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Ni-P-Acetylacetonate-TiO_2 Composite Plating with Electroless Plating: Plating Parameters and Corrosion Resistance

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Abstract

In this study, the chemical plating parameters for Ni-P-acetylacetonate-TiO_2 composite particles and the corrosion resistances of the deposition layer obtained by electroless plating are investigated. The effects of the TiO_2 concentration, process time, temperature, and pH of the plating materials are examined, and optimal parameters are determined. The corrosion resistance of samples obtained by Ni-P-acetylacetonate-TiO_2 composite plating is assessed by comparison to a Ni plating layer, and it is found to be superior to that of both the Ni plating layer and the Ni-P plating layer Ni-P plating layers in a 3.5% NaCl salt spray, as well as in 15% H_2SO_4 and 20% HCl solutions. The origin of this corrosion resistance in composite plating layers is discussed.

Key Words

"Chemical plating, composite material, deposition rate, corrosion resistance, Ni plating, acetylacetonate"

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1. INTRODUCTION

Electroless plating is a temperature-dependent plating process that creates a metallic layer by chemically reducing metal ions dissolved in a plating solution in the vicinity of a metal surface. Electroless plating does not depend on physical parameters like pressure (Farzaneh et al., 2017), and it has several advantages, including the ability to create uniformly thick layers and a cost that is lower than electroplating (Soares et al., 2017). Therefore, electroless plating is more suitable than electrolytic plating for metallic samples of complex shape, and it can be used to plate the inner surface of these samples. Furthermore, it can be used with materials containing polymeric formations. Layers plated with electroless plating are typically harder than those deposited using galvanic methods, and they exhibit perfect abrasion resistance and excellent corrosion resistance. For these reasons, electroless plating is used in several industrial processes (Soares et al., 2017; Ru et al., 2017).

The pH of the Ni-TiO_2 plating solution is the most important parameter affecting the Ni plating process. At low pH the plating speed decreases, and the plating layer quality is reduced. To prevent these effects, phosphates can be added to the Ni-TiO_2 plating solution, or, alternatively, the solution temperature can be increased. Temperature is in fact another important parameter in electroless plating, which promotes the formation of uniform layers (Promphet et al., 2017; Han et al., 2017).

In recent years, composite plating techniques have evolved substantially, to exploit the ability to plate large surfaces and to produce plating layers with high corrosion resistance. Composite materials are particularly important in the plating of carbon steel surfaces, because of the versatility achievable by the use of chemical additives, like phosphates and acetylacetonates (Gezerman et al., 2013). Undissolved particles in the electroless plating solution can however affect the thickness of the final plating layer, which compromises hardness, abrasion, corrosion properties, and oxidation resistance at high temperature (Kolev et al., 1999). Recent developments in Ni-TiO_2 plating techniques are based on the use of phosphate salts and Al_2O_3 (Yongfeng et al., 2017). The aim of this study is therefore to investigate the effects of the addition of sodium dimethylacetylacetonate salts to the plating solution during the Ni-TiO_2 plating process, and to examine how some physical properties of the layers obtained using this method, including corrosion and abrasion resistance, are affected by the presence of this additive.

2. MATERIALS AND METHODS

All materials used in this study for preparing the plating bath and the surface treatment bath were supplied by Merck Chemicals, Turkey.

2.1 Sample Preparation

The composition of the surface treatment bath is shown in Table 1. Stainless steel samples of size 50 mm × 30 mm × 2 mm were used in this study, which were immersed prior to plating in a prepassivation solution (20% HCl and 15% H_2SO_4) for 15 min and then washed with distilled water, to remove all surface impurities.

Table 1. Composition of the surface treatment bath for pre-plating at 90 °C.

Composition (g/L)	Chemical formula	CAS number	Concentration
Sodium hydroxide	NaOH	1310-73-2	35
Sodium carbonate	Na2CO3	497-19-8	35
Trisodium phosphate dodecahydrate	Na3PO4·12 H2O	10101-89-0	15
Sodium metasilicate nonahydrate	Na2SiO3	6834-92-0	15

The plating parameters and the composition of the Ni-P-acetylacetonate-TiO_2 plating bath used in this study are shown in Table 2. It is important to ensure that acetylacetonate-TiO_2 particles diffuse uniformly within the plating layers. To achieve uniform diffusion, physical and chemical dispersion methods were used. For the chemical dispersion, an anion surfactant (lauryl sodium sulfate) was added to the plating solution. Physical dispersion was achieved by ultrasonication and mechanical mixing. TiO_2 particles were then added to the plating solution, and the mixture was then treated at 20 W and 20 kHz for 10 min using a Q-100DE ultrasonicator. The plating solution was then stirred with a magnetic mixer.

