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Effect of Polyethyleneimine Cationic Surfactant on Morphology and Corrosion Resistance of Electrodeposited Ni-Co-SiC Composite Coatings

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Abstract: Ni-Co-SiC composite coatings were prepared by modified watt-type plating solution with 40 nm SiC particles. The effects of polyethyleneimine (PEI) on the dispersion of SiC nanoparticles and the hardness and corrosion resistance of Ni-Co-SiC coatings were studied. The electrode reaction process was measured by cyclic voltammetry. The results showed that when the PEI concentration was 0.06 g/L, the peak current was the highest. SiC distribution in Ni-Co-SiC coatings was relatively uniform and the coating was flat and dense. With the increase in PEI concentration, the hardness and corrosion resistance showed a trend of increasing first and then decreasing. The hardness and corrosion resistance were at their best with 0.06 g/L PEI. Pretreatment effectively avoided the competitive adsorption of surfactant and other additives on the surface of SiC particles. PEI was preferentially adsorbed on the surface of SiC particles by pretreatment. Steric resistance was formed, which inhibited the agglomeration of nanoparticles and make SiC particles more evenly dispersed into the coating. The hardness was significantly increased by 119.26 Hv, and the corrosion resistance improved accordingly.

Keywords: cationic surfactant PEI; Ni-Co-SiC composite coatings; hardness; corrosion resistant

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1. Introduction

The electrodeposition method has the advantages of requiring simple equipment, having low requirements on the shape and size of the workpiece, being a simple process with small technical difficulty, and being low cost [1]. The composite coatings prepared by the electrodeposition method are smooth in appearance and have good bonding with various substrates [2,3]. With the improvement of material performance requirements, the composite coatings prepared by adding nanoparticles with unique properties to the plating solution have both the properties of the matrix and the nanoparticles, and the prepared nanocomposites have higher hardness and better oxidation resistance, wear resistance, and corrosion resistance [4]. The cobalt atoms in the Ni-Co alloy coating enter the crystal lattice in the way of the replacement, which causes the lattice distortion and increases the number of grain boundaries. Co can refine the grain size and the composite coating is more compact. The corrosion resistance and high-temperature resistance of the composite coating are stronger than that of the pure nickel coating [5–7], and the Ni-Co structure has hydrogen evolution catalytic performance [8,9]. Nano-SiC particles have excellent wear resistance and corrosion resistance [10]. When SiCs were deposited into Ni-Co composite coating as a reinforcement phase, they can effectively inhibit the growth of matrix grain, reduce grain size, and make the surface of Ni-Co-SiC composite coatings more compact. At the same time, the addition of SiC particles has the effect of solution strengthening and dispersion strengthening, which hinders the movement of dislocations to enhance the hardness and

corrosion resistance of the coating [11]. The uniform distribution of SiC in the coating reduces the effective area of the substrate exposed to the corrosive medium. Moreover, the SiC and the Ni-Co alloy coating act as the anode and cathode of the micro-galvanic cell, respectively. The corrosion mechanism changes local corrosion to uniform corrosion, which can effectively improve the corrosion resistance of the composite coating [12].

Due to the high surface activity and random Brownian motion in the plating solution, nano-sized particles are easy to collide and agglomerate, which affects the deposition rate and the content of nanoparticles in the composite coating, and in turn, affects the performance of the composite coating [13,14]. A convenient and efficient way to solve the problem of nanoparticle agglomeration is to add a surfactant to the plating solution. The surfactant can effectively disperse the agglomerated nanoparticles and increase the number of nanoparticles deposited in composite coatings. The types and concentrations of the surfactant added to the electrolyte affect the nature and quality of charge of the particle surface, which in turn affects the content of SiC particles deposited in the coatings. The results show that the maximum SiC content in the coating is 54% when the non-ionic surfactant coumarin is added. The addition of surfactant changes the microstructure of the coating, from matte to bright, from porous to spherical and dense. With the increase in SiC content, the wear resistance and hardness of the Ni-SiC nanocomposite coating gradually increase [15]. The anionic surfactant sodium dodecyl sulfate (SDS) is beneficial to improve the stability of the plating solution. The Ni-P-Al_2O_3 composite coatings prepared by adding SDS have no pores and carbon black defects on the surface, and the hardness and corrosion resistance of the composite coating is good [16]. Ahmad and co-workers reported that surfactants can change the surface charge (Zeta potential), the hydrophilic and hydrophobic balance of nanoparticles, and change the agglomeration and incorporation tendency of particles. Adding ammonium lauroyl ether sulfate (ALES) and cetyl trimethyl ammonium chloride (CTAC) to the electrolyte can change the embedding and doping mode of SiO_2 deposited into the nickel coating and increase the SiO_2 content in the composite coating. Moreover, the corrosion resistance, hardness, and wear resistance of the Ni-SiO_2 composite coating prepared by adding ALES is much higher than that of adding CTAC [17].

In recent years, the research on the surfactant added during the preparation of Ni-Co-SiC composite coatings focused on SDS [11,12,18,19]. In order to prepare Ni-Co-SiC composite coatings with high SiC content and excellent performance, cationic surfactant polyethylenimine (PEI) was introduced. The effect of PEI on the dispersion and deposition amount of SiC nanoparticles in the composite coatings is studied, and the effect of PEI on the hardness and corrosion resistance of the Ni-Co-SiC composite coatings is analyzed.

2. Experimental Procedure

Ni-Co-SiC composite coatings were electrodeposited from a modified Watts bath, the electrolyte compositions and electrodeposition parameters are given in Table 1. Pure nickel (99%) with dimensions of 15 mm × 20 mm × 3 mm was used as an anode, copper was used as substrate as a plate of 1 cm^2 in area, and the distance between the two electrodes is 1 cm. The substrates were polished with 600#, 1200#, and 1500# sandpaper in turn, and then cleaned with deionized water after alkali washing and acid pickling and dried for later use.

