



Roles of Graphene Additives in Optimizing the Microstructure and Properties of Ni–Cr–Graphene Coatings

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Abstract: The electrodeposition technique was used to fabricate graphene and Cr particle-reinforced Ni–Cr–graphene coatings. The Rietveld refinement was utilized to analyze the microstructure of Ni deposits in the coatings. The properties including micro-hardness and corrosion behaviors of the coatings were also tested. Results showed that the addition of graphene particles contributed to the dendrite like structure on the surface of the Ni–Cr–graphene coating. The crystallite size and [200] texture of the Ni deposits in the Ni–Cr–graphene coatings were significantly decreased by the graphene particles. The crystallite size of 149.8 nm in the Ni-25–Cr-0–graphene coating was reduced to 35 nm in the Ni-25–Cr-8–graphene coating due to the addition of 8 g/L graphene to the electrolyte. The microstructure evolution of the Ni–Cr–graphene coatings brought about an enhancement in micro-hardness and corrosion resistance of the coatings. The micro-hardness of the coatings was improved from 260.1 HV_{0.2} of the pure Ni coating to 285.9 HV_{0.2} of the Ni-25–Cr-0–graphene coating and continually to 461.8 HV_{0.2} of the Ni-25–Cr-8–graphene coating. In corrosion solution (3.5 wt.% NaCl), the corrosion current (6.22 μ A/cm²) of the Ni-25–Cr-0–graphene coating could be decreased by about an order of magnitude through the addition of graphene particles, which was 0.33 μ A/cm² for the Ni-25–Cr-8–graphene coating.

Keywords: Ni–Cr–graphene coating; electrodeposition; microstructure; micro-hardness; corrosion resistance

1. Introduction

As one of the most important surface engineering coatings, Ni-based composite coatings possess superior resistance to oxidation, wear, and corrosion, and they are extensively used to cope with severe environments [1,2]. Particle reinforcements including nonmetallic and metallic particles (such as Al₂O₃, CeO₂, Al, Cr, and Ti particles) can be co-deposited onto Ni deposits to establish Ni-based composite coatings by electrodeposition [1,3–9]. The co-deposition behaviors of the particle additives contribute to an optimized microstructure, e.g., decreased crystallite size and diminished preferential growth orientation of nickel deposits, which consequently enhance the properties of the Ni composite coatings [5,9].

Among the particle additives, Cr particles are extensively adopted to fabricate Ni–Cr composite coatings with enhanced micro-hardness, high temperature oxidation, and corrosion and wear resistance [6–8]. Peng et al. [1] electrodeposited Ni–Cr coatings and suggested that the Ni–Cr coatings possessed decreased crystallite size with respect to Ni deposits, which was induced by the co-deposition of Cr particles. Meanwhile, the incorporation of Cr particles reduced the possibility of localized corrosion in NaCl solution and consequently enhanced the corrosion resistance of the coatings.



Zhao et al. [6] suggested that Cr particles gave birth to the crystallite refinement of Ni deposits and consequently enhanced the micro-hardness and wear resistance of the Ni–Cr coatings. Additionally, some kinds of particles such as CeO₂, Al, and SiC worked as modification particles to further optimize the microstructure and properties of the Ni–Cr coatings [7,10,11]. Dong et al. [7] suggested that CeO₂ modification particles lowered the oxidation kinetics of Ni–Cr composite coatings by further modifying the microstructure of Ni–Cr coatings and promoting the formation of oxide scale. Therefore, these modification particles can further decrease the crystallite size of the Ni deposits, thereby improving the properties of the Ni–Cr coating with the intrinsic roles of the modification particles.

As an emerging two-dimensional structure of free-standing carbon atoms, graphene attracts lots of scientific attention due to its desirable electrical, thermal, mechanical, and physical properties [12]. Graphene is extensively used as a particle additive to fabricate Ni–graphene composite coatings, which exhibit superior corrosion resistance, wear resistance, and micro-hardness [13–16]. The electrodeposition behaviors of graphene can enable the graphene particles to be incorporated into the Ni–Cr composite coating and consequently establish an Ni–Cr–graphene composite coating. Therefore, an idea of the preparation of graphene-modified Ni–Cr–graphene composite coatings was established, in which the graphene works as the modification particle. These coatings can have potentially desirable properties including superior corrosion resistance and micro-hardness. Investigations into the modification effects of graphene additives on the microstructure and properties of the Ni–Cr–graphene coatings need to be comprehensively carried out, which can greatly contribute to the broad applications of graphene-modified Ni–Cr–graphene coatings.