Table 2. Composition of the plating solution.

Component	Chemical formula	CAS Number	Concentration
Nickel sulfate	NiSO4·7H2O	10101-98-1	40 g/L
Nickel acetylacetonate	Ni(C5H7O2)2	3264-82-2	8 g/L
Sodium acetate	CH3COONa	127-09-3	10 g/L
Citric acid	C6H8O7	5949-29-1	15 g/L
Lactic acid	CH3CH(OH)CO2H	50-21-5	6%(v/v)
Lauryl sodium sulfate	CH3(CH2)11OSO3Na	151-21-3	30 mg/L
Sodium monophosphate	NaH2PO4·H2O	7558-80-7	20 g/L

After pre-treatment, the plating samples were immersed in the composite plating solution, washed with distilled water, and dried. The plating temperature was measured with an electronic thermometer, and the pH was monitored with a digital pH-meter. During the plating process, the solution temperature was controlled using a hot water bath. To obtain a uniform plating thickness, a rotating plating device was used. An air pump was used to shake and mix the plating solution.

2.2 The Orthogonal Test

To optimize the Ni-P-acetylacetonate-TiO_2 composite plating layer parameters in acidic conditions, the effects of the TiO_2 concentration, plating time, temperature, and pH on the plating process were examined. TiO2 concentrations of 1, 2, 3, and 4 g/L were used, with plating times of 1, 1.5, and 2 h, temperatures of 70, 80, and 90 °C, and pH values of 3.8, 4.8, and 5.8. For each of these plating conditions, the plating layer deposition speed and the corrosion speed in standard corrosion solutions were determined.

2.3 Performance of the Composite Plating Layer

1. Performance of the composite plating layer: The morphology of the plating layer was studied with a Quanta 200 scanning electron microscope, and its elemental composition was determined using energy dispersive spectroscopy. Representative scanning electron microscopy and elemental analysis results obtained on a composite layer are shown in Figure 1 and Figure 2, respectively.

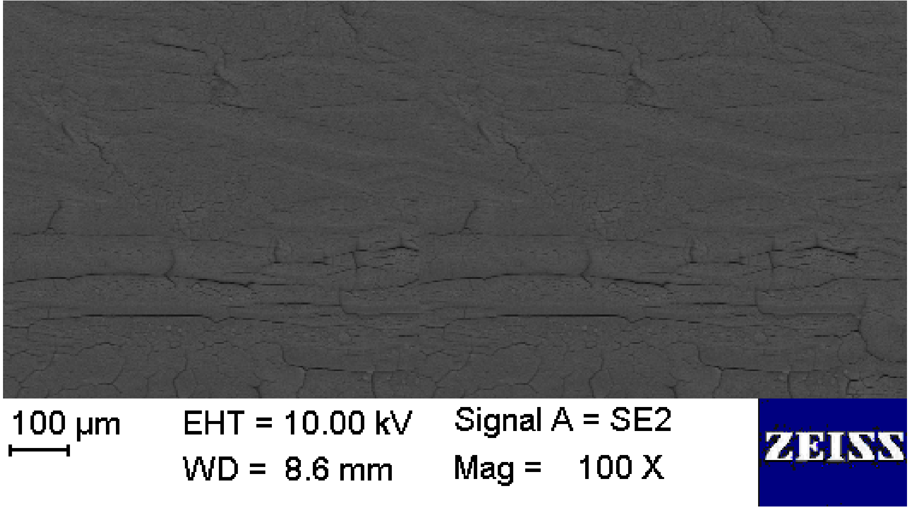


Fig. 1. Morphology of the Ni-P-acetylacetonate-TiO_2 composite plating layer.

