Influence of Silica Particle Size on the Corrosion Behavior of Electroplated Silica–Ni Hybrid Layer

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ABSTRACT: Silica–Ni hybrid layers were electroplated on a Q235 steel plate in a Watt nickel plating solution with varying sizes of silica, and a pure nickel layer was prepared as a blank sample. The surface morphology, composition, and crystal structure of the electroplated layers were examined using a field emission scanning electron microscope (FESEM), an energy-dispersive spectrometer (EDS), and a X-ray diffractor (XRD). The corrosion resistance of the samples was evaluated by the experiments of potentiodynamic polarization, electrochemical impedance spectroscopy, and salt spray test in NaCl solutions. The results showed that the smaller the particle size of silicon, the higher the content of silicon in the layer was, and the better the corrosion resistance of the layer was. However, when the particle size is 10 nm, agglomeration would happen, which leads to a decrease in the corrosion resistance performance, 50 nm silica–Ni hybrid layer showed the optimal corrosion resistance with the highest silica content.

1. INTRODUCTION

Electroplated nickel is an effective way to extend the service life of the steel workpiece, but the potential corrosion and porosity of the electroplated layer limit the corrosion resistance of electroplated nickel. The research on corrosion resistance of electroplating nickel is the focus of practical engineering applications. Compared to the single metal layer, metal-based hybrid layers have attracted much attention due to high hardness, high wear resistance, and excellent corrosion resistance.1–4 The introduction of oxide particles can improve specific properties and optimize the performance of the electroplated nickel layer. The presence of second-phase particles in the nickel matrix could reduce the porosity and improve the mechanical properties and the corrosion resistance of the layer. At present, a great variety of nanoparticles have been embedded into the nickel matrix hybrid layers, such as silica, Al2O3, ZrO2, TiO2, TiN, SiC, etc. Xu et al.5,6 reported that nickel matrix hybrid layers reinforced with sub-microsized Al2O3 particles were produced by pulse electrodeposition. The wear resistance of hybrid layers increased with the increase of volumetric content of Al2O3 particles under oil-lubricated wear conditions. Ahmadi et al.7 reported that the Ni–ZrO2 hybrid layers were prepared by conventional electrodeposition methods. The results showed that the content of particles in the plating layer increases first and then decreases as the concentration of ZrO2 in the plating solution increases. The electroplated sample in the bath containing 90 g/L ZrO2 has the maximum particle content and the best corrosion resistance. Pavlatou et al.11 reported that the Ni–TiO2 composites were prepared by applying direct current on a rotating disk electrode (RDE). It has been observed that the presence of TiO2 nanoparticles favors the (100) texture of the nickel matrix. As the titania incorporation percentage is increased, nickel crystals get a considerable degree of grain refinement. Wu et al.13 reported that nano Ni–TiN layers are prepared by ultrasonic electrodeposition on the surface of mild steel. Ni–TiN hybrid layers showed better corrosion resistance than Ni layers. Nowak et al.14 reported on nickel-based hybrid layers containing nano-SiC particles prepared under separate
pulse conditions. It has been proved that the presence of nanoparticles changes the crystal orientation, resulting in a hybrid layer with a smaller grain size than the pure Ni layer.

Due to the low cost and superior physical/chemical properties, silica as a second-phase particle was widely used in electroplated nickel, copper, zinc, and gold layers. The corrosion resistance of the film can be effectively improved by the hybrid layer of silica particles and electroplating nickel. The improvement of the corrosion resistance of the hybrid layers mainly depends on the co-deposition amount of the nanoparticles. Therefore, the focus of the current research was mainly on how to increase the content of nanoparticles in the hybrid layer. Some of the literature focused on the effect of the added amount and the surface modification of silica particles on the properties of the electroplated layer. Also, the agglomeration of nanoparticles was likely to occur; some works explored the effects of surfactant and solvent on the mechanical properties and corrosion resistance of the layers. However, little attention had been paid to the impact of particle size of silica on the corrosion resistance of the layer.

