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Full Length Article

Microstructural, surface and electrochemical properties of a novel Ni–B/Ni–W–BN duplex composite coating by co-electrodeposition

Baosong Li[a,*], Weiwei Zhang[b], Dandan Li[a], Yuxing Huan[a], Jia Dong[a]

[a] College of Mechanics and Materials, Hohai University, Nanjing 211100, China
[b] College of Mechanical and Electrical Engineering, Hohai University, Changzhou 213022, China

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ABSTRACT

In this study, a novel Ni–B/Ni–W–BN duplex nanocomposite coating was successfully developed by co-electrodeposition. Their microstructural, surface and electrochemical properties were evaluated and compared to that of monolayer Ni–B, Ni–W, and Ni–W–BN coating by SEM, AFM, EDS, XRD and XPS. The electrochemical behaviors of the coatings were investigated by EIS in 3.5 wt% NaCl aqueous solution. The effects of graphite-like BN nanoparticles on the properties of the duplex coating were discussed. The mechanism of electrochemical co-deposition was proposed. Results show that all the coatings are uniform, compact and crack-free. The crystal size of the Ni-B/Ni-W-BN duplex composite coating is smaller compared to monolayer Ni–W–BN coating. The inclusion of BN nanoparticles in Ni-W matrix affect the content of nickel and tungsten of the deposits, increase the hardness and reduce the wear weight loss of the duplex composite coating. As a newly deposited layer with more active sites, the underlayer Ni–B much affects the morphologies of the top layer Ni–W–BN of the duplex coating. The incorporation of graphite-like BN nanoparticles into spherical-like Ni–W matrix increased the surface roughness and decreased the porosity. The Ni–B/Ni–W–BN duplex composite coating exhibited higher corrosion resistance than Ni–W and Ni–W–BN coating. The corrosion resistance was firstly increased and then decreased with the increase of BN. The optimum corrosion resistance could be obtained at 5 g L^{-1} BN nanoparticles in bath. However, a higher concentration of BN nanoparticles is detrimental to the properties of the duplex coating.

1. Introduction

Electrodeposition is a simple, low-cost technique to obtain various coatings uniformly at high growing rate on industrial scale [1]. It is commonly and extensively used to fabricate metal or alloy coating [2,3]. Recently, owing to the advantages and unique possibility in the nanostructure synthesis, electrodeposition has attracted much attention to producing nanocomposite coating which exhibits superior or completely new properties compared to traditional coating [4,5]. Incorporation of well-distributed solid nanoparticles (NPs) in a metallic matrix by electrodeposition can produce nanocomposite coating with enhanced surface hardness, corrosion resistance, wear resistance and self-lubrication et al. [6], which promotes its potential application in the field of engineering [7–9].

Ni–W alloy has the advantages of high hardness, favorable anti-wear and anti-corrosion properties and has applications in a variety of industries [10]. However, the need for further development of their properties to address more challenging applications prompts scientists to explore new method to enhance its performance [11]. Based on existing literature [6], it is an effective method to further enhance the properties of alloy by introducing a second strengthening phase or developing a more advanced coating. To data, nanoparticles, including SiC [12], diamond [13], MWCNT [14], ZrO_2 [15], Al_2O_3 [16], have been co-deposited into Ni–W matrices due to their unique physical and chemical properties [14,17–21]. Among which graphite-like boron nitride (BN) with hexagonal structure owns several excellent characteristics, such as chemically inert, high resistance to oxidation, anti-wear and lubricating properties in various environment, exhibiting an ideal reinforcing phase for composite coatings [6,22]. Thus, the BN NPs were adopted as a strengthening phase for alloy modification and had received considerable research attention. However, there are not many literatures regarding the Ni–W–BN nanocomposite coatings [23]. For instance, Han Li et al.[23] successfully produced functionally graded Ni–W/BN coatings and illustrated that the wear resistance and microhardness were enhanced and its corrosion resistance increased with the BN nanoparticles incorporated in the deposit. Karahan et al. [6] fabricated Ni–B/BN composite coating through electrodeposition and reported that its microhardness was 10% lower than Ni–B coating, but the

* Corresponding author.
E-mail address: bsli@hhu.edu.cn (B. Li).

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corrosion resistance was better than Ni–B coating. Kalaignan et al. [24] electrodeposited Ni–W/BN coatings and verified that the anti-wear and anti-corrosion properties were improved through the addition of BN in the electrolyte. Although several aspects of Ni–W/BN has been studied, there is still an intractable challenge that the coating is prone to crack or peeling off when the coating is too thick or too many nanoparticles are incorporated [24–27], which will worsen the adhesion and deteriorate the performance of the coating. Moreover, few literature are known about the microstructure, surface and electrochemical properties of the Ni–W–BN composite coating [28,29].

To explore new performance or better combination properties, a novel duplex coating was designed which comprises an outer layer with high wear resistance, physical shielding feature, and an inner layer possessing high corrosion resistance [7]. This concept of duplex coating is to make full use of the synergistic effect of the two coatings, taking full of their advantages and making up for their deficiency, respectively. Therefore, it is valuable to develop a novel duplex composite coating via co-electrodeposition which has the advantages of adhesion and corrosion resistance of the underlayer with the top layer which enhances the wear resistance [17,21].

In the present work, the concept of a novel Ni–B/Ni–W–BN duplex nanocomposite coating was firstly proposed and prepared by co-electrodeposition. The underlayer Ni–B coating assures the good adhesion and corrosion resistance. The outer layer Ni–W–BN composite coating was fabricated to enhance the wear resistance and combination properties. The microstructural, surface and electrochemical properties of the coatings in 3.5 wt% NaCl aqueous solution were investigated. The co-electrodeposition mechanism of the Ni–B/Ni–W–BN duplex composite coating was proposed. To the best of our knowledge, no relevant studies have been reported on the Ni–B/Ni–W–BN duplex nanocomposite coating prepared by electrodeposition in literature.

