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Abstract: In this study, using 45# carbon steel as the substrate, a first experimental analysis was carried out on the polarisation behaviour of different component wattage plating solutions in order to determine the reasonable content of nanodiamond particles in a nickel/nanodiamond composite plating solution. Secondly, the effect of double-pulse forward and reverse duty cycle and reverse working time on the performance of nickel/nanodiamond composite plating was then investigated by testing the thickness, hardness and surface roughness of the composite plating and observing the surface micromorphology. The experimental results show that, when the content of nanodiamond particles in the plating solution is 5 g/L, the anti-pulse working time, forward and reverse pulse duty cycle of the double-pulse plating parameters are 20 ms, 0.3 and 0.2, respectively, and the composite plating layer prepared by double pulse has good comprehensive performance. This research work provides technical support for the optimisation of process parameters for the preparation of nickel/nanodiamond composite coatings by double-pulse electrodeposition.

Keywords: double-pulse electrodeposition; optimisation of process parameters; composite coatings performance; nanodiamond particles

1. Introduction

Compared to the ordinary composite coating, nanocomposite coating improves hardness, abrasion resistance and friction reduction. It is an attractive candidate for next-generation coating systems [1,2]. Nickel metal, as the most commonly used protective coating material, possesses high ductility, corrosion resistance and chemical stability, which has been studied by many researchers [3–5]. Researchers are paying more and more attention to Ni matrix reinforced with nanoparticles, especially nanodiamond particles [6–8]. Unique mechanical and tribological properties, including high hardness and a low friction coefficient of ultra-fine nanodiamond powders, have caused researchers to conduct further investigations into their utilisation as coatings and as composite coatings. There are various methods of preparing deposits by the electrodeposition process, which, according to the deposition principle, can be divided into anodic electrodeposition and cathodic electrodeposition. Depending on the operating conditions of the electroplating power supply, electrodeposition can be classified as DC electrodeposition, pulsed electrodeposition, jet electrodeposition, ultrasonic electrodeposition, etc. Among them, DC electrodeposition and pulsed electrodeposition are more frequently used in production practice and have been widely used in precision instruments, electronic components, semiconductor nano-array preparation, etc. [9–16]. The electrodeposition process has two processes: nucleation and crystal growth, which directly affect the microscopic morphology and properties of the deposit. When using DC electrodeposition to prepare deposits, the cations in the cathode area are constantly depleted and the ion concentration is not compensated in time. The result is a certain gradient of concentration of cations and solutions in the cathode area.
The surface of the prepared deposits is not homogeneous and hydrogen precipitates easily on the cathode, resulting in many defects on the deposited surface, such as hydrogen embrittlement, pitting, blistering, etc. During pulsed electrodeposition, the concentration of particles in the vicinity of the cathode can be changed due to the periodic pulsed current [17,18]. During the preparation of a coating by pulsed electrodeposition, the interval between pulses inhibits the growth of the coating grains and controls the growth trend of the deposit, thus avoiding the appearance of coarse grains and resulting in a finer grain size in the deposit than that prepared using DC electrodeposition. Pulsed power currents for pulsed electrodeposition are available in a variety of waveforms, including rectangular, sinusoidal half-wave, sawtooth and intermittent americium waves. Rectangular pulses are usually chosen for double-pulse preparation of metal coatings. In addition, the pulsed electrodeposition preparation process has three independent parameters, namely pulse current density ($I_p$), pulse on time ($T_{on}$) and pulse off time ($T_{off}$). During the pulsed electrodeposition process, the properties of the prepared deposits are affected to varying degrees as the three separate parameters are adjusted. Double-pulse electrodeposition is the introduction of a reverse pulse current after the output of a forward pulse current. During the forward pulse operation of pulsed electrodeposition, the metal ions in the plating solution are deposited onto the base metal, and the reverse pulse operation dissolves the metal already plated on the base metal. This allows the uneven distribution of plating thickness to be improved and at the same time the plating thickening to be reduced. Therefore, the forward pulse working time in pulsed electrodeposition is greater than the reverse working time.