In the present work, different concentrations of graphene particles accompanied by a given concentration of Cr particles were co-deposited to establish the Ni–Cr–graphene coatings. The roles of graphene modification particles in optimizing the microstructure, including crystallite size and crystallographic orientation, and properties of the Ni–Cr–graphene coatings were comprehensively investigated. The micro-hardness and corrosion behaviors of the Ni–Cr–graphene coatings were also comprehensively evaluated.

2. Materials and Methods

2.1. Preparation of Ni-Cr-Graphene Coatings

The electrodeposition technique was adopted to fabricate the Ni–Cr–graphene composite coatings. The electrodeposition electrolyte was a Watts bath containing a certain concentration of 25 g/L Cr particles and different concentrations of graphene particles (0, 1, 2, 4, and 8 g/L). The expression of Ni-*x*–Cr-*y*–graphene was used to describe the coating electrodeposited at *x* g/L concentration of Cr and *y* g/L concentration of graphene particles. The sizes of the as-received Cr and graphene particles were about 1 and 10 µm (see Figure 1), respectively. The agglomeration of Cr particles can be seen in Figure 1a. The substrate materials, which worked as the cathode in electrodeposition, were nickel aluminum bronze alloys (NAB) with a surface area of 2 cm². Meanwhile, the anode materials were nickel plates with a surface area of 5 cm². These two electrodes were fixed in parallel, with a distance of 30 mm. In electrodeposition, magnetic agitation at 350 rpm was maintained to suspend the particles. A direct current of 5 A/dm² was adopted to fabricate the coatings until the thicknesses reached ca. 60 µm. The electrodeposition parameters are shown in Table 1.



Figure 1. SEM morphologies of the Cr (a) and graphene particles (b).

Bath Composition	Concentration (g/L)	Electrodeposition Conditions
NiSO ₄	240	Current density: 5 A/dm ²
NiCl ₂	40	pH: 3.5
H ₃ BO ₃	30	Temperature: 45 °C
C ₁₂ H ₂₅ SO ₄ Na	0.2	Stirring rate: 350 rpm
Cr particles	25	-
Graphene	0–8	-

Table 1. Bath composition and electrodeposition conditions.

Prior to electrodeposition, the NAB substrates were ground and then ultrasonically degreased in 1 mol/L NaOH solution for 10 min, which was followed by ultrasonic cleaning with pure water. Then, 10% HCl acid solution was used to activate the NAB substrates, which was followed by rinsing in pure water. To uniformly disperse particles, the electrodeposition electrolytes were magnetically stirred for 3 h and ultrasonically treated for 0.5 h. Once each electrodeposition process ended, the Ni–Cr–graphene coating was ultrasonically cleaned in pure water.

2.2. Characterization of Ni-Cr-Graphene Coatings

The morphologies of the Ni–Cr–graphene coatings were characterized by scanning electron microscopy (SEM, Hitachi TM3030, Tokyo, Japan). Raman spectroscopy (LabRAMHR, Horiba Jobin Yvon, France), energy-dispersive spectroscopy (EDS, Oxford Swift 3000, Oxford, UK), and X-ray diffraction (XRD, Rigaku Ultima IV, Tokyo, Japan) analysis were employed to analyze the chemical composition and microstructure of the coatings. Rietveld refinements were utilized to analyze the XRD results of the coatings with the MAUD software (version 2.33) [17]. The crystallite information of Ni deposits, including crystallite size and crystallographic orientation, was obtained. In Rietveld refinements, the pseudo-Voigt (pV) function [18] was adopted to fit K_{a1} and K_{a2} [19], which was expressed as follows:

$$pV(2\theta) = \sum_{a_1a_2} I_{nt}[(1-\delta)(1+S^2)^{-1} + \delta \exp(-\ln 2 \times S^2)]$$
(1)

