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# Fabrication of Ni-W-$B_4C$ composite coatings and evaluation of its micro-hardness and corrosion resistance properties

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ABSTRACT

Boron carbide ($B_4C$) particles were embedded in nickel-tungsten (Ni-W) coatings by pulse current electrodeposition technique. Physical properties of the composite coatings were studied by XRD, SEM, EDS and Vickers micro-hardness instrument. Corrosion protection of the deposited films was investigated utilizing potentiodynamic polarization and Electrochemical Impedance Spectroscopy (EIS). Results exhibited that the addition of $B_4C$ nanoparticles into the Ni-W alloy can significantly improve the surface morphology and the micro-hardness of the composite coatings. The corrosion resistance of Ni-W-$B_4C$ nanocomposite is much better than Ni-W alloy deposit, especially when the concentration of $B_4C$ nanoparticles is 2 g/L in plating bath, the obtained Ni-W-$B_4C$ composite coating has the best surface morphology, the highest micro-hardness and the excellent corrosion resistance.

## 1. Introduction

Carbon steel is widely used in the field of petroleum chemical industry, construction and all kinds of machinery manufacturing industry because of its excellent physical properties and economic performance [1,2]. But the friction and corrosion are considered as the main causes of material failure and resulted in huge economic losses [3]. To improve the service life of mechanical parts, various materials surface modification techniques have been developed. And electro-plating is one of the most time saving and economical ways. Electrodeposition method is divided into direct current plating (DC) and pulse current plating (PC), where PC method is more advantageous than DC method [4–7]. PC technique can obtain the deposits with highly dense layer of deposits; eliminate hydrogen embrittlement and improve the strength and corrosion resistance of the coatings.

With more attention paid to environment, cadmium and hard chromium plating have been gradually replaced by other composite coatings. Particularly in recent years, nickel-tungsten (Ni-W) coatings have been applied to improve the hardness, wear and corrosion resistance of the substrate, like steel and alloy [8–10]. To further enhance the mechanical properties of coatings, various types of particles reinforcements, such as $Al_2O_3$ [11], MWCNT [12,13], SiC [14–16,20], $SiO_2$ [17,18], $MoS_2$ [19], $TiB_2$ [21] and TiN [22] have been embedded in composite coatings.

Wang et al. [17] fabricated Ni-W-$SiO_2$ nanocomposite coatings through DC method and the results indicated that nano-$SiO_2$ can significantly enhance the hardness of Ni-W coating, while the corrosion protection of the coating was less affected. Sassi et al. [18] further investigated the influence of pH on the physical properties and corrosion protection of Ni-W-$SiO_2$ composite coatings fabricated by pulse electroplating method, and the outcomes found the surface of Ni-W/$SiO_2$ (pH 4) coating was glossier than Ni-W-$SiO_2$ (pH 3) coating, showing a better corrosion resistance. Swarnima et al. [20] reinforced SiC (0–5 g/L) in Ni-W alloy matrix and evaluated its corrosion performance in 0.5 M NaCl solution, and the results indicated that SiC particles can effectively suppress the localized corrosion. Similarly, Li et al. [16] investigated the influence of the electrodeposition parameters and the concentration of SiC particles (0–12 g/L) on the Ni-W coating, resulted that Ni-W-SiC (6 g/L) coating produced with the deposition time varied from 10 to 30 min obtain the highest corrosion and wear resistance. In addition, Our lab has explored the effects of four nanoparticles ($Si_3N_4$, BN(h), MWCNT, Mica) on the Nickel-tungsten alloy coatings, these nanocomposite coatings both exhibit good wear and corrosion resistance [13,23–25]. From the above mentioned studies, it can be concluded that the adding nano-scale ceramic particles to the Ni-W coating is an effective way to improve the coating performance.

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Because of unique properties such as super-hardness (HV > 30 GPa), excellent chemical and thermal stabilities, Boron carbide ($B_4C$) has attracted considerable attention as a reinforcing agent [26,27]. Rezagholizadeh et al. [28] prepared Ni-B-$B_4C$ composite coating on the C45 carbon steel, and found that heat treatment can significantly increase the hardness of coatings, which increased from 870 Vickers to 1350 Vickers. Araghi et al. [29] studied the properties of Ni-W-P-$B_4C$ coatings and found that the anti-corrosion performance of Ni-W-P-$B_4C$ nanocomposite coatings is stronger Ni-P coatings but worse than Ni-P-$B_4C$ coatings. Dhananjay et al. [31] reinforced 24 wt% $B_4C$ in nickel matrix coating and fabricated the Ni-$B_4C$ composite coating on copper substrate utilizing DC method. It demonstrated that the physical and corrosion resistance of the deposited films can be enhanced by adding $B_4C$ to the metal matrix. However, in a study of corrosion resistance of Al-$B_4C$ metal matrix composites obtained a different conclusion, not only the Al-$B_4C$ composites showed lower corrosion protection than Al-based alloy, but increasing the concentration of $B_4C$ particles will result in reduced corrosion resistance of Al-$B_4C$ composites [30].

To our best knowledge, studies on the co-deposition of $B_4C$ particles into Ni-W alloy coatings have not been reported. To further heighten the micro-hardness and corrosion resistance of Ni-W alloy coatings, $B_4C$ nanoparticles as the promising nanoparticles is embedded into the Ni-W alloy coatings for improving its microstructure and mechanical properties. Hence, the present work aimed to produce Ni-W-$B_4C$ composite coatings by means of pulsed electrodeposition method and the effect of $B_4C$ nanoparticles reinforcement on the microstructural, micro-hardness and corrosion resistance properties of the composite coatings are also investigated.

