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Increasing the Adsorption of Reinforcement Alumina Nanoparticles in Ni-alumina Nanocomposite Coatings by Using Methanol Organic Solvent

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Abstract: To enhance the mechanical properties in Ni-alumina nanocomposite coatings, it is necessary to increase the amount of alumina nanoparticles participation in nickel matrix. The aim of this study is the compassion investigation of Ni-Al2O3 nanocomposite coatings' embedded nanoparticles affected by methanol addition to the electrolyte. In this investigation the composition of electrolyte was modified by adding methanol organic solvent. The coating were produced by pulse current and under ultrasonic agitation .After the electroplating process, the coatings' cross sectioned and the amount of incorporated alumina nanoparticles and the morphology of each coating was analyzed by Energy X-ray spectroscopy (EDX) coupled with an Scanning Electron Microscopy (SEM). The results showed that with adding the methanol organic solvent to the Watt's solution the zeta potential of the nanoparticles increased from -4.1mV to +24.5mV and subsequently, the content of alumina reinforcement nanoparticles increased from 4.6vol. % to 11vol. %. It has been assumed that methanol surfactant may act as a surface agent that affected the hydrated layer on the nanoparticles and it promoted the co-deposition of nano alumina particles with nickel.

Keywords: Nickel-alumina nanocomposite, Al2O3 nanoparticles, Methanol, Pulse electrodeposition.

1. Introduction

Metal matrix composite coatings (MMCs) can show unique physical, mechanical and chemical properties, e. g. they can be used as high wear resistant coatings [1, 2]. This makes them promising low cost advanced materials which can be produced by means of electrodeposition [3, 4]. The advantages of the electrochemical fabrication method compared to other coating methods such as physical vapor deposition (PVD), chemical vapor deposition (CVD) and powder

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metallurgy include more homogenous distribution of particles, reduced waste materials and ability of continuous processing [5, 6]. However, the dispersion of the particles (particularly for nano particles) in a common plating bath can be problematic. In most cases agglomeration and sedimentation of the particles take place which makes successful co-deposition [7, 8]. These nano-composite coatings can be achieved through electrochemical deposition of the matrix material from a solution containing suspended particles such as: oxides, carbides, nitrides, metal powder [9, 10]. This technique has been applied in the present work using nanometer size Al_2O_3 particles for the production of the composite coatings. Ni-Al_2O_3 composites have been studied extensively and commercialized successfully for the protection of mechanical parts under friction corrosion, due to their high wear resistance and the low cost of ceramic powder. The usual dimensions of Al_2O_3 powder in such applications are in the range of micrometers. To our knowledge, there is not a comprehensive study on comparing the effects of adding methanol organic solvent to electrolyte on the morphology of nanocomposite coatings and the content of alumina reinforcement nanoparticles. In this study, the role of adding methanol organic solvent on the formation of Ni-Al_2O_3 nanocomposite coatings was analyzed. The effect of the addition of methanol organic solvent to the electrolyte solution on the zeta potential of every solution containing alumina nanoparticles and methanol and the solution with nanoparticles and without methanol was measured. The amount of deposition of alumina nanoparticles in the nanocomposite coatings and their nanostructure was also studied.

2. Materials and methods

Ni-Al_2O_3 nanocomposite coatings used in this study were deposited from a solution containing alumina nanoparticles under pulse current conditions on the Ck45 steel specimens. The chemical composition of the bath, galvanic sol parameters and pulse current are shown in Table 1.

