Corrosion resistance of AZ91D magnesium alloy with electroless plating pretreatment and Ni–TiO$_2$ composite coating

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In this paper, a protective multilayer coating, with electroless Ni coating as bottom layer and electrodeposited Ni–TiO$_2$ composite coating as top layer, was successfully prepared on AZ91D magnesium alloy by a combination of electroless and electrodeposition techniques. Scanning electron microscopy and X-ray diffraction were employed to investigate the surface, cross-section morphologies and phase structure of coatings, respectively. The electrochemical corrosion behaviors of coatings in 3.5 wt.% NaCl solutions were evaluated by electrochemical impedance spectroscopy, open circuit potential and potentiodynamic polarization techniques. The results showed that the corrosion process of Ni–TiO$_2$ composite coating was mainly composed of three stages in the long-term immersion test in the aggressive media, and could afford better corrosion and mechanical protection for the AZ91D magnesium alloy compared with single electroless Ni coating. The micro-hardness of the Ni–TiO$_2$ composite coating improved more than 5 times than that of the AZ91D magnesium alloy.

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1. Introduction

The inherent lightness and high stiffness to weight ratio makes magnesium alloys become the choice for weight reduction in portable microelectronics, automotive industry and biomaterials [1,2]. The high reactive nature of magnesium is clearly indicative of its low standard electrode potential ($E = -2.37 \text{ V}$) which makes magnesium and its alloys highly susceptible to corrosion in aggressive media. Many reports about corrosion research of AZ91D magnesium alloy could be found in the previous literatures [3–6]. For the die-cast AZ91D magnesium alloys, corrosion starts preferentially at the boundaries between $\alpha$ and $\beta$ phases [5] which restrict their wide applications. Hence, various methods for applying protective coatings on AZ91D magnesium alloy, such as electrochemical plating, chemical conversion coating, hydride coating, anodizing, gas phase deposition, and organic/polymer coatings have been tried [7–12].

Electrodeposition of ceramic, polymer and metal particles within metal matrix that produces composite coatings with the attractive properties such as high wear and corrosion resistance, higher hardness, and more excellent self-lubricating, has been wildly studied [13–19] on various substrates. However, electrodeposition of Ni–TiO$_2$ composite coating on magnesium alloy, which is well known for the properties of wear-resistance and corrosion-resistance [13,19], has not yet been reported.

It has been well accepted that magnesium alloys are “difficult to plate metals” [20,21] due to the oxide film with...
low electrical conductivity and bonding ability which is always present on the light metal surface, which prevents the adhesion of the metallic coating. Thus, several pretreatments used to produce an interlayer on the surface of AZ91D magnesium alloy have been proposed for electrodeposition. It was found that electroless nickel coating does not only show a good adherence on AZ91D magnesium alloy after special pretreatment, but also shows a lot of excellent properties including corrosion resistance and conductivity which can provide an excellent interlayer for electrodeposition [10,22–24].

The aim of the present study is to form a dense multilayer coating with electroless Ni coating as the inner layer and electroplating Ni–TiO2 composite coating as the top layer for the AZ91D magnesium alloy. The surface morphology and corrosion resistance of both single Ni electroless coating and Ni–TiO2 composite coating were investigated. Finally, the degradation process of the multilayer in 3.5 wt.% NaCl was investigated by electrochemical impedance spectroscopy (EIS) and the corrosion mechanisms were discussed.

2. Experimental

Die-casted AZ91D magnesium alloys were the experimental materials used for the investigation. The chemical compositions were mainly composed of 8.77 wt.% Al, 0.74 wt.% Zn, 0.18 wt.% Mn and Mg balance. Samples with sizes 10 × 25 × 4 mm were cut and the substrate was mechanically ground with No. 2000 SiC paper before the pretreatment processes. The composition and operating conditions of the electroless Ni coating and the electroplating Ni–TiO2 coatings on the AZ91D magnesium alloy were shown in Table 1. The samples were cleaned thoroughly with deionized water as quickly as possible between any two steps of the treatments. Anatase TiO2 powder was purchased from Shanghai CaiYu Nano technique Co., Ltd., (China) with a mean diameter of 10 nm. A nickel plate with the purity of 99.99% was used as anode on the side of the electrolytic cell.