The surface morphology of Ni-Co-SiC composite coatings was investigated using a Hitachi S4800 scanning electron microscope (SEM, Hitachi, Tokyo, Japan). An energy-dispersive X-ray detector (EDS, Oxford, UK) coupled with SEM was used to determine the chemical composition and the SiC content of the coatings. The Vickers microhardness measurements were carried out using a 402 MVD hardness tester (Shanghai Zhujin Analytical Instrument Co., Ltd, Shanghai, China). The hardness test condition is 40 times the objective lens, the shooting brightness value is 100, each load pressure is 100 g, and maintains 15 s, the average of the five measurement results is the final hardness value of the composite coating. Electrochemical experiments were performed at the IVIUM Electrochemical Workstation (Ivium Technologies, Eindhoven, Netherlands) in a three-electrode cell. Platinum

wire of 0.1 cm in diameter was used as a working electrode (WE), a 1 cm × 1 cm platinum plate as a counter electrode (CE), and a saturated calomel electrode as a reference electrode (RE). Cyclic voltammograms were carried out at a potential sweep rate of 5 mV/s. The test voltage range is −1 V~0.2 V, and the step is set as 10 mV. The corrosion resistance of the composite coating was characterized by the polarization curve method and AC impedance method. The AC impedance test was carried out in a 3.5% NaCl corrosive medium, with a frequency of 0.01 Hz–100,000 Hz and a scanning speed of 5 mV/s. The polarization curve was scanned from the potential of −1 V to the potential of 0.5 V, and the remaining parameters are the same as above.

Table 1. Electrolyte compositions and electrodeposition parameters.

Electrolyte Ingredients	Concentration (g/L)
$NiSO_4 \cdot 7H_2O$	250
$NiCl_2 \cdot 6H_2O$	40
$CoSO_4 \cdot 7H_2O$	50
H_3BO_3	40
SiC	3
Deposition parameters	**Amount**
SiC particle size	40 nm
Type of current	DC
Current density (A/dm^2)	3
Temperature (°C)	50
Solution pH	4.3
Magnetic agitation rate (rpm)	500
electrodeposition cell voltage (V)	1.1
deposition time (min)	75
bath volume (mL)	100

3. Results and Discussion

3.1. Effect of PEI Concentration on Ni-Co-SiC Composite Coatings

3.1.1. Effect of PEI Concentration on Ni-Co-SiC Co-Deposition Process

Figure 1 shows the cyclic voltammetry curves of electrodeposited Ni-Co-SiC composite coatings under different PEI concentrations. PEI concentrations are 0.02 g/L, 0.04 g/L, 0.06 g/L and 0.08 g/L, respectively. It can be seen from the figure the cathode polarization current gradually increases with the increase in the PEI concentration. When the concentration of PEI is 0.06 g/L, the cathode polarization current in the cyclic voltammetry curve is the highest. Then, the cathode polarization current decreased with the increase in the PEI concentration. The reason is that as a long-chain polymer, one end of PEI is adsorbed on the surface of nano-SiC and the other end may be adsorbed on the surface of other nano-SiC or other long chains of PEI, which results in flocculation and deposition of nanoparticles, that is, the bridge effect [20]. When the PEI concentration is small, PEI is adsorbed on the surface of the nanoparticles. It fails to form an effective steric hindrance and neutralizes the heterogeneous charges on the surface of the SiC particles. The electrostatic repulsion force decreases and the agglomeration of the nanoparticles occurs on the surface of the electrode. The shielding is larger and it reduces the effective reaction area of Ni^{2+} and Co^{2+}, resulting in a lower discharge current. When the content of PEI increases, a large amount of PEI is adsorbed on the surface of nano-SiC, which not only increases the surface charge of particles, but also increases the electrostatic repulsion force, and a large amount of PEI on the surface of particles forms a thick steric barrier, and the particles are dispersed again. At the same time, the shielding on the electrode surface decreases, the effective reaction area of Ni^{2+} and Co^{2+} increases, and the cathode polarization current increases continuously. As the PEI concentration continues to increase, the excessive PEI will re-flocculate particles together and nanoparticle flocculation will occur. When PEI concentration is 0.06 g/L, it is the most favorable condition for the co-deposition of SiC particles and matrix metal.

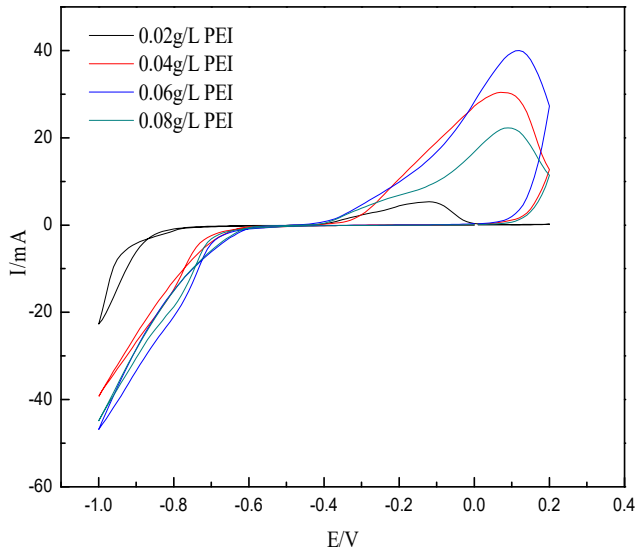
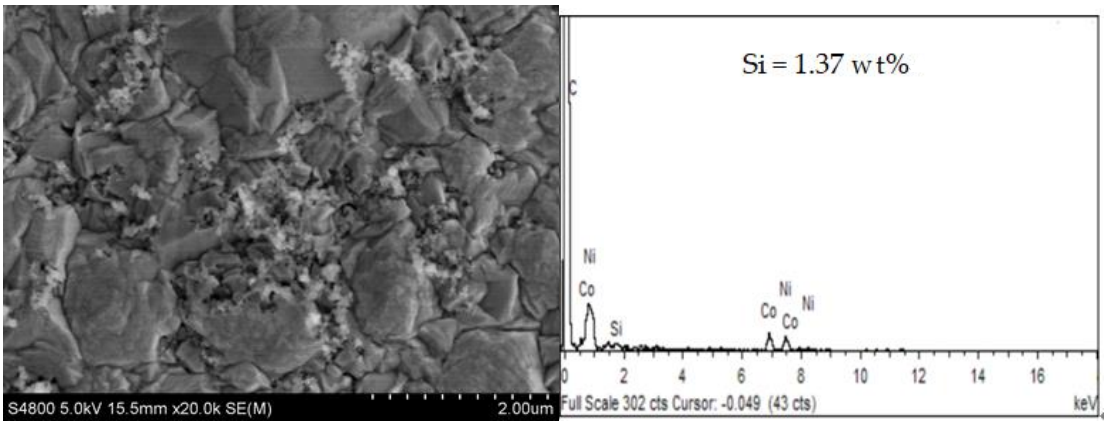


