Mechanical and anti-corrosion properties of TiO$_2$ nanoparticle reinforced Ni coating by electrodeposition

Wei Shao$^{1,2*}$, David Nabb$^3$, Nathalie Renevier$^4$, Ian Sherrington$^4$, Yongqing Fu$^5$ and Jikui Luo$^{1*}$

$^1$Institute for Renewable Energy and Environmental Technologies, University of Bolton, Bolton, BL3 5AB, UK
$^2$College of Chemical Engineering, Nanjing Forestry University, Nanjing 210037, China
$^3$MSC Copperflow Ltd, Bolton, BL1 2SX, UK
$^4$Jost Institute for Tribotechnology, University of Central Lancashire, Preston, PR1 2HE, UK
$^5$Thin Film Centre, University of West of Scotland, Paisley, PA1 2BE, UK

Abstract: Nanocomposite metallic coatings containing various reinforced nanoparticles to improve their tribological and mechanical properties enhance and improve their use in industry and have been developed in last few decades. The main purpose of the current work is to investigate mechanical and anti-corrosion properties of the electroplated nickel nanocomposite with a small percentage of titania nanoparticles. The surface morphology, hardness, wear and corrosion resistance were investigated in detail. The results showed the nanocomposite coatings have a smoother and more compact surface than the pure nickel layer, and have higher hardness and lower wear rate than the pure Ni coating. The preferred orientation of the nanocomposite coating changes from (200) crystal plane to (220) plane. The anti-corrosion property of nanocomposite coating was carried out in 3.5 % and 35 % NaCl solution, respectively. The results also showed that the nanocomposite coating improves the corrosion resistance significantly. This present work reveals that incorporation of titania nanoparticles in nickel nanocomposite coating can achieve much improved corrosion resistance and mechanical properties of both hardness and wear resistance performances, and the improvement becomes stronger as the content of titania is increased.

Key words: Electroplating; nanocomposite; hardness; wear resistance; corrosion resistance

* Corresponding author. Tel.: +44-1204-903523; fax: +44-1204-399074.
E-mail address: w.shao@bolton.ac.uk (W.shao) and J.Luo@bolton.ac.uk (J.Luo)
1. Introduction

Although metallic composite coating deposited by plating is not a new technique, it has continuously been developed since the 1970s and is still one of the most commonly used high-value added technologies [1]. There are several reasons for this steadily increased interest, including easy maintainability and low cost for materials, equipment and process. The composite coatings by plating have many attractive mechanical, tribological and anti-corrosion properties, and can be easily tailored by adjusting the concentrations of the materials in the composites, the process conditions and post-treatment [2].

During composite plating process, insoluble micro- or nano-sized materials are normally suspended in a conventional plating electrolyte and embedded inside the growing metal films [3]. These second-phase materials can be powder, fine fibres or particles such as silicon carbide (SiC), alumina (Al$_2$O$_3$), titania (TiO$_2$), carbon nanotubes (CNTs) and polymers such as polytetrafluoroethylene (PTFE) and polyethylene (PE) with sizes from micrometres to nanometres [4-7]. Generally, microhardness, yield strength, tensile strength, friction, wear, and corrosion resistance of the composites can all or partially be improved by the presence of these second-phase particles [8], depending on the nature of these reinforcement materials incorporated.

Since Ni is one of the most common coatings used in engineering, Ni-composite coatings have been intensively studied [5, 7-9]. Among the reinforcement materials, TiO$_2$ is one of the most important nanoparticles used in the engineering coatings, and the titania-based material normally offers high strength, good corrosion and better oxidation resistance [6]. Therefore, it is expected that incorporation of TiO$_2$ nanoparticles into Ni matrix can greatly improve the mechanical, tribological properties and corrosion resistance, hence the TiO$_2$ enhanced Ni coating can be used in industry either in a single layer or multilayer structures. These nanocomposite coatings have various applications for automotive parts, aviation, aerospace, electronics, petroleum, chemistry, machinery, textiles, printed circuitry, and decorative door, light and bathroom fittings [10].