In this work, silica–nickel hybrid layers were electroplated in a Watt nickel plating solution with the silica particles. The effects of silica particle sizes on the corrosion resistance of the silica–nickel hybrid layer have been explored, which would promote the application of silica–nickel hybrid plating.

2. RESULTS AND DISCUSSION

2.1. Transmission Electron Microscopy (TEM) Measurement. The four sizes of silica particles are shown in Figure 1. Among them, the silica particles with sizes of 50, 100, and 150 nm have good dispersibility and are basically nonblocking. The 10 nm silica particles agglomerate to a certain degree, and the actual particle size is between 10 and 500 nm.

2.2. Field Emission Scanning Electron Microscopy (FESEM) and Energy-Dispersive Spectrometry (EDS) Measurements. FESEM images of the pure Ni layer and the silica–Ni hybrid layers with silica particles of varying sizes are shown in Figure 2. It could be clearly observed that the surface of the pure Ni layer has a hill-like rough structure with varying sizes, and a microstructure with deep valleys was formed on the surface between different sizes, and there were few pores on the surface. By adding silica emulsion to the plating solution, the morphology of the surface was changed from Figure 2b to e. The pores of the silica–Ni hybrid layers disappeared, which indicated that the density of the layer increased, and the presence of second-phase particles changed the morphology of the layer. There are two main reasons to explain this phenomenon: (1) Silica particles are co-deposited on the cathode surface with nickel ions under the action of electric current and can fill the pores generated during the growth of nickel crystals. (2) The presence of silica particles increases the nucleation position of nickel crystals and reduces the growth rate of nickel crystals. Thus, the pores between dendritic nickel crystals are reduced. It was observed from the enlarged view in Figure 2 that silica particles with different contents are aggregated on the layer surface.

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2.3. X-ray Diffraction (XRD) Analysis. The XRD pattern of the Ni layer and silica–Ni hybrid layers are shown in Figure 4. The main peak was around 51.8°, which corresponds to the Ni(200) crystal plane, and the peak at 44.5° corresponds to the Ni(111) crystal plane. No diffraction peak of silica was observed, indicating that the content of silica in the layer is lower than the detection intensity of XRD. The phase of all

Figure 1. TEM images of silica particles (a) 10 nm, (b) 50 nm, (c) 100 nm, and (d) 150 nm.
samples was same, which indicated that the particle size of silica had no effect on the diffraction angle.\textsuperscript{26} However, the intensity of the (200) peak of the silica–Ni hybrid layers were lower than that of the pure Ni layer. It could be explained that the incorporation of the second-phase particles provides more nucleation sites for the Ni grains, which limits the growth of the crystal plane and reduces the grain size.\textsuperscript{27} As the particle size of silica changes, the relative intensity of the (200) peak changes. For the (200) lattice plane of the 50 nm silica–Ni hybrid layer, the intensity of the peak was the lowest. This shows that the second-phase particles introduced in the hybrid layer have an optimal size of 50 nm, and the grain size of the hybrid layer obtained at the optimal size was the smallest.

2.4. Corrosion Resistance. To evaluate the corrosion resistance of the silica–Ni hybrid layers with varying sizes of silica, electrochemical property and salt spray tests were performed in 3.5 and 5 wt % NaCl solutions.

