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Synthesis of a duplex Ni-P-YSZ/Ni-P nanocomposite coating and investigation of its performance

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ABSTRACT

In this study, a duplex Ni—P with yttria-fully stabilised zirconia (YSZ) nanoparticle composite coating was prepared by electroless deposition on a carbon steel substrate. The characteristics of the coatings were evaluated using scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The electrochemical and corrosion behaviour of the coating in a 3.5 wt.% NaCl solution was investigated using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). In addition, the effects of the YSZ nanoparticle concentration on the properties of the coatings were also discussed. The results show that the structures of the as-deposited duplex Ni-P-YSZ/Ni-P coating are amorphous, and it changes to a crystalline state after heat treatment. The surface roughness and morphology of the coating are affected by the addition of YSZ nanoparticles. The duplex coating exhibits both good microhardness and wear resistance as well as excellent corrosion resistance because of its special duplex structure.

1. Introduction

Electroless nickel-phosphorous coatings (Ni—P) are widely used in engineering fields because of their remarkably high hardness, wear resistance and exceptional corrosion resistance [1–3]. They can even be used as in manufacturing solid oxide fuel cell anodes in solid oxide fuel cells (SOFCs) [4]. The Ni—P coatings are produced in a bath solution containing the nickel ions (oxidizing agent) and sodium hypophosphite (reducing agent). The microstructure and properties of the coating depend on many factors, such as the chemical composition of the bath solution, heat treatment, and second-phase particles, among others [5–7].

The crystal structure and property of the coating can be influenced by the content of phosphorus within the coating [8,9]. Coatings containing 1–5 wt.% phosphorus (low phosphorus) show high hardness and good wear resistance, but poor corrosion resistance. Conversely, high-phosphorus coatings exhibit good corrosion resistance and poor mechanical properties. Developing multilayer coatings is an effective way to enhance both mechanical properties and corrosion resistance [10,11], for example, a duplex coating with an outer layer with low phosphorus and an inner layer with high phosphorus. This type of coating demonstrated the beneficial combination properties. Furthermore, co-deposition of a third element (*M*) was developed to improve the mechanical or corrosion resistance properties. The *M* could be any of various transition metal elements such as Cu, Zn, W, Fe, Sn, Re, Mo, among others. The ternary Ni-*M*-P coating significantly improved the coating properties compared with the normal binary Ni—P coating. Researchers demonstrated that the transition metal elements co-deposited in the nickel matrix could improve the electrochemical, thermal and mechanical properties of the coatings [12–14].

Nanoparticles have many well-know and unique physical and chemical properties because of their quantum size effect [15]. Incorporating solid nanoparticles into the Ni—P matrix also improved its hardness and corrosion resistance [16], and broadened its potential application in engineering fields, as another effective method to improve the protective performance of the coating. To data, two types of nanoparticles, solid lubricant particles and hard ceramic particles, have been deposited into Ni—P matrices. The lubricating particles include MoS_2, graphite, carbon nanotubes, and PTFE [17–19], while the hard ceramic particles are Al_2O_3, CeO_2, ZrO_2, and diamond [20–23]. Of these nanoparticles, the ZrO_2 particles possess several notable properties, such as chemical inertness, low thermal conductivity, high hardness, fracture toughness, and excellent wear resistance. The Ni-P/ZrO_2 coating showed good corrosion and tribological properties after incorporating ZrO_2 into the Ni—P matrix [24,25]. The yttria-fully stabilised zirconia (YSZ) has a unique combination of properties, such as excellent thermal stability,

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high fracture toughness, and hardness. Its Young's modulus and thermal expansion coefficient are close to those of steel [26]. Thus, the YSZ can be selected as an improved candidate for numerous applications.

To the best of our knowledge, there are few reports on the design of electroless of YSZ nanoparticles strengthening duplex Ni—P composite coatings. In the present work, a duplex Ni-P-YSZ/Ni-P coating was designed by electroless methods. The inner layer of the coating contained a high phosphorus coating (Ni—P) to assure the good adhesion and corrosion resistance. A low phosphorus layer including the YSZ nanoparticles was developed as the outer layer to enhance the combination properties. The properties of the coatings, such as their structure, surface morphology, roughness, microhardness, and composition as well as the corrosion behaviour in the 3.5 wt.% NaCl solutions were observed.

2. Experimental procedures

2.1. Sample and solution preparation

Duplex Ni-P-YSZ/Ni-P coatings were prepared by the electroless deposition on a normal medium-carbon steel substrate, with a size of $10 \times 10 \times 2$ mm^3. The sample surface was ground sequentially using SiC paper from 400 to 2000 grit. Then, the surface was polished with 0.1 μm and 0.05 μm alumina polishing powders. The substrates were rinsed with deionized water and alcohol, and then they were moved into an ultrasonic bath with alcohol for 10 min followed by cleaning in distilled water and alcohol. The following two steps aid the adhesion between the coating and substrate. First, the sample was cleaned in an alkaline solution for 15 min at 50– 60 °C, rinsed with deionized water, and dried with cool air. Second, they were moved into a 10 wt.% hydrochloric acid solution for 1 min, allowing the surface of the samples to form many surface-active sites, improving the subsequent interaction between the surface and the bath solution. The detailed deposition processes includes the following steps: first, immediately after activation of the surface in the hydrochloric acid solution, the specimen was transferred to the Ni-high P bath solution, which was placed in a constant temperature water bath for the electroless process. Second, after depositing for some time, the specimen was quickly transferred to the Ni-low P bath containing the YSZ particles to form the outer layer. Fig. 1 shows the TEM morphology of the YSZ powder demonstrating sizes on the nanoscale. Because the YSZ nanoparticles easily agglomerated in the bath solution during the electroless process, nanoparticles agglomeration influenced the uniform distribution and homogeneous quality of the coatings. An effective way to avoid agglomeration was to mix the YSZ nanoparticles with a small quantity of the bath solution by ultrasonic dispersion for 120 min before adding them to the bulk bath solution.