The main parameters of the pulsed electrodeposition process include the forward and reverse average current density, the forward and reverse duty cycle, the forward and reverse operating time and the pulse frequency. In this study, 45# steel was used as the substrate and the polarisation behaviour of the plating solution containing nanodiamond particles was first analysed to determine the reasonable content of nanodiamond particles in the plating solution. On the basis of this work, the hardness, thickness and surface morphology of the plated layers were measured and the effect of the process parameters of the double pulses, such as forward and reverse duty cycle and forward and reverse working time, on the deposited nickel/nanodiamond composite coatings was experimentally investigated. The aim is to find the best process route for the preparation of high-strength nickel-nanodiamond composite coatings by pulsed electrodeposition and to provide technical support for further research.

2. Experimental Preparation
2.1. Substrate Selection and Pre-Treatment

The substrate specimen size was 60 mm $\times$ 15 mm $\times$ 3 mm and the plating area on the substrate was 20 mm $\times$ 15 mm. The dark part in the middle of the electroplating region in Figure 1 is the measurement region, with an area of 10 mm $\times$ 5 mm. The pre-treatment of the specimen was: rough grinding of the sample pre-plating area with corundum wheels of 60# and 80#, then fine grinding of the surface with sponge wheels of 300# and 800# grit, followed by chemical degreasing of the surface, distilled water washing and blowing dry.

![Figure 1](image-url)

**Figure 1.** The 45 carbon steel substrate specification diagram: (a) electroplated surface, and (b) non-electroplated surface.
2.2. Analysis of the Polarisation Behaviour of Nanodiamond Particles in Plating Solutions

The polarisation behaviour in composite plating solutions containing nanodiamond particles were analysed by using a three-electrode, two-loop system. As shown in Figure 2, the study electrode was 45 carbon steel, the auxiliary electrode was a nickel plate and the reference electrode was a saturated glycol electrode. The electrolyte was a watt nickel plating solution with the addition of diamond and the reference electrode was placed in a saturated potassium chloride solution system. The two systems were connected by a salt bridge with a Rugin capillary biased towards the research electrode end. The test conditions were: starting from an open circuit potential, a scanning speed of 1 mV/s and an end-point potential of −1.6 V. With reference to the literature [19–23], the following plating process parameters were selected: bath temperature 40 °C, pH 4.2, current density 3 A/dm², stirring speed 10 r/min and plating time of 45 min. Nanodiamond concentrations in the plating solution were 1, 5, 10 and 50 g/L, respectively. The instrumentation required for electrochemical testing included: CHI660E Electrochemical Workstation from Beijing Huake Putian Technology Co. (Beijing, China), DF-101S Collective Heating Magnetic Stirrer from Gongyi Yuhua Instruments Co. (Gongyi, China) and CHI150 reference electrode (saturated glycerol electrode) from Tianjin Aida Hensheng Technology Development Co. (Tianjin, China).

![Figure 2. Schematic diagram of the three-electrode system.](image)

2.3. Selection of Parameters for Double-Pulse Electrodeposition

Existing research shows that the forward and reverse pulse parameters affect the crystallinity, deposition rate, thickness distribution, impurity content, etc. in double-pulse electrodeposition [24,25]. When the average current in the forward direction is constant, as the duty cycle of the forward pulse decreases, the impurity content in the coating decreases and the grain size gradually becomes smaller. When the coating thickness distribution increases with the reverse duty cycle, the deposition rate is slower. After analysing and comparing the effect of duty cycle on the plating properties prepared by double-pulse electrodeposition, the duty cycle of positive and negative pulses is usually chosen to be 10%–30%. In general, the average current of the forward pulse is chosen to be equal to or slightly greater than the current of the DC plating, and the peak current of the reverse pulse is equal to or greater than the peak current of the forward pulse when preparing the plating in double pulses. For this experiment, the average current of the forward pulse was chosen to be equal to the current of the DC plating and the peak current of the reverse pulse was 1.45 times the peak current of the forward pulse. The value was determined to meet the requirement that the peak forward pulse current was less than or equal to the peak reverse pulse current, and also to meet the projected average reverse current, which met the requirements for the accuracy of the pulse power setting used in the experiment.
This experimental study focuses on the preparation of composite coatings by double-pulse plating by varying the forward duty cycle, reverse duty cycle and the working time of the reverse pulse, with the specific process parameters shown in Table 1.