X-ray diffraction patterns (XRD) of the AZ91D magnesium alloy and the coated samples were obtained from an X-ray diffractometer (XD-3, Beijing Purkinje general instrument Co., Ltd. China) with a diffractometer operating at 36 kV, 20 mA, using Cu Kα target. The samples were run at 2θ from 10° to 80° with a step size of 0.01° (2θ) and a scanning rate of 4° min⁻¹. In order to study the adhesion and thickness, the cross sectional microstructure of the electroless Ni coating and Ni–TiO2 composite coating, all samples were carefully mounted, ground and polished. The corrosion behaviors of the samples were compared using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements. The testing equipment was a CS350 Electrochemical Workstation (Wuhan CorroTest Instrument Co., Ltd., China). A conventional three-electrode cell, with the specimens as the working electrode, a saturated calomel electrode (SCE) as reference and a platinum sheet as counter electrode, were employed in those tests. Working electrodes were embedded into epoxy resin with an exposure area of 1 cm². The specimens were immersed in the electrolyte for 30 min prior to each test, allowing the system to be stabilized. The test electrolyte was neutral 3.5 wt.% NaCl solution and the test temperature was maintained at 30 °C. The scan rate for potentiodynamic polarization curves was 1 mV s⁻¹. Open circuit potential (OCP) was monitored before the immersion EIS test for the Ni–TiO2 composite coating. EIS

<table>
<thead>
<tr>
<th>Operation</th>
<th>Plating bath composition</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grinding</td>
<td>No. 2000 SiC sandpaper</td>
<td>Time 10 min</td>
</tr>
<tr>
<td>Ultrasonic cleaning</td>
<td>Aceton degrease</td>
<td>Temperature 65 °C</td>
</tr>
<tr>
<td>Alkaline cleaning</td>
<td>NaOH 10 g/L</td>
<td>Time 5 min</td>
</tr>
<tr>
<td></td>
<td>Na2CO3 20 g/L</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C₆H₄H₂N₂SO₄ 0.5 g/L</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PtCl₂ 0.5 g/L</td>
<td></td>
</tr>
<tr>
<td></td>
<td>EtOH 20 g/L</td>
<td>Time 5–10 s</td>
</tr>
<tr>
<td>Pretreatment</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electroless Ni coating</td>
<td>NiCO3 2Ni(OH)₄·4H₂O 10 g/L</td>
<td>Temperature 65 °C</td>
</tr>
<tr>
<td></td>
<td>NaH₂PO₄·H₂O 20 g/L</td>
<td>Time 60 min</td>
</tr>
<tr>
<td></td>
<td>C₃H₆O₂·H₂O 5 g/L</td>
<td>pH 6.1±0.2</td>
</tr>
<tr>
<td></td>
<td>NH₄HF₂ 20 g/L</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NH₃·H₂O 30 mL/L</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SC(NH₂) 2 1 mg/L</td>
<td></td>
</tr>
<tr>
<td>Electroplating Ni–TiO2 coating</td>
<td>NiSO₄··7H₂O 300 g/L</td>
<td>Temperature 50 °C</td>
</tr>
<tr>
<td></td>
<td>NaCl 60 g/L</td>
<td>Time 30 min</td>
</tr>
<tr>
<td></td>
<td>HBO3 30 g/L</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Anatase TiO2 8 g/L</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SDS 0.1 g/L</td>
<td>pH 5</td>
</tr>
</tbody>
</table>

Table 1 - Composition and operating conditions of the electroless Ni coating and Ni–TiO2 composite coating on AZ91D magnesium alloy (the samples were cleaned thoroughly with deionized water as quickly as possible between any two steps of the treatments).
tests were conducted at the OCP and the measuring frequency was ranged from $10^5$ Hz down to $10^{-2}$ Hz, with ac excitation amplitude of 5 mV. The acquired EIS data were curve fitted and analyzed using ZsimpWin 3.10 software.

The Vickers micro-hardness of the magnesium alloy and the coatings were evaluated using an HXD-1000TMC (China) micro-hardness tester with Vickers indenter, at a load of 100 g and duration of 15 s. For each specimen, the average hardness value was taken from at least 10 tests.

