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Effect of Formaldehyde on Pulsed Electro-Plated Nickel-Alumina Nanocomposite Coatings

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Abstract

Metal-based nanocomposite coating prepared by plating method can exhibit unique mechanical, chemical, and physical features which have led to their extensive application in various high-tech industries. Nickel-based nanocomposite coatings can pose far lower pollution toward the environment and related staff as compared with chromium-based ones. In this research, a novel compound was developed to coat nickel-alumina nanocomposite by adding formaldehyde to the plating bath. The concentration of alumina nanoparticles (NPs) in the plating bath was 10 g/L. The nickel-alumina nanocomposite coatings were prepared by a pulsed electrical current under ultrasound turbulence in the plating bath. Two Ni bathes in combination with Watt's compound were used with and without formaldehyde addition. Before plating, the zeta potential of alumina NPs was measured in the two different baths. After plating, the cross-section of the coatings and the alumina content participated in the coating, as well as the coating morphology, were analyzed by scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDX). Based on the results, incorporation of formaldehyde into the Watt's solution increased the zeta potential of the nanoparticles from -4.1 to +30.5 mV; consequently, the nanoparticle content of the coatings enhanced from 4.6 to 8.5 vol.%.

Keywords: Composite Electrodeposition, Nickel Alumina Nanocomposite, Formaldehyde, Zeta Potential.

1. Introduction

Nickel-based coatings have found increasing popularity due to their desirable properties such as proper mechanical features, wear and corrosion resistance. Regarding the current industrial advancements, pure nickel coatings fail to fulfill the available needs. Therefore, huge efforts have been dedicated to modifying the Ni coatings using various methods. One of these methods involves the formation of a secondary phase in the form of non-metallic particles dispersed in the matric; known as the Ni-based composite coatings [1]. These coatings are often created by ceramic particles and the global research trend has been focused on the application of these coatings using nano-sized particles [2]. Ni-based composite coatings can offer unique physical, mechanical, and chemical features. They can be employed as wear- and corrosion-resistant coatings [3-5]. These low-cost promising advanced materials can be prepared by electrochemical plaiting [6,7]. Compared to other methods such as physical vapor deposition, chemical vapor deposition, and powder metallurgic approaches, electrochemical plating can offer advantages such as more homogenous particle distribution, lower wastes, higher processability, and continuous production [8,9]. However, particle (especially nanoparticle) dispersion in a common plating bath could be problematic. Problems such as agglomeration can lead to unsuccessful deposition or non-uniform particle distribution in the composite [10, 11]. Electrochemically plated nanocomposite coatings are achieved by electrochemical deposition of the base material along with the floating reinforcing agents. Composite plating baths encompass the solutions containing the ions of the base metal and floating particles such as oxides, carbides, nitrides, and metallic powders [12, 13].

This method was employed in the present research using nano-sized alumina particles to produce nanocomposite coatings.

Thanks to their high wear resistance and low costs, alumina-nickel composites have been extensively applied and commercialized for protecting mechanical workpieces exposed to wearing corrosion [14, 15].

Regarding the research made by the present group, no comprehensive study has compared the effect of adding formaldehyde solvent to the electrolyte on the microstructure of the plated alumina-containing nanocomposite coatings.

In this study, the role of formaldehyde solvent in the formation of nickel-alumina nanocomposite coatings, the structure of the nanocomposite coatings, and the zeta potential of the nanoparticles was assessed.

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2. Materials and Methods

CK45 steel sheet was cut into 80× 25 × 20 mm^3 pieces. The surface of the samples was polished by sandpaper No. 1000 followed by degreasing in 20 wt.% sodium hydroxide and potassium hydroxide solution. Prior to plating, the samples were acid-washed with sulfuric acid (10 wt.%). The samples were also washed with distilled water and alcohol followed by drying after each step.

Steel samples were placed in the plating cell as the cathode. The dissolving anode of the plating cell was a high-purity (99.9%) nickel sheet. Fig. 1. schematically shows the connection of anode and cathode to the current source.

The nickel-alumina nanocomposite coatings were deposited on the steel samples using Watt's solution. Table. 1. lists the composition of the electrolyte bath and the constant operational parameters.

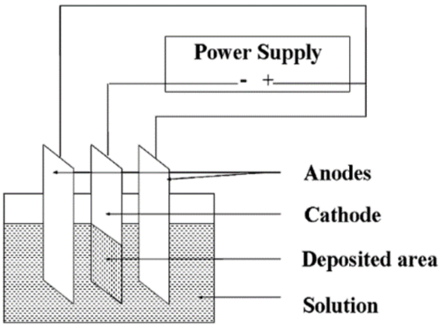

Fig. 1. Schematic of the experimental electrodeposition cell.