Table 1. Selection of process parameters for double-pulse electrodeposition.

| Sample Number | Average Current/A | Working Time/ms | Duty Cycle |
|---------------|------------------|-----------------|------------|
|               | Positive Direction | Reverse Direction | Positive Direction | Reverse Direction | Positive Direction | Reverse Direction |
| 1             | 0.14             | 0.01            | 100         | 10           | 0.2               | 0.1               |
| 2             | 0.14             | 0.01            | 100         | 10           | 0.2               | 0.1               |
| 3             | 0.14             | 0.01            | 100         | 13           | 0.2               | 0.1               |
| 4             | 0.14             | 0.02            | 100         | 20           | 0.2               | 0.2               |
| 5             | 0.14             | 0.02            | 100         | 10           | 0.2               | 0.1               |
| 6             | 0.14             | 0.03            | 100         | 13           | 0.2               | 0.2               |
| 7             | 0.14             | 0.04            | 100         | 20           | 0.2               | 0.2               |
| 8             | 0.14             | 0.03            | 100         | 10           | 0.2               | 0.3               |
| 9             | 0.14             | 0.04            | 100         | 13           | 0.2               | 0.3               |
| 10            | 0.14             | 0.06            | 100         | 20           | 0.2               | 0.3               |
| 11            | 0.14             | 0.02            | 100         | 10           | 0.1               | 0.1               |
| 12            | 0.14             | 0.03            | 100         | 13           | 0.1               | 0.1               |
| 13            | 0.14             | 0.04            | 100         | 20           | 0.1               | 0.1               |
| 14            | 0.14             | 0.04            | 100         | 10           | 0.1               | 0.2               |
| 15            | 0.14             | 0.05            | 100         | 13           | 0.1               | 0.2               |
| 16            | 0.14             | 0.08            | 100         | 20           | 0.1               | 0.2               |
| 17            | 0.14             | 0.06            | 100         | 10           | 0.1               | 0.3               |
| 18            | 0.14             | 0.08            | 100         | 13           | 0.1               | 0.3               |
| 19            | 0.14             | 0.12            | 100         | 20           | 0.1               | 0.3               |
| 20            | 0.14             | 0.01            | 100         | 10           | 0.3               | 0.1               |
| 21            | 0.14             | 0.02            | 100         | 13           | 0.3               | 0.1               |
| 22            | 0.14             | 0.01            | 100         | 20           | 0.3               | 0.1               |
| 23            | 0.14             | 0.01            | 100         | 10           | 0.3               | 0.2               |
| 24            | 0.14             | 0.02            | 100         | 13           | 0.3               | 0.2               |
| 25            | 0.14             | 0.03            | 100         | 20           | 0.3               | 0.2               |
| 26            | 0.14             | 0.02            | 100         | 10           | 0.3               | 0.3               |
| 27            | 0.14             | 0.03            | 100         | 13           | 0.3               | 0.3               |
| 28            | 0.14             | 0.04            | 100         | 20           | 0.3               | 0.3               |

2.4. Components of the Compound Plating Solution

The chemical preparation was produced by Tianjin Guangfu Fine Chemical Research Institute, including nickel chloride (NiCl₂·6H₂O) 15 g/L, nickel sulphate (NiSO₄·6H₂O) 240 g/L, boric acid (H₃BO₃) 30 g/L, sodium dodecyl sulphonate (CH₃(CH₂)₁₀CH₂-OSO₃Na) 0.1 g/L and nanodiamond particles. Figure 3 shows a diagram of the pulse plating reaction unit.

![Diagram of the pulse plating reaction unit](image-url)
2.5. Testing of Plating Properties

The thickness of the coating was measured using a JDG-S2 digital vertical optical meter from Shanghai Optical Instrument Factory with a minimum display value of 0.1 µm, testing accuracy of 0.3 µm. Plated surface roughness measurement was carried out with a Harbin Gauge & Cutting Tools Group’s Surface Profile Gauge 2302A. The grain and surface morphology of the composite coating were observed using a ZEISS Sigma 300 scanning electron microscope. Plating hardness was tested by using the DUH-W201 micro hardness tester. The hardness test parameters were: a loading time of 15 s, a load of 490 mN and a loading speed of 14 mN/s. The final composite thickness and hardness values were averaged from 5 measurements.