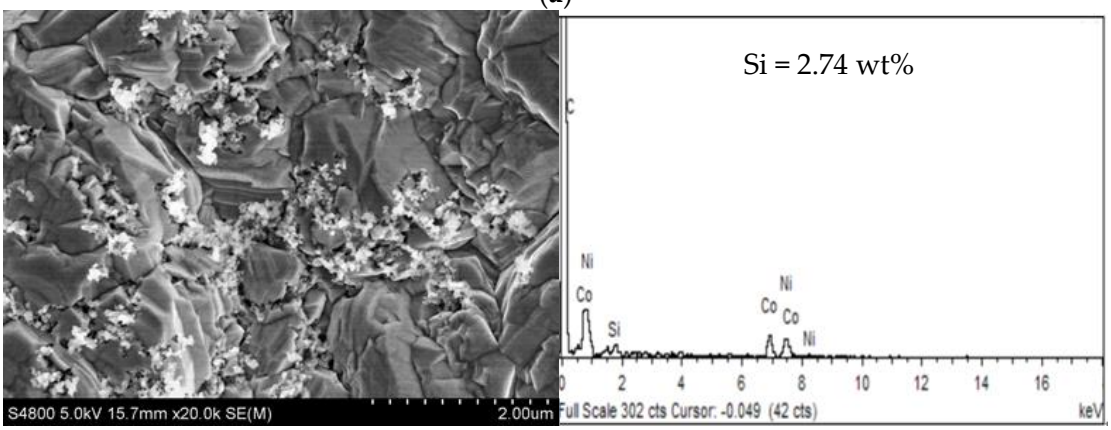
Figure 1. Cyclic voltammetry curves of Ni-Co-SiC electrolytes under different PEI concentrations.

3.1.2. Effect of PEI Concentration on Ni-Co-SiC Composite Coatings

Figure 2 shows the SEM and EDS spectra of Ni-Co-SiC composite coatings with PEI content of 0.02 g/L, 0.04 g/L, 0.06 g/L, and 0.08 g/L, respectively.



(**a**)



(**b**)

Figure 2. *Cont.*

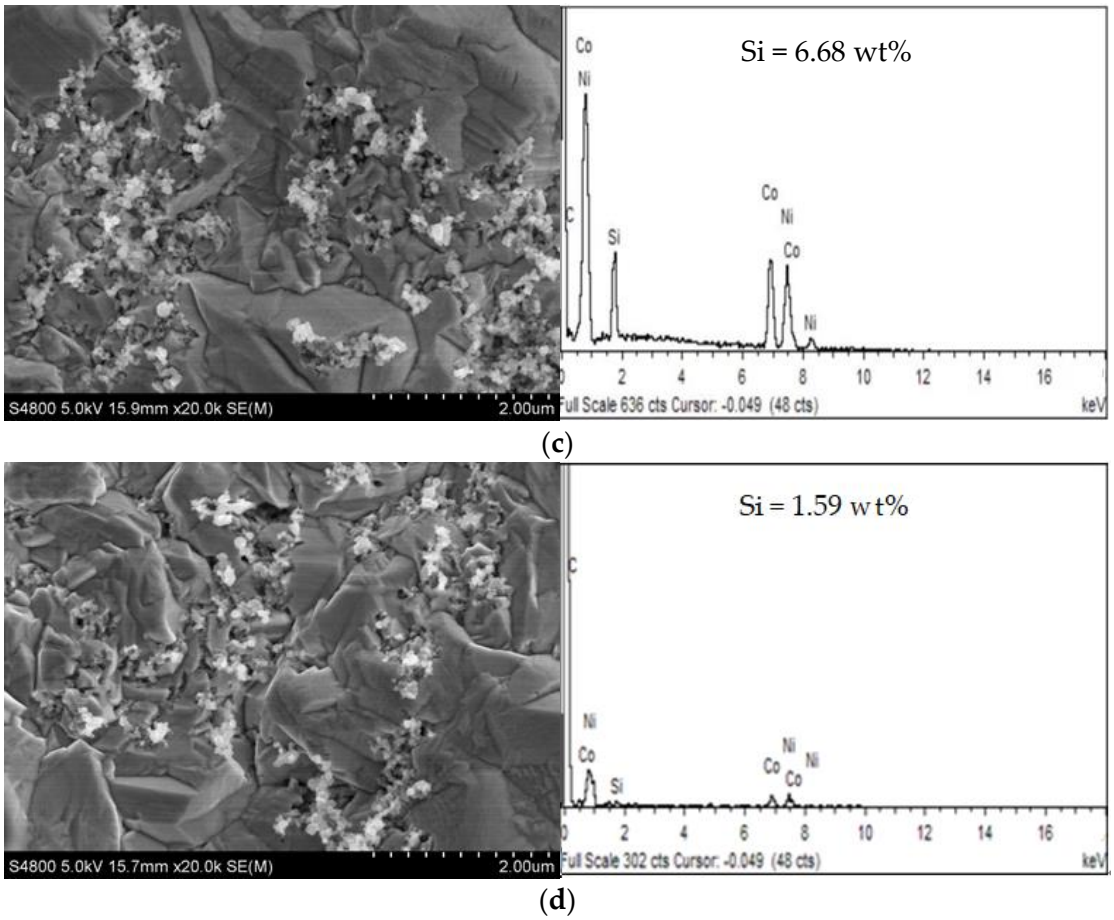


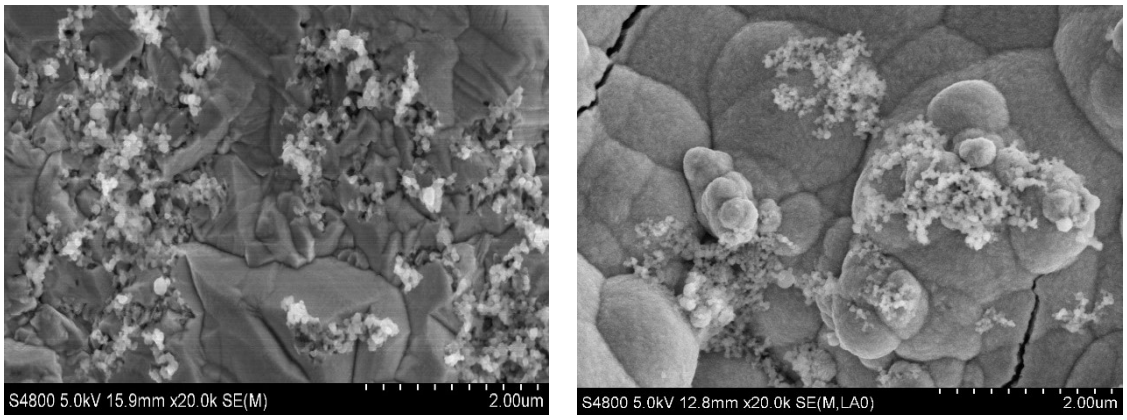
Figure 2. SEM images and EDS spectra of Ni-Co-SiC composite coatings under different PEI concentrations. (**a**) 0.02 g/L; (**b**) 0.04 g/L; (**c**) 0.06 g/L; (**d**) 0.08 g/L.