Development of Ni nanocomposite coatings has been focused on electroless plating mainly due to its simple process, but in the form of Ni-P-TiO$_2$ [9, 11-15]. The corrosion resistance and mechanical properties of Ni-P-TiO$_2$ nanocomposite coatings using electroless plating and sol-gel combined methods have been investigated by Song et al. [10] and Chen et al. [11],
and results demonstrated the improved hardness, wear and corrosion resistance. For electroplating Ni-TiO$_2$ composite, Parida et al. [16] studied the surfactant effect on the mechanical properties of the composite coatings, and showed that the plating solution with 0.3 g/L surfactant can generate higher microhardness and wear resistance. Baghery et al. [17] demonstrated that electroplating parameters significantly affect the properties Ni-TiO$_2$ composite coatings. Chen et al. [18] reported improved mechanical property and corrosion resistance of Ni-TiO$_2$ composite coatings by using a combined sol-gel and electroplating method. However, research on the electroplating Ni-TiO$_2$ nanocomposites is relatively limited, and the mechanisms of particle co-deposition and performance-enhancement are far from clear, and the processes are far from optimized. In the present paper, incorporation of TiO$_2$ nanoparticles in a Ni matrix electroplated in a Watts nickel bath was systematically investigated. The effect of TiO$_2$ nanoparticles on microstructure, hardness and corrosion resistance as well as wear resistance of TiO$_2$-Ni nanocomposite coatings were studied and reported.

2. Experiments

2.1 Coating preparation

Mild steel plates with dimension of 20 mm × 20 mm × 1 mm were used as the substrates. Before electroplating, the steel substrates were cleaned in alkaline solution followed by an acid etch process. De-ionized water was used to rinse the substrates after each step and finally the samples were dried with N$_2$ gas. The details of pretreatment on the mild steel plates are listed in Table 1. Ni depositions were performed from a Watts nickel bath and the general composition and conditions of the electroplating bath are summarized in Table 2. In this experiment, the suspension was prepared by adding TiO$_2$ nanoparticles with average size of 50 nm (from Sigma) into the solution to reach a TiO$_2$ concentration up to 12 g/L in the Ni plating electrolyte. The mild steel was used as the cathode and a pure Ni plate was used as the anode. Electrodeposition took place in the bath at a stirring rate of 200 rpm at a temperature of 50 °C and a current density of 2 A/dm$^2$ for one hour for all the samples. The film thickness is about 25 μm for all coatings without visible change when nanoparticles are added in the plating solution. The cathode current efficiency is estimated to be about 95%, consistent with most Ni-electroplating process.

2.2 Surface analysis of the coatings
After the plating, the coatings were cleaned ultrasonically in acetone for 10 min in order to remove the loosely adsorbed TiO$_2$ nanoparticles from the coatings. The coatings were rinsed using distilled water and dried. A Philips XL30 Scanning Electron Microscope (SEM) operating at an accelerating voltage of 15 keV was used to investigate the surface morphologies of the coated samples. The concentrations of Ni and TiO$_2$ in the nanocomposite films were analyzed using a Phoenix EDAX X-ray microanalysis system (EDX) embedded within the SEM system operating at an accelerating voltage of 10 or 15 keV. X-ray diffraction (XRD) analysis was used to determine the crystal structure of the deposited coatings. A Bruker GADDS X-Ray Diffractometer with a Cu K$_\alpha$ radiation (40 kV/30 mA) was employed to obtain XRD spectra using a two-theta (2$\theta$) range from 35 to 80°.

2.3 Mechanical tests

After electropolating, the coated samples were mounted on sample holders to polish the top surface of the coating prior to the nano-indentation test to minimize the effect of rough surface. Hardness of the coatings were obtained by indentation on the polished surface of the Ni nanocomposite coatings using a nanoindentation system (The Nanotest™, Micro Materials, UK) at room temperature. A three-sided pyramidal diamond tip with an angle of 104.3° was used for the test. The indenter was lowered at a rate of 50 nm/s to indent the matrix up to a depth of 500 nm and then retrieved from the coating surface. A total of five indentations were made at randomly selected positions on each specimen surface and the average values were calculated and discussed.

