Jet Electrodeposition of Ni-SiO₂ Nanocomposite Coatings with Online Friction and Its Performance

Yihao Wang, Lida Shen, Mingbo Qiu, Zongjun Tian, Xia Liu, and Wei Zhuo
College of Mechanical and Electrical Engineering, Nanjing University of Aeronautics and Astronautics, 210016 Nanjing, People's Republic of China

To improve the surface quality and performance of Ni-SiO₂ nanocomposite coatings, jet electrodeposition of SiO₂ nanoparticles (diameter 20–30 nm) with Watt's nickel solution was used to process on graphite substrate accompanied by ceramic stick rolling and friction (R&F) online. The crystal structure and microstructure of coatings were analyzed by using X-ray diffraction and field emission scanning electron microscope, respectively. The corrosion resistance of the samples was evaluated by potentiodynamic polarization (Tafel). By studying the influences of different concentrations of SiO₂ in the solution and the effect of R&F on the coatings, we found that adding a certain amount of nano-SiO₂ in the solution can significantly increase the microhardness of coatings (from 550 HV to 627 HV or a 14% increase). R&F further caused the microhardness to reach 711 HV, which is a 20% increase relative to pure Ni coatings. Moreover, R&F can help to remove cellular bulge on the surface of nanocomposite coatings, thereby improving surface quality. The corrosion resistance of Ni-SiO₂ nanocomposite coatings is better than that of pure Ni coatings.

© The Author(s) 2016. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0241610jes] All rights reserved.

Experimental

Experimental device.—The experimental device is shown in Figure 1. The workpiece is fixed in a plating bath with a special fixture as the cathode. Plating solution is pumped into the anode chamber from the plating bath and then injected onto the surface of the workpiece. A nickel stick is inserted through the anode chamber to remove grease through ultrasonic cleaning. Deionized water was used to remove the surface texture and then placed in an alcohol solution to remove the surfactant. Water bath was used to heat the electrolyte at a temperature of 65 ± 5 °C, and the DC power supply output was set at approximately 0.18 A. The distance between the nozzle and the cathode was 1 mm. The flow velocity was calculated as follows:

\[ V = \frac{Q}{A} = \frac{200 \times 10^{-3}}{1 \times 18 \times 10^{-6} \times 3600} = 3.09 \text{ m/s} \]

(Q: flow; A: export cross-sectional area)

Experiment content and parameters.—The electrolyte composition and composite electrodeposition parameters in the experiment are shown in Table II. The diameter of nano-SiO₂ was 20–30 nm (as shown in Figure 3). Two experiments (with or without R&F) were conducted with different SiO₂ concentrations.

Pretreatment.—To conveniently strip the coating for the test, a 30 mm × 15 mm square graphite substrate was selected. The actual area of deposition was 20 mm × 10 mm. Before the experiment, the graphite substrate was polished sequentially with #1–#6 sandpaper to remove the surface texture and then placed in an alcohol solution to remove grease through ultrasonic cleaning. Deionized water was used in the ultrasonic generator to remove residual alcohol and other substances.

Nano-SiO₂ powder was added to the electrolyte, placed in an ultrasonic generator, and oscillated for 60 minutes. A glass rod was used for stirring to scatter the agglomerate powder as much as possible. Water bath was used to heat the electrolyte at a temperature of approximately 50 ± 1 °C, and the DC power supply output was set at approximately 0.18 A. The distance between the nozzle and the cathode was approximately 1 mm while the voltage fluctuated at 28 V. The calculation result of current density was 100 A/dm².

Characterization of Ni-SiO₂ composite coating.—The instruments and parameters for coating characterization are shown in Table III.

In recent years, nanocomposite coating processed by electrodeposition has received widespread attention because it performs better than pure metal coating. In the process of electrodeposition, nanoparticles deposited in the coating as the second phase, thereby improving the performance of the coating. P. Bagheri obtained Ni-TiO₂ nanocomposite coating by using electrodeposition, which greatly improved the wear resistance and corrosion resistance of the coating. Ping Yu improved the high-temperature oxidation resistance of Ni coatings by adding nano-SiO₂ to the solution. Yi Wang obtained a Ni-W-SiO₂ coating by direct electrodeposition, which increased the microhardness by nearly 60 HV but worsened the surface quality.