As can be seen from Figure 2a, when the PEI concentration is 0.02 g/L, the grain size of the Ni-Co matrix is not uniform, the coating surface is not smooth, and the amount of SiC particles in the composite coating is very small, and there is obvious agglomeration. When PEI concentration is increased to 0.04 g/L, as shown in Figure 2b, the deposition amount of SiC particles increases and the agglomeration phenomenon weakens, but the surface of the coating is still uneven. When the concentration of PEI continues to increase to 0.06 g/L, as shown in Figure 2c, the amount of SiC in the coating increases and SiC particles are relatively uniformly dispersed in the coating. The Ni-Co grains around SiC are refined, and the coating is flat and compact. When the amount of PEI reaches 0.08 g/L, the amount of SiC in the coating decreases, the larger grains become obvious again, and the surface flatness of the composite coating is poor. Surfactants PEI can promote co-deposition. The cationic surfactant PEI is adsorbed on the surface of SiC particles and electrodes. The hydrophilic group of PEI faces the hydrophobic SiC and electrode surface, and the hydrophobic group of PEI is away from the particle and electrode surface. Then the PEI on the electrode surface separates SiC and water. The dipole moment of organic molecules is the smallest, which helps the co-deposition process. When PEI is 0.06 g/L, the dispersion effect of SiC is better, and the coating is relatively smooth and compact.

3.1.3. The Effect of Higher Concentration PEI on Ni-Co-SiC Composite Coatings

In order to investigate the influence of higher concentration PEI on Ni-Co-SiC composite coatings, the concentration of PEI is increased to 0.6 g/L, and the surface morphology of Ni-Co-SiC composite coatings is observed. Figure 3 are SEM images of Ni-Co-SiC composite coatings at different PEI concentrations. The PEI concentration is 0.06 g/L and 0.6 g/L,

respectively. It can be seen from the figure that when the PEI concentration is increased to 0.6 g/L, the crystal grains of the nickel-cobalt matrix layer has changed from the angular cones to ellipsoids. There are cracks in the coating, and the dispersion of SiC is poor. The reason is that the increase of an order of magnitude of PEI fails to disperse nano-sized SiCs better. A high concentration of PEI promotes lattice distortion of composite coatings, which weakens the edges and corners of Ni-Co matrix grains to become round and makes them grow in layers. The crack may be due to the high concentration of PEI. With the growth of the composite coating, excessive polymer remains on the coating, which leads to the decrease of the internal stress and the ductility of the coating, and the occurrence of cracks. Therefore, the concentration of PEI has a great influence on the Ni-Co-SiC composite coatings prepared by electrodeposition.

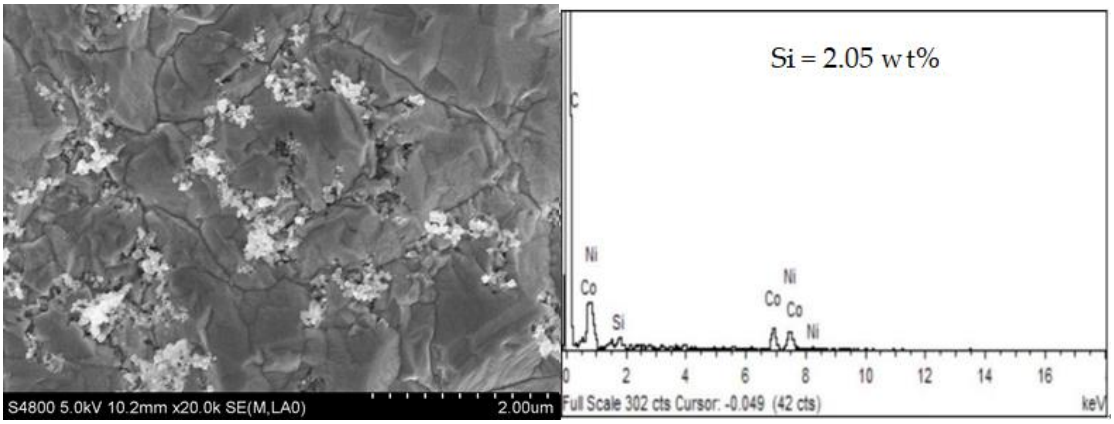


(**a**) (**b**)

Figure 3. SEM images of Ni-Co-SiC composite coatings at different PEI concentrations. (**a**) 0.06 g/L; (**b**) 0.6 g/L.

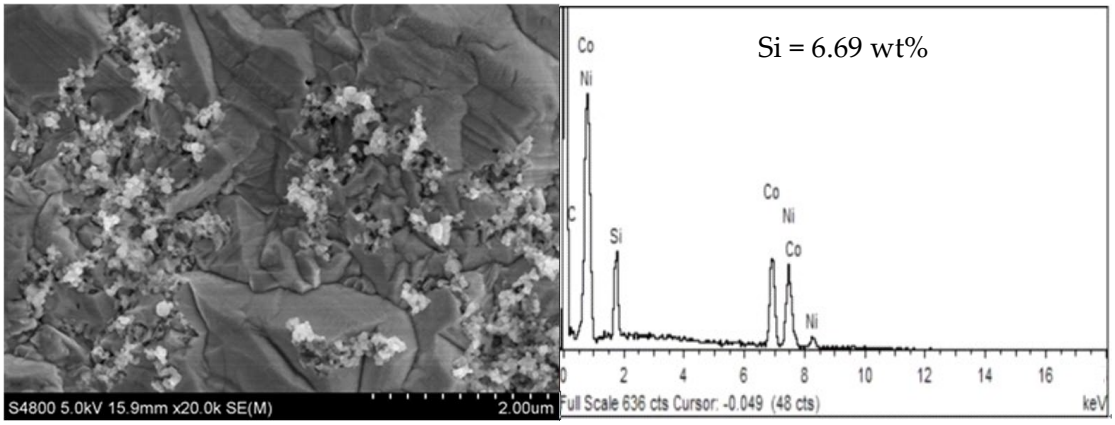
3.2. Effect of Pretreatment on Ni-Co-SiC Composite Coatings

This experiment will pre-treat SiC particles to achieve a better dispersion effect. Surfactant PEI and SiC will be mixed first to achieve SiC particles being pre-coated by PEI, and then pre-coated SiC will be added to prepare the electroplating solution. The dispersion effects of SiC particles are compared by pre-coated SiC and uncoated SiC in the experiment. In order to better disperse the easily agglomerated nano-SiC particles to obtain better composite coatings, the effect of pre-coating on the Ni-Co-SiC composite coating is studied when 0.06 g/L cationic surfactant PEI is added, as shown in Figure 4.