Wear resistance properties of the Ni composite samples were evaluated on a reciprocating ball-on-disk computer-controlled oscillating tribotester. A tungsten carbide (WC) ball (diameter 6 mm, hardness HV: 15500 N/mm$^2$) was used as the counter body. All the wear tests were performed using a load of 12 N and a speed of 12 mm/s in a dry sliding mode at room temperature. The sliding amplitude was 5 mm and the total sliding length was 10 meters with the data recorded automatically during the tests. After the tests, the specimen was washed with distilled water to remove the debris from the specimen. The wear behavior and wear rate of the test samples were studied by analyzing the profile of wear tracks. The degree of wear resistance of the coatings was evaluated on the basis of the worn surface area (examined using SEM). The wear rates were calculated based on the profiles of wear tracks vs. duration of wear and the corresponding wear scar depth and length were determined by an Omniscan MicroXAM 5000B optical profiler. If the profile of a vertical section of a wear
track can be measured, the area of the profile can be calculated. The area of the profile multiplied by the mean track length represents the volume loss \( V \) of the test material. The \( V \) can be calculated using the British Standard BS EN 1071-12:2010 which is shown as follows:

\[
V = (l - w_a)w_a d_a + \left(\pi w_a^2 d_a\right)/4
\]

(1)

where \( w_a \) and \( d_a \) are the average width and depth of the wear scar; \( l \) is the overall length of the wear scar. The average width and depth of the wear scar were determined by five points. Wear rate, \( R \), can then be calculated by dividing this volume loss by both the load and the total sliding distance on the disk specimen, as given by

\[
R = \frac{V}{2LSN}
\]

(2)

where \( V \) is volume loss of material during the test duration; \( L \) is the applied load; \( S \) is the stroke length; \( N \) is the total number of reciprocations.

2.4 Corrosion tests

Electrochemical measurements were carried out using the PG581 potentiostat system with CorrTest software. Potentiodynamic polarization measurements were carried out in a 250 mL cell with three standard electrodes: saturated calomel electrode (SCE) as a reference, a platinum electrode as the counter and a coating sample as the working electrode. All the potentials were recorded and compared with the SCE. Prior to Tafel polarization, the specimens were allowed to immerse in the electrolyte while the open circuit potential (OCP) was measured as a function of time until it reaches a stable value. All the specimens were washed with acetone and distilled water to remove possible surface contamination prior to each experiment. The experiments were performed in a 3.5 % NaCl solution at room temperature. Potentiodynamic polarization curves were recorded from a starting potential of 500 mV below the OCP and scanned towards the positive direction at a scan rate of 1 mV s\(^{-1}\), until the potential reached 500 mV. The polarization tests were repeated at least three times for each specimen. The corrosion potential (\( E_{corr} \)) and corrosion current density (\( I_{corr} \)) were determined from the Tafel curve by the extrapolation method. Corrosion resistance of coatings was also assessed by weight loss method. The specimens were immersion into 35 % NaCl solution at room temperature in order to accelerate the corrosion rates. The weight differences of the specimens were recorded after 5 days, 10 days, 15 days and 20 days.
immersion. The weight losses were measured using an electric balance (with a resolution of $10^{-5}$ g) and were compared for the Ni coating and Ni nanocomposite coatings.

3. Results and discussions

3.1 Crystalline structure

Figure 1 shows SEM morphologies of a pure Ni coating and Ni-TiO$_2$ nanocomposite coating containing 12 g/L TiO$_2$ nanoparticles. The morphologies between the pure Ni coating and Ni-TiO$_2$ nanocomposite coating are quite different. The Ni coating has a clear crystal structure with an average grain size in the range of 2~4 µm (Fig. 1a). The addition of TiO$_2$ nanoparticles would increase deposition over potential [19, 20] and disordered the regular crystal structure, thus the structure of nickel matrix became uniform and fine crystalline with fine crystal sizes of 0.1~1 µm (Fig. 1b). The co-deposited TiO$_2$ nanoparticles are much uniformly distributed in the Ni matrix as white spherical globules as can be seen in Fig. 1b. The Ni-TiO$_2$ nanocomposite coating has a fairly uniform, continuous and compact morphology.

Figure 2 shows XRD patterns of the pure Ni and Ni-TiO$_2$ nanocomposite coatings, respectively. As shown in Fig. 2a, the pure Ni coating has a preferred orientation of (200) crystal plane with weak peak at (220). The addition of TiO$_2$ nanoparticles changes the preferred orientation from (200) to (220) plane. During deposition, there is a competition between the nucleation and crystal growth of Ni crystals. It is believed that the TiO$_2$ nanoparticles deposited on the surface of the coating provide more nucleation sites, hence inhibit the rapid crystal growth, resulting in a Ni nanocomposite with smaller grain sizes [21].