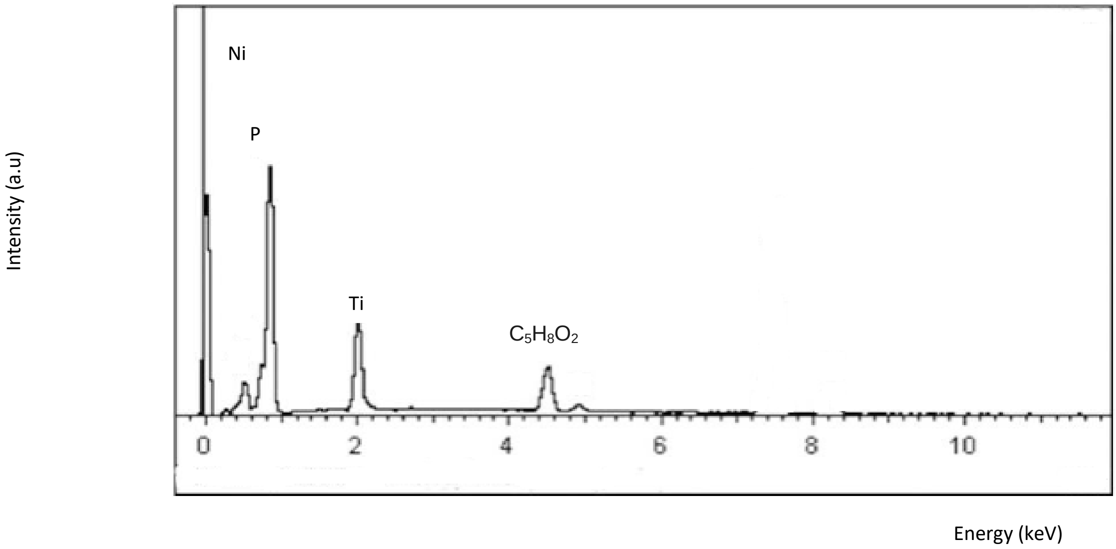


Fig. 2. Energy-dispersive X-ray spectrum of the Ni-P-acetylacetonate-TiO_2 composite plating layer.

2.Abrasion potential and corrosion resistance: To determine the abrasion potential of the plating layer, polarization curves were used. The polarization curves were obtained at room temperature in a 3.5% NaCl corrosive solution with a calomel reference electrode, a platinum auxiliary electrode, a scanning speed of 0.1 mV s-1, a potential step of 0.5 mV, a starting potential of -0.6 V, and a final potential of -0.1 V. The same conditions were used for all plating layers.

The corrosion resistance was assessed by immersing the plating layers in 15% H_2SO_4 and 20% HCl solutions at room temperature for 9 h. The samples were then removed, cleaned, dried, and weighed. The corrosion resistance was determined from the change in weight after immersion in the acidic solutions.

3. RESULTS AND DISCUSSION

3.1 Optimization of the Ni-P-acetylacetonate-TiO_2 Composite Plating Parameters

Previous corrosion resistance studies of Ni-P-TiO_2 composite plating were performed with a variety of methods and parameters (Yongfeng et al., 2017). In this study, the effects of four plating parameters (TiO_2 concentration, plating speed, solution temperature, and pH) on the deposition speed and corrosion speed were investigated.

3.2 Effects of TiO_2 Particle Addition on the Deposition Speed

Table 3 shows the dependence of the layer deposition speed on the concentration of TiO_2 in the plating solution. As the concentration of TiO_2 particles increases, the deposition speed initially also increases. The highest plating speed is reached when a TiO_2 concentration of 3 g/L is used. At higher TiO_2 concentrations the plating speed is reduced. The initial increase of the deposition speed with TiO_2 concentration can be explained by the fact that TiO_2 in the plating solution has an abrasive effect, which prepares the surface of the sample for the subsequent plating process and layer deposition.

Table 3. Plating parameters obtained from orthogonal tests for 8 plating solutions.

Plating solution no	TiO2 (g/L)	Plating duration (h)	Temperature (°C)	pH	Deposition ratio (μm/h)	Corrosion concentration (g)
1	1	1	70	3.8	8.20	0.0551
2	2	1.5	80	4.8	12.01	0.0332
3	2	2	90	5.8	12.69	0.0412
4	3	1	70	4.8	10.00	0.0433
5	3	1.5	80	4.8	12.7	0.0225
6	3	2	90	5.8	10.66	0.0234
7	4	1	70	3.8	12.77	0.0241
8	4	1.5	80	5.8	15.12	0.0211

When all the other process parameters are kept fixed, the highest deposition rate is obtained for a TiO_2 concentration of 3 g/L TiO_2. Xu et al. (2015) have reported that a maximum TiO_2 concentration of 10 g/L can be used in Ni-TiO_2 plating. Other studies have addressed the relation between the TiO_2 concentration and the relative density and metal shape (Hoye et al., 2012; Sahu et al., 2013; Kumar et al., 2015). Takeda et al. (2000) investigated the use of TiO_2 and SiO_2 during Ni plating, which were found to promote the plating process.