Ni-based coating is widely used as a protective layer for various mechanical instruments because of its excellent anti-corrosion property, wear resistance, high hardness, and good appearance. Our team has conducted related research on this coating for years. Nano-SiO₂ has a spherical microstructure, which can improve the strength and chemical resistance of materials. However, when nano-SiO₂ are deposited with nickel, the surface will form cellular bulges, which influence the surface quality. Few studies focus on improving the surface quality of Ni-SiO₂ coating. To improve the hardness of Ni-based coated and solve the problem of cellular bulge, this paper proposes the use of jet electrodeposition to process nanocomposite coatings accompanied by ceramic stick rolling and friction (R&F) online. R&F prevents reunited particles from depositing into the coatings and removes surface bulge, thereby improving the quality of the coatings.
Results and Discussion

Surface morphology.—The photos taken by field emission scanning electron microscope are shown in Figure 4. The surface morphology of pure nickel coating (Figure 4a) is smooth and has no obvious surface defects. However, after adding nano-SiO2 particles to the solution (Figure 4b), the surface formed cellular bulges (The bulges is not SiO2 but Ni-coating with some nano-SiO2 embedded) with diameters that ranged from 20–100 μm. With the increase of SiO2 content, the size of the cellular bulge increased. When the concentration of SiO2 reached 10 g/L (Figure 4d), a large number of small cellular bulges increased in size. The morphology also changed, becoming higher and larger than that shown in Figure 4b (4 g/L). This change is due to the increased particle density of SiO2; these particles dispersed in the solution, thereby increasing the number of cellular bulges with SiO2 as nucleation. However, cellular bulges were not removed on time. Thus, nickel deposited on the bulges, thereby causing a point discharge effect. Thus, the cellular bulges grew bigger and became uncontrolled, thereby affecting the surface quality of the coatings.

After introducing the method of mechanical friction, cellular bulges were smoothed by the effect of R&F in a timely manner, leaving behind very small scratch marks, as shown in Figure 5a. Moreover, the surface morphology of coatings greatly improved. But when the content of SiO2 improved, the effect of R&F declined (Figure 5b). The principle of R&F is shown in Figure 6. In the electrodeposition process, the effect of mechanical R&F could smooth the rapidly growing crystal on time, thereby hindering the point discharge. As a result, the

| Table I. Parameters of device. |
|--------------------------------|
| Parameters                  | Value |
| Modulus of elasticity (N/m)  | 200   |
| Spring deformation (mm)      | 0.8   |
| Ceramic weight (g)           | 5.4   |

| Table II. Plating solution composition. |
|----------------------------------------|
| Composition | Content (g/L) | Temperature (°C) | PH | Effect             |
| NiSO4·6H2O  | 280           | 50°C ± 1         | 4 ± 0.1 | Ni source          |
| NiCl2·6H2O  | 40            |                   |     |                   |
| H3BO4       | 5             |                   |     | Adjust PH          |
| Saccharin   | 5             |                   |     | Refined grain      |
| Nano-SiO2   | 0, 2, 4, 6, 8, 10 |                 |     | Second phase       |
Figure 3. Nano-SiO₂.

Table III. Instruments and parameters.

| Characterization          | Instruments(Type) | Parameters                                    |
|---------------------------|-------------------|-----------------------------------------------|
| Surface morphology        | FESEM(S-4800)     |                                               |
| Structure analysis        | XRD (D/max 2500VL/PC) | 20.0/80.0/0.02/12(sec), Cu(40 kV,100 mA):     |
| Microhardness             | Micro-hardness tester (ZHVST-1000D) | Test force 0.98N, autoload                    |
| Corrosion resistance      | Electrochemical workstation (CHI660E) | TAFEL&EIS                                     |

Figure 4. Pure Ni coating and Ni-SiO₂ nanocomposite coating (b, 6 g/L; c, 10 g/L).

Figure 5. Composite coating with R&F (a, 6 g/L; b, 10 g/L).

Current line distributed uniformly and induced uniform growth of the coating.

Compositions of different coatings were analyzed by means of EDS analysis and the results are shown in Figure 7, in which the SiO₂ content corresponding to Si content in the coating. As shown in Figure 7, SiO₂ content increased slightly with the increase of SiO₂ nano-particles in electropainting bath. But the coating with R&F has slightly lower SiO₂ content which caused by the friction that brought away some particles during electrodeposition.

Coating structure.—Figure 8 shows the X-ray diffraction patterns of pure Ni coating (a) and Ni-SiO₂ composite coating (b, 6 g/L; c, 10 g/L) without friction. A comparison with the Ni standard map shows that the structure is face-centered cubic structure. Crystal surfaces (111) and (200) of the pure nickel coating grows uniformly, whereas the Ni-SiO₂ composite coating has an obvious preferred orientation in the (111) surface.

Phase analysis indicates that no SiO₂ diffraction peak existed in the patterns, but the ‘b’ and ‘c’ diffraction peak shifted to the left contrast to the ‘a’. This shift implies that the crystal lattice constant became larger; some particles whose diameters were larger than that of the nickel atoms were mixed into the coating, thereby resulting in crystal lattice distortion. Thus, a possible reason for the absence of a SiO₂ diffraction peak is that the SiO₂ content in the coating is too low (The highest content of SiO₂ is only 0.83%) to be detected.