No TiO$_2$ peak was detected from the XRD spectra in Fig. 2b, probably due to the formation of low quantity and highly dispersive distribution of the fine TiO$_2$ nanoparticles [11]. To confirm the existence of TiO$_2$ in the films, EDX was used to measure the TiO$_2$ concentration and the result is shown in Fig. 3, which clearly confirms the presence of TiO$_2$ nanoparticles in the Ni matrix. The inset in Fig. 3 is the relationship between the TiO$_2$ concentration in weight percentage measured and the concentration of nanoparticles in the plating solution, showing gradual increase and saturation of TiO$_2$ content with the increase of the nanoparticle content in the plating solution.

3.2 Hardness
Figure 4 shows the hardness of the Ni coating and Ni-TiO$_2$ nanocomposite coatings with the different contents of TiO$_2$ nanoparticles, obtained from nano-indentation tests. It can be seen that the hardness of Ni-TiO$_2$ nanocomposite coatings increases with increasing the content of TiO$_2$ nanoparticles. The hardness values of the Ni coating and Ni nanocomposite coatings can be found in Table 3. The hardness of the pure Ni coating is 316 HV, in agreement with the typical values of pure Ni metal. The coating electroplated with a 12 g/L TiO$_2$ nanoparticles solution has the maximum hardness of 387 HV, about 20 % larger than that of the pure Ni layer. The improvement in hardness is compatible to those of electroless plating Ni-P-TiO$_2$ with a similar TiO$_2$ nanoparticle concentration as reported here, though the absolute value of the hardness for electroless plated Ni-P-TiO$_2$ is much higher owing to the inclusion of P-element. [31]. The effect of increasing the hardness may be attributed to three different factors. Firstly, the co-deposited TiO$_2$ nanoparticles in the Ni matrix can restrain the growth of large Ni grains, resulting in the fine grain structure. Secondly, dispersive strengthening effects can be resulted from the reinforcing phase itself which acts as barriers to retard the plastic deformation of Ni matrix, leading to a higher hardness of Ni-TiO$_2$ nanocomposite coatings [22]. The fine grain and dispersive strengthening effects become stronger with increasing the content of the TiO$_2$ nanoparticles in the nanocomposite coatings, which leads to the increase of hardness of the Ni-TiO$_2$ nanocomposite coating with the TiO$_2$ nanoparticles content [23]. The third factor is the structural modification of Ni crystallites through the changes of the preferred orientation [23]. The diffraction pattern of the pure Ni coating showed the dominant (200) texture (Fig. 2a), and it changed to (220) structure once the TiO$_2$ nanoparticles are included in the matrix. Ni layers with (200) texture is associated with the minimum hardness and internal stress, and the maximum ductility among different oriented crystal structures of Ni [24, 25]. The Ni-TiO$_2$ nanocomposite coating modifies the “soft” (200) structure to a (220) orientation which has a higher hardness.

3.3 Anti-wear properties

Figure 5 shows the effect of TiO$_2$ nanoparticles on the wear rate of Ni matrix nanocomposite coatings. The wear rate decreases continuously with the increase of the content of TiO$_2$ nanoparticles in the nanocomposite coatings. The wear rate values can be found in Table 3. For example, the wear rate of the Ni-TiO$_2$ nanocomposite coating with 12 g/L TiO$_2$ is 9.1×10$^{-9}$ mm$^3$/Nmm, improved by about 48 % compared to that of the pure Ni coating of 14.88×10$^{-9}$ mm$^3$/Nmm. The improvement is believed to be twofold. Firstly, an increase in the surface
fraction of TiO$_2$ nanoparticles reduces the direct contact between the Ni matrix and WC ball, while the TiO$_2$ particles have higher wear resistance than Ni. The TiO$_2$ coatings also have finer and smoother surface that may increase the load-carrying area and reduce the stress concentration between the friction couples which leads to the improvement of wear resistance of the nanocomposite coating [26]. Secondly, the TiO$_2$ nanoparticles have a much higher wear resistance [27], hence reduce the overall wear rate of the nanocomposite coating. Also the nanocomposite coating is much denser with smaller grain sizes as seen in Fig. 1b, which may also contribute to the improvement of the wear resistance. Therefore the more TiO$_2$ nanoparticles there are, the higher the wear resistance will be [28].

The SEM images of worn coating surfaces are shown in Figure 6. The wear tracks on all the coatings showed dark grey to black appearance and scratches parallel to the direction of motion, which are typical for an abrasive wear mode [29]. Clearly, the width of the worn track of the pure Ni coating (Fig. 6a) is larger than that of the TiO$_2$ reinforced Ni nanocomposite coating as shown in Fig. 6b under the same load.