### 2.4.1. Electrochemical Characterization

The potentiodynamic polarization (pp) curves of pure Ni and silica–Ni hybrid layers in a 3.5 wt % NaCl solution are shown in Figure 5. According to the polarization curve, the corrosion current density and the corrosion rate of different specimens were fitted by the Tafel method. The electrochemical parameters of the corresponding specimens are listed in Table 2. The corrosion potential, corrosion current, and corrosion rate of the pure Ni layer were $-0.5155$ V, $4.6103 \times 10^{-5}$ A/cm$^2$, and 0.53718 mm/a, respectively. The silica–Ni hybrid layers showed a more positive corrosion potential and smaller corrosion current and corrosion rate than that of the pure Ni layer, which indicates that the silica–Ni hybrid layers have a higher corrosion resistance than that of pure Ni in a 3.5 wt % NaCl solution. However, the varying sizes of silica particles have different degrees of enhancing the corrosion resistance of the silica–Ni hybrid layers. The corrosion potential of the
A hybrid layer was positively shifted to $-0.43701 \text{ V}$ when the particle size of silica added to the plating solution was 50 nm, which was slightly smaller than the corrosion potential of $-0.43089 \text{ V}$ of 100 nm. The corrosion current and corrosion rate of Ni-50 nm silica nanohybrid layer were the smallest, $1.8518 \times 10^{-5} \text{ A/cm}^2$ and 0.21577 mm/a, respectively. The corrosion potentials of a 10 nm silica–Ni and a 150 nm silica–Ni hybrid layers were more negative than that of a 50 nm silica–Ni nanohybrid layer and the corrosion current and corrosion rate were higher than those of the Ni-100 nm silica layers. In summary, the corrosion resistance of the 50 nm silica–Ni hybrid layer was the best. Silica plays an important role in improving the corrosion resistance of layers, mainly in two aspects. First, in the process of electroplating, silica particles are embedded in the Ni matrix to fill the pores of the layer. This will increase the density of the layer, extend the time when the corrosive medium reaches the substrate, and improve the corrosion resistance of the layer. Second, since the Ni layer is a cathode layer, the deposition of silica particles on the surface of the layer can reduce the cathode area and avoid the generation of a large cathode and a small anode. Based on the above reasons, the corrosion resistance of the hybrid layer was improved. In addition, the smaller the size of the silica particles is, the better the interstitial effect, and the higher the specific surface area. More the particles deposited on the cathode surface under the action of current and the silica–Ni hybrid layers, better the corrosion resistance.

From the TEM image of silica in Figure 1, it could be seen that when the size of silica was 10 nm, the particle tended to agglomerate, which was no longer the original nanometer size. Therefore, the corrosion resistance of the 50 nm silica–Ni hybrid layer is better than that of the 10 nm silica–Ni hybrid layer.

The corrosion behavior of the pure Ni layer and the silica–Ni hybrid layers cannot be estimated from the corrosion current and the corrosion rate alone. Electrochemical impedance spectroscopy (EIS) is a powerful nondestructive electrochemical technique used to confirm and study the corrosion behavior of materials. Moreover, EIS can provide valuable information about the mechanism of corrosion and the effectiveness of protective layers. In this study, EIS was employed to investigate the corrosion behavior of Ni and silica–Ni hybrid layers. The results showed that the corrosion resistance of the hybrid layers was significantly improved compared to the pure Ni layer. The impedance spectra of the layers were analyzed using the equivalent circuit model, and the resistance to corrosion was calculated. The results indicated that the hybrid layer with 50 nm silica particles showed the highest corrosion resistance, with a significantly lower corrosion rate than the pure Ni layer. This finding was consistent with the polarization curve results, which showed that the hybrid layer had a lower corrosion current and a more negative corrosion potential, indicating better protection against corrosion.

Figure 3. EDS results of silica–Ni hybrid layers.

Figure 4. XRD pattern of the electroplating (a) Ni layer and silica–Ni hybrid layers with varying sizes of silica: (b) 10 nm, (c) 50 nm, (d) 100 nm, and (e) 150 nm.

Figure 5. Polarization curves of Ni and silica–Ni hybrid layers in a 3.5 wt % NaCl solution.