$$S = \frac{2\theta - 2\theta_0}{\beta} \tag{2}$$

where I_{nt} , θ_0 , β , and δ are the scale parameter of the pV function, the Bragg angle of Ka₁ radiation, the full width at half maximum, and the Gaussian component, respectively. The Popa LB model and Popa rules were used to calculate the line broadening and anisotropic crystallites [20]. The deformation and twin faults could induce shifts, broadening, and asymmetry in the XRD profile, which was refined by the Warren model [21]. The pole figures of (111), (200), and (220) planes could be obtained from

the harmonic texture model, which could be verified by the relative texture coefficients (RTC) of (hkl) peaks as follows [22]:

$$RTC_{(hkl)} = \frac{I_{(hkl)}/I_{0(hkl)}}{\sum I_{(hkl)}/I_{0(hkl)}} \times 100\%$$
(3)

where $I_{(hkl)}$ and $I_{0(hkl)}$ are the (hkl) peak intensities of the coatings and the standard Ni powders, respectively.

The Vickers micro-hardness of the Ni–Cr–graphene coatings was measured using a micro-hardness tester (HXD-1000TMC/LCD, Shanghai TaiMing optical instruments, Shanghai, China) with 200 g of load and 15 s of dwelling time. In a 4 mm × 4 mm square area of the surface, the micro-hardness of 25 points was evenly measured at an interval of 1 mm. The final micro-hardness of the coating was obtained from the average values of micro-hardness of 25 points.

In 3.5 wt.% NaCl solution, the electrochemical corrosion experiments were carried out using an electrochemical workstation (Autolab PGSTAT302N, Metrohm, the Netherlands) at 25 °C. Electrochemical impedance spectra (EIS) and potentiodynamic polarization experiments were conducted. The Ni–Cr–graphene coatings with surface area of 1 cm², platinum sheet, and saturated Ag/AgCl electrode (+198 mV) built a three-electrode system, which acted as the working, counter, and reference electrodes, respectively. In potentiodynamic polarization experiments, the anodic/cathodic Tafel slopes (b_a and b_c), corrosion potential (E_{corr}), and corrosion current (I_{corr}) were obtained with a scanning speed of 1 mV/s. At the open circuit potential, EIS experiments, including Nyquist plots and Bode plots, were conducted. The scanning frequency was from 0.01 to 100,000 Hz, and the potential amplitude was 10 mV. Before corrosion measurements, the coatings were immersed in 3.5 wt.% NaCl solution for 1 h.

3. Results

3.1. Morphology and Composition of the Ni-Cr-Graphene Coatings

The different amounts of graphene particles were incorporated into the Ni–Cr–graphene coatings. Figure 2 exhibits the surface morphologies of the coatings. It can be observed that the pure Ni coating possessed a typical pyramidal surface structure [5,9], while a dendrite-like structure appeared on the surface of the Ni–Cr coating (see Figure 2b). This property increasingly appeared as the graphene concentration increased. When the graphene concentration reached 8 g/L, the dendrite-like structure became compact and its porosity was reduced in the surface layer of the Ni-25–Cr-8–graphene coating.



Figure 2. SEM morphologies of the Ni–Cr–graphene coatings electrodeposited with 0 g/L Cr particles (**a**) and 25 g/L Cr particles with various graphene concentrations of 0 (**b**), 1 (**c**), 2 (**d**), 4 (**e**), and 8 (**f**) g/L.

The contents of Cr particles in the Ni–Cr–graphene coatings are exhibited in Figure 3. It can be found that the Cr contents changed little among all the coatings, approaching ca. 7.7 wt.% on average. Figure 4 shows the EDS analysis results of the different coatings. With careful observation, the shapes of Ni and Cr peaks remained almost consistent among different coatings. However, the peak intensity of C gradually increased as the graphene concentration increased, which demonstrated the increase in graphene content in the coatings. To verify the EDS results, the Raman analysis of graphene in the Ni–Cr–graphene coatings is exhibited in Figure 5. Two strong peaks of D and G appeared for the graphene particles, located at 1348 cm⁻¹ and 1590 cm⁻¹, respectively. For the Ni–Cr–graphene coatings electrodeposited at 0, 1, and 2 g/L, the D and G peaks of graphene were not obvious, while they were strong in the coatings electrodeposited at graphene concentrations of 4 and 8 g/L, which demonstrates the increase in graphene content in the Ni–Cr–graphene coatings.



Figure 3. Content of Cr particles in the Ni–Cr–graphene coatings.



