 300.
12. K.H. Lee, D. Chang and S.C. Kwon, *Electrochim. Acta*, 50 (2005) 4538.
13. Y.N. Bekish, S.K. Poznyak, L.S. Tsybulskaya and T.V. Gaevskaya, *Electrochim. Acta*, 55 (2010) 2223.
14. T.V. Gaevskaya, I.G. Novotortseva and L.S. Tsybulskaya, *Met. Finishing*, 94 (1996) 100.
15. O. Hammami, *Int. J. Corros.*, (2012) 8.
16. N.S. Qu, D. Zhu and K.C. Chan, *Scripta Mater.*, 54 (2006) 1421.
17. A.G. McCormack, M.J. Pomeroy and V.J. Cunnane, *J. Electrochem Soc.*, 5 (2003) 356.
18. A.B. Radwan, R.A. Shakoor and A. Popelka, *Int. J. Elctrochem. Sci.*, 10 (2015) 7548.
19. S. Yuan, S.O. Pehkonen, B. Liang, Y.P. Ting, K.G. Neoh and E.T. Kang, *Corros. Sci.*, 53 (2011) 2738.