Table 1. Si Content of Silica–Ni Hybrid Layers

| size (nm) | 10  | 50  | 100 | 150 |
|----------|-----|-----|-----|-----|
| Si (atom %) | 0.66 | 2.47 | 2.24 | 1.98 |

Table 2. Fitting Parameters of Polarization of Ni Layer and Silica–Ni Hybrid Layers in 3.5 wt % NaCl Solution

|          | 0 nm | 10 nm | 50 nm | 100 nm | 150 nm |
|----------|------|-------|-------|--------|--------|
| $E$ (V)  | -0.5155 | -0.48812 | -0.43701 | -0.43089 | -0.46917 |
| $I_0$ (A/cm$^2$) | $4.6103 \times 10^{-5}$ | $2.6165 \times 10^{-5}$ | $1.8518 \times 10^{-5}$ | $2.0568 \times 10^{-5}$ | $3.4688 \times 10^{-5}$ |
| corrosion rate (mm/a) | 0.53718 | 0.30487 | 0.21577 | 0.23965 | 0.40417 |
corrosion behavior at the electrode/electrolyte interface and is used to study the impedance information corrosion of sediment exposed in corrosion solutions. To better understand the corrosion behavior of pure Ni and silica−Ni hybrid layers, the electrochemical impedance spectroscopy (EIS) of the samples in a 3.5 wt % NaCl solution was further tested. Before undergoing EIS, the samples were tested in the mentioned solution for 1 h to stabilize the layer/electrolyte system and measure the open-circuit potential (OCP). The test results are shown in Figure 6. Compared to that of the pure Ni layer (−0.50846 V), the potentials of the silica−Ni hybrid layers were more positive, especially the potential of the 50 nm silica−Ni hybrid layer was −0.42547 V, so a hybrid layer presents excellent anticorrosion properties.

The Nyquist and Bode plots of the pure Ni and silica−Ni hybrid layers are shown in Figure 7a,b, respectively. The θ−f curves of all layers have two peaks in Figure 7b, indicating that the impedance spectrum has two time constants. The incorporation of silica did not change the corrosion principle of the layer. From the Bode diagram (Figure 7a), it could be seen that the capacitive arc radius of all silica−Ni hybrid layers was larger than that of the pure Ni layer. This indicated that the silica−Ni hybrid layers had better resistance corrosion than the Ni layer, the incorporation of silica particles was conducive to enhancing the corrosion resistance of the layer. However, the capacitive arc radius of the hybrid layers obtained from silica with varying particle sizes was not the same. The radius of the 50 nm silica−Ni hybrid layer had the largest radius and the best corrosion resistance.

The corresponding mathematical physical model was determined according to the characteristics of the impedance spectrum and the related electrochemical experience. The corresponding equivalent circuit is shown in Figure 8. Similar equivalent circuits were proposed to explore the corrosion behavior of the Ni matrix hybrid layers. Schematic for the equivalent circuit model was used to fit EIS measurement results, R, is the solution resistance, the pore resistance Rcp indicates that the corrosion medium extends inwardly through the defects in the layer to the substrate, layer interface galvanic corrosion caused, charge-transfer resistance (Rct) is a measure of electron transfer across the surface, which is proportional to the corrosion resistance. Due to the unevenness of the layer surface, the frequency response characteristics of the double-layer capacitors of all the samples did not match the pure capacitance. A constant phase element (CPE) was used instead of the pure capacitance C, which is expressed as follows

\[
Z_{CPE} = \frac{1}{Y_{0}(j\omega)^{n}}
\]