Figure 4. Energy-dispersive spectroscopy (EDS) analysis of the Ni–Cr–graphene coatings electrodeposited at different graphene concentrations: 0 (**a**), 2 (**b**), and 8 (**c**) g/L.



Figure 5. Raman spectra of the Ni–Cr–graphene coatings with different concentrations of graphene.

3.2. Microstructure of the Ni–Cr–Graphene Coatings

The XRD results of the Ni–Cr–graphene coatings are exhibited in Figure 6, where three peaks of (111), (200), and (220) of Ni deposits can be observed for all the coatings. However, the relative intensities of the three peaks varied greatly for the various coatings. In the XRD result of the pure Ni coating, the (200) peak possessed greater relative intensity. With the co-deposition of Cr and graphene particles, the relative intensities of (200) and (111) peaks gradually decreased and increased, respectively. When the graphene concentration reached more than 4 g/L, the (111) peak intensity predominated significantly. In the magnified image of the dotted area (Figure 6b), the Cr peaks of (200) and (211) can be observed, illustrating that the Cr particles were co-deposited onto Ni deposits. However, the peak of graphene was not exhibited in the XRD patterns, which was induced by the low content of graphene in the coatings.



Figure 6. (**a**) X-ray diffraction (XRD) results of the Ni–Cr–graphene coatings with different concentrations of graphene and (**b**) the magnified XRD result of the dotted area in figure of (a).

The Rietveld refinement of XRD results of the Ni–Cr–graphene coatings were adopted to calculate the crystallite size, crystallite shape, and crystallographic or ientation of Ni deposits. A typical Rietveld plot of the Ni-25–Cr-8–graphene coating is exhibited in Figure 7. The value of goodness of fit (sigma, R_{wp}/R_{exp}) was 1.69. For all the Ni–Cr–graphene coatings, the sigma values were all less than two, indicating that all refinements were feasible [23]. The crystallite sizes of Ni deposits along the [200] orientation were obtained from the Rietveld refinements (see Figure 8). The crystallite size of Ni deposits in the Ni–Cr–graphene coating decreased from 149.8 to 35.0 nm as the graphene concentration increased from 0 to 8 g/L, always remaining smaller than that in the pure Ni coating (175.3 nm).



Figure 7. Rietveld plot of the Ni–Cr–graphene coatings of 8 g/L graphene (sigma = 1.69, $R_w = 1.13\%$, $R_{exp} = 0.67\%$).



Figure 8. Crystallite size of Ni deposits in Ni-Cr-graphene coatings obtained from Rietveld refinements.

The crystallite shapes of the pure Ni and Ni-25–Cr-8–graphene coatings are exhibited in Figure 9. The white lines represent the crystallography coordinate frames (*XYZ*). In the crystallography coordinate system, the crystallite shapes reflect the anisotropic level of crystallite size [20,24]. It can be observed that the Ni crystallite in the pure Ni coating (Figure 9a) possessed a branched shape with larger length along the crystallography coordinate frame. The branched shape changed to a spherical shape in the Ni-25–Cr-8–graphene coating (Figure 9b) due to the co-deposition of 8 g/L graphene particles. These results demonstrate that the crystallite sizes of Ni deposits in the pure Ni coating were much larger along the [100] direction. There was no obvious difference in the crystallite sizes of Ni deposits in the Ni-25–Cr-8–graphene coating along all directions.

The crystallite shape evolution in Figure 9 reflects the changes in the crystallographic orientation of the Ni deposits in the Ni–Cr–graphene coatings, which were also pictorially built using Rietveld refinement. The detailed crystallographic orientation evolution of the Ni–Cr–graphene coatings with various concentrations of graphene is exhibited in Figure 10. It can be observed that a strong [200] fiber texture appeared in the pure Ni coating, while the [200] texture gradually diminished with increasing graphene concentration. A random crystallographic orientation appeared in the Ni-25–Cr-8–graphene coating.



Figure 9. Crystallite shapes of Ni deposits in the pure Ni (**a**) and Ni-25–Cr-8–graphene (**b**) coatings obtained from Rietveld refinements.



Figure 10. Pole figures of the Ni-Cr-graphene coatings obtained from Rietveld refinements.