Table. 1. Chemical composition of the electrolyte bath and plating condition.

Composite Plating Solution Composition	**Concentration**	**General Conditions of Composite Plating**	
$NiSO_4.6(H_2O)$	300 (gr/lit)	**Temperature**	55 (^oC)
$NiCl_2. 6(H_2O)$	50 (gr/lit)	**Time**	35 (min)
H_3BO_4	40 (gr/lit)	**PH**	3.7
Alumina Nanoparticles	10 (wt%)	**Cathodic Current Density**	5 (A/dm^2)

The alumina nano-powder was investigated by transmission electron microscope (TEM) analysis for determining the shape and size of them. The solution was ultrasonically stirred before and during the experiments. Table. 2. also presents the homogenization condition and the parameters of the pulsed current. Moreover, magnetic stirring was used during the plating process.

The first state of deposition involved no formaldehyde addition. Then, deposition was continued by adding the organic compound of formaldehyde. Each experiment was carried out in triplicates. Prior to electro-plating, the zeta potential of the alumina nanoparticles was measured in both plating solutions with and without formaldehyde. This measurement was also carried out in triplicates.

Table. 2. Magnetic Homogenization, Ultrasonication, and Pulsed Current Parameters.

Process	**Current Frequency**	**Work Cycle**	**Time on and off**
Pulse Current	1000 Hz	50 %	500 µsec
Homogenization (Magnetic and Ultrasonic)	1000 Hz	50 %	500 µsec

First, the cross-section of the samples was prepared for microscopic analysis. After surface preparation, a scanning electron microscopy MIRA 3 equipped with EDX with acceleration voltage of 15 kV was utilized for microstructural observations.

The contribution of the nanoparticles in the Ni-based composite coatings was determined by EDX. To determine the volume percentage of alumina NPs, the densities of Ni (8.9 g/cm^3) and alumina (3.95 g/cm^3) were used to convert the weight percentage into volume percentage.

4. Results and Discussions

4.1. Characterization of Alumina NPs and Surface Morphology of the Coating

Transmission electron microscopy (TEM) images of alumina NPs are depicted in Fig. 2. As can be observed, the nanoparticles had an elliptical shape in the diameter range of 30-40 nm. These results confirmed the mean value presented by the manufacturer (30 nm).

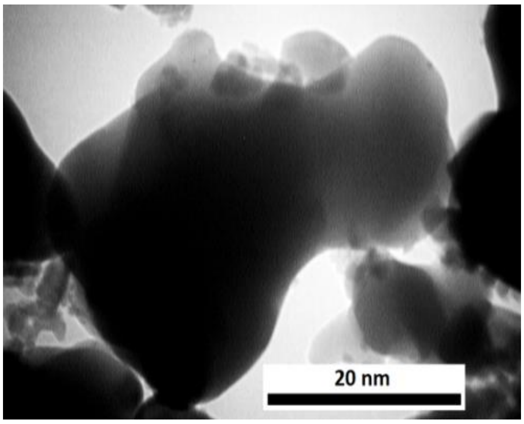

Fig. 2. TEM images of alumina NPs.

The plated composite coatings were investigated by an optical microscope as well as an EDX-equipped scanning electron microscope.

As mentioned earlier, the steel samples were exposed to pulse electro-plating in a plating bath with/without formaldehyde for 30 min at 55℃ to create nickel-alumina nanocomposite coatings.

Naked eye assessment of the samples removed from the plating solution indicated the formation of the coatings. Fig. 3. shows the electron micrograph of the outer surface of the plated coating from the formaldehyde-containing bath.

As seen in Fig. 2., alumina NPs can be detected as white phases on the coatings as confirmed by EDX analysis.

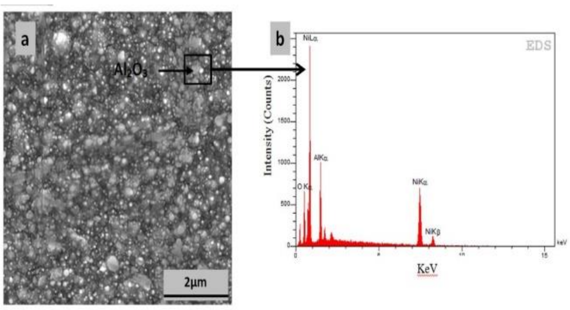

Fig. 3. Electron micrograph of the outer surface of nickel-alumina nanocomposite coatings plated in formaldehyde-containing Watt's solution a) surface morphology b) EDX analysis of the region shown in (a).