(**a**)

Figure 4. *Cont.*



(**b**)

Figure 4. SEM images and EDS spectra of different pretreatment procedures on Ni-Co-SiC composite coatings. (**a**) without pretreatment; (**b**) pretreatment.

Pretreatment refers to the process of mixing and stirring the surfactant and insoluble particles and then dispersing them by ultrasonic waves. As can be seen from Figure 4, in the Ni-Co-SiC composite coatings prepared without pretreatment, SiCs agglomerate and distribute along the grain boundaries of the matrix grains. The amount of SiCs in the coating is less, and the matrix grain size is generally larger. After pretreatment, the deposition amount of SiCs increases and is relatively uniformly distributed in the coating. The grain size around SiCs decreases obviously. Pre-coating SiCs with cationic surfactants effectively avoids the competitive adsorption of surfactants and other additives in the plating solution on the SiC particle surface, which optimizes the composition of the plating solution and improves the dispersion of nano-SiC particles. Therefore, the pretreatment of PEI and SiC particles can effectively disperse the agglomerated SiC and further refine the grain size of the composite coating.

3.3. Effect of PEI on Hardness of Ni-Co-SiC Composite Coatings

3.3.1. Effect of PEI Concentration on Hardness of Ni-Co-SiC Composite Coatings

The microhardness of Ni-Co-SiC composite coatings prepared by different PEI concentrations is shown in Figure 5. It can be seen from Figure 5 that the hardness of Ni-Co-SiC composite coating gradually increases with the increase of PEI concentration. When the addition of PEI is 0.06 g/L, the hardness of the composite coating reaches 509.50 HV. As the concentration of surfactant continues to increase, the hardness of the composite coating decreases. PEI is a high molecular polymer surfactant that can efficiently ionize cations. Under the condition of magnetic stirring and ultrasonic dispersion, the hard particle SiCs and PEI are fully wrapped and dispersed well. After moving to the cathode surface, SiCs are deposited into the composite coatings, and the content in the composite coatings increases, which effectively improves the hardness of Ni-Co-SiC composite coatings.

There are two ways of existence of nano-SiC particles in the Ni-Co-SiC composite coating prepared by electrodeposition. One is grain boundary inlay and the other is inlay in crystal grains. With the increase of PEI concentration, the more SiC particles deposit into the coatings, the stronger the effect of dispersion strengthening, the more dislocation and twins, and the hardness of the composite coatings is higher. The greater the amount of SiC embedded into the composite coating, the greater the hindering effect on the growth of grains, the stronger the inhibiting effect on the growth of matrix grain, the smaller the size of Ni-Co metal matrix grain, the denser of Ni-Co-SiC composite coating. According to Hall-Petch's formula:

$$Hv = Ho + kd^{-1/2} \quad (1)$$

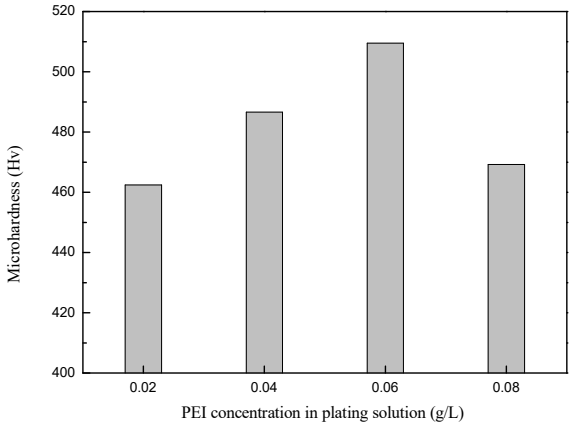
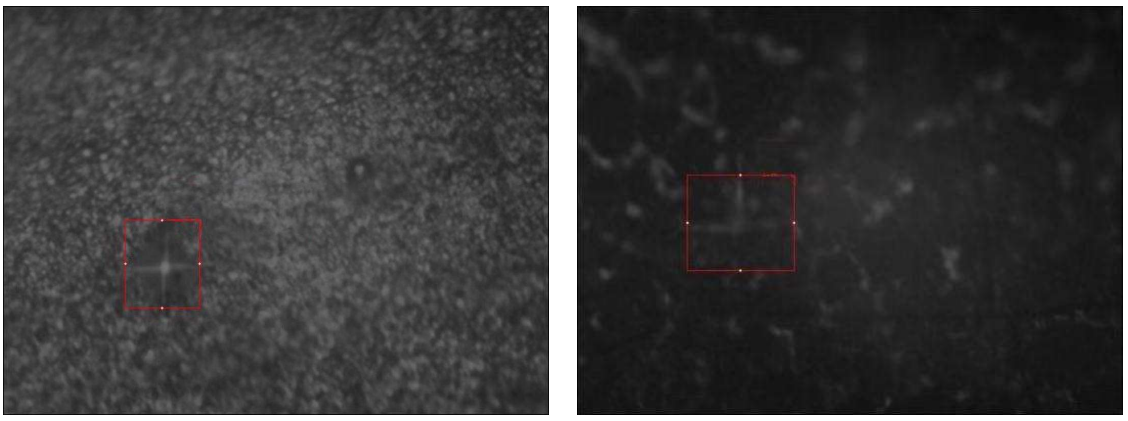


Figure 5. Effect of PEI concentration on the microhardness of Ni-Co-SiC composite coatings.

