Ni/TiO₂ Nanocomposite Coating Prepared by Direct and Pulse Current Methods

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Abstract

Pure nickel and nickel matrix composite coatings containing nano-TiO₂ particles were produced under both direct and pulse current conditions from an additive-free nickel Watts’ type bath. The surface morphology, crystal size, crystallographic orientation and microhardness of nickel matrix and the amount of embedded nano-TiO₂ particles in the composite coatings were investigated. The corrosion performance of the coatings was investigated by potentiodynamic polarization and electrochemical impedance spectroscopy methods. The TiO₂ particles embedded in the nickel matrix exerted strong influence on the texture of the growing nickel layer, changing its texture under both direct and pulse current conditions.

1. Introduction

The development of modern technology requires metallic materials with better surface properties [1]. The surface is the most important part of any engineering component. It is well known that most components fail from surface initiated defects such as wear, corrosion, fatigue or fracture. Applying a coating on the surface is a method to improve the surface properties. A variety of preparation techniques, such as plasma thermal spraying, combination of chemical and physical vapor deposition, powder metallurgy and electroplating have been applied to produce protective coatings [2, 3]. Among those, the process of electroplating has the advantages of uniform depositions on complexly shaped substrates, low cost, good reproducibility, low processing temperature, and the reduction of waste [4].

Electroplating composite coatings is an effective method to prepare composite coatings through the co-deposition of metallic particles, or non-metallic particles. Even polymer particles with metal, and the properties such as wear-resistance, lubrication, or corrosion resistance can be improved remarkably [5-7].

The composition, structure and properties of the composite coatings are affected by electroplating parameters, such as composition and particle concentration of the plating bath, particle characteristics, temperature, pH, agitation, type of applied current and current density [8-10]. Recently, researches focused on the preparation processes developed from direct current (DC) electrodeposition to pulse current (PC) electrodeposition. Compared with DC composite electrodeposition, the application of PC results with the production of composite coatings with higher percentages of particle incorporation, reduced grain sizes and a more uniform distribution of particles in the Ni matrix. Consequently, more wear-resistant and more corrosion-resistance composites can be obtained [10-12].

In the present work, the electrodeposition technique has been applied using nanometer size TiO₂ particles for the production of the composite coatings. The goal of this study is to produce Ni–TiO₂ composite with high corrosion resistance.

2. Experimental

Ni/TiO₂ composites were electrodeposited from an organic free Watts’ nickel electrolyte with suspended nano-sized TiO₂ particles. The composition of the plating solution, as well as the plating parameters, is given in Table 1.

<table>
<thead>
<tr>
<th>Bath composition</th>
<th>g/L</th>
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<tbody>
<tr>
<td>NiSO₄·6H₂O</td>
<td>250</td>
</tr>
<tr>
<td>NiCl₂·6H₂O</td>
<td>40</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>40</td>
</tr>
<tr>
<td>TiO₂ (dₐ=21 nm)</td>
<td>50</td>
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Electrodeposition conditions

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<tr>
<td>pH</td>
<td>4.0 ±0.1</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>55 ±1</td>
</tr>
<tr>
<td>CD (DC) (Adm⁻²)</td>
<td>6</td>
</tr>
<tr>
<td>PCD (PC) (Adm⁻²)</td>
<td>12</td>
</tr>
<tr>
<td>Pulse frequency (Hz)</td>
<td>10</td>
</tr>
<tr>
<td>Duty cycle (%)</td>
<td>50</td>
</tr>
<tr>
<td>Stirring speed (rpm)</td>
<td>240</td>
</tr>
<tr>
<td>Time (min.)</td>
<td>60</td>
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</table>

TiO₂ particles were maintained as suspension in an electrolytic bath by continuous magnetic stirring at rotating speed of 250 rpm for at least 24 h before deposition. A polished pure copper sheet and platinized Ti plate were used as cathode and anode, respectively. Ag/AgCl electrode was used as the reference electrode.

The electrochemical properties of composite coatings have been investigated by electrochemical techniques. Potentiodynamic polarization measurements were carried out in an open to air conventional three electrode cell, containing 250 mL of electrolyte.
Measurements were performed in 0.5 M NaCl solution at the room temperature. Coated specimens were used as working electrode and platinum electrode and saturated Ag/AgCl electrode were used as counter electrode and the reference electrode. Polarization studies were conducted using computer controlled Gamry Reference 600 DC 105-DC Corrosion at a scan rate of 1 mV s\(^{-1}\).

Electrochemical impedance spectroscopy (EIS) measurements were performed between 0.01 Hz and 100000 Hz frequency range using computer controlled Gamry Reference 600 EIS 300. Electrochemical Impedance at the room temperature. The EIS was measured after 1 hour of holding of the open circuit.

3. Results and Discussion

The XRD diagrams of all coatings prepared at different current regime are illustrated in Fig. 1.

![Figure 1. XRD diagram of the Ni and Ni/TiO\(_2\) composite coatings prepared under DC (6 A/dm\(^2\)) and PC (12 A/dm\(^2\), 50% dc, 10 Hz) conditions](image)

The co-deposition of the inert particles in matrix is based on two consecutive adsorption steps. In the first step, the dispersed particles in the bath are transported to the Helmholtz’s double layer of the electrode by mechanical action and adsorbed weakly at the cathode due to Van der Waals forces. In the second step, these physically adsorbed particles dehydrate because of the strong electric field of Helmholtz layer of the electrode, and a strong irreversible chemical adsorption of particles on the electrode takes place. Thus, the particles are then buried with depositing metal [1,5-8].