3. Results and Analysis

3.1. Analysis of the Cathodic Polarisation Behaviour of Plating Solutions Containing Nanodiamond Particles

The evaluation of the plating properties such as the crystalline fineness, brightness, levelling and dispersion of the plating are all related to the polarisation behaviour. By analysing the cathodic polarisation behaviour of the particles in the plating solution, the influence of the electrodeposition process conditions on the coating properties was theoretically analysed, and the optimal process parameters were determined as a result. Figure 4 shows the cathodic polarisation curves for the three wattage plating solutions mentioned earlier, including those without dispersant, those with dispersant and those with different levels of nanodiamond particles.

According to Figure 4, nickel deposition currents in solutions containing diamond nanoparticles were low when the cathodic potential was between –0.5 and –0.85 V, indicating that significant reduction of Ni²⁺ had not begun. When the voltage was negative to –0.85 V, the reduction of Ni²⁺ accelerated and the current rose significantly as the voltage continued to decrease. Comparing curves 1 and 2 in Figure 4, the addition of dispersant sodium dodecyl sulphate caused a significant increase in the polarisation of the Ni²⁺ cathodic reduction process, which was due to the addition of sodium dodecyl sulphate adsorbed on the electrode surface, hindering the reduction of Ni²⁺ and thus increasing the degree of cathodic polarisation. Comparison of curves 2 and 3 in Figure 4 shows that the polarisation of the Ni²⁺ cathodic reduction process was reduced by the addition of nanodiamond particles. This was due to the fact that the dispersant sodium dodecyl sulphate used in the plating solution improved the wettability and surface charged polarity of the nanodiamond particles, acted as a spatial site barrier, hindered the agglomeration of the nanodiamond particles and maintained the dispersion of the nanodiamond particles, making them conducive to migration transfer to the cathode and capture by the cathode surface. When nanodiamond particles were added to the plating solution, a portion of the
dispersant should have been adsorbed on the surface of the nanodiamond particles, making them less of an impediment to Ni\(^{2+}\) reduction, which in turn would lead to a reduction in cathodic polarisation. As the amount of nanodiamond particles added increased, more of the dispersant sodium dodecyl sulphate would be adsorbed onto the surface of the nanodiamond particles, improving the dispersion of the nanodiamond in the plating solution and thus reducing the hindering effect of the dispersant sodium dodecyl sulphate on the reduction of Ni\(^{2+}\). Thus, the degree of cathodic polarisation of curves 3, 4 and 5 in Figure 4 decreased with increasing nanodiamond concentration. When the concentration of nanodiamond particles was further increased, the adsorption of the dispersant sodium dodecyl sulphate on the nanodiamond reached saturation, making its hindering effect on the reduction of Ni\(^{2+}\) manifest again. Based on the test results, a reasonable content of 5 g/L of nanodiamond particles in the composite plating has been determined here.

3.2. Effect of Different Deposition Methods on the Morphology of Composite Coatings

According to the above study, and also with reference to the literature [16,17], the appropriate amounts of dispersant sodium dodecyl sulphonate and nanodiamond particles with a content of 5 g/L were added to the watt plating solution. The nickel/nanodiamond composite plating was prepared by plating power supply with DC, single and double pulses respectively, and other plating parameters are the same. Figures 5 and 6 show the microscopic morphology of the nickel/nanodiamond composite coating obtained using SEM at different magnifications, respectively, with Figure 6 showing the morphology of the green box in Figure 5 at 50,000 times magnification.