The diffraction peak of ‘b’ is obviously wider than that of ‘a’, while that of ‘c’ is slightly narrower. Calculation indicates that the grain size of ‘c’ is the biggest (12.33 nm), ‘a’ is the second (11.53 nm), and ‘b’ is the minimal (10.93 nm). This finding is consistent with the idea that adding nanoparticles can refine the grains, but the added amount of SiO₂ must be appropriate.

Figure 9 shows the XRD patterns of coatings with R&F. Compared to the coatings without R&F, preferred orientation in the (111) surface weakened, and the diffraction peaks shifted to the left slightly. Calculation indicates that the grain size of ‘a’ and ‘b’ is 11.86 nm and 12.00 nm, which is a little bigger than ‘a’ and ‘b’.

Figure 6. Grain growth figure of traditional and R&F electrodeposition. (a) Traditional electrodeposition; (b) R&F electrodeposition.
Microhardness.—Figure 10 shows the effect of different SiO₂ concentrations and the influence of R&F on the microhardness of the coating when other parameters are the same. Within a certain concentration range, the increase of the microhardness of the coating was approximately linear with the increasing of SiO₂ concentration. The microhardness of the coating with R&F was obviously superior to that without R&F. When the concentration of SiO₂ reached 6 g/L, the microhardness peaked (627 HV), exhibiting a 14% increase over that of pure nickel coating. As the concentration increased, the microhardness decreased gradually. With R&F, the microhardness peaked (711 HV) when the concentration of SiO₂ was 8 g/L, thereby indicating a 29.3% increase. Then, as the concentration increased, the microhardness decreased continuously.

The microhardness increased for the following reasons: Nanoparticles were dispersed in the plating solution, which provided a large number of nucleation areas for the deposition process. Thus, the coating grain number increased. During the process of grain growth, nanoparticles embedded into the Ni-coating, thereby resulting in lattice distortion, which induced micro-distortion strengthening in the coating. Also, nano-SiO₂ as the 2nd phase co-deposit with Ni matrix which acted as strong obstacles to dislocation movement, thereby strengthening dispersion. However, the microhardness declined when...
the SiO$_2$ concentration exceeded a certain value. The high density of dispersed SiO$_2$ affected the discharge process of nickel ions, and the reunion rate increased greatly as concentration increased. The reunited particles in the coating obviously affected the coating performances.

Microhardness peaks at different concentrations with or without R&F, thereby proving that R&F can improve the surface quality, remove surface defects in a timely manner, and eliminate some negative effects due to high SiO$_2$ concentration, thus improving the coating performance. However, when the concentration of SiO$_2$ is too high, the effect of R&F cannot improve the coating performance very well, thereby reducing the hardness.

Electrochemical corrosion behavior.—The potentiodynamic polarization curves of pure Ni and Ni-SiO$_2$ nanocomposite coatings in 3.5 wt% NaCl solution are depicted in Figure 11. The corrosion potential ($E_{\text{corr}}$) and corrosion current ($i_{\text{corr}}$) are obtained from the intersection of cathodic and anodic Tafel curve tangents and listed in Table IV. (d, e′ with R&F; others without).

Table IV shows that the corrosion resistance of nanocomposite coating is better than that of pure nickel coating and is influenced by the concentration of SiO$_2$. The $E_{\text{corr}}$ and $i_{\text{corr}}$ of the pure Ni coating are $-0.37$ V and $3.58 \mu$A/cm$^2$, respectively. For the Ni-SiO$_2$ nanocomposite coatings, however, the $E_{\text{corr}}$ values are more positive, and the $i_{\text{corr}}$ values are lower than those of pure Ni coating, thereby indicating that the Ni-SiO$_2$ nanocomposite coatings have higher corrosion resistance than the pure Ni coating in 3.5 wt% NaCl solution. With the increase of the concentration of SiO$_2$, the corrosion resistance improved. However, the performance dropped when the concentration reached 8–10 g/L, similar to the result of microhardness. The nanoparticle can refine the grain. However, excess nanoparticles causes many nanoparticles to reunite, thereby resulting in cellular bulges and surface defects. As a result, the corrosion resistance drops.

A comparison between ‘d’ and ‘d′’ shows that at the concentration of 6 g/L, the coating with R&F has more negative $E_{\text{corr}}$ but lower $i_{\text{corr}}$. To better understand the corrosion behavior, the electrochemical impedance spectra (EIS) in 3.5 wt% NaCl solution were obtained and shown as Nyquist plots in Fig. 12. The capacitive loops of the coating with R&F has a larger radius than that without R&F, which means R&F can improve the corrosion resistance. Compare ‘e’ and ‘e′’, it shows that at the concentration of 8 g/L, the coating with R&F has more positive $E_{\text{corr}}$ and lower $i_{\text{corr}}$, which also means coating with R&F has better corrosion resistance. The corrosion of materials originates from the surface, especially micro-holes, micro-cracks, and other defects. R&F can make the coating compact and uniform, thereby improving the corrosion resistance.