3. Results and Discussion

3.1. X-ray Diffraction Pattern Analysis

The XRD patterns of the AZ91D magnesium alloy, electroless nickel coating and Ni–TiO$_2$ composite coating are shown in Fig. 1. Fig. 1a showed the sharp peaks for AZ91D magnesium substrate, which was for comparison. Fig. 1b showed a broad peak at diffraction angle $2\theta$ between 40° and 50° corresponding to the dominant peak of Ni (111), and some additional weak peaks corresponding to AZ91D magnesium substrate, which was similar to reports in the previous work [25], while the spectra of Ni–TiO$_2$ composite coating in Fig. 1c showed typical peaks of Ni with the peaks of (111), (200) and (220). The characteristic peak of TiO$_2$ in the composite coating was not observed in the XRD patterns due to the low content of TiO$_2$ in the coatings. However, the EDS analysis testified the existence of TiO$_2$ particles in the composite coating. In each measurement an area of 10 µm in diameter was examined to a depth of about 2 µm. The examinations showed that the TiO$_2$ content in the composite coatings amounted to 2.2 ± 0.2 wt.%.

3.2. Scanning Electron Microscopy Analysis

The typical surface morphologies of the electroless Ni coating at low and high magnifications are shown in Fig. 2a and b, respectively. The surface of the sample was fully covered by the electroless Ni coating with regular round nodules. The
The dimension of these nodules was smaller than 5 µm. Fig. 2c showed that the electroless Ni coating was compact and uniform, and there was not any chink between the Ni coating and the substrate. It can be seen that the AZ91D magnesium substrate was coated by a thin Ni coating with the thickness of about 4 µm which depicted an interlayer homogeneously distributed onto the surface of the substrate.

Composite plating of Ni–TiO$_2$ was carried out on the surface of electroless Ni coating and the surface and cross-section morphologies of multilayer coating were shown in Fig. 3. The surface of Ni–TiO$_2$ composite coating was rough with different dimensions of nodules due to the co-electrodeposition of TiO$_2$ nano-particle. The boundaries of every nodule were cycloidal. Fig. 3c showed the cross-section morphologies of the Ni–TiO$_2$ composite coating. The thickness of the total coating layer was about 15 µm. Good adhesion between the magnesium alloy substrate and electroless Ni coating, the electroless Ni coating and the Ni–TiO$_2$ composite coating were both observed, because no abruption or cracks were observed along the interfaces of the three coatings. There was only a gleaming boundary between the electroless coating and the Ni–TiO$_2$ composite coating.

3.3. Corrosion Analysis

3.3.1. Electrochemical Impedance Spectroscopy Test for the Samples
Electrochemical impedance spectroscopy and polarization potentiodynamic methods are powerful techniques to investigate the corrosion protection of different coatings for substrate. The EIS characteristics of the bare magnesium alloy substrate, electroless Ni coating and the Ni–TiO$_2$ composite coating in 3.5 wt.% NaCl solution were respectively examined at open circuit potential to illuminate their different corrosion resistance as shown in Fig. 4. Taking into account the different characteristics of EIS plots of AZ91D magnesium alloy, the electroless Ni coating and the Ni–TiO$_2$ composite coating, the corrosion resistance was significantly improved by the composite coating. The thickness of the total coating layer was about 15 µm. Good adhesion between the magnesium alloy substrate and electroless Ni coating, the electroless Ni coating and the Ni–TiO$_2$ composite coating were both observed, because no abruption or cracks were observed along the interfaces of the three coatings. There was only a gleaming boundary between the electroless coating and the Ni–TiO$_2$ composite coating.

Fig. 4 – Bode plots of bare magnesium alloy substrate, electroless Ni coating and the Ni–TiO$_2$ composite coating in 3.5 wt.% NaCl solution.
substrate with and without coatings, two equivalent circuits are proposed as shown in Fig. 5.