3.3 Effects of Plating Time on the Deposition Speed

The variation of the deposition speed over time was determined from the analysis of the orthogonal test results, summarized in Table 3. The plating speed increased with the deposition time, with the highest deposition speed achieved during the 1.5 h plating test. This is because as the plating time increases, the plating solution degrades, and the metal ion concentration increases. The degradation of the plating solution therefore reduces the deposition speed at longer plating times. Zou et al. (2006) investigated the effects of the plating time with SiC particles on a Ni plating layer, and they reported that Al_2O_3 and SiC promote the formation of layers of uniform thickness in Ni plating. Suiyuan et al. (2012) investigated the effect of Al_2O_3 and polytetrafluoroethylene in Ni plating. Gawad et al. (2013) performed Ni-P-TiO_2 plating for 1 h and they showed that the resulting materials exhibit good corrosion resistance to a 3.5% NaCl solution.

3.4 Effects of Temperature on the Deposition Speed

Temperature is one of the most important parameters affecting the plating speed, the stability of the plating solution, and the plating layer quality. In general, the catalytic reactions involved in electroless Ni plating take place at temperatures higher than room temperature. When the temperature increases, the plating speed increases, but the stability of the plating solution decreases. The results from the orthogonal tests concerning the effects of the temperature change on the deposition rate of the composite plating layer are shown in Table 3. As the temperature increases to 80 °C from 75 °C, the deposition ratio decreases. This is caused by the fact that, as the temperature increases, the TiO_2 particles in the plating solution move faster, and the deposition increases with the concentration of the metal ions and TiO_2 particles.

3.5 Plating Layer Polarization Measurements

Polarization measurements in NaCl of a Ni plating layer, a Ni-P plating layer and a Ni-P-acetylacetonate-TiO_2 composite plating layer are shown in Figure 3. For the Ni-P plating layer, the following parameters were determined: corrosion potential φ_c = -0.351 V, corrosion current density i_{correc} = 1.08 × 10-5 A/cm^2, anodic and cathodic polarization b_a= 0.0362 V/decade and b_c= 0.0224 V/decade. The corresponding parameters for Ni-P/TiO_2 plating layers were φ_c = -0.381 V, i_{correc} = 7.11 × 10-6 A/cm2, b_a= 0.0305 V/decade, and b_c= 0.0208 V/decade. From these results, it is clear that the Ni-P-TiO_2 composite plating layer shows lower corrosion current density than the Ni-P plating layer.

The addition of TiO_2 to the Ni-P-acetylacetonate plating layer increases its corrosion resistance by decreasing the corrosion current density, making it higher than that of a Ni-P plating layer. Chen et al. reported similar results (Chen et al., 2010). The results obtained here are also consistent with other studies, which have shown that the addition of TiO_2 to a Ni-P plating layer enhances its corrosion resistance (Ranganatha et al., 2010; Balaraju et al., 2003; Balaraju et al., 2001).

Measurements of the plating layer polarization have been performed for composite platings such as Ni-P-TiO_2. Different from the case of the main metal surface, this method is used for composite layer platings. Therefore, measurements have not been performed for Ni platings.