Ho and k in Formula (1) are constant values, which are only related to the type of crystal. According to the formula, it can be concluded that the smaller the grain diameter is, the higher the hardness value is, which is an inversely proportional relationship. The experimental conclusion is consistent with this formula. Therefore, the hardness of Ni-Co SiC composite coatings is the highest when the PEI concentration is 0.06 g/L. Excess PEI will further flocculate and increase agglomeration of SiC particles when the amount of PEI reaches 0.08 g/L, then the hardness decreases.

3.3.2. The Effect of Higher PEI Concentration on Hardness of Ni-Co-SiC Composite Coatings

Figure 6 are the surface indentation morphologies of Ni-Co-SiC composite coatings prepared with PEI concentrations of 0.06 g/L and 0.6 g/L. The surface indentation area with PEI 0.06 g/L is smaller than that of PEI 0.6 g/L. According to the principle of the micro-hardness test, when the area of the quadrangular pyramid on the coating is smaller, the hardness value is larger, indicating that the hardness of Ni-Co-SiC composite coatings is higher when the PEI concentration is 0.06 g/L. According to the results, the hardness of the coating was 441.31 Hv when the PEI concentration was 0.6 g/L, which was less than 509.50 Hv when the amount of PEI was 0.06 g/L. It can be concluded that an order of magnitude increase in PEI does not improve the hardness of the coating. Increasing the amount of PEI changes the morphology of Ni-Co-SiC composite coatings from cones to spheres with inconspicuous corners but does not increase the content of hard SiC particles in the coating and refine the matrix crystals. Therefore, increasing PEI concentration by one order of magnitude does not increase the hardness of the coating.



(**a**) (**b**)

Figure 6. Indentation identification results of Ni-Co-SiC composite coatings with different orders of PEI concentration. (**a**) 0.06 g/L; (**b**) 0.6 g/L.

3.3.3. Effect of Pretreatment on Hardness of Ni-Co-SiC Composite Coatings

Table 2 shows the hardness of Ni-Co-SiC composite coatings with different pre-coating procedures. It can be concluded from the table that the composite coating prepared by pre-coating has a hardness of 119.26 Hv higher than the composite coating prepared without pre-coating. The pre-coating makes the PEI fully adsorb the nano-SiC particles, which will form steric hindrance and effectively inhibit the agglomeration of nanoparticles. The SiC particles fully coated by cationic surfactant PEI are positively charged, which increases the residence time of SiC on the cathode and increases the content of SiC particles in the coating. The pretreatment of SiC particles with PEI can effectively disperse the agglomerated SiC and further refine the grain size of the composite coating, and the hardness of the coating is increased.

Table 2. Data of hardness measurement of Ni-Co-SiC composite coatings with different procedures.

Coating Conditions	1	2	3	4	5	Average Value
pretreatment	472.45 Hv	519.22 Hv	504.71 Hv	528.12 Hv	523.02 Hv	509.50 Hv
without pretreatment	437.96 Hv	327.45 Hv	407.89 Hv	472.63 Hv	305.26 Hv	390.24 Hv

3.4. Effect of PEI on Corrosion Resistance of Ni-Co-SiC Composite Coatings

3.4.1. Effect of PEI Concentration on Corrosion Resistance of Ni-Co-SiC Composite Coatings

Figure 7 shows the polarization curves of Ni-Co-SiC composite coatings with different concentrations of PEI. The four curves are roughly similar in shape and have a relatively wide passivation zone. With the increase of the concentration of PEI in the plating solution, the polarization curve first moves in the more positive direction, the corrosion becomes slower, and the corrosion resistance is better. When PEI exceeds 0.06 g/L, it moves in a more negative direction, and the corrosion becomes faster. It indicates that as the PEI concentration increases, the corrosion resistance of the Ni-Co-SiC composite coating gradually becomes better. When the PEI concentration exceeds 0.06 g/L, the corrosion resistance of the composite coatings decreases.

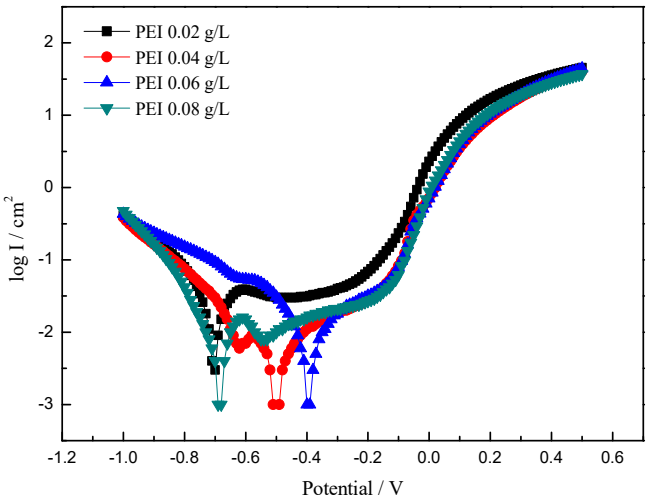


Figure 7. The polarization curves of Ni-Co-SiC composite coatings with different PEI concentrations.

The extrapolated fitting parameter analysis of the Tafel curve is shown in Table 3. According to the data in the table, as the concentration of PEI increases, the corrosion potential becomes more positive, and the corrosion current density and corrosion rate decrease gradually. When it exceeds 0.06 g/L, the corrosion current and corrosion rate increase and the corrosion potential becomes more negative. The higher the concentration of PEI, the

better the dispersion effect of SiC. As is observed in Figure 2. More SiC nanoparticles are uniformly deposited in the composite coating, refining the grain size of the Ni-Co matrix, and the composite coating is more compact, greatly reducing the defects in the composite coating, such as pores and cracks, improving the corrosion resistance of the coating. When the concentration of PEI is greater than 0.06 g/L, excessive PEI will flocculate SiC particles together again, and the nanoparticles will agglomerate. The amount of SiC particles in the coating decreases, the matrix grain size of the coating increases, and the corrosion resistance of the composite coating decreases. The more SiC content, The smaller the matrix grain of the composite coating, and the better the corrosion resistance of the coating. The results of the polarization curve method are consistent with the AC impedance method. When the concentration of PEI is 0.06 g/L, the corrosion resistance of the Ni-Co-SiC composite coatings is the best.

Table 3. Corrosion Tafel-Parameters of Ni-Co-SiC composite coatings with different PEI concentrations.