3.4 Corrosion resistance

The potentiodynamic polarization curves of pure Ni coating (line 1) and Ni-TiO$_2$ nanocomposite coatings with 12 g/L TiO$_2$ (line 2) in 3.5 % NaCl solutions are presented in Figure 7. The electrochemical parameters such as corrosion potential ($E_{corr}$), corrosion current ($I_{corr}$) and the calculated corrosion rates ($R_{corr}$) using Tafel extrapolation method are listed in Table 4. The corrosion rate of the 12 g/L TiO$_2$ nanoparticles reinforced Ni coating has been decreased up to 25 % compared with that of the pure Ni coating. With the increase of TiO$_2$ content in the nanocomposite coating, the corrosion current decreases and the corrosion potential shifts to a positive side, resulting in a decreased corrosion rate. TiO$_2$ nanoparticles played a major role for improving the corrosion protection, possibly in three mechanisms. Firstly, these incorporated TiO$_2$ particles filled in the pores and cracks of Ni matrix, acting as inert physical barriers to the initiation and development of corrosion, and contributing to the improvement of anti-corrosion resistance. Secondly, dispersion of the TiO$_2$ nanoparticles in the nickel matrix results in formation of many “corrosion micro-cells”, in which the TiO$_2$ nanoparticles act as the cathode and while nickel metal acts as the anode as the standard potential of TiO$_2$ is more positive than that of nickel. Such corrosion micro-cells facilitate the anode polarization. Therefore, in the presence of TiO$_2$ nanoparticles, localized corrosion is inhibited, and homogeneous corrosion dominates [7, 17]. Finally, the corrosion must proceed
along a circuitous path along the nanoparticles to reach the substrate since the crystallite size of the coating is in the nanometer range. The length of the circuitous path will be longer in Ni-TiO$_2$ composite coating compared to that in the pure Ni coating owing to the smaller crystallite size in composites. As a result, the composite coatings have improved corrosion resistance over pure Ni coating [30]. The corrosion resistances of our samples are in the range between 0.011-0.015mm/year as summarized in table 3, better than or comparable to those of electroless Ni-P-TiO$_2$ coatings with similar TiO$_2$ concentrations [12].

A 35 % NaCl solution was used as a corrosive medium to speed up the corrosion test. Figure 8 shows the weight losses for different Ni-based coatings immersed in a 35 % NaCl solution for 5 days, 10 days, 15 days and 20 days, respectively. As shown in Fig. 8, the weight losses of both Ni coating and Ni-TiO$_2$ nanocomposite coating increased with the immersion time. The Ni-TiO$_2$ nanocomposite coating exhibited a smaller weight loss than the pure Ni coating for all TiO$_2$ contents tested and corrosion durations. For a fixed corrosion duration, the weight loss decreases with the increase of the TiO$_2$ particle content, but the percentage of decrease in weight loss as compared to that of the pure Ni coating remains almost unchanged for each duration. For instance, for the 5-day test, the weight loss for the 12 g/L coating is improved by 22 %, similar to that of the 20-day test. The results have clearly shown that the TiO$_2$ nanoparticle reinforced Ni nanocomposite coatings have a better corrosion resistance compared with that of the pure Ni coatings in the NaCl solution.

4. Conclusions

TiO$_2$ nanoparticles reinforced Ni nanocomposite coatings were prepared by electroplating method. The pure Ni coating has a regular crystal surface. Introduction of the TiO$_2$ nanoparticles into the plating solution resulted in a much smoother surface morphology with excellent mechanical properties. The Ni-TiO$_2$ nanocomposite coatings exhibited a higher hardness and higher wear resistance in comparison with that of the pure Ni coating. Meanwhile, the corrosion resistance of the nanocomposite coating has been enhanced significantly.

Although electroless plating Ni-P-TiO2 composite coating have higher hardness, electroplating process is easier for controlling the thickness, contents of the coating, and for plating in patterned structure, therefore electroplated Ni-TiO2 composite have better and broad applications in engineering and researches.
Acknowledgements

The authors would like to acknowledge the financial support by Knowledge Transfer Partnership and TSB (KTP007867) and The Knowledge Centre for Materials Chemistry under Grant No. of X00680PR.