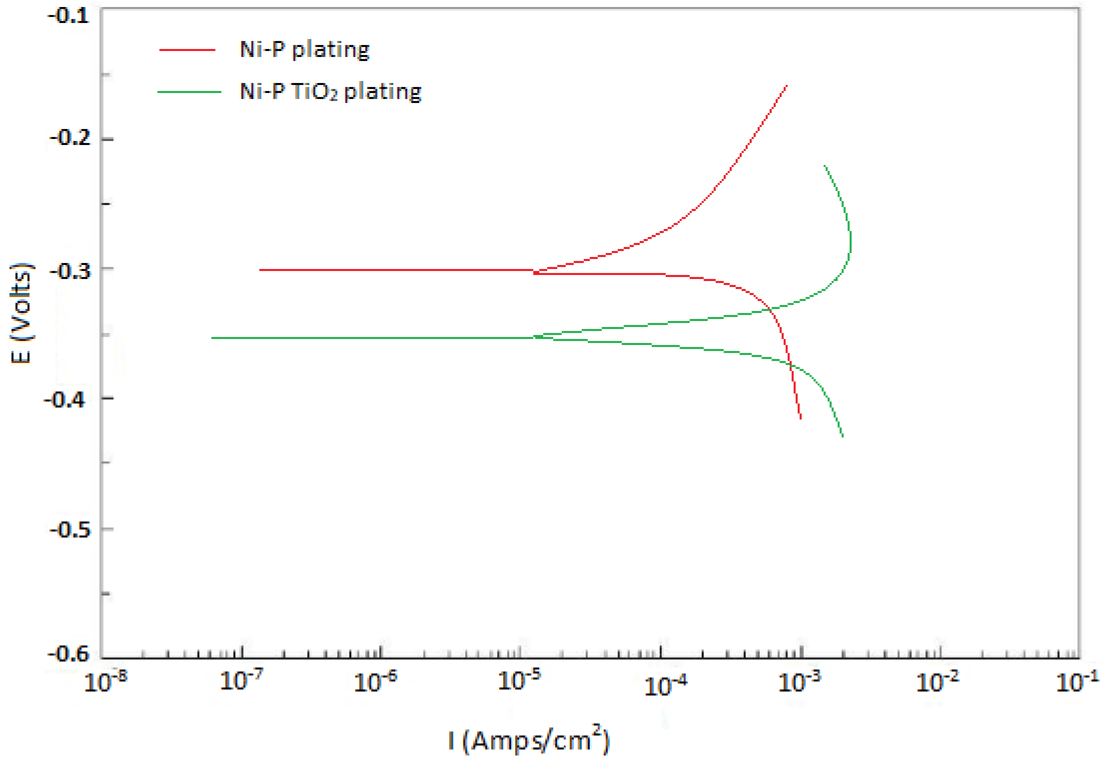
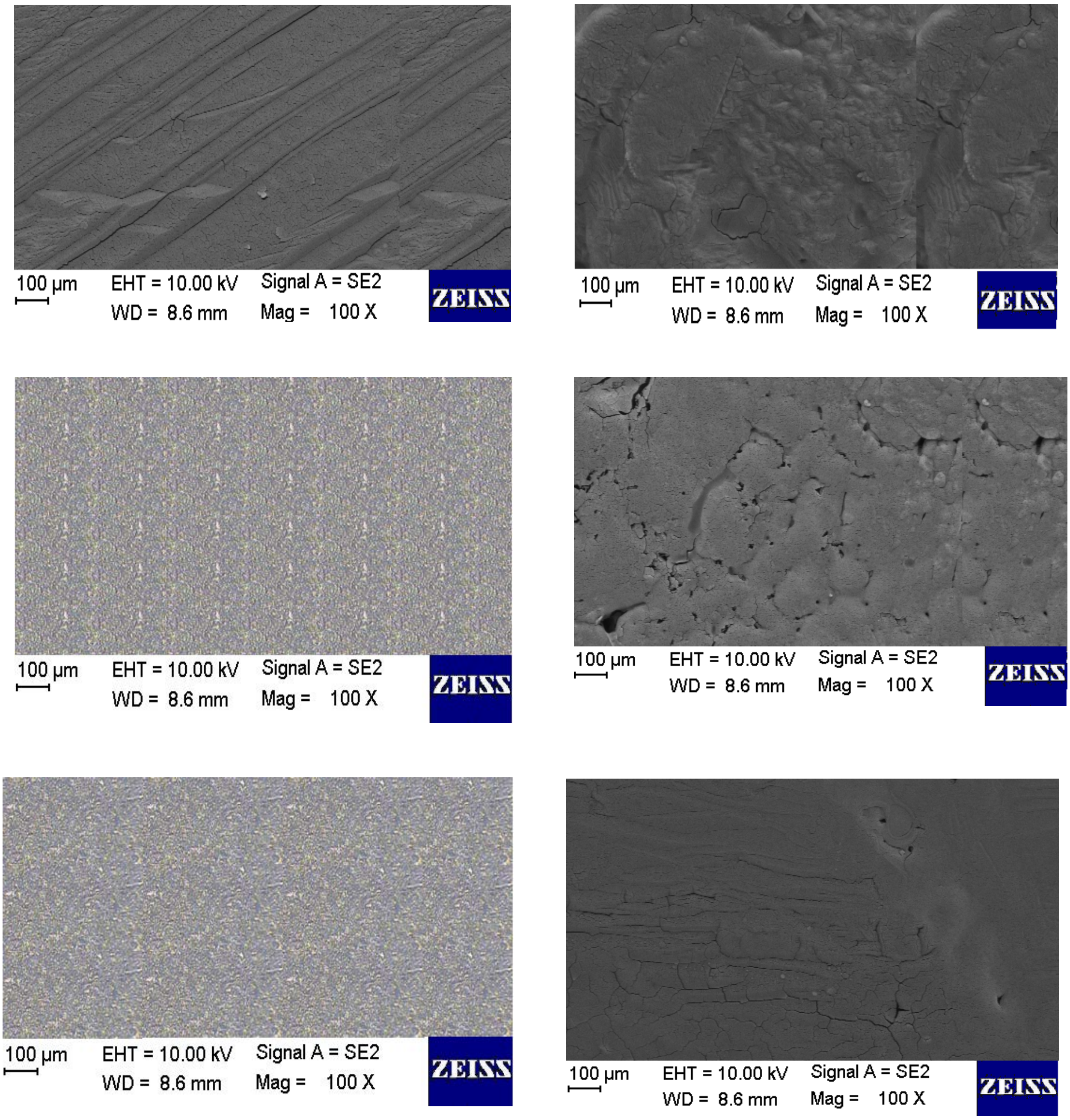