4.2. Cross-Section Observation and Comparison of the Alumina NP Contents of the Coatings

The cross-section of the nickel-alumina nanocomposite coatings plated in formaldehyde-free and formaldehyde-containing plating baths are presented in the SEM micrographs of Fig. 4. Based on Fig. 4.a, the nickel-alumina coatings plated in a formaldehyde-free bath had a bright background with a small number of dark points. Based on EDX results, these dark points are alumina NPs entrapped in the nickel matrix.

A comparison of the electron micrographs of Fig. 4.a and Fig. 4.b indicated the increased deposition of alumina in the nanocomposite coatings upon adding formaldehyde to the plating bath. Fig. 5. also illustrates the influence of the formaldehyde on the difference in alumina absorption of the nanocomposite coatings as well as the measured zeta potential of the plating baths.

According to Fig. 5., the percentage of deposited alumina NPs on the nickel matrix was recorded up to 8.5 vol% with adding formaldehyde to the plating bath. Nanocomposite coatings plated in a formaldehyde-free plating bath contained 4.6 vol% alumina NPs. These results showed that the contribution of nanoparticles in the coating was almost doubled by adding formaldehyde to the plating bath. According to Lee et al. [16], the maximum alumina deposition in the coating occurs upon a stable equilibrium at the cathode surface. This means that the number of alumina NPs entering the coating and trapped in the coating is equal to the number of alumina NPs approaching the cathode surface. When the amount of suspended alumina NPs near the cathode exceeds the maximum amount of alumina deposition in the stable equilibrium, they will agglomerate, hence declining the amount of NPs introduced into the nickel base [17].

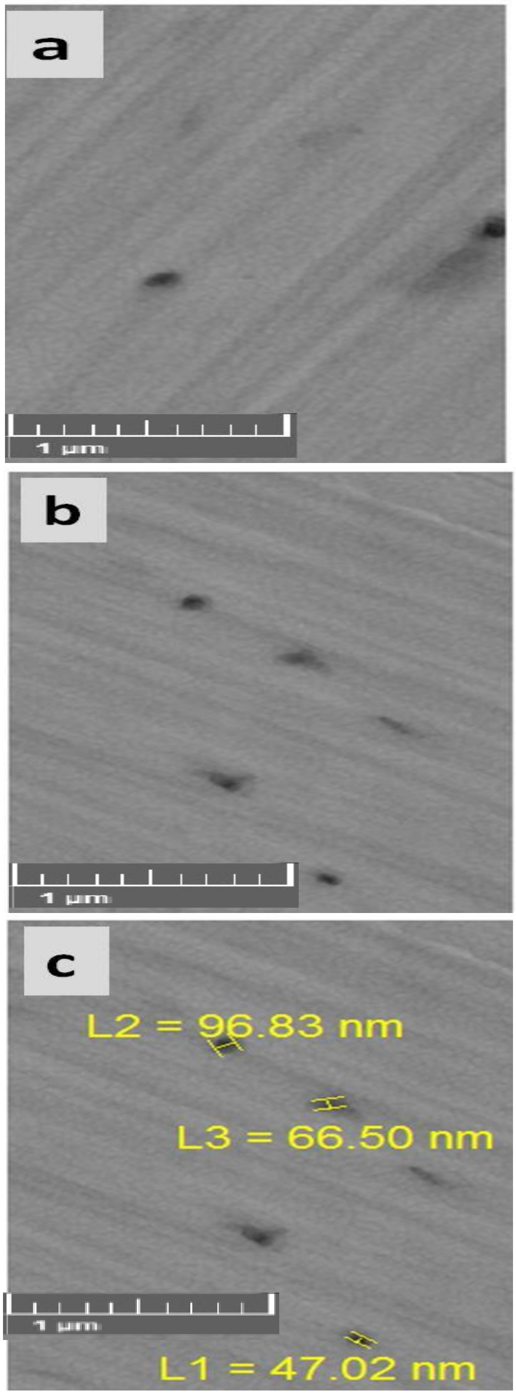

Fig. 4. SEM micrographs of the cross-section of nickel-alumina nanocomposite coatings plated in Watt's solution a) without formaldehyde, b) with formaldehyde (20%), and c) size of the alumina NPs in Fig. b.