where \( Y_{0} \) always takes a positive value, \( j \) is a complex operator \((-1)^{1/2}\), \( \omega \) is the angular frequency, and \( n \) is an empirical exponent that is applied to describe the surface roughness. In this formula, \( 0 \leq n \leq 1 \). If \( n = 1 \) and 0, the CPE shows the behavior of pure capacitance and pure resistance, respectively. The least-square method was used to fit the established model with Zsimwin software, and the parameter values of each equivalent element in the mathematical model were obtained (Table 3). From the fitted data, it can be seen that the values of Rct of the silica−Ni hybrid layers are much higher than the values of Rct of the pure Ni layer, and the Rct values dramatically increased when the particle diameter of silica is increased from 10 to 50 nm and then decrease with increasing particle size. The above phenomenon indicates that the corrosion resistance of the layer can be significantly improved by incorporating silica particles into the Ni matrix. The particle size of silica has an effect on the corrosion resistance of the Ni hybrid layer, and the corrosion resistance of the 50 nm silica−Ni hybrid layer is the best. The corrosion resistance results
Table 3. EIS Fitting Results of the Samples in the 3.5 wt % NaCl Solution

| samples     | $R_s$ (Ω·cm$^2$) | $C$ (μF/cm$^2$) | $R_{cp}$ (Ω·cm$^2$) | CPE_d (μF/cm$^2$) | $n$    | $R_d$ (Ω·cm$^2$) |
|-------------|------------------|-----------------|---------------------|-------------------|-------|-----------------|
| Ni          | 1.046            | 28.31           | 54.36               | 281.3             | 0.7087| 1532            |
| 10 nm SiO$_2$–Ni | 1.13            | 18.31           | 39.82               | 277.8             | 0.7234| 2850            |
| 50 nm SiO$_2$–Ni | 1.241          | 17.69           | 46.75               | 114.9             | 0.8869| 4364            |
| 100 nm SiO$_2$–Ni | 1.662          | 8.304           | 41.42               | 114.4             | 0.8498| 3931            |
| 150 nm SiO$_2$–Ni | 1.51           | 22.4            | 56.59               | 112.7             | 0.8727| 2176            |

Figure 9. Morphology of the electroplating layers after the salt spray test in a 5 wt % NaCl solution for 90 h. (a) Ni layer and silica–Ni hybrid layers with varying sizes of silica: (b) 10 nm, (c) 50 nm, (d) 100 nm, and (e) 150 nm.
obtained from the EIS chart are consistent with the polarization test results.

2.4.2. Salt Spray Test (SST). Figure 9 shows the surface morphology of the sample in a 5 wt % NaCl solution for 90 h in the salt spray test, which visually revealed the difference in corrosion resistance of each layer. It can be clearly observed in Figure 9a that there are corrosion pits on the surface of the traditional pure Ni layer, which indicates that the corrosion resistance is poor, and many pits are formed by bubbles generated during the plating process on the layer surface, which is not decorative. Compared with the pure Ni layer, the surface rust of the silica−Ni hybrid layers is significantly reduced, and no corrosion pits appear (Figure 9b−e), which indicates that the addition of silica particles is beneficial to improving the corrosion resistance of the Ni layer. The silica−Ni hybrid layer is prepared when the silica particle size of 50 nm can hardly see corrosion. If the size is too large or too small, the corrosion resistance will be reduced. By studying the corrosion resistance mechanism of silica particles to enhance the layer, it can be known that the higher the content of silica in the layer is, the better the corrosion resistance of the layer.9,27 The content of silica in the layer is related to the size, and the content of particles in the 50 nm silica−Ni hybrid layer is the highest (Figure 2 and Table 1). The results of corrosion resistance are consistent with a decrease in the corrosion current (Figure 5) and an increase in the impedance value (Figure 7).

3. CONCLUSIONS

The silica−Ni hybrid layers were electroplated by embedding the varying sizes of silica into Ni layers and the corrosion resistance of the layers was evaluated. The results are as follows:

(1) The embedded silica particles reduced the pores of the electroplated Ni layer.
(2) When the particle size of silica was 50 nm, the content of silica in the hybrid layer reached a maximum (2.47 atom %).
(3) The size of the silica particles limited the growth of Ni on the (200) crystal plane, and the (200) peak intensity of the 50 nm silica−Ni hybrid layer was the lowest.
(4) Embedding nanosilica particles into the Ni matrix increased the corrosion resistance of the electroplated hybrid layer. The 50 nm silica−Ni hybrid layer presented the best corrosion resistance.