For the AZ91D magnesium substrate, the high frequency capacitance loop corresponding to the solution resistance explained with \( R_s \), \( R_{ct} \) and CPE and the low frequency inductive loop explained with \( R_L \) (inductance resistance) and \( L \) (inductance) was obtained as shown in Fig. 5a. \( R_s \) referred to the solution resistance. \( R_{ct} \) was named as charge transfer resistance representing the resistance of electron transfer during electrochemical reaction course. Taking into account the rough metal surface, the constant phase element of CPE \( (\theta) \) was used instead of the electric double layer capacitance. The low frequency relaxation process could be attributed to the occurrence of corrosion nucleus, slow reaction, such as adsorbed reaction intermediates during the metal dissolution process. In the case of the samples with electroless Ni coating and the Ni–TiO\(_2\) composite coating, only a capacitance loop was observed and the EIS spectra were similar except for the difference in the diameter of the loops. This meant that the corrosion mechanisms of the samples were similar, but their corrosion rates were different, and both the EIS plots could be well fitted by the equivalent circuit shown in Fig. 5b. As shown in Fig. 4, it can be seen that for the Ni–TiO\(_2\) composite coating, the spectrum revealed the broadest phase angle and highest impedance value, which could be ascribed to the good protective property of Ni–TiO\(_2\) composite coating rather than the electroless nickel coating. This indicated that the corrosion resistance was improved by composite coating.

3.3.2. Open Circuit Potential
The open circuit potential of the substrate with Ni–TiO\(_2\) composite coating immersed in 3.5 wt.% NaCl solution at different immersion times was monitored to reach a relatively stable stationary value before each experiment (Fig. 6). All the curves were characterized by a slow increase or decrease of the potential with time until it reaches a plateau. The difference of the curves is presented in the tendency of the two curves, it slowly climbed and reached a higher value for the samples’ immersion for 0.5 h and 24 h, while for the rest of the samples, all the curves are down to a steadily value. The open circuit potential of the sample immersion for 0.5 h was found to be more positive compared with the sample immersion for a longer time.

3.3.3. Immersion Test
The impedance spectra of the specimen treated with composite coating immersion for different times are shown in Fig. 7. In order to further understand the corrosion mechanisms, the corresponding equivalent circuits for EIS tests of the immersion samples are shown in Fig. 8. The plots are fitted

![Fig. 5](image5.png)

**Fig. 5** – Equivalent circuits used to fit the experimental data of EIS plots in Fig. 4, (a) AZ91D magnesium alloy, and (b) electroless Ni coating and the Ni–TiO\(_2\) composite coating.

![Fig. 6](image6.png)

**Fig. 6** – Open circuit potential versus time for the Ni–TiO\(_2\) composite coating immersion in 3.5 wt.% NaCl solution for different immersion time.

![Fig. 7](image7.png)

**Fig. 7** – Bode plots of the Ni–TiO\(_2\) composite coating immersed in 3.5 wt.% NaCl solution at different times.
using Zsimpwin 3.10 software and the results are listed in Table 2. A good correspondence between the fitted and measured spectra is obtained. The corrosion and degradation processes of the Ni-TiO$_2$ composite coating immersion in 3.5 wt.% NaCl solution could be described by three stages as follows.

The first stage was the immersion time of 0.5 h in which only one time constants could be observed and the impedance modulus $|Z|$ of multilayer coating remained in the very high value suggesting the excellent anticorrosion properties provided for the substrate. At the first half an hour of immersion, only a capacitance loop existed in the spectra, and the composite coating exhibited a low activity of reaction. At the moment, the composite coatings showed relatively high resistance as shown in Fig. 7 (0.5 h). The dissolution of Ni-TiO$_2$ composite coating was negligible at this period. The corresponding equivalent expression of the impedance of the electrode system [26]

$$Z = \frac{1}{j\omega L + R_s + 1/(Y_0(j\omega)^n + 1/R_{ct})}$$

where $Y_0$ is a constant that is independent of frequency, $w$ is the angular frequency, $j = \sqrt{-1}$ and $n$ is the exponential index which represents a dispersion of relaxation.