Conclusions

1. Adding a proper amount of nano-SiO$_2$ in the plating solution can refine the grains and improve the microhardness of the coating significantly from 550 HV to 627 HV. However, when the content of nano-SiO$_2$ is too high, microhardness drops.
2. R&F can remove cellular bulges caused by the addition of SiO$_2$ and improve the surface quality. Moreover, R&F can increase the microhardness from 627 HV to 711 HV.

3. The corrosion resistance of the composite coating is better than that of pure nickel coating and can be improved further by R&F.

Acknowledgments

The project is supported by the National Natural Science Foundation of China (grant No. 51475235, No. 51105204). We also extend our sincere thanks to all who contributed in the preparation of these instructions.

References

1. S. C. Tjong, Nanocrystalline materials and coatings, Materials Science and Engineering R, 45, 1 (2004).
2. Jiang Peng-fei, Effect of grain size on the corrosion resistance of corten-B weathering steel, Iron and Steel, 44(12), 67 (2009).
3. S. Kasturibai and G. P. Kalaignan, Characterizations of electrodeposited Ni-CeO$_2$ nano-composite coatings, Materials Chemistry and Physics, 147, 1042 (2014).
4. Soroor Ghaziof and Wei Gao, Zn-Ni-Al$_2$O$_3$ nano-composite coatings prepared by sol-enhanced electroplating, Applied Surface Science, 351, 869 (2015).
5. E. Pavlatou, M. Stroumboudi, and P. Glyfou, Hardening effect induced by incorporation of SiC particles in nickel electrodeposits, Journal of Applied Electrochemistry, 36 385 (2006).
6. V. Viswanathan, Challenges and advances in nanocomposite processing techniques, Materials Science and Engineering R, 54, 121 (2006).
7. V. Zarghami and M. Ghorbani, Alteration of corrosion and nanomechanical properties of pulse electrodeposited Ni-SiC nanocomposite coatings, Journal of Alloys and Compounds, 598, 236 (2014).
8. Kenneth Hili and Daniel Fan, Nickel electroplating for high-resolution nanostructures, Microelectronic Engineering, 141, 122 (2015).
9. B. U. Lu-xia and S. H. I. Jun, Electrodeposition and Corrosion Resistance of Ni-SiO$_2$ Nano-particles Composite Coating, Plating & Finishing, 33(21906), 13 (2011).
10. Lidia Benca, Eliza Danaila, and Jean-Pierre Celis, Influence of electro-co-deposition parameters on nano-TiO$_2$ inclusion into nickel matrix and properties characterization of nanocomposite coatings obtained, Materials Science & Engineering A, 610, 106 (2014).
11. Iram Ul Haq, Electrodeposition of Ni–Fe$_2$O$_3$ nanocomposite coating on steel, Surface & Coatings Technology, 235, 691 (2013).
12. Yuxin Wang, Mechanical properties and microstructure of Au-Ni-TiO$_2$ nano-composite coatings, Materials Characterization, 102, 189 (2015).
13. Wu Hua and Li Xue-song, Preparation and wear performance of electrodeposited Ni-SiC composite coatings with nano-sized SiC addition, Corrosion Science and Protection Technology, 66, 28 (2005).
14. P. Baghery, Ni-TiO$_2$ nanocomposite coating with high resistance to corrosion and wear, Surface & Coatings Technology, 204, 3804 (2010).
15. Ping Yu and Tan Cheng-yu, Study on Properties of Ni-SiC and Ni-SiO$_2$ Composite Plated Coatings, Surface Technology, 63, 27 (2001).
16. Yi Wang, Preparation of Ni–W–SiO$_2$ nanocomposite coating and evaluation of its hardness and corrosion resistance, Ceramics International, 41, 79 (2015).
17. Chen Jin-song and Huang Yin-hui, New Study Tendency of Electrodeposited Composite Coatings, Plating & Finishing, 28(2), 21 (2006).
18. Wang Jing-li and Liu Zhi-dong, Research on Fractal of Growth in Jet-Electrodeposition, Electroplating and Pollution Control, 28(5), 11 (2008).
19. Zhu Jun, Tian Zong-jun, and Liu Zhi-dong, Preparation of Bright Nano-Crystalline Nickel via Friction-Aided Jet Electrodeposition, Journal of South China University of Technology (Natural Science Edition), 39(11), 92 (2011).
20. Zhu Jun, Friction auxiliary jet electrodeposition technology test research [D], Nanjing: Nanjing University of Aeronautics and Astronautics, 54 (2011).