![Figure 5. Cont.](image-url)
According to Figures 5 and 6, the surface grain shape of the composite layer prepared by using different plating methods during plating was different, where the surface grain of the plated layer obtained by pulse plating was spherical, while the grain size of the composite layer prepared by double pulse was finer. The surface morphology of the composite layer prepared by pulse plating was better than that prepared with DC plating conditions under the same conditions of other plating parameters, while the surface grains of the composite layer prepared by double-pulse plating were finer and flatter compared to single-pulse plating. In double-pulse electrodeposition for the preparation of coatings, the energisation and de-energisation were alternated. In double-pulse plating, Ni/nanodiamond particles were deposited on the cathode to form the layer when the positive current was applied, while when the reverse current was applied, the anodic oxidation of the layer dissolved and the dissolution occurred preferentially on the raised parts of the layer. The reverse current flow in double-pulse plating had a levelling effect on the surface of the plated layer, which helps to improve the microscopic morphology of the plated layer, resulting in smaller and more uniformly distributed crystalline particles and a denser microstructure.
3.3. The Effect of Reverse Working Time on the Properties of Composite Plating

In order to further optimise the double-pulse electrodeposition parameters, this study experimentally investigates the effect of forward and reverse duty cycle and reverse working time on the performance of the composite coating. Firstly, the effect of reverse working time on the performance of the composite plating prepared by double-pulse plating was studied. The same plating parameters were chosen as follows: the forward and reverse duty cycle was 0.2, the average forward current was 0.1395 A and the working time was 100 ms. In order to prevent the reverse working time from dissolving the layer due to the excess of the reverse working time in double-pulse plating, the forward working time was generally chosen to be 5–10 times the reverse working time. In this experiment, the forward working time was chosen to be 5, 7.5 and 10 times the reverse working time, and the reverse working time rotation was 20, 13 and 10 ms, respectively. The measured layer thickness, hardness and roughness results are listed in Table 2, and all results were the average of five measured point data.
Table 2. Results of the effect of changes in reverse working time on the properties of composite plating.

| Reverse Working Time/ms | Thickness/mm | Hardness/kgf·mm² | Roughness/µm |
|-------------------------|--------------|------------------|--------------|
| 10                      | 0.2589       | 269              | 1.509        |
| 13                      | 0.3374       | 285              | 1.791        |
| 20                      | 0.1944       | 291              | 1.423        |

The reverse work during double-pulse plating was the process by which the plated projections were dissolved. Theoretically, the longer the reverse working time, the thinner the prepared layer, the smoother the surface and the denser the layer organisation. Table 2 shows that with a reverse working time of 20 ms, the final layer prepared, 0.1944 mm, had the greatest hardness, the smallest surface roughness $Ra$ and the smoothest surface.

Figure 7 shows the microscopic morphology of the composite layer prepared by using three different reverse working times during double-pulse plating. As observed in Figure 7, the surface grains of the prepared composite layer were coarse when the reverse working time was selected as 10 ms during the double-pulse plating. Compared with 10 ms and 13 ms, the surface grains of the composite layer prepared when the reverse working time was 20 ms were denser and more uniform, and the surface was flatter and smoother, which was consistent with the above surface roughness test results. The comprehensive analysis concluded that the overall performance of the plated layer was better when the reverse working time of 20 ms was selected for double-pulse plating.

Figure 7. Cont.
3.4. Effect of Reverse Duty Cycle on the Performance of Composite Coatings

The effect of different reverse duty cycles on the performance of the composite plating during double-pulse plating was investigated here. The same plating parameters were chosen as follows: forward duty cycle 0.2, reverse working time 20 ms, forward average current 0.1395 A and forward working time 100 ms. The reverse duty cycles chosen were 0.1, 0.2 and 0.3. The measured thickness, hardness and surface roughness of the composite plated layers are listed in Table 3 and all results were the average of five replicates.

| Reverse Duty Cycle | Thickness/mm | Hardness/kgf·mm⁻² | Roughness/µm |
|--------------------|--------------|--------------------|--------------|
| 0.1                | 0.3018       | 279                | 1.942        |
| 0.2                | 0.1944       | 291                | 1.423        |
| 0.3                | 0.118        | 275                | 0.85         |

As the plating process proceeds, along with the continuous deposition of nickel ions, the content of embedded nanodiamond particles in the prepared composite coating increased and the hardness of the coating increased. However, in double-pulse plating, as the reverse duty cycle increased, the reverse average current also increased, causing more of the prepared composite layer to dissolve off the projections. As a result, the thickness of the layer was reduced, but the layer crystalline grains were fine and uniform with a smooth surface. When the reverse duty cycle in the double-pulse plating parameters was greater than 0.2, the average reverse current was higher, resulting in the dissolution of the nanodiamond particles embedded in the protruding part of the composite plating solution. This made the composite layer less hard. When the reverse duty cycle of the double-pulse plating parameter was chosen to be 0.2, the overall performance of the plating was better. Figure 8 shows the microscopic morphology of the composite layer prepared by selecting different reverse duty cycle parameters in double-pulse plating. According to the analysis of Figure 8, the surface of the composite layer prepared with the reverse duty cycle parameter of 0.2 during double-pulse plating was relatively smooth and the grain size was uniform, which was consistent with the above surface roughness test results.