## 2. Experimental

### 2.1. Samples fabrication

Table 1 listed the composition of the electroplating bath and operational conditions. All chemicals were used without further purification. Different concentration of $B_4C$ nanoparticles were ultrasonically scattered in the bath solution for 30 min and then mechanical stirring for 30 min to improve the dispersion of nanoparticles within the plating solution. The Scanning electron microscope (SEM) figure of $B_4C$ nanoparticles is shown in Fig. 1.

Ni-W alloy coating and Ni-W-$B_4C$ composite coatings were prepared on C45 carbon steel sheet (10 × 30 mm). Before the electrodeposition, these steels have already been pre-treated by 600#、800#、1000#、1200# sand-papers to eliminate the surface passive oxide film, obtaining a smooth and bright surface. After that, the steels were degreased using acetone, washed by deionized water and active with 1 M $H_2SO_4$ solution for 30 s and then immediately placed in the bath. After pulse electrodeposition process, the surface of samples was cleaned by distilled water to remove loosely adsorbed $B_4C$ nanoparticles.

**Table 1**
Bath composition and electroplating conditions.

| Composition and conditions | |
|---|---|
| Bath | $NiSO_4 \cdot 6H_2O$ 16 g/L |
| | $Na_2WO_4 \cdot 2H_2O$ 46 g/L |
| | $NH_4Cl$ 27 g/L |
| | NaBr 16 g/L |
| | SDS 0.1 g/L |
| | $Na_3C_6H_5O_7 \cdot 2H_2O$ 147 g/L |
| | $B_4C$ from 0 to 5 g/L |
| temperature | 70 ± 2 °C |
| pH | 7–7.5 (adding citric acid when necessary) |
| Pulse frequency (Hz) | 1000 |
| Duty cycle (%) | 80 |
| Deposition time (min) | 60 |
| Current density (A $dm^{-2}$) | 5 |

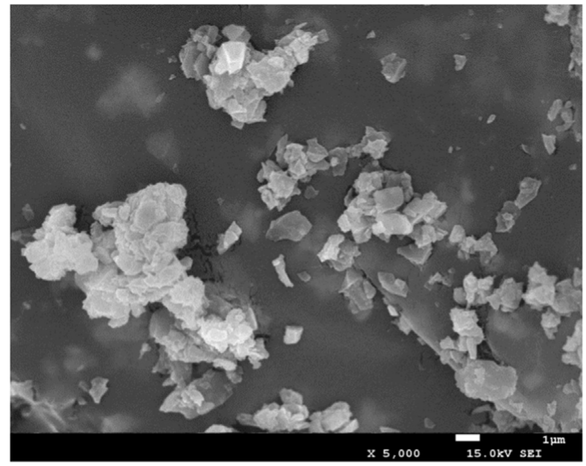


**Fig. 1.** The SEM image of $B_4C$ particles used in this study.

### 2.2. Characterizations

Scanning electron microscope (SEM, JSM-7500F, JEOL), X-ray diffraction (XRD, PANalytical X′Pert Pro diffractometer) and X-ray energy dispersive spectrometry (EDS, INCA) were applied to characterize surface morphologies, microstructures and chemical composition of the deposited films. The micro-hardness of the as-prepared coatings was identified by a Vickers micro-hardness instrument (DUH-W201) at a load of 100 g for a period of 10 s and each samples measured 3 times. The coating thickness was tested by QNix 4500 coating thickness gauge, and then calculated by averaging over four tests for each sample.

### 2.3. Corrosion resistances of the samples

The anti-corrosion property of the deposited coatings was measured using polarization techniques (Tafel curve) and electrochemical impedance spectroscopy (EIS). The measurements were carried out by a three electrode electrochemical cell, which including a platinum plate as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The surface area of the as-prepared composite coatings (as the working electrode) exposed to the test solution was 1 $cm^2$. When the open circuit potential (OCP) remained stable, electrochemical impedance spectroscopy were measured with a sinusoidal AC signal of 1 mV (rms) amplitude applied to the electrode over the frequency ranged from $10^{-2}$ to $10^5$ Hz. Potentiodynamic polarization curves were carried out in a potential range from $-250\,mV_{SCE}$ to $+1000\,mV_{SCE}$ at a scan rate of 1 mV/s. Experiments were tested in 3.5% NaCl corrosive medium at room temperature of 25 °C. Electrochemical measurements were repeated three time for each sample to make sure the satisfactory reproducibility.

## 3. Results and discussion

### 3.1. SEM and EDS studies

Fig. 2 presents the SEM micrographs of the Ni-W alloy and Ni-W-$B_4C$ composite coatings. It is obvious that the incorporation of $B_4C$ nanoparticles to the nickel-tungsten coatings has a great effect on the surface morphologies of the coatings. As presented in Fig. 2a, the surface of Ni-W alloy is obscure and covered with cluttered and various sized nodules. In contrast, Ni-W-$B_4C$ coatings show a clear and smooth surface (Fig. 2b-f). when the addition amount of the $B_4C$ particles in the electroplating solution increased from 0 g/L to 2 g/L, the surface of Ni-W-$B_4C$ composite coatings become smoother, and the nodules become