Fig. 3. Polarization curves of Ni-P, and Ni-P-acetylacetonate-TiO_2 plating layers in a 3.5% NaCl solution.

For the corrosion tests, plating layer samples were immersed in 15% H_2SO_4 and 20% HCl standard solutions. After 9 h at room temperature, average corrosion ratios were calculated from the sample weight before and after corrosion. Ni, Ni-P-acetylacetonate-TiO_2 composite, and Ni-P plating layers showed weight losses of 0.444; 0.035; 0.024 g/cm2, respectively. The corrosion resistance of the Ni-P-acetylacetonate-TiO_2 composite plating layer is similar to that of the Ni-P plating layer, and much higher than that the Ni-plating layer.

Figure 4 shows the surface morphology of test samples before and after corrosion. The surface of the Ni-P plating layer is less sensitive to corrosion than that of the Ni-P-acetylacetonate-TiO_2 layer, although the degrees of corrosion in the two samples are comparable. Balaraju et al. (2001) investigated the corrosion resistance of Ni-P-TiO_2 plating layers in 3.5% NaCl using electrochemical impedance spectroscopy. They reported that composite plating layers have superior corrosion resistance relative to Ni-P layers. The higher corrosion resistance of Ni-P-acetylacetonate-TiO_2 composite plating layers relative to Ni-P layers is related to their non-crystalline structure.



(a)

(b)

Fig. 4. Surface morphology of Ni (top), Ni-P and Ni-P-acetylacetonate-TiO_2 in 15% H_2SO_4 and 20% HCl standard corrosion solutions, before (a) and after (b) corrosion**.**

The addition of TiO_2 particles leads to the formation of smoother layers and to an increase in the layer surface porosity. The corrosion resistance of Ni-P-acetylacetonate-TiO_2 composite plating layers therefore increases and is higher than that of Ni-P plating layers.

In this study, the advantages of the Ni-P-TiO_2 plating over the Ni- P plating in terms of the corrosion resistance and plating deposition speed are discussed. In addition, the plating properties are analyzed by polarization measurements and compared with those of the Ni-P plating. Thus, the effects of TiO_2 on the plating layer are investigated. Acetylacetonate addition to the Ni plating bath is considered an important strategy to minimize wastewater generation from the bath in industrial applications.

4. CONCLUSIONS

During the Ni-P-acetylacetonate-TiO_2 composite plating process, the deposition ratio decreases as the plating time increases, and, according to the results of this study, the most suitable plating time is 1 h. The optimal temperature range is 70 to 80 °C. The plating layer deposition rate is highest when the TiO_2 particle concentration is 3 g/L. The pH of the plating solution was maintained at 3.8-5.8 (for 1-2 h) in this study. Polarization measurements and immersion tests were used to compare the corrosion resistance of different plating layers. The corrosion resistance of Ni-P-acetylacetonate-TiO_2 layers in a 3.5% NaCl solution is higher than that of Ni-P plating layers in the absence of TiO_2 particles. The corrosion resistance of Ni-P is higher than that of Ni-P-TiO_2 composite layers for immersion in 15% H_2SO_4 and 20% HCl. In summary, the corrosion resistance of Ni-P and Ni-P-acetylacetonate-TiO_2 composite plating layers is higher than that of Ni plating layers, which makes the former more suitable for applications in the metal plating industry.

The advantages of the Ni-P-TiO_2 plating over those of the Ni- P plating, in terms of the corrosion resistance and plating deposition speed are discussed. The plating properties are measured and compared with those of the Ni-P plating to reveal the effects of TiO_2 on the plating layer. Addition of acetylacetonate to the bath is important for mitigating wastewater formation in industrial applications.

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