Figure 7. Micrographs of composite coatings prepared by different reverse working times (×5000): (a) 10 ms, (b) 13 ms, (c) 20 ms.

Table 3. Results of the effect of reverse duty cycle on plating properties.
3.5. Effect of Forward Duty Cycle on the Performance of Composite Plating

In this part, the influence of the forward duty cycle in double-pulse plating on the performance of the composite layer was investigated, and the forward duty cycle parameters were chosen as 0.1, 0.2 and 0.3, respectively. The same plating parameters were chosen as follows: reverse duty cycle of 0.2, reverse working time of 20 ms, forward average current of 0.1395 A and working time of 100 ms. The measured thickness, hardness and surface roughness of the composite plating are listed in Table 4 and all results were averaged over five tests.
Table 4. Results of the effect of forward duty cycle on the performance of composite plating.

| Forward Duty Cycle | Thickness/mm | Hardness/kgf mm⁻² | Roughness/µm |
|--------------------|--------------|-------------------|--------------|
| 0.1                | 0.1064       | 444               | 1.075        |
| 0.2                | 0.1565       | 297               | 1.865        |
| 0.3                | 0.0394       | 569               | 1.755        |

During double-pulse plating, as the value of the forward duty cycle became larger, the current off time during plating was reduced. The plating solution was well replenished with nickel ions and the forward deposition rate became faster. As a result, the thickness of the prepared composite layer increased continuously. However, the degree of polarisation of the nickel ion concentration also increased, increasing side reactions and reducing current efficiency, resulting in a less dense nickel layer and a rougher and less hard surface. The maximum hardness of the plated layer was 569 kgf mm⁻² with a surface roughness Ra of 1.755 µm, which may be related to the nanodiamond particles embedded in the surface of the plated layer, an issue to be further investigated. The microscopic morphology of the composite layer prepared by selecting different forward duty cycles during double-pulse plating is shown in Figure 9. In terms of surface smoothness, the surfaces of the composite coatings prepared by double-pulse plating under the three conditions were relatively close to each other and were consistent with the surface roughness test results above. However, a comprehensive analysis of the hardness, thickness and surface morphology of the plated layer showed that the composite layer prepared with a value of 0.3 for the forward duty cycle had a better overall performance.

Figure 9. Cont.
Figure 9. Micrographs of composite coatings prepared by different forward duty cycles (×2000): (a) 0.1, (b) 0.2, (c) 0.3.

4. Conclusions

A pulsed electrodeposition method was used to prepare a nickel/nanodiamond composite plating on a 45# steel substrate. The effect of forward and reverse duty cycle and reverse working time on the plating performance during double-pulse plating was experimentally studied. Based on testing the thickness, surface roughness and hardness of the composite coating, as well as analysing the surface micromorphology of the composite coating, the following conclusions were obtained: (1) in double-pulse plating, when the forward and reverse duty cycles were constant, the thickness and surface roughness of the composite layer increased and then decreased with the increase in the reverse working time. When the reverse working time was 20 ms, the overall performance of the composite layer was better. (2) When the reverse working time and forward duty cycle remained unchanged, the thickness and surface roughness of the composite coating showed a decreasing trend as the reverse duty cycle increased. When the reverse duty cycle was 0.2, the composite coating performance was better. (3) When the reverse working time and the reverse duty cycle were unchanged, with the increase in the forward duty cycle, the thickness of the composite coating showed a trend of first increasing and then decreasing, while the hardness of the composite coating showed the opposite trend, and the surface roughness of the composite coating did not change much. When the forward duty cycle was 0.3, the performance of the composite layer was better. The optimised double-pulse electrodeposition parameters have been explored. The process will be researched deeply and will be applied to actual production such as of bearings and cylinders [26–28].