The second stage was the immersion time ranging from 24 h to 96 h in which two well-defined time constants could be observed and the impedance modulus $|Z|$ of multilayer coating decreases properly. The two capacitance loops indicated the presence of two reaction courses. The high frequency capacitance loop corresponding to the charge transfer reaction still could be explained by $R_{an}$, $R_{ct}$ and CPE$_1$. The low frequency capacitance loop was correlative with the transitional electrolyte penetrating into the micro-cracks, infiltrated through the porous layer by diffusion, and reached the interface of porous layer and the compact inner barrier layer, which could be explained by $R_{cor}$ and CPE$_2$. Generally, the impedance magnitude of the composite coating decreased slightly, which illuminated that the composite coating was stable and the corrosion resistance could be maintained for long immersion time in 3.5 wt.% NaCl solution. The corresponding equivalent circuits for this period were shown in Fig. 8, and the mathematical expression of the impedance of the electrode system [26] could be described by the equation as follows:

$$Z = \frac{1}{j\omega L + R_s + 1/(Y_0(j\omega)^n + 1/R_{ct} + 1/(Y_0(j\omega)^n + 1/R_{cor}))}$$

The values of capacitance (CPE$_3$) and $R_c$, which was the sum of $R_{ct}$ and $R_{cor}$, at different times are illustrated in Fig. 9. With the increasing immersion time, the $R_c$ values reduced gradually. On the contrary, the capacitance values increased with the increasing immersion time, and then trended to be stable.

The third stage was the immersion time after 96 h in which visible corrosion pits were observed. Once the corrosion pits penetrate the coatings, serious galvanic corrosion will destroy the substrate quickly and the EIS tests cannot be carried out again in the third stage of immersion.

### 3.3.4. Potentiodynamic Polarization

Fig. 10 showed the potentiodynamic polarization curves for the bare magnesium alloy substrate, electroless Ni coating and the Ni-TiO$_2$ composite coating. For the bare magnesium alloy substrate, an activation-controlled cathodic process occurred in the cathodic branch, and the main reaction was hydrogen evolution. When the applied potential increased into the anodic branch, an activation-controlled anodic process was observed. The polarization current increased by increasing the applied anodic potential and no passivation occurred. For the AZ91D magnesium substrate with electroless Ni coating and

![Fig. 8 – Equivalent circuit used to fit the experimental data of EIS plots in Fig. 7.](image8)

![Fig. 9 – Changes of $R_c$ and capacitance with different immersion times.](image9)

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>$L$ (H.cm$^{-2}$)</th>
<th>$R_0$ (Ω.cm$^2$)</th>
<th>$Y_{D1}$ (Ω$^{-1}.$cm$^{-2}$ s$^{-n}$)</th>
<th>$n_1$</th>
<th>$R_{cor}$ (Ω.cm$^2$)</th>
<th>$Y_{D2}$ (Ω$^{-1}.$cm$^{-2}$ s$^{-n}$)</th>
<th>$n_2$</th>
<th>$R_{cor}$ (Ω.cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>3.5E–6</td>
<td>4.2</td>
<td>8.6E–5</td>
<td>0.90</td>
<td>98200</td>
<td>6.0E–4</td>
<td>0.72</td>
<td>7869</td>
</tr>
<tr>
<td>24</td>
<td>3.9E–6</td>
<td>2.6</td>
<td>1.9E–4</td>
<td>0.85</td>
<td>1783</td>
<td>7.4E–4</td>
<td>0.61</td>
<td>9405</td>
</tr>
<tr>
<td>48</td>
<td>3.8E–6</td>
<td>3.2</td>
<td>2.2E–4</td>
<td>0.83</td>
<td>811</td>
<td>7.4E–4</td>
<td>0.61</td>
<td>7717</td>
</tr>
<tr>
<td>72</td>
<td>4.5E–6</td>
<td>1.5</td>
<td>3.4E–4</td>
<td>0.80</td>
<td>449</td>
<td>1.1E–3</td>
<td>0.67</td>
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<tr>
<td>96</td>
<td>4.5E–6</td>
<td>1.4</td>
<td>3.3E–4</td>
<td>0.79</td>
<td>935</td>
<td>1.0E–3</td>
<td>0.61</td>
<td>9031</td>
</tr>
</tbody>
</table>

Table 2 – Fitting results of EIS plots for Ni-TiO$_2$ composite coating with different immersion times in neutral 3.5 wt.% NaCl solutions.
Ni–TiO2 composite coating, the cathodic reaction was still hydrogen evolution, an obvious passivation occurred in the anodic branch, and the passivation range reached 200 mV and 350 mV, respectively. This meant that the Ni–TiO2 composite coating presented an excellent corrosion resistance.