4. EXPERIMENTAL PROCEDURE

4.1. Preparation of Layers. A nickel plate of dimension 70 mm × 35 mm × 3 mm was used as the anode, and a Q235 steel plate of dimension 2 mm × 5 mm × 0.3 mm was used as a cathode. The chemical composition of low-carbon steel is shown in Table S1. The steel plate was degreased with the solution of Na2CO3 and Na3PO4 and rinsed with distilled water, immersed in a 10% H2SO4 solution for 1 min to remove the oxides, and washed thoroughly with distilled water.

DC plating was used to deposit Ni and silica−Ni hybrid layers on a Q235 steel plate. The composition of the bath and the electroplating parameters are shown in Table 4. Before electroplating, the silica emulsion was added dropwise to the plating solution under rapid stirring and then stirred for 100 min and ultrasonic cleaning for 30 min. The pH of the plating solution was adjusted to 4 using 10% H2SO4 or 10% NaOH solution.32 After deposition, the plate was rinsed with distilled water and blow-dried for testing.

4.2. Characterization of the Electroplating Layers. The electrochemical corrosion properties of the layers were tested using an electrochemical workstation (CS350). At room temperature, the corrosion resistance of the layers was evaluated in a 3.5 wt % NaCl solution by potentiodynamic polarization (pp) and electrochemical impedance spectroscopy (EIS). The standard three-electrode system included the layer samples with 1 cm2 exposed area as the working electrode, the platinum wire electrode as the counter electrode, and the saturated calomel electrode as the reference electrode. The working electrode was immersed in the test solution, and the open-circuit potential was measured for 1 h until the electrochemical system became stable. The EIS measurements were carried out from 100 kHz to 10 MHz, accompanied by 5 mV amplitude perturbations. The EIS data were presented as Nyquist plots. The plot fitting was implemented using ZSimWin software. All potential dynamic scanning experiments were set to a scanning speed of 5 mV/s and a relative open-circuit potential of ±0.25 V. All of the tests were performed in the same condition.

To characterize the corrosion resistance of the layers in the presence of a corrosive medium, a salt spray test (SST) was performed on all samples for 90 h at 35 °C using a 5 wt % NaCl solution (ASTM Standard). An area of 4 cm2 was exposed in the center of the sample, and other areas were closed with nail polish. The results of the salt spray test were evaluated by comparing the extent of corrosion defects on the samples.

Table 4. Composition of the Electroplating Liquid and Electroplating Parameters

| composition and parameters | quantity |
|----------------------------|----------|
| NiSO4·6H2O                 | 300 g/L  |
| NiCl2·6H2O                 | 45 g/L   |
| H3BO3                      | 40 g/L   |
| silica                     | 10, 50, 100, 150 nm |
| current                    | 4 A/dm2  |
| pH                         | 4        |
| temperature                | 55 °C    |
| deposition time            | 4 min    |
| layer solution stirring     | 100 rpm  |

Main components of Q235 steel, Hull cell test, and calculation of porosity (PDF)
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Notes