The RTC values of different crystalline planes were also utilized to evaluate the level of crystallographic orientation [25]. In this work, the RTC values of (111), (200), and (220) planes were calculated (see Figure 11). It can be observed that the $\text{RTC}_{(200)}$ decreased while $\text{RTC}_{(111)}$ and $\text{RTC}_{(220)}$ increased gradually with increasing graphene concentration. The values of $\text{RTC}_{(200)}$ were 0.93 and 0.89 in the pure Ni coating and the Ni-25–Cr-0–graphene coating, respectively, illustrating that the coatings possessed a strong [200] fiber texture. The RTC results were consistent with the built pole figures of the coatings.



Figure 11. Relative texture coefficient (RTC_(hkl)) values of the Ni–Cr–graphene coatings with respect to graphene concentration in the electrolyte.

3.3. Micro-Hardness of the Ni-Cr-Graphene Coatings

The surface micro-hardness variation of the Ni–Cr–graphene coatings with respect to graphene concentration in the electrolyte is exhibited in Figure 12a. The micro-hardness of the Ni–Cr–graphene coating was improved by the addition of the graphene particles, always remaining higher than that of the pure Ni coating (260.1 HV_{0.2}). When 8 g/L graphene was employed as the modification particles, the micro-hardness of the Ni-25–Cr-8–graphene reached 461.8 HV_{0.2}. Furthermore, the surface micro-hardness distribution of the pure Ni and the Ni-25–Cr-8–graphene coatings are exhibited in Figure 12b,c. The micro-hardness of the Ni-25–Cr-8–graphene coating was apparently larger than that of the pure Ni coating, whereas their distributions became less uniform.



Figure 12. Micro-hardness variation of the Ni–Cr–graphene coatings (**a**); surface micro-hardness distribution of the pure Ni (**b**) and Ni-25–Cr-8–graphene (**c**) coatings.

3.4. Corrosion Behaviors of the Ni–Cr–Graphene Coatings

The potentiodynamic polarization curves of the Ni–Cr–graphene coatings are shown in Figure 13. Based on these curves, the extrapolation method was used to calculate the E_{corr} and I_{corr} of the coatings (see Table 2). The E_{corr} of the Ni–Cr–graphene coatings gradually improved from -0.36 to -0.20 mV with increasing graphene concentration from 0 to 8 g/L. The E_{corr} of the Ni–Cr–graphene coatings were obviously more positive than that of the pure Ni coating (-0.41 mV). Meanwhile, the I_{corr} decreased from 7.01 μ A/cm² for the pure Ni coating to 0.33 μ A/cm² for the Ni-25–Cr-8–graphene coatings with increasing graphene concentration. The Ni-25–Cr-8–graphene coating possessed the best corrosion resistance with the highest E_{corr} and the lowest I_{corr} .



Figure 13. Potentiodynamic polarization curves of the Ni–Cr–graphene coatings in 3.5% NaCl solution.

Ni–Cr–Graphene	$E_{\rm corr}$ (V)	$R_{\rm p}$ (k $\Omega \cdot {\rm cm}^2$)	b_{a} (V·dec ⁻¹)	$b_{\rm c}$ (V·dec ⁻¹)	$i_{\rm corr}$ (μ A/cm ²)
Ni	-0.41	4.38	0.16	-0.13	7.01
Ni-25–Cr-0–Graphene	-0.36	5.39	0.16	-0.15	6.22
Ni-25-Cr-1-Graphene	-0.29	6.17	0.21	-0.12	5.32
Ni-25-Cr-2-Graphene	-0.27	15.29	0.33	-0.13	2.67
Ni-25-Cr-4-Graphene	-0.26	18.38	0.15	-0.19	1.93
Ni-25–Cr-8–Graphene	-0.20	85.50	0.12	-0.14	0.33

Table 2. Corrosion characteristics of the Ni–Cr–graphene coatings in 3.5% NaCl solution.

