Characterization and Properties of Ni-W-ZrO₂ Composite Coating by Ultrasonic Electrodeposition

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Abstract. Ni-W-ZrO₂ composite coating was prepared on N80 steel plate by composite electrodeposition in the Ni-W bath with ZrO₂ nanoparticles. The microstructure of the coating was observed by scanning electron microscopy, and the micro-hardness of the coating was measured as well. The results showed that the optimum working current density of composite electrodeposition was 1.5A/dm². Lower current density will cause the nonuniform coating, and higher current density will cause the coating to crack. The addition of ZrO₂ nanoparticles in the composite coating significantly improved the micro-hardness of the coating. When the concentration of ZrO₂ nanoparticles in the bath was 10 g/L, the surface of the composite coating was more compact and the micro-hardness was higher.

1. Introduction

Composite electrodeposition [1-3] refers to the process of adding one or more insoluble solid particles to a metal matrix or alloy plating layer to form a composite coating. The change of the concentration of the particles in the base solution is closely related to the physical and chemical properties, mechanical properties and corrosion resistance of the coating. The addition of the particle, especially the nanoparticles, can greatly enhance the performance of the coating. Therefore, the composite electrodeposition has been a hot topic [4-6].

Lee et al. [7] prepared a nickel-diamond nano-composite coating with a hardness of three times than that of pure nickel. The properties of the coating prepared by pulsed electrodeposition were better than that of DC electrodeposition. M.H. Sarafrazi et al. [8] added micron-sized Si and nano-sized TiO₂ particles to the Ni-based coating, which significantly reduced the nickel-based crystal size. The micro-hardness and corrosion resistance of the composite coating were significantly improved. Anna Góral [9] found that Ni- Al₂O₃ composite coating have a refinement of the Ni grains and higher micro-hardness compared with the pure nickel coating. The presence of alumina nanoparticles in the solution changed the microstructure of the nickel deposit, while the addition of both ceramic and saccharide did not affect the preferential crystallization orientation of the Ni grains but reduced the residual stress in the coating. A. Laszczyńska et al. [10] prepared a Ni-Mo-ZrO₂ composite coating from a citrate electrolyte containing dispersed ZrO₂ nanoparticles. They found that the crystallite size of the composite coating decreased gradually with the increase of molybdenum and ZrO₂ nanoparticles. Compared with the Ni-Mo alloy coating, the micro-hardness of Ni-Mo-ZrO₂ composite coating was higher and the presence of ZrO₂ nanoparticles in Ni-Mo alloy matrix can improve the corrosion resistance.

In this paper, Ni-W alloy coating was prepared by composite electrodeposition at different current
density. The microstructure of the coating was observed by scanning electron microscopy, investigating the effect of current density on the morphology. The process parameters of the composite electrodeposition were optimized, on the basis of which, Ni-W-ZrO₂ composite coating was prepared on N80 steel plate at different concentration of ZrO₂ nanoparticles. The microstructure observation and micro-hardness test of composite coatings with different nanoparticle contents were carried out. The effect of ZrO₂ nanoparticle contents in the coating was studied.

2. Experimental
During the electrodeposition process, a pure nickel plate was used as the anode, whereas N80 steel plate (30 mm × 20 mm × 3 mm) was used as the cathode. Before electrodeposition, one side of the cathode plate was mechanically polished to get a smooth, bright, and uniform surface, and the other five sides were encapsulated in silicone. Then, the cathode was put in an alkaline washing solution (NaOH: 20 g/L, Na₂CO₃: 20 g/L, Na₃PO₄: 10 g/L, Na₂SiO₃: 10 g/L) for 10 min to remove the oil on the surface. After caustic washing, the cathode was activated by the mass fraction of 10% dilute hydrochloric acid. The composition and content of the base bath during the composite electrodeposition were listed in Table 1. The pH of the solution was adjusted to ~7 using citric acid and ammonia, and the temperature was kept at 60 °C. The ultrasonic stirring was carried out at 45 kHz and 300 W for 2 hours. In the preparation of Ni-W-ZrO₂ composite coating, ZrO₂ nanoparticles with a diameter of 50nm were added to the bath, and the additions were 5, 10 and 20 g/L, respectively. To prevent agglomeration of nanoparticles, the plating bath was electromagnetically stirred at 500 rpm for 2 hours.