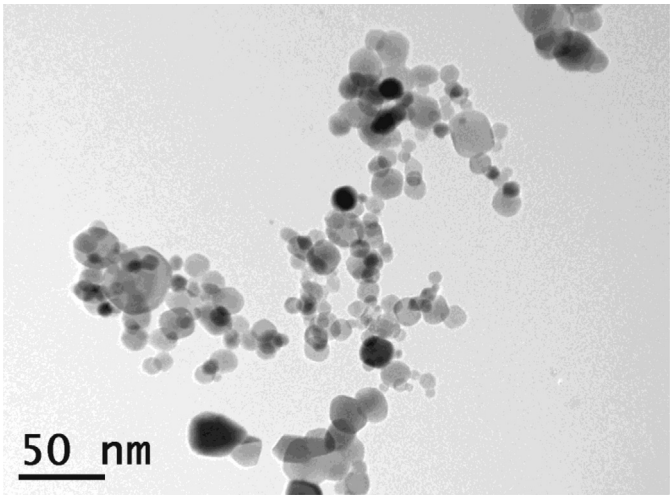

Fig. 1. TEM morphology of the YSZ nanoparticles.

Table 1
Bath composition and plating parameters for the Ni-high P coating.

Bath constituent	Quality	Plating conditions
$NiSO_4 \cdot 6H_2O$	16 g·L^{-1}	pH: 4.5– 5.0
$NaH_2PO_2 \cdot H_2O$	33 g·L^{-1}	Agitation: 250 rpm
Lactic acid	20 mL·L^{-1}	Temperature: 83 ± 1 °C
Succinic acid	12 g·L^{-1}	Time: 60 min
Thiourea	1 mg·L^{-1}	

Moreover, the bath solution was agitated by ultrasonic vibration and a magnetic stirrer with a speed of 250– 300 rpm.

The main compositions of the two types of electroless bath solution and the detailed electroless process conditions are shown in Tables 1 and 2. $NiSO_4$ and NaH_2PO_2 were the main chemicals, and other auxiliary chemicals were added to improve the electroless processes. According to the reports that the surfactant sodium dodecyl sulphate (SDS) was suitable for producing a smooth surface and reducing the deposit porosity [27], an appropriate quantity of SDS was added to the bath solution. All reagents used here were of analytical grade.

2.2. Characterization of the composite coating

The crystal structure of the duplex Ni-P-YSZ/Ni-P coating, in as-deposited and heat-treated (400 °C for 1 h) states was observed by X-ray diffraction (XRD) performed using Cu K_α radiation and a 2θ range from 20° to 80° with a scanning step of 0.02°. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to obtain the surface morphology, roughness and cross-sectional micrographs of the duplex layer coatings. The microhardness of the duplex coatings was determined by a Vickers microhardness indenter. The load weight was 100 g with a load time of 10 s after which the microhardness results were recorded. The results were obtained from the average of five samples. The friction and wear behaviour of the duplex Ni-P-YSZ/Ni-P composite coatings were measured at room temperature under dry friction. The rotating speed was 250 rpm with a loading of 30 N, and the test lasted 30 min.

The detailed composition of the duplex coating was investigated by an XPS with a hemispherical electron analyser operating by with a monochromatic Al K_α radiation source and at a pass energy of 10 eV. The XPS spectra fitting was conducted after a Shirley background subtraction using a Gaussian and mixed Gaussian/Lorentzian function.

The corrosion behaviour of the Ni-P-YSZ/Ni-P composite coating was performed in a 3.5 wt.% NaCl solution by the PAR 2273 electrochemical workstation in a conventional three-electrode cell. The 3.5 wt.% NaCl solution was used to simulate a seawater environment. A saturated calomel electrode (SCE) was the reference electrode, with a platinum plate acting as the counter electrode and the coating samples being the working electrode. Prior to the corrosion test, the samples were immersed into the solution for a certain time to reach a steady-state potential. The EIS measurement was conducted at the open-circuit potential (OCP), with a perturbation amplitude of 10 mV and a frequency ranging from 100 kHz to 10 mHz. The ZSimpWin 3.2 software and an equivalent

Table 2
Bath composition and plating parameters for the Ni- low P-YSZ coating.

Bath constituent	Quality	Plating conditions
$NiSO_4 \cdot 6H_2O$	16 g·L^{-1}	pH: 7.0– 7.5
$NaH_2PO_2 \cdot H_2O$	20 g·L^{-1}	Agitation: 300 rpm
CH_3COONa	15 g·L^{-1}	Temperature: 83 ± 1 °C
$Na_3C_6H_5O_7 \cdot 2H_2O$	23 g·L^{-1}	Time: 60 min
YSZ nanoparticles	0– 18 g·L^{-1}	
Thiourea	1 mg·L^{-1}	