Different parameters including corrosion current density ($i_{corr}$) and corrosion potential ($E_{corr}$) calculated from the polarization curves displayed in Fig. 10 using Tafel extrapolation are summarized in Table 3. It can be seen from Table 3 that Ni–TiO2 composite coating exhibited the noblest $E_{corr}$ with a value of −325 mV and the lowest $i_{corr}$ with a value of 0.44 $\mu$A cm$^{-2}$, while bare substrate showed the lowest $E_{corr}$ with a value of −1491 mV and the highest $i_{corr}$ with a value of 10.80 $\mu$A cm$^{-2}$. The polarization potential $E_{corr}$ of the electroless coating coated sample and Ni–TiO2 composite coating shifts positively about 1027 mV and 1166 mV compared with that of the substrate, respectively. The polarization resistance values calculated with the Stern–Geary formula from potentiodynamic diagrams were in good agreement with those obtained from the impedance measurements. The polarization resistance of Ni–TiO2 composite coating was by far the largest and also suggested that it could provide the good protection for the AZ91D magnesium substrate.

From the analysis mentioned above, it can be seen that Ni–TiO2 composite coating and electroless nickel coating both provided excellent protection for the bare magnet, but nobler $E_{corr}$, $E_{pit}$ and much lower $i_{corr}$ for the Ni–TiO2 composite coating indicated the better protection provided for the AZ91D magnesium substrate. The polarization resistance values obtained from both methods are in good agreement.

### 3.3. Micro-hardness Analysis

The micro-hardness of the Ni–TiO2 composite coating on AZ91D substrate was about 445 HV, which was far higher than that of the AZ91D magnesium alloy substrate (about 78 HV), and that of the electroless Ni coating on AZ91D substrate (about 145 HV). Therefore, the magnesium alloy coated by the Ni–TiO2 composite coating with high hardness would be expected to greatly improve its mechanical properties.

### 3.4. Conclusions

In summary, the following conclusions can be concluded in this article.

The electroless Ni coating was formed on AZ91D magnesium substrate as an interlayer for electrodeposition of Ni–TiO2 composite coating, and both coatings were well formed. The electroless Ni coating could provide some protection for AZ91D magnesium substrate, and Ni–TiO2 composite coating provided a longer corrosion protection in 3.5 wt.% NaCl solution.

Three stages could be concluded for the corrosion and degradation mechanism of the Ni–TiO2 composite coating immersed in a 3.5 wt.% NaCl solution. The immersion time of 0.5 h with highest resistance value was named as the early stage of immersion. The immersion time of 24 h to 96 h with stable resistance value was named as the middle stage and the visible corrosion pits were observed after immersion time of 96 h that was the final stage of immersion. Once the corrosion pits penetrate the coatings, serious galvanic corrosion will destroy the substrate quickly.

The micro-hardness of the Ni–TiO2 composite coating on AZ91D substrate was far higher than that of the AZ91D magnesium alloy substrate.

### Table 3 – Electrochemical parameters of bare magnesium alloy substrate, electroless Ni coating and the Ni–TiO2 composite coating, obtained by polarization in 3.5 wt% NaCl solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>OCP, mV</th>
<th>$E_{corr}$, mV</th>
<th>$i_{corr}/\mu$A cm$^{-2}$</th>
<th>Corrosion rate mm/a</th>
<th>$R_p$/Ω cm$^2$</th>
<th>Passive region/mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ91D magnesium substrate</td>
<td>−1585</td>
<td>−1491</td>
<td>10.80</td>
<td>0.11</td>
<td>1609</td>
<td>−</td>
</tr>
<tr>
<td>Electroless nickel coating</td>
<td>−514</td>
<td>−464</td>
<td>0.96</td>
<td>0.01</td>
<td>17853</td>
<td>200</td>
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<tr>
<td>Ni–TiO2 composite coating</td>
<td>−251</td>
<td>−325</td>
<td>0.44</td>
<td>5.18E−03</td>
<td>34847</td>
<td>330</td>
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</table>
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