Table 1. Composition and concentration of the base plating solution

| Composition       | Concentration (g/L) |
|-------------------|---------------------|
| NiSO₄ • 6H₂O      | 50                  |
| Na₃C₆H₇O₇ • 2H₂O | 80                  |
| Na₂WO₄ • 2H₂O    | 60                  |
| NiCl₂ • 6H₂O     | 10                  |

3. Results and Discussion

3.1. Effect of Current Density on Cracking of Coatings
Figure 1 showed the SEM micrographs of Ni-W alloy coatings prepared at different current densities. It can be seen that the micro-morphology of the coating was flat and uniform, when the current density was 1 A/dm². However, when the current density was 2 A/dm², there was a small crack occurring in the center of the coating, indicating that the current density was slightly larger. When the current density was 3 A/dm², the center of the coating was seriously cracked, indicating that the current density was too large. Only when the current density was 1.5 A/dm², no crack and unevenness in the coating were observed. Therefore, the current density used in the preparation of the Ni-W-ZrO₂ composite coating was 1.5 A/dm². Zhu et al. [11] reported that the cracks in the composite coating occurred because of hydrogen embrittlement. Near the cathode, in addition to the reduction of nickel ions, hydrogen ions also react to generate hydrogen gas, resulting in hydrogen embrittlement. The excessive current density accelerated the rate of reduction of the cathode surface, so that the hydrogen generation rate increased. In this case, it cannot be discharged in time, resulting in cracking of the coating. In addition, the current density can affect the thickness of coating, so that the stress in the coating will be changed. With the increasing of current density, the amount of atoms deposited on the cathode per unit time increased, and the thickness of the coating increased, which may cause the stress of the coating to increase, leading to the cracking of coating.
3.2. Effect of ZrO$_2$ Content on Micro-hardness of Coatings

![Figure 1. Microstructure of Ni-W alloy coatings at different positions at different current densities](image1)

![Figure 2. Micro-hardness of Ni-W alloy coating and Ni-W-ZrO$_2$ composite coatings](image2)

The micro-hardness of Ni-W alloy coating and Ni-W-ZrO$_2$ composite coating were shown in Figure 2. The micro-hardness of Ni-W alloy coating was 346.74 HV$_{0.2}$. The micro-hardness of Ni-W-ZrO$_2$ composite coatings was obviously improved when ZrO$_2$ nanoparticles were added into the bath. The micro-hardness of the composite coatings prepared by adding 5, 10 and 20 g/L ZrO$_2$ nanoparticles reached 501.6, 522.62 and 520.16 HV$_{0.2}$, respectively. As a result of the increase in the micro-hardness
of the composite coating after the addition of nanoparticles, Han Li et al. [12] suggested that the addition of nanoparticles increased the nucleation sites and thus reduced the grain size. At the same time, the presence of nanoparticles in the composite coating prevented the dislocation movement and the occurrence of plastic deformation. In addition, ZrO$_2$ is the ceramic material with very high hardness, evenly distributed in the composite coating can also play a role in dispersion enhancement [10].

3.3. Effect of ZrO$_2$ Content on Morphology of Coatings

![Figure 3. The microstructure of Ni-W-ZrO$_2$ composite coating: ZrO$_2$ concentration (a) 0 g/L, (b) 5 g/L, (c) 10 g/L, (d) 20 g/L](image)

The surface morphology of Ni-W alloy coating and Ni-W-ZrO$_2$ composite coatings were shown in Figure 3. It can be clearly observed from Figure 3 (a) that the surface morphology of Ni-W alloy coating was dense and uniform. After the addition of ZrO$_2$ nanoparticles, the surface of Ni-W-ZrO$_2$ composite coatings produced a protrusion structure similar to pyramid. It was not difficult to find from Figure 3 (b), (c) and (d) that the surface of the composite coating was the most dense and smooth when the amount of ZrO$_2$ nanoparticles was 10 g/L. This may be because that the low content (5g/L) in the plating bath leading to the low nanoparticles content of the deposition into the composite coating. When the content was 20 g/L, the chance of collision between the nanoparticles in the bath increased, resulting in agglomeration and settlement of nanoparticles during the process of electrodeposition.

4. Conclusions
(1) Ni-W-ZrO$_2$ composite coating was prepared on N80 steel plate successfully by composite electrodeposition in the Ni-W bath with ZrO$_2$ nanoparticles.
(2) The effect of current density on the morphology of Ni-W alloy coatings was investigated. The
optimum current density was 1.5 A/dm$^2$. Lower current density will cause no uniformity between the center and edge of the coating, and higher current density will lead to cracks on the coating.

(3) The addition of ZrO$_2$ nanoparticles in Ni-W base bath can significantly improve the micro-hardness of the coating. When the concentration of ZrO$_2$ nanoparticles in the bath was 10 g/L, the micro-hardness was the highest and the surface of the composite coating was the most compact and uniform.

5. References
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