Study of Corrosion Resistance of Electro-Deposition Ni-CBN Composite Coatings

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Abstract. In this paper, Ni-cubic boron nitride (cBN) composite coating with different volume fractions (from 2.45% to 45.66 vol.%) of cBN particle was successfully prepared by electro-deposition method on steels. The polarization curves (Tafel), electrochemical impedance spectroscopy(EIS), X-ray diffraction (XRD), energy dispersive spectrometer (EDS) and scanning electron microscopy (SEM) were used to characterize the protection performance of coatings. The potentiodynamic polarization and electrochemical impedance spectroscopy of Ni-cBN coatings in 3.5wt% NaCl solution were performed to investigate the effects of cBN particles friction on composite coatings. The results of corrosion studies revealed that while addition of 45.66% of cBN particles resulted in potent protection performance of composite coatings, a low amount of cBN particles content exhibited a reverse effect.

1. Introduction

Steels were widely used in modern industry. However, the low corrosion resistance performances has restricted its further practical application in certain field, such as chemical industry and ships. To our best knowledge, surface treatment method is widely used to improve the wear resistance of the Ti alloys, such as physical vapor deposition (PVD) [1], chemical vapor deposition (CVD) [2], electro-less plating [3] and electroplating [4]. Compared to other methods, Electro-deposition is one of the most important techniques for producing composites of metallic and non-metallic constituents, because of its simple process and fast deposition rate. Coatings containing solid particles such as SiC, Al2O3, WC, CNT and diamond, etc. have been developed for better wear resistance or dispersion hardening [5-6]. Cubic boron nitride (cBN) has outstanding physical and chemical properties similar to diamond such as high hardness, high thermal conductivity, large band gap, and high breakdown field [7]. So cubic boron nitride (cBN) particles are chosen as the second phase to enhance the corrosion resistance property of the coating.

In this paper, Ni-cBN composite coatings with different volume fractions of cBN particles were deposited on steels by electroplate. The effect of the volume fraction of cBN particles on corrosion resistance properties of the Ni-cBN composite coatings were investigated.
2. Experimental

2.1. Preparation of Ni-cBN composite coating
The commercialized carbon steels was used as the substrate with the size of 18 mm×12 mm×8 mm. Before preparation of coatings, the steel was ground up to a grit of #600 using SiC papers, and then ultrasonically cleaned in acetone for 5 min. The pre-treatment process of the steels included washing in an alkaline solution containing 60~80 g/L NaOH, 20~40 g/L Na₂CO₃, 20~40 g/L Na₃PO₄ and 3~10 g/L Na₂SiO₃ at 70 °C for 30 min, and activating in a solution containing 50 mL/L HCl and 40 mL/L HF at room temperature for 1~3 min, and finally washing thoroughly with distilled water before conducting the plating, as shown in Table 1. After pre-treatment, a double-layered Ni/Ni-cBN coating was prepared on the steels substrate, that is, the Ni coating was firstly electroplated on the steels, and then the Ni-cBN composite coating was electroplated as the outmost layer. Washing was conducted in distilled water for a short duration of less than 30s after the Ni and Ni-cBN layers were plated, respectively. The detailed electro-deposition parameters and process are also shown in Table 1.

Table 1. The pre-treatment and electro-deposition processes of the steels.

| Process              | Chemicals    | Concentration | Conditions          |
|----------------------|--------------|---------------|---------------------|
| Alkaline cleaning    | NaOH         | 60—80 g/L     | 70°C,30min          |
|                      | Na₂CO₃       | 20—40 g/L     |                     |
|                      | Na₃PO₄       | 20—40 g/L     |                     |
|                      | Na₂SiO₃      | 3—10 g/L      |                     |
| Activation           | HCl          | 50 mL/L       | Room temperature,   |
|                      | HF           | 40 mL/L       | 1~3min              |
| Ni electroplating    | NiSO₄·6H₂O   | 150—300 g/L   |                     |
|                      | NiCl₂        | 45 g/L        | 50°C, 20min, 3A/dm² |
|                      | H₃BO₃       | 35 g/L        |                     |
| Ni-cBN electroplating| NiSO₄·6H₂O   | 150—300 g/L   |                     |
|                      | NiCl₂        | 45 g/L        | 50°C,120min,        |
|                      | H₃BO₃       | 35 g/L        | 1~5A/dm²            |
|                      | cBN particles| 1-20 g/L      |                     |