The variation of weight percentage of reinforced nanoparticles in the nickel composite coating as a function of co-deposition conditions. The reinforcement content is lower in the coatings deposited using DC co-deposition. The periodic alternation of current (between positive and zero values for PC) discharges the electric double layer formed around the cathode, and thereby allowing better penetration of nanoparticles (with adsorbed ions on the surface) towards cathode [5]. The adsorbed ions on the surface of the nanoparticles subsequently get reduced at the cathode causing entrapment (reinforcement) of the nanoparticles in the growing coating.

When pure nickel was deposited under DC conditions, intense (200) and quite weak (111) and (311) diffraction lines were observed. The nickel crystallites grew predominantly in the direction of the [100] plane, detected by the intensive reflection at (200). On the other hand, Ni crystallites produced at 50% duty cycle under PC condition were characterized by an intense (200) diffraction line corresponding to a [100] texture. As a result, the crystallographic orientation study of the Ni (PC) crystallites in deposits prepared at duty cycle of 50% and prepared under DC conditions, preferred oriented was obtained (Fig. 1).

Comparing Ni and Ni/TiO\(_2\) coatings prepared under DC conditions, it is proved that the presence of TiO\(_2\) nanoparticles in the bath promoted a loss of [100] texture, reflected by the reduction of the line (200) and the relative enhancement of the (111) and (311) lines. This changing of diffraction lines at (200), (111) and (311) intensities was attributed to the dispersed [211] orientation. It was revealed that the embedding of the TiO\(_2\) particles in the Ni matrix presented a tendency to modify the [100] texture to a mixed orientation of nickel crystallites through [100] and [211] axes under PC conditions.

SEM micrographs showing surface morphologies of DC, and PC electrodeposited pure nickel (Ni) and nickel composite (Ni/TiO\(_2\)) are presented in Fig. 2.
Figure 2. SEM images of Ni films (a-b) and Ni/TiO2 coatings (c-d), prepared by DC and PC conditions

Figure 2a presents nickel crystals oriented through [100] axis composing long fibers with twins that end up to the shape of tetragonal pyramids. Ni films electrodeposited by PC (Fig. 3b) methods have a uniform surface morphology with defined repetitive patterns across the surface. Pulse-plated Ni deposits exhibited reduced grain size compared to DC deposits. When PC is applied, the current distribution and mass transfer are improved. Based on the Tafel equation, one can conclude that the larger the current density, the higher the overpotential. The high cathodic overpotential decreases the activation energy of nucleation and leads to an increased nucleation rate. The TiO2 particles codeposited with nickel radically changed the structure of the deposit from regular [211] to disordered crystal structure, and the structure of the nickel matrix became fine (Fig. 3c and d).

The potentiodynamic polarization curves of pure Ni and Ni/TiO2 composite coatings in 0.5 M NaCl solution in Fig. 3. It can be clearly seen that the corrosion resistances of all these composite coatings are higher than that of pure nickel coating. With increasing of TiO2 nanoparticle content in the composite coating the corrosion current decreases and the corrosion potential shifts towards more positive values. The Tafel curve for Ni/TiO2 (PC) in coating has the lowest corrosion current density (0.72 μA/cm²) and the highest corrosion potential (-232 mV) amongst others.

Figure 3. Tafel polarization curves for pure Ni and Ni/TiO2 composite coating in 0.5 M NaCl solution

The measured impedance spectra of this coatings in 0.5 M NaCl solution are shown as Nyquist plot in Fig. 4.

Figure 4. Nyquist impedance diagrams for pure Ni and Ni/TiO2 composite coating in 0.5 M NaCl solution

The shape of Nyquist plots of the pure Ni and Ni/TiO2 composite coatings (DC and PC) was similar with respect to their shape, but they differ considerably in their sizes. This indicates that the same fundamental processes must be occurring on the coatings but over a different effective area in each case. It can be said that the Ni/TiO2 composite coatings exhibits better corrosion resistance. It can be observed that by changing the current type, the diameters of the capacitance loops also change. Ni/TiO2 composite electrodeposited by PC method has the maximum diameter, whereas this value decreases for Ni/TiO2 composite electrodeposited by the methods of DC. This means that the corrosion resistances of Ni/TiO2 films are reduced by changing the deposition conditions from PC to DC.

It is clear that the TiO2 nanoparticles played a major role for improving the corrosion protection in two mechanisms. Firstly, these TiO2 nanoparticles act as inert physical barriers to the initiation and development of defect corrosion, modifying the microstructure of the nickel layer and hence improving the corrosion resistance of the coating. Secondly, the codeposition of the TiO2 particles in composite coating
can help to prevent the corrosive pits from growing up, and the incorporation of nano-particles contributes to accelerate the passivation process of the metal matrix as well [1,3-5].

4. Conclusions

In this work, Ni reinforced by nano-sized (21 nm) TiO₂ particle was successfully codeposited by DC and PC methods. The presence of TiO₂ influences the evaluation of the texture for both DC and PC. With regard to the XRD patterns, Ni exhibits [100], while [211] is dominant in Ni/TiO₂ in DC. For PC, in Ni, at 50% duty cycles and 10 Hz (111) is loss, and (100) became apparent. For Ni/TiO₂ in PC, the intensity of (111) and (311) increases. However, the general orientation lies in the mixed [100]+[211]. The changes in the texture and crystal size of nickel and composite coatings may be attributed to the existence or formation of different interfacial inhibitors such as H₂, H_ads, or Ni(OH)₂, in the electrode/electrolyte interface during the electrodeposition process which occurred as results of the varying electrolysis conditions.

References