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REFERENCES

(1) Gyftou, P.; Pavlatou, E. A.; Spyrellis, N. Effect of pulse electrodeposition parameters on the properties of Ni/nano-SiC composites. *Appl. Surf. Sci.* 2008, 254, 5910–5916.
(2) Katamipour, A.; Farzam, M.; Danaee, I. Effects of sonication on anticorrosive and mechanical properties of electrodeposited Ni–Zn–TiO2 nanocomposite coatings. *Surf. Coat. Technol.* 2014, 254, 358–363.
(3) Li, R.; Chu, Q.; Liang, J. Electrodeposition and characterization of Ni–SiC composite coatings from deep eutectic solvent. *RSC Adv.* 2015, 5, 44933–44942.
(4) Dong, D.; Chen, X. H.; Xiao, W. T.; Yang, G. B.; Zhang, P. Y. Preparation and properties of electrolless Ni-P-SiO2 composite coatings. *Appl. Surf. Sci.* 2009, 255, 7051–7055.
(5) Wang, Y.; Zhou, Q.; Li, K.; Zhong, Q.; Bui, Q. B. Preparation of Ni–W–SiO2 nanocomposite coating and evaluation of its hardness and corrosion resistance. *Ceram. Int.* 2015, 41, 79–84.
(6) Li, R.; Hou, Y.; Liang, J. Electro-codeposition of Ni-SiO2 nanocomposite coatings from deep eutectic solvent with improved corrosion resistance. *Appl. Surf. Sci.* 2016, 367, 449–458.
(7) Chen, L.; Wang, L.; Zeng, Z.; Xu, T. Influence of pulse frequency on the microstructure and wear resistance of electropolished Ni-Al2O3 composite coatings. *Surf. Coat. Technol.* 2006, 201, 609–605.
(8) Chen, Y.; Hao, Y.; Huang, W.; Ji, Y.; Yang, W.; Yin, Y.; Liu, Y.; Ling, X. Corrosion behavior of Ni-P-nano-Al2O3 composite coating in the presence of anionic and cationic surfactants. *Surf. Coat. Technol.* 2017, 310, 122–128.
(9) Arghabani, R.; Ahmadi, N. P. Electrodeposition of Ni–ZrO2 composite coatings and evaluation of particle distribution and corrosion resistance. *Surf. Eng.* 2011, 27, 649–654.
(10) Wang, W.; Hou, F.-Y.; Wang, H.; Guo, H.-T. Fabrication and characterization of Ni–ZrO2 composite nano-coatings by pulse electrodeposition. *Scr. Mater.* 2005, 53, 613–618.
(11) Sparou, S.; Pavlatou, E. A.; Spyrellis, N. Ni/nano-TiO2 composite electrodes: Textural and structural modifications. *Electrochim. Acta* 2009, 54, 2547–2555.
(12) Sarafraz, M. H.; Alizadeh, M. Improved characteristics of Ni-electrodeposited coatings via the incorporation of Si and TiO2 particulate reinforcements. *J. Alloys Compd.* 2017, 720, 289–299.
(13) Xia, F. F.; Liu, C.; Wang, F.; Wu, M. H.; Wang, J. D.; Fu, H. L.; Wang, J. X. Preparation and characterization of Nano Ni–TiN coatings deposited by ultrasonic electrodeposition. *J. Alloys Compd.* 2010, 490, 431–435.
(14) Nowak, P.; Socha, R. P.; Kaisheva, M.; Fransaer, J.; Celis, J. P.; Stoinov, Z. Electrochemical investigation of the codeposition of SiC and SiO2 particles with nickel. *J. Appl. Electrochem.* 2000, 30, 429–437.
(15) Li, H.; Wan, Y.; Liang, H.; Li, X.; Huang, Y.; He, F. Composite electroplating of Cu–SiO2 nano particles on carbon fiber reinforced epoxy composites. *Appl. Surf. Sci.* 2009, 256, 1614–1616.
(16) Zamblau, I.; Varvara, S.; Muresan, L. M. Corrosion behavior of Cu–SiO2 nanocomposite coatings obtained by electrodeposition in the presence of cetyl trimethyl ammonium bromide. *J. Mater. Sci.* 2011, 46, 6484–6490.