The EIS plots (Nyquist plots and Bode plots) of the Ni–Cr–graphene coatings are shown in Figure 14. In Figure 14a, the Nyquist curves of all the coatings exhibited a single semicircle, and the semicircle diameter of the Ni–Cr–graphene coating increased with increasing graphene concentration, always remaining larger than that of the pure Ni coating. In Figure 14b, both the Bode phase maximum and the Bode impedance modulus (Z_{mod}) of the Ni–Cr–graphene coating increased as graphene concentration increased. Moreover, the Bode phase evolution (Figure 14b) reflected a fixed constant for all coatings. The equivalent circuit (Figure 15) was used to fit Nyquist curves, in which CPE_{dl} , R_{ct} , and R_s represent the non-ideal double-layer capacitance, the charge transfer resistance, and the solution resistance, respectively. Table 3 exhibits the calculated values of each circuit element. The R_{ct} value of the Ni–Cr–graphene coating increased from 37.3 to 861.5 k Ω ·cm² as the graphene concentration increased from 0 to 8 g/L, always remaining larger than that of the pure Ni coating (10.2 k Ω ·cm²).



Figure 14. Nyquist plots (a) and Bode plots (b) of the Ni–Cr–graphene coatings in 3.5% NaCl solution.



Figure 15. Equivalent circuit of the Ni-Cr-graphene coatings in 3.5% NaCl solution.

Ni–Cr–Graphene	$R_{\rm ct}$ (k $\Omega \cdot {\rm cm}^2$)	$R_{\rm s}$ ($\Omega \cdot { m cm}^2$)	CPE _{dl} (µF·cm ^{−2})	n
Ni	10.2	7.5	85.5	0.65
Ni-25–Cr-0–Graphene	37.3	6.8	426.8	0.61
Ni-25-Cr-1-Graphene	137.6	8.7	115.7	0.79
Ni-25-Cr-2-Graphene	272.1	7.1	189.2	0.79
Ni-25-Cr-4-Graphene	280.4	9.1	37.9	0.75
Ni-25–Cr-8–Graphene	681.5	8.4	233.5	0.84

Table 3. Corrosion factors from equivalent circuits of the Ni-Cr-graphene coatings.

4. Discussion

In Figure 2, it can be seen that the regular pyramidal surface structure of the pure Ni coating changed to the dendrite like structure of the Ni–Cr–graphene coating as the graphene concentration increased in the electrolyte. The results suggested that the addition of graphene particles to the electrolyte strongly influenced the surface morphology evolution of the Ni–Cr–graphene coatings, which was believed to be induced by the electric conductivity of the graphene [9,26].

Figure 3 shows that the Cr contents in the Ni–Cr–graphene coatings were almost consistent (ca. 7.7 wt.%). This was caused by the certain Cr concentration of 25 g/L in the electrolyte for all the coatings. The electrodeposition behaviors of Cr particles were sustainable and stable, and they were seldom disturbed by the co-deposition of graphene particles. In Figures 4 and 5, it can be observed that the graphene content in the Ni–Cr–graphene coating increased with increasing graphene concentration. This was caused by the increased possibility of graphene particles adsorbing onto the cathode as the graphene concentration in the electrolyte increased [27]. The EDS (Figure 3) and Raman (Figure 5) results further illustrated that the Ni–Cr–graphene composite coatings were successfully established.

The XRD evolution in Figure 6 reflected the microstructure changes of Ni deposits in the Ni–Cr–graphene coatings with increasing graphene concentration. The calculated crystallite size of Ni deposits by Rietveld refinement is exhibited in Figure 8. Comparing the crystallite size evolution (Figure 8) with the results of EDS and Raman analysis (Figures 3–5), it was rational to consider that the addition of particles induced the decreased size of the Ni crystallites. In the electrodeposition process,

the locations where the suspended particles were adsorbed could be deemed as the growth centers of Ni crystallites [2,28]. The adsorbed Cr particles prevented the further growth of Ni crystallites, simultaneously acting as the new nucleus to promote the crystallite refinement of Ni deposits in the Ni–Cr coating [2,28]. With the further addition of graphene particles, the graphene particles could also work as the new nucleus, consequently leading to further crystallite refinement in the Ni–Cr–graphene coatings.

Figures 9–11 reflected the crystallite shape and crystallographic orientations of the Ni deposits in the Ni–Cr–graphene coatings. It was authenticated that the [100] orientation was the preferred orientation of the pure Ni coating in the Watts bath without particle additives, which could be changed by the co-deposition of particle additives in the electrolyte [2,4,29]. McCormack et al. [2] suggested that the co-deposition of Y_2O_3 particles led to the increase of [111] orientation of Ni–Y2O3 coatings. For the Ni–Cr–graphene coatings, the [100] growth orientation of the Ni crystallites could be disturbed by the co-deposition of Cr and graphene particles. The co-deposited particles precluded further growth of the Ni crystallites, consequently shielding the growth sites of Ni ions in the Watts bath [2,28]. Meanwhile, the nucleation of Ni crystallites took place on the particles, and the [111] orientation formed. Thus, the higher concentration of graphene particles led to a weaker [200] fiber texture in the Ni–Cr–graphene coatings.