The surface and cross-sectional morphologies of the coatings were characterized by a scanning electron microscope (SEM). The composition of the coatings was identified by an energy dispersive spectrometer (EDS) and a X-ray diffraction (XRD).

2.2. Corrosion resistance properties of Ni-cBN composite coating
All electrochemical measurements were done by using an electrochemical workstation equipment with a frequency response analyzer. A conventional three electrode cell system was used for all electrochemical measurements. The coated samples were used as the working electrode (Fig.1 3) whereas an saturated calomel electrode and a platinum wire electrode were used as the reference (Fig.1 2) and counter electrodes (Fig.1 1) respectively. For EIS measurements, the coated samples were exposed to a 3.5 wt% NaCl solution. The impedance measurements were carried out at the open circuit potential over a frequency range of 0.1 MHz to 10MHz using a 10mV amplitude of the sinusoidal voltage. The electrochemical data were analyzed by using the Zsimp Win software. All measurements were conducted at room temperature.
3. Results and discussion

Fig. 2 shows a SEM image of the cubic boron nitride (cBN) particles. It can be found that the size of cBN particles ranges from $3 \mu$m to $5 \mu$m.

The volume fractions of cBN in the composite coatings were calculated by the image analysis system. As shown in Table 2, the volume friction of cBN particles in Ni-cBN composite coatings decreases with the increase of current density. Fig. 3 shows the surface and cross-sectional morphology of the Ni-cBN composite coatings with 45.66 vol. % cBN particles. It can be found that cBN particles are well dispersed and embedded in the nickel matrix. The micro-hardness of the composite coatings with different volume fractions of cBN particles are also listed in Table 2. It is evident that the Ni-cBN composite coatings reveal higher hardness then pure Ni coating. The hardness of the Ni-cBN composite coatings increase with the increase of the volume fraction of cBN particles. As shown in Table 2, the hardness of the composite coating with 45.66 vol. %cBN particles is the highest. Fig. 4 shows the XRD patterns of the Ni-cBN composite coatings with 45.66 vol. %, which shows that the composite coatings are crystalline nickel and cBN particles.
Table 2. Volume fraction of cBN and micro-hardness of Ni-cBN composite coatings.

| Current density (A·dm^{-2}) | Volume fraction of cBN in coatings (%) | Micro-hardness of coatings (Hv 100) |
|-----------------------------|---------------------------------------|-------------------------------------|
| 1.0                         | 45.66                                 | 625.83                              |
| 2.0                         | 29.45                                 | 432.85                              |
| 3.0                         | 20.05                                 | 331.12                              |
| 4.0                         | 11.84                                 | 306.03                              |
| 5.0                         | 2.45                                  | 212.48                              |

Figure 3. The SEM images of: (a) surface morphology; (b) cross-sectional morphology.

Figure 4. XRD patterns of Ni-cBN composite coating

Fig. 5 shows the potentiodynamic polarization curves of the coatings clad with different cBN particles content in 3.5 wt% NaCl solution at room temperature. All coatings clad with different cBN particles content exhibit low corrosion current and passive current, which indicates that the films formed on the surfaces of coatings are very stable and exhibit outstanding ability to withstand corrosion. It can be seen from the graph that the polarization curves are similar and the anodic polarization curves are more distinct. Ni-cBN coatings clad in 3.5 wt% NaCl solution is active dissolution reaction and the corrosion current density increases with the increase of anode voltage.