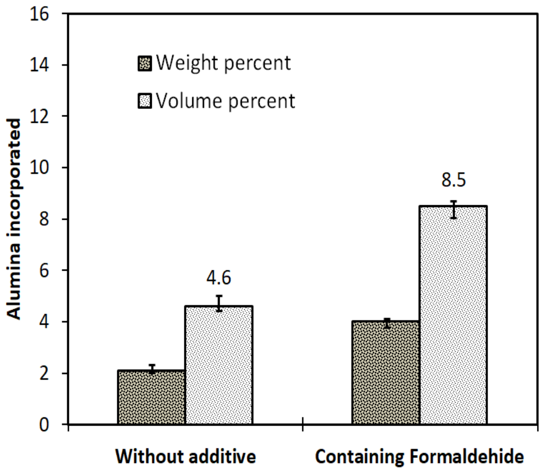

Fig. 5. Effect of formaldehyde in Watt's solution on the alumina deposition within the plated nickel-alumina nanocomposite coatings.

Moreover, the nanoparticle agglomerates themselves can block other NPs from further entering the nanocomposite coating. This phenomenon is called obstruction effects [18].

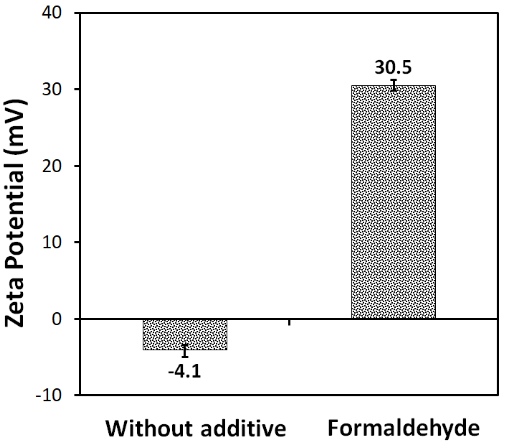

Fig. 6. Measurement of zeta potential of alumina nanoparticles in formaldehyde-containing and formaldehyde-free plating solutions.

The zeta potential of alumina NPs in pure and formaldehyde-containing Watt's solution is depicted in Fig. 6. The zeta potential of alumina NPs in a formaldehyde-free plating bath was measured to be -4.1 which is very low according to the previous results [18, 19].

These studies introduced the zeta potential as a key value for the suspension of nanoparticles and preventing their agglomerating in plating electrolytes.

Chen and colleagues [19] stated that the reason for this phenomenon is the modification of the surface charge of nanoparticles by adsorption of ions and molecules and thus the increase in the electrophoretic motion of suspended nanoparticles. According to Gull et al. [18] and Chen et al. [19], if no surfactant is added to the Watt's solution, the potential of the nanoparticles in the electrolyte will be very low or close to zero (absolute value less than 8 mV), therefore, resulting in the lowest particle adsorption on the coatings.

This result is repeated in the present study for the formaldehyde-free Watt's solution. In other words, when the potential of nanoparticles is significantly lower than other samples (here, 4.1 mV), the nanoparticle content of the coating will be the lowest (Fig. 5 and Fig. 6.). Low and near-zero zeta potential increases the probability of agglomeration of nanoparticles, hence, reduces their adsorption in the coating. It can be stated that the hydrated or double-layer formed around the nanoparticles is not sufficiently thick to maintain the nanoparticles separated [20]. One of the properties of the hydrated layer formed around the nanoparticles is to prevent their agglomeration and modify their dispersion in the electrolyte [21].

It seems that the addition of formaldehyde to the Watt's bath can increase the thickness of the hydrated layer around the alumina NPs. According to Fig. 5., the zeta potential has increased to 30.5 with adding formaldehyde.

Therefore, it can be concluded that the effect of formaldehyde in this study in increasing the zeta potential of alumina nanoparticles could be a very effective factor in enhancing the adsorption of alumina NPs in the coating. As illustrated in Fig. 6., the incorporation of formaldehyde led to a significant increment in the zeta potential which almost doubled the content of reinforcing nanoparticles in the plated nanocomposite coating.

6. Conclusions

Nickel and alumina metal-based nanocomposite coatings were successfully plated on a steel surface using a Watt's bath containing formaldehyde organic solvent and alumina NPs. The morphology, the alumina NP content of the coatings, and the zeta potentials of the NPs in the plating bath were examined. The following statements can be considered as general conclusions:

1. The zeta potential of alumina NPs increased from - 4.1 mV to +30.5 mV upon the addition of formaldehyde organic solvent to the Watt's solution.
2. With the incorporation of formaldehyde into the Watt's solution, the alumina content of the plated nanocomposite coatings almost doubled and enhanced from 4.6 vol.% to 8.5 vol.%.
3. It seems that the increase in alumina content of the nickel-alumina nanocomposite coatings from 4.6 vol.% to 8.5 vol.% could be due to a) declined probability of the elastic collision of NPs at the cathode-electrolyte interface, b) reduced the barrier effect, and c) lower possibility of agglomeration in the electrolyte.

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