References

Fig. 1 Surface morphologies of Ni based coatings (a) Ni coating, (b) Ni-TiO$_2$ nanocomposite coating. The surface becomes smoother with much smaller grain sizes once the TiO$_2$ particles are included in the Ni matrix.
Fig. 2 XRD pattern of pure Ni deposit (a) and Ni-TiO$_2$ nanocomposite coating (b), showing a clear crystal orientation change once nanoparticles are included in the coatings.
Fig. 3 EDX analysis of Ni-TiO$_2$ nanocomposite coatings. The inset is the TiO$_2$ concentration in the Ni matrix as a function of TiO$_2$ nanoparticle concentration in the plating solution.
Fig. 4 Hardness for Ni based nanocomposite coatings, demonstrated improved hardness with enclosure of nanoparticles.
Fig. 5 Wear rates for Ni based nanocomposite coatings, showing significant improvement in wear resistance.
Fig. 6 SEM images of worn surfaces (a) pure Ni coating, (b) Ni-TiO$_2$ nanocomposite coating
Fig. 7 Tafel curves of Ni and Ni-TiO$_2$ nanocomposite coatings
Fig. 8 Weight loss results after 5 days, 10 days, 15 days and 20 days immersion in 35% NaCl solution
### Table 1 Pretreatment of mild steel before Ni plating

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Bath composition and operating conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline cleaning</td>
<td>NaOH:30 g/L; Na₃PO₄:30 g/L; Na₂CO₃:30 g/L; Na₂SiO₃:10 g/L; 80 °C; 10 min</td>
</tr>
<tr>
<td>Rinsing</td>
<td>Water, room temperature</td>
</tr>
<tr>
<td>Electropolishing</td>
<td>NaOH:30 g/L; Na₃PO₄:30 g/L; Na₂CO₃:30 g/L; Na₂SiO₃:10 g/L; room temperature; 2 min; voltage:5~7 V</td>
</tr>
<tr>
<td>Rinsing</td>
<td>Hot water, then cold water</td>
</tr>
<tr>
<td>Pickling</td>
<td>HCl (30 %); room temperature, 5 min</td>
</tr>
<tr>
<td>Rinsing</td>
<td>Water, room temperature</td>
</tr>
</tbody>
</table>
Table 2 Electroplating solution composition

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiSO₄·7H₂O</td>
<td>300 g/L</td>
</tr>
<tr>
<td>NiCl₂·6H₂O</td>
<td>35 g/L</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>40 g/L</td>
</tr>
<tr>
<td>TiO₂ nanoparticles</td>
<td>0-12 g/L</td>
</tr>
<tr>
<td>Surfactant</td>
<td>suitable</td>
</tr>
</tbody>
</table>
Table 3 Hardness and wear rates of Ni based composite coatings

<table>
<thead>
<tr>
<th>Samples</th>
<th>Hardness (GPa)</th>
<th>Hardness (HV)</th>
<th>Wear rates (mm³/Nmm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni coating</td>
<td>3.1</td>
<td>316</td>
<td>14.88</td>
</tr>
<tr>
<td>Ni-TiO₂ (4 g/L)</td>
<td>3.23</td>
<td>329</td>
<td>13.1</td>
</tr>
<tr>
<td>Ni-TiO₂ (8 g/L)</td>
<td>3.45</td>
<td>352</td>
<td>11.87</td>
</tr>
<tr>
<td>Ni-TiO₂ (12 g/L)</td>
<td>3.8</td>
<td>387</td>
<td>9.1</td>
</tr>
</tbody>
</table>
Table 4 Electrochemical parameters and calculated corrosion rates for tested coatings

<table>
<thead>
<tr>
<th>Samples</th>
<th>$E_{corr}$ [mV]</th>
<th>$I_{corr}$ [µA]</th>
<th>$R_{corr}$ [µm/y]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni coating</td>
<td>-755</td>
<td>333</td>
<td>15.3</td>
</tr>
<tr>
<td>Ni-TiO$_2$ (4 g/L)</td>
<td>-742</td>
<td>314</td>
<td>14.4</td>
</tr>
<tr>
<td>Ni-TiO$_2$ (8 g/L)</td>
<td>-733</td>
<td>296</td>
<td>13.6</td>
</tr>
<tr>
<td>Ni-TiO$_2$ (12 g/L)</td>
<td>-727</td>
<td>258</td>
<td>11.5</td>
</tr>
</tbody>
</table>