The polarization curve in figure 5 is processed by software fitting to get the corrosion data in the electrode reaction processed as shown in the table 3. It can be seen from the table that the self
etching point of electroplated pure nickel is the most negative and the corrosion current density is the largest. With the increase of the cBN particles content, the corrosion rate of the composite coating decreases, and reaches the minimum when the cBN particle content is 45.66%.

![Polarization Dynamic Polarization Curve of Ni-cBN Composite Coatings in 3.5% NaCl Solution](image)

**Figure 5.** Polarization dynamic polarization curve of Ni-cBN composite coatings in 3.5% NaCl solution.

**Table 3.** Parameter of polarization polarization curve of Ni-cBN composite coatings in 3.5% NaCl solution.

| Volume fraction of cBN | Corrosion potential (Ecorr/mV) | Corrosion current (Icorr/μA.cm⁻²) |
|------------------------|--------------------------------|-----------------------------------|
| 45.66%                 | -325.70                        | 0.1024                            |
| 29.45%                 | -366.56                        | 0.2236                            |
| 20.05%                 | -370.52                        | 0.2899                            |
| 11.84%                 | -338.94                        | 0.3678                            |
| 2.45%                  | -268.34                        | 0.4163                            |
| 0% (Nickel coating)    | -401.43                        | 0.8585                            |

The EIS analysis could provide useful information about the corrosion process and the protection performance of coating systems. The EIS analysis was conducted to investigate the influence of cBN particles on the percolation properties and electrochemical activity of coating layers during the immersion times in 3.5wt% NaCl solution.

Fig. 6 shows the EIS Nyquist and Bode plots of various coated samples during 10 days of immersion. According to EIS analysis, the shape of EIS patterns of different components are similar, which perform a capacitive arc. The impedance matching of composite coatings with different components is carried out by Zsimp Winsoftware, and the equivalent circuit diagram is shown in figure 7. The fitting equivalent circuit parameters are shown in table 4. In figure 7 the corrosion resistance of the coating is expressed by R2, the greater the R2, the corrosion resistance performance is better. It can be seen from the table 4 that with the increase of cBN particle content, the polarization resistance of composite coating increases gradually. The result is consistent with the measured by Tafel method.
Figure 6. EIS of Ni-cBN composite in 3.5wt% NaCl with different cBN content (a) Nyquist; (b) and (c) Bode.

Table 4. Parameter values of equivalent circuit.

| Volume fraction of cBN | $R_1$(omh/cm²) | $C_d$(μF/cm²) | $R_2$(omh/cm²) |
|------------------------|----------------|--------------|---------------|
| 45.66%                 | 1.634          | 2.964        | 85440         |
| 29.45%                 | 1.699          | 2.842        | 57090         |
| 20.05%                 | 1.855          | 9.247        | 19210         |
| 11.84%                 | 1.749          | 1.842        | 14900         |
| 2.45%                  | 1.618          | 1.802        | 8570          |
| 0(Nickel coating)      | 2.292          | 8.127        | 223.9         |

Figure 7. Equivalent circuit diagram of EIS of Ni-cBN composite coatings.
Figure 8. The schematic representation of the percolating structure.

Analysis thinks that due to the uniform distribution of particle in the coating, the porosity of the coating is small, and the compactness of the coating is increased. The chemical properties of cBN particles in this coating are not active, and the uniform distribution in the coating separates the corrosive medium from the grain. The cBN particles increase the path of the corrosive permeating the coating to the substrate surface, which slow the occurrence of corrosion. Therefore, the Ni-cBN composite coatings have higher corrosion resistance compared with the pure nickel coating.

4. Conclusion

(1) Ni-cubic boron nitride (cBN) composite coatings have been successfully deposited on a steel substrate by electro-deposition technology. The cBN particles can be well dispersed and embedded in the nickel matrix.

(2) All of composite coating layers exhibit excellent corrosion resistance, even more superior than that nickel coating layer in NaCl solution. The cBN particles may be the main factors attributing the excellent corrosion resistance for composite coating layers.

(3) With the increase of particle content in composite coatings, the corrosion current density of composite coating decreases, polarization resistance of composite coating increases gradually.

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