(17) Khan, T. R.; Vimalanandan, A.; Marlow, F.; Erbe, A.; Rohwerder, M. Existence of a lower critical radius for incorporation of silica particles into zinc during electro-codeposition. *ACS Appl. Mater. Interfaces* 2012, 4, 6221–6227.
(18) Tsuweri, T. J.; Wilcox, G. D. Behaviour of Zn-SiO2 electrodeposition in the presence of n-n-dimethyldecylamine. *Surf. Coat. Technol.* 2006, 200, 5921–5930.
(19) Chang, C. C.; Yang, K. H.; Liu, Y. C.; Hsu, T. C.; Mai, F. D. Surface-enhanced raman scattering-active Au/SiO2 nanocomposites prepared using sonochemical pulse deposition methods. *ACS Appl. Mater. Interfaces* 2012, 4, 4700–4707.
(20) Attunya, C. U.; Ekweghariiri, D. I.; Obele, C. M. Experimental study on the microstructural and anti-corrosion behaviour of Co-deposition Ni-Co–SiO2 composite coating on mild steel. *Dif. Technol.* 2018, 14, 64–69.
(21) Sassi, W.; Dhoubi, L.; Berco, P.; Rezzazi, M. The effect of SiO2 nanoparticles dispersion on physico-chemical properties of modified Ni–W nanocomposite coatings. *Appl. Surf. Sci.* 2015, 349, 369–379.
(22) Ratajski, T.; Kalemba-Rec, I.; Indyka, P.; Ledwig, P.; Szczepia, M. J.; Dubiel, B. Effect of PDDA surfactant on the microstructure and properties of electrodeposited SiO2/Ni nanocomposites. *Mater. Charact.* 2020, 163, No. 110229.
(23) Li, R.; Hou, Y.; Liu, B.; Wang, D.; Liang, J. Electrodeposition of homogenous Ni/SiO2 nanocomposite coatings from deep eutectic solvent with in-situ synthesized SiO2 nanoparticles. *Electrochem. Acta* 2014, 222, 1272–1280.
(24) Li, R.; Liang, J.; Hou, Y.; Chu, Q. Enhanced corrosion performance of Zn coating by incorporating graphene oxide electrodeposit from deep eutectic solvent. *RSC Adv.* 2015, 5, 60698–60707.
(25) Salehi, M.; Mozammel, M.; Emarati, S. M. Superhydrophobic and corrosion resistant properties of electrodeposited Ni-TiO2/ TMPSi nanocomposite coating. *Colloids Surf., A* 2019, 573, 196–204.
(26) Li, B.; Li, D.; Zhang, J.; Chen, W.; Zhang, W. Electrodeposition of Ni-W/TiN-Y2O3 nanocrystalline coating and investigation of its surface properties and corrosion resistance. *J. Alloys Compd.* 2019, 787, 952–962.
(27) Chen, W.; Gao, W. Sol-enhanced electroplating of nanostructured Ni–TiO2 composite coatings-the effects of sol concentration on the mechanical and corrosion properties. *Electrochim. Acta* 2010, 55, 6865–6871.
(28) Zargarhami, V.; Ghorbani, M. Alteration of corrosion and nanomechanical properties of pulse electrodeposited Ni/SiC nanocomposite coatings. *J. Alloys Compd.* 2014, 598, 236–242.
(29) Baghery, P.; Farzam, M.; Mousavi, A. B.; Hosseini, M. Ni–TiO2 nanocomposite coating with high resistance to corrosion and wear. *Surf. Coat. Technol.* 2010, 204, 3804–3810.
(30) Zhou, Q.; Wang, Y.; Wu, H.; Zhong, Q.; Jiang, J. Preparation of passive Cu–Ni–Fe coating on low-carbon steel for improving corrosion resistance. *Surf. Coat. Technol.* 2012, 207, 503–507.
(31) Jythoender, K. S.; Srivastava, C. Ni-graphene oxide composite coatings: Optimum graphene oxide for enhanced corrosion resistance. *Composites, Part B* 2019, 175, No. 107145.
(32) Lee, H.-K.; Lee, H.-Y.; Jeon, J.-M. Codeposition of micro- and nano-sized sic particles in the nickel matrix composite coatings obtained by electroplating. *Surf. Coat. Technol.* **2007**, *201*, 4711−4717.