Author Contributions: Conceptualization, D.W. and M.L.; methodology, F.L.; validation, D.W., M.L. and F.L.; formal analysis, M.L.; investigation, D.W.; resources, F.L.; data curation, Y.Z.; writing—original draft preparation, M.L.; writing—review and editing, D.W.; visualization, D.W.; supervision, D.W.; project administration, F.L.; funding acquisition, M.L. All authors have read and agreed to the published version of the manuscript.

Funding: The authors gratefully acknowledge the Tianjin Municipal Science and Technology Bureau (No. 20YDTPJC00080) for financial support of this research work.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Sørensen, P.; Kill, S.; Johansen, D.K.; Weinell, C. Anticorrosive coating: A review. J. Coat. Technol. 2009, 6, 135–176. [CrossRef]
2. Müller, K.; Bugnicourt, E.; Latorre, M.; Jorda, M.; Sanz, Y.E.; Lagaron, J.M. Review on the processing and properties of nanocomposites and nanocoating and their applications in the packing, automotive and solar energy fields. Nanomaterials 2017, 7, 74. [CrossRef]
3. Mariello, M.; Guido, F.; Mastronardi, V.M.; Giannuzzi, R.; Algieri, L.; Qualteri, A.; Maffezzoli, A.; De Vittorio, M. Reliability of Protective Coatings for Flexible Piezoelectric Transducers in Aqueous Environments. *Microachines* 2019, 10, 739. [CrossRef]

4. Bao, W.; Deng, Z.; Zhang, S.; Ji, Z.; Zhang, H. Next-Generation Composite Coating System: Nanocoating. *Front. Mater.* 2019, 6, 72. [CrossRef]

5. Safavi, M.S.; Rasooli, A. Ni-P-TiO₂ nanocomposite coatings with uniformly dispersed Ni₃Ti intermetallics: Effects of current density and post heat treatment. *Surf. Coat. Technol.* 2019, 372, 252–259. [CrossRef]

6. Abdoli, M.; Rouhaghdam, A.S. Preparation and characterization of Ni–P/nanodiamond coatings: Effects of surfactants. *Diam. Relat. Mater.* 2012, 31, 30–37. [CrossRef]

7. Sajjadnejad, M.; Omidvar, H.; Javanbakht, M.; Mozafari, A. Textural and structural evolution of pulse electrodeposited Ni/diamond nanocomposite coatings. *J. Alloys Compd.* 2017, 704, 809–817. [CrossRef]

8. Ogihara, H.; Safuan, M.; Saji, T. Effect of electrodeposition conditions on hardness of Ni–B/diamond composite films. *Surf. Coatings Technol.* 2012, 212, 180–184. [CrossRef]

9. Deng, S.-H.; Gong, Z.-Q.; Chen, W.-G. Research status and development of nano-material electrodeposition. *Electropl. Finish.* 2001, 30, 35–39. (In Chinese)

10. Li, L.; Yang, Y.W.; Huang, X.H.; Li, G.; Zhang, L. Pulsed electrodeposition of single-crystalline Bi₂Te₃ nanowire arrays. *Nanotechnology* 2006, 17, 1706–1712. [CrossRef]

11. He, X.K.; Chen, B.Z.; Wu, L.Y.; Li, X.D.; He, Q.G. Process of pulse electrodeposition of nanocrystalline Ni-Cr alloy from trivalent chromium bath. *Chin. J. Nonferrous Met.* 2006, 16, 1281–1287.

12. Xiang, G.-P.; Zhou, E.-B. Study of Ni-Co Alloy Pulse-Plating. *Electropl. Finish.* 1994, 13, 18–22.

13. Xie, J.-L.; Zhu, H.-F. Research of Pulse Plating Gold Process Technology. *Microelectron. Comput.* 1999, 22, 21–23.

14. Shivagan, D.D.; Shirage, P.M.; Pawar, S.H. Studies on the fabrication of Ag/Hg₁Ba₂Ca₁Cu₂O₆ + &/CdSe heterostructures using the pulse electrodeposition technique. *Semicond. Sci. Technol.* 2004, 19, 323–330.