PEI Concentration (g/L)	Ecorr (V)	Icorr (A/cm^2)	Corr.Rate (mm/y)
0.02	−0.4085	5.04×10^{-6}	5.854×10^{-2}
0.04	−0.3817	2.13×10^{-6}	2.476×10^{-2}
0.06	−0.2943	2.62×10^{-7}	3.045×10^{-3}
0.08	−0.4616	8.20×10^{-7}	9.527×10^{-3}

3.4.2. The Effect of Higher PEI Concentration on Corrosion Resistance of Ni-Co-SiC Composite Coatings

Figure 8 shows the polarization curves of Ni-Co-SiC composite coatings obtained with different PEI concentrations. PEI concentration is 0.06 g/L and 0.6 g/L, respectively. As can be seen from Figure 9, when the concentration of PEI increases by an order of magnitude, the curve shifts to the left, the corrosion potential moves negatively, and the passivation interval is not obvious. This indicates that the corrosion resistance of Ni-Co-SiC composite coating prepared by adding 0.6 g/L PEI is weakened.

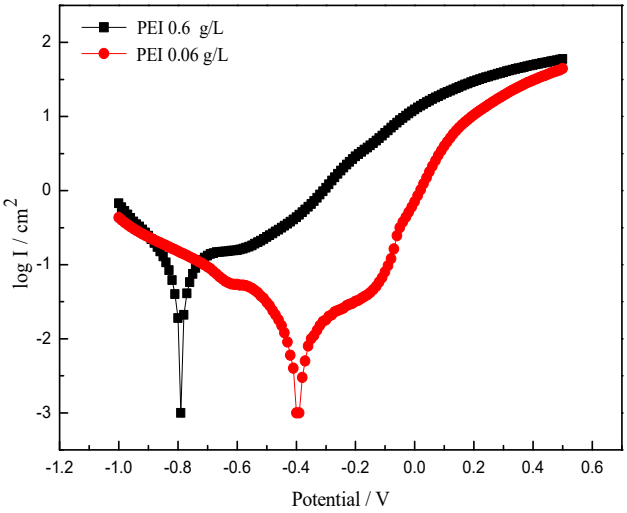


Figure 8. The polarization curves of Ni-Co-SiC composite coatings with different PEI concentrations.

The parameters obtained by analyzing the polarization curve with IVIUM Soft software(version 2.594) are shown in Table 3. As can be seen from Table 4, the corrosion potential is more negative with the increase of PEI concentration, and the corrosion rate and corrosion current density both increase, indicating that the corrosion resistance of the composite coating is worse. Most of the SiC in the composite coating is present in the composite coating in agglomerated state increasing PEI concentration, the effect of refining grain is not obvious and the average grain size increases. There are cracks distributed in

the coating. As is observed in Figure 3. The corrosive liquid penetrates into the composite coating along the cracks, which intensifies the corrosion of the Ni-Co-SiC composite coating. Therefore, increasing the PEI concentration by an order of magnitude failed to improve the corrosion resistance of the Ni-Co-SiC composite coating.

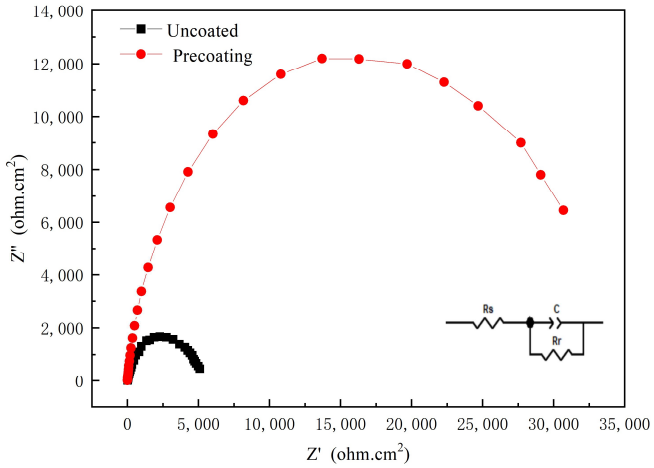


Figure 9. Nyquist diagram of Ni-Co-SiC composite coatings with different pre-coated procedures.

Table 4. Corrosion Tafel-Parameters of Ni-Co-SiC composite coatings with different orders of PEI concentration.

PEI Concentration (g/L)	Ecorr (V)	Icorr (A/cm^2)	Corr.Rate (mm/y)
0.06	−0.2943	2.62×10^{-7}	3.045×10^{-3}
0.6	−0.7406	2.57×10^{-5}	2.986×10^{-1}

3.4.3. Effect of Pretreatment on Corrosion Resistance of Ni-Co-SiC Composite Coatings

In order to investigate the influence of pretreatment on the corrosion resistance of Ni-Co-SiC composite coatings, the electrochemical impedance test was carried out on the Ni-Co-SiC composite coatings prepared without pretreatment and with pretreatment. The results are shown in Figure 9, and the fitting parameters of its equivalent circuit are shown in Table 5. It can be concluded from the Nyquist diagram that the high-frequency capacitive reactance arcs fall in the first quadrant, and the semicircular diameter of the capacitive reactance arc of the Ni-Co-SiC composite coating prepared by the pretreatment is larger than the coating obtained without pretreatment, which means that its reaction resistance is higher, and the corrosion resistance is stronger. The data in Table 4 shows that the polarization resistance of Ni-Co-SiC composite coating prepared with pretreatment is more than 4 times greater than that of Ni-Co-SiC composite coating without pretreatment, that is, the Ni-Co-SiC composite coating prepared by pretreatment has better corrosion resistance. As is observed in Figure 4. the pretreatment of PEI and SiC particles can effectively disperse the agglomerated SiC and further refine the grain size of the composite coating. Furthermore, the corrosion resistance is better.

Table 5. Equivalent circuit fitting parameters of Ni-Co-SiC composite coatings with different procedures.

Coating Conditions	R_P (ohm)	C_d (10^{-5} F)
Without pretreatment	5126	5.120
pretreatment	21,558	4.624

4. Conclusions

1. When the PEI concentration was 0.06 g/L, the coating was flat and dense. The dispersion of SiC nanoparticles in the coating was the best, the grain size in the Ni-Co-SiC composite coating was smaller.
2. With the increase in PEI concentration, the hardness and corrosion resistance of Ni-Co-SiC composite coatings showed a trend of first increasing and then decreasing. When the PEI concentration was 0.06 g/L, the hardness and corrosion resistance of Ni-Co-SiC composite coating was the best.
3. When the PEI concentration was increased by an order of magnitude to 0.6 g/L, the microscopic morphology of the Ni-Co-SiC composite coating changed from the original cone to an ellipsoid with unclear edges, and obvious cracks occurred on the surface of the coating. The grain in the coating became larger, and the agglomeration of nano-SiC particles was obvious. The hardness and corrosion resistance of Ni-Co-SiC composite coatings were not improved with the increase of PEI concentration by an order of magnitude.
4. Compared with the Ni-Co-SiC composite coating prepared without pretreatment, the Ni-Co-SiC composite coating prepared by pretreatment was denser and uniform, the hardness of the composite coating was increased by 119.26 Hv, and the corrosion resistance also improved.