2. Experimental

2.1. Electrolyte and substrate preparation

The bath composition and operating parameters employed for Ni–B (bath 1), Ni–W and Ni–W–BN (bath 2) are listed in Tables 1 and 2. The boron nitride (BN) nanoparticles are provided by Shanghai Chaowei Nano Technology Co., Ltd. Its purity is 99.99% and the average particle size is 50 nm. All reagents were of analytical reagent and were used as received without any further treatment. The electrolyte consists of nickel sulfate and nickel chloride as the nickel precursors, trimethylamine borane (TMAB) as boron precursor, boric acid as a buffer, BN as reinforcing particles, saccharine as surfactants. Carbamide was not adopted during the deposition of Ni–B, Ni–W monolayer, and was employed when preparing the Ni-W-BN composite coating to suspend BN nanoparticles and prevent possible aggregation. In addition, ultrasonic dispersion for more than 10 min just before electrodeposition is beneficial to homogeneous electrolyte.

Nickel plate and copper sheet were adopted as the anode and cathode during electrodeposition, respectively. Before deposition, the substrate was sequentially grounded by SiC sandpaper from 600 to 1500 grit. After sanding process, the surface was polished with 0.2 μm alumina polishing powders. Then, the substrates were cleaned in an ultrasonic bath with ethanol and rinsed with deionized water. At last, they were immersed in 5 wt% HCl solution for 0.5–2 min to provide active sites. Finally, the surface was thoroughly washed using distilled water and was ready for electrodeposition.

Table 1
Bath composition and electrodeposition parameters of Ni–B coating.

Electrolyte composition		Electrodeposition parameters	
$NiSO_4·6H_2O$	230 g L^{-1}	Temperature	45 °C
$NiCl_2·6H_2O$	40 g L^{-1}	Current density	2 A dm^{-2}
H_3BO_3	30 g L^{-1}	Agitation rate	300 rpm
Trimethylamine borane	3 g L^{-1}	Electrode distance	3 cm
Saccharin	1 g L^{-1}	Deposition time	10–30 min
pH	3.5	Anode	Ni plates

Table 2
Bath composition and electrodeposition parameters of Ni–W or Ni–W–BN composite coatings.

Electrolyte composition		Electrodeposition parameters	
$NiSO_4·6H_2O$	40 g L^{-1}	Average NPs size	50 nm
$NiCl_2·6H_2O$	12 g L^{-1}	pH	8.0–8.5
H_3BO_3	10 g L^{-1}	Temperature	65 °C
$Na_2WO_4·2H_2O$	66 g L^{-1}	Current density	2 A·dm^{-2}
$Na_3C_6H_5O_7·2H_2O$	118 g L^{-1}	Agitation rate	300 rpm
NH_4Cl	27 g L^{-1}	Electrode distance	3 cm
Urea	0–10 g L^{-1}	Deposition time	10–30 min
BN particles	0–10 g L^{-1}	Anode	Ni plates

2.2. Electrodeposition process

The Ni–B/Ni–W–BN duplex coatings were synthesized by co-electrodeposition. The electrodeposition setup is shown in Fig. 1. The detailed deposition processes as follows. Initially, Ni–B coating was fabricated in bath 1 (Table 1) in a thermostat water bath. Subsequently, an outer layer Ni–W–BN coating was synthesized in bath 2 (Table 2) on the Ni–B underlayer. Continuous magnetic stirring at 300 rpm was adopted throughout the electrodeposition process. Meanwhile, 10 g L^{-1} carbamide was adopted to fabricate a smooth and crack-free surface [20,30]. It is worth noting that carbamide and BN nanoparticles were firstly mixed with a small amount of electrolyte, and ultrasonic stirring for 10 min before pouring them into the bulk bath. As for the duplex coating, it needs to be pointed out that the deposition time given in this paper is the summation of the deposition time for each layer. The deposition time for each layer is designed to be equal.

2.3. Characterization of the coatings

XRD (D8 Advance model) with Cu Kα radiation was used to analysis the phase structure and preferred orientation of the Ni–B/Ni–W–BN duplex coating in as-deposited state. Scherer's equation was used to

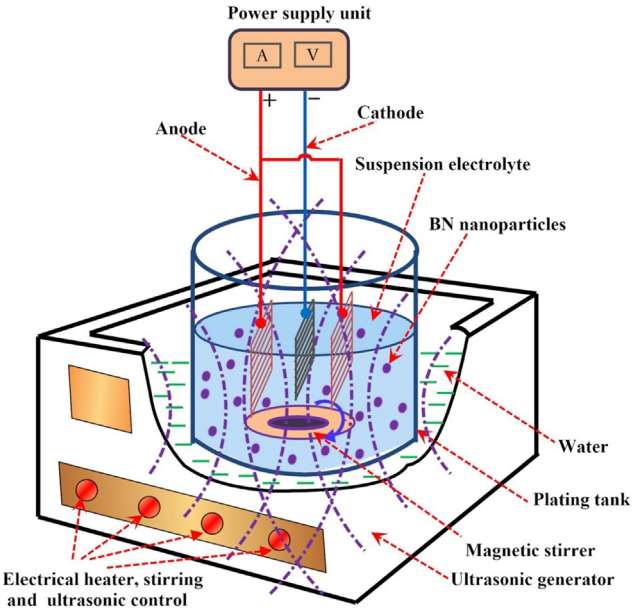

Fig. 1. Schematic diagram of the co-electrodeposition setup. The magnetic stirring was continuously working during deposition.