15. Yin, Y.-T. Research and application of pulse power supply in local high-speed silver plating process. *Microelectron. Technol.* 2001, 29, 58–59.

16. Yang, F.Z.; Xu, S.; Yao, S.; Chen, B.; Zheng, X.; Zhong, X.; Zhou, S. A Study on the Elect rodeposition of Palladium and it’s Nucleation. *Electrochemistry* 1997, 3, 103–108.

17. Xu, J.-X.; Jiang, L.-H.; Liu, D.-Z.; Chen, S.-Y.; Feng, W.-S. Effect of Average Electric Current Density on Deposition Rate and Appearance of Structure of Pulse Electrodeposited Fe Coating. *J. Mater. Prot.* 2006, 39, 13–15.

18. Xiang, G. *Theory and Application of Pulse Electroplating*; Tianjin Science and Technology Press: Tianjin, China, 1989; pp. 13–14.

19. Liu, M.; Zhao, Y.; Meng, Y.; Li, F.-H.; Gong, Y.-I.; Feng, L. Morphology and Mechanial Properties of Ni/Nano-Diamond Composite Coatings Prepared at Different Current Density in Different Nano-Diamond Concentrations. *J. Mater. Prot.* 2016, 1, 1–6.

20. Liu, M.; Liu, H.; Wang, D.; Chu, Y.; Li, F.; Liu, S. Influence of Electrodeposition Parameters on Properties of Ni-Nanometer Diamond Composite Coating. *J. Mater. Prot.* 2018, 1, 62–66.

21. Liu, M.; Wang, D.; Han, H.; Shi, Y.; Liu, B.; Li, F.; Gong, Y.; Zhang, W. Study on Optimization Technology to Strengthen Ni-Based Composite Coating Electroplate Containing Nanodiamond. *Materials* 2019, 12, 1654. [CrossRef] [PubMed]

22. Liu, M.; Liu, H.; Wang, D.; Liu, B.; Shi, Y.; Li, F.; Gong, Y.; Li, L.; Li, L.; Zhang, W. Effect of Nanodiamond Concentration and the Current Density of the Electrolyte on the Texture and Mechanical Properties of Ni/Nanodiamond Composite Coatings Produced by Electrodeposition. *Materials* 2019, 11, 1105. [CrossRef]

23. Zhao, Y.; Liu, M.; Feng, L.; Meng, Y.; Li, F.-H.; Chen, Z. Optimization of Technology for Electro-deposition of Nickel Coating on Q235A Steel Substrate. *J. Mater. Prot.* 2014, 37, 33–36.

24. Wang, Y.; Yuan, X.-T.; Yu, H.-Y.; Sun, D.-B.; Li, H.-Q. Influence of pulse parameters on the micro-structure and microhardness of nickel electrodeposits. *Mater. J. Prot.* 2010, 18, 90–95.

25. Zhang, Z.; Liu, H.; Meng, Q.; Wang, X.; Li, Y.; Yang, H. Effect of Duty Cycle on Ni-Cr-Mn Alloy Coating Prepared by Pulse Electroplating. *Hydrometall. China* 2017, 36, 115–118.

26. Bhuiyan, E.H.; Moreno, S.; Wang, C.; Minary-Jolandan, M. Interconnect Fabrication by Electroless Plating on 3D-Printed Electroplated Patterns. *ACS Appl. Mater. Interfaces* 2021, 13, 19271–19281. [CrossRef] [PubMed]

27. Wang, C.; Bhuiyan, E.H.; Moreno, S.; Minary-Jolandan, M. Direct-Write Printing Copper–Nickel (Cu/ Ni) Alloy with Controlled Composition from a Single Electrolyte Using Co-Electrodeposition. *ACS Appl. Mater. Interfaces* 2020, 12, 18683–18691. [CrossRef] [PubMed]

28. Cao, X.; Xu, L.; Wang, C.; Li, S.; Wu, D.; Shi, Y.; Liu, F.; Xue, X. Electrochemical Behavior and Electrodeposition of Sn Coating from Choline Chloride–Urea Deep Eutectic Solvents. *Coatings* 2020, 10, 1154. [CrossRef]