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References

1. Mousavi, S.M.A.; Pitchumani, R. A study of corrosion on electrodeposited superhydrophobic copper surfaces. *Corros. Sci.* **2021**, *186*, 109420. [CrossRef]
2. Wang, L.; Lu, J.L.; Liu, K.; He, L.; Zheng, Q.; Luo, X. Effect of Electrodeposition Method on Properties of Ni-SiC Nanocomposite Coatings. *Surf. Technol.* **2017**, *46*, 180–184.
3. Raghavendra, C.R.; Basavarajappa, S.; Sogalad, I.; Naik, K.; Karthik, K.Y. Study on Ni composite coating on Al6061 substrate material with different nano particle reinforcement by electrodeposition process. *Mater. Today Proc.* **2020**, *24*, 1680–1685. [CrossRef]
4. Noorbakhsh Nezhad, A.H.; Mohammadi Zahrani, E.; Alfantazi, A.M. Erosion-corrosion of electrodeposited superhydrophobic Ni-Al_2O_3 nanocomposite coatings under jet saline-sand slurry impingement. *Corros. Sci.* **2022**, *197*, 110095. [CrossRef]
5. Masoumi Balashadehi, M.; Nourpour, P.; Sabour Rouh Aghdam, A.; Allahyarzadeha, M.H.; Heydarzadeh, A.; Hamdi, M. The formation, microstructure and hot corrosion behaviour of slurry aluminide coating modified by Ni/Ni-Co electrodeposited layer on Ni-base superalloy. *Surf. Coat. Technol.* **2020**, *402*, 126–283. [CrossRef]
6. Liu, Y.; Liu, Y.; Gao, Y.; Dong, C.; Wang, S. Microstructure and Properties of Ni-Co Composite Cladding Coating on Mould Copper Plate. *Materials* **2019**, *12*, 2782. [CrossRef] [PubMed]
7. Karimzadeh, A.; Aliofkhazraei, M.; Walsh, F. A review of electrodeposited Ni-Co alloy and composite coatings: Microstructure, properties and applications. *Surf. Coat. Technol.* **2019**, *372*, 463–498. [CrossRef]
8. Gorospe, A.E.; Balela, M.D.L. Ni-Co nanocomposites deposited on carbon fiber paper as an electrocatalyst towards hydrogen evolution reaction. *Mater. Today Proc.* **2020**, *22*, 255–261. [CrossRef]
9. Feng, J.W.; Zhou, Q. Effect of Different Co contents on Structure of Nanoporous Ni-Co and Catalytic Performance of Hydrogen Evolution. *Chin. J. Inorg. Chem.* **2019**, *35*, 1746–1754.
10. Huang, P.C.; Hou, K.H.; Hong, J.J.; Lin, M.H.; Wang, G.L. Study of fabrication and wear properties of Ni–SiC composite coatings on A356 aluminum alloy. *Wear* **2021**, *477*, 203772. [CrossRef]
11. Bakhit, B.; Akbari, A.; Nasirpouri, F.; Hosseini, M.G. Corrosion resistance of Ni–Co alloy and Ni–Co/SiC nanocomposite coatings electrodeposited by sediment codeposition technique. *Appl. Surf. Sci.* **2014**, *307*, 351–359. [CrossRef]

12. Dheeraj, P.R.; Patra, A.; Sengupta, S.; Das, S.; Das, K. Synergistic effect of peak current density and nature of surfactant on microstructure, mechanical and electrochemical properties of pulsed electrodeposited Ni-Co-SiC nanocomposites. *J. Alloys Compd.* **2017**, *729*, 1093–1107. [CrossRef]
13. Babu, C.V.; Ramji, K. Influence of SiC Nano Particles on Microhardness and Corrosion Resistance of Electroless Ni-P Coatings. *J. Bio Tribo Corros.* **2018**, *4*, 1–8.
14. Liu, J.H.; Liu, Y.D.; Pei, Z.L.; Li, W.H.; Shi, W.B.; Gong, J.; Sun, C. Influence of particle size and content on the friction and wear behaviors of as-annealed Ni–Mo/diamond composite coatings. *Wear* **2020**, *452–453*, 203300. [CrossRef]
15. Walsh, F.C.; Low CT, J.; Bello, J.O. Influence of surfactants on electrodeposition of a Ni-nanoparticulate SiC composite coating. *Trans. IMF* **2015**, *93*, 147–156. [CrossRef]
16. Song, Y.T.; Min, M.; Yi, Y.; Zhao, T.; Zhang, X.; Li, Z.L. Effect of Surfactant on Properties of Electrodeposited Ni-P-Al_2O_3 Coatings. *Mater. Prot.* **2018**, *51*, 66–69.
17. Rouhollahi, A.; Fazlolahzadeh, O.; Dolati, A.; Ghahramanifard, F. Effects of different surfactants on the silica content and characterization of Ni–SiO_2 nanocomposites. *J. Nanostruct. Chem.* **2018**, *8*, 139–152. [CrossRef]
18. Baghal, S.L.; Amadeh, A.; Sohi, M.H.; Hadavi, S.M.M. The effect of SDS surfactant on tensile properties of electrodeposited Ni–Co/SiC nanocomposites. *Mater. Sci. Eng. A* **2013**, *559*, 583–590. [CrossRef]
19. Kan, H.M.; Meng, Y.Y.; Ramana, G.R.J. Influence of particle size and surfactants on uniformity and quantity of silicon carbide particles in electrodeposited nickel-silicon carbide coatings. *Cent. South Univ.* **2021**, *28*, 1627–1636. [CrossRef]
20. Zhang, W.L.; Wang, Y.; Sun, D.B.; Li, H.Q. Study on dispersion effect of some surfactants upon Ni-P-SiC amorphous composite electroplating. *Electroplat. Finish.* **2006**, *25*, 4–7.

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