As mentioned above, the co-deposition of the graphene particles gave birth to the decreased crystallite size and [200] texture of nickel deposits, which played important roles in the enhancement of the micro-hardness of the Ni–Cr–graphene coatings (see Figure 12a) based on the strengthening of crystallographic orientation and crystallite refinement. The crystallite refinement strengthening played an important role based on the Hall–Petch formula [30].

$$\sigma_v = \sigma_0 + kd^{-1/2} \tag{4}$$

$$Microhardness = 3\sigma_{y} \tag{5}$$

where k, d, σ_y , and σ_0 are the constant, the crystallite size, the yield stress, and the friction stress, respectively. The crystallographic orientation strengthening was based on the orientation relationship between the crystallographic orientation and the slip systems [31]. The {111} <110> plane represented the slip system of Ni deposits. When the external stress was perpendicular to the (111) plane, the resolved shear stress in the slip system was zero, consequently resulting in the higher micro-hardness of (111) planes with respect to other planes. During the electrodeposition of the Ni–Cr–graphene coatings, more graphene particles brought about the further crystallite refinement and decreased [200] texture of Ni deposits. Therefore, the micro-hardness of the Ni–Cr–graphene coatings increased as the graphene concentration in the electrolyte increased. In Figure 12c, the less uniform distribution of the micro-hardness of the Ni–25–Cr-8–graphene coating could be understood by the surface irregularity of the coating. The co-deposition of graphene particles caused the surface irregularity of the coatings (see Figure 2), which led to the nonuniform distribution of micro-hardness [32].

In Figure 13 and Table 2, the E_{corr} and I_{corr} of the Ni–Cr–graphene coating increased and decreased with increasing graphene concentration, respectively. In Figure 14, showing the Nyquist and Bode plots, the corrosion resistance of the coatings could be determined by the magnitude of the semicircle diameter, Bode phase maximum, and Z_{mod} [33,34]. A larger semicircle diameter, Bode phase maximum, and Z_{mod} indicated the better corrosion resistance of the Ni–Cr–graphene coatings. Therefore, the results of I_{corr} and R_{ct} indicated that the corrosion resistance of the Ni–Cr–graphene coating increased with increasing graphene concentration.

The incorporation of graphene particles and the microstructure changes of Ni deposits significantly enhanced the corrosion resistance of the Ni–Cr–graphene coatings. Firstly, the addition of graphene particles brought about further crystallite refinement and the a diminution of the [200] texture of Ni deposits in the Ni–Cr–graphene coatings compared to the Ni and Ni–Cr coatings, reducing rapid corrosion paths and facilitating the formation of a passivation film [34,35]. Secondly,

the graphene particles worked as "physical barriers" in the corrosion paths to hinder the spread of the corrosion [36]. Thus, the corrosion resistance of the Ni–Cr–graphene coating increased when the graphene concentration in the electrolyte increased.

5. Conclusions

As modification additives, different amounts of graphene particles, together with 25 g/L Cr particles, were used to fabricate Ni–Cr–graphene coatings in a Watts bath by electrodeposition. The co-deposition of graphene particles led to a dendrite-like structure of the Ni–Cr–graphene coating instead of the regular pyramidal surface structure of the pure Ni coating. For all coatings, the amounts of Cr particles incorporated in the coatings were ca. 7.7 wt.%, while the graphene content in the coatings increased when the graphene concentration in the electrolyte increased.

The increased graphene content in the coating brought about microstructure changes of the Ni deposits in the Ni–Cr–graphene coatings, such as crystallite size, crystallite shape, and crystallographic orientation. With increasing graphene concentration in the electrolyte, the crystallite size and [200] texture of the Ni deposits gradually decreased. The microstructure changes of the Ni deposits contributed to the enhancement in micro-hardness and corrosion resistance of the Ni–Cr–graphene coatings. Therefore, the graphene particles successfully played the role of modification particles for the Ni–Cr coating by further optimizing the microstructure and properties of the coatings.

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