Table 1.
Bath composition and Deposition conditions

Plating bath and process	Composition and conditions
$NiSO_4.6H_2O$	250 (gL^{-1})
$NiCl_2.6H_2O$	40 (gL^{-1})
H_3BO_3	35 (gL^{-1})
Al_2O_3 nanoparticles (50nm)	10 (gL^{-1})
pH	3.6 ± 0.2
Temperature	53 ± 2 (°C)
Stirring speed during electrodeposition	100 (rpm) + ultrasonic agitation
Maximum current density	10 (Adm^{-2})
Pulse frequency	1000 (Hz)

Alumina nanoparticles used in the experiments were purchased from US Research Nanomaterials, Inc. Based on the information provided by the producer; the alumina nanoparticles with an average diameter of 50nm have more than 99.9% purity. Alumina nanoparticles were stirred by magnetic stirrer under 600 rpm. To ensure the uniform distribution the nanoparticles become turbulent by the ultrasonic probe with a power of 1 wmm-3 in the plating bath 30 minutes before electroplating. The steel sheet-shaped specimens were cut with dimensions 5×3×0.2 to be used as cathode in the cell. The plating cell soluble anode was made of a nickel plate with high purity (99.9%) and located at the distance of 3 cm from the cathode. Before electroplating, the surface preparation operation was done. First, the surface of specimens was mechanically polished up to 1000-grit sandpaper. Then the specimens were degreased in acetone and NaOH 10%. Finally, the specimens' surface was activated by immersion in a solution of HCl 5%. Then the specimens were washed with distilled water and immediately placed in the plating bath. Next, nanocomposite plating process was performed on them. During the deposition, the electrolytic plating, in addition to being stirred at 100 rpm, became turbulent using an ultrasonic probe and ultrasonic waves.

Before the coatings analysis, all specimens were washed thoroughly with distilled water for 1 min in acetone and ultrasonic cleaner and then dried out. To prepare the cross-sections of the coatings, first, the specimens were mounted and then cut. The cut-off specimens were mechanically ground and polished using the sandpapers up to 2000-grit and alumina powder (0.3 mμ).

Nanocomposite coating microstructure was observed by using a field emission scanning electron microscope (FESEM MIRA 3). The nanoparticles' participation in the Ni matrix nanocomposite coatings was determined using X-ray spectroscopy (EDX) coupled with an SEM. The weight percentage of each element (Al, Ni) was obtained by the average of the three measurements from three random points of each specimen in 800X zoom. To determine the volume percentage of alumina nanoparticles in the coatings, the densities of nickel (8.9 g/cm3) and alumina (3.95 g/cm3) were used to convert the weight percentage to volume percentage. Before the electroplating, 20 min agitating was repeated by the ultrasonic probe. Zeta potential of nanoparticles suspended solutions was measured by a Malvern zetasizer Nano series instrument (Nano-ZS model).

3. Results and discussion

3.1. The characterization of alumina nanoparticles

The TEM image of the alumina nanoparticles is presented in Figure 2. As seen, the nanoparticles have an oval shape, and their particle size is between 30 and 40nm.

3.2. The coatings' cross-sections and the amount of incorporated alumina

Ni-Al_2O_3 nanocomposite coatings were plated by pulse plating of the alumina nanoparticles in the nickel matrix under the ultrasonic probe using magnetic stirrer and the plating Watt's bath with and without methanol organic solvent. The SEM micrographs of their cress sectional view are presented in Figure 2.

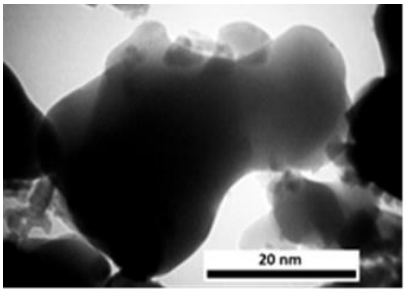

Fig. 1. TEM of the Al2O3 nanoparticles

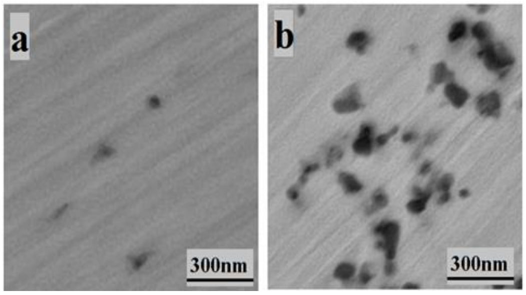

Fig. 2. TEM of SEM micrographs of cross sectional view of Ni-Al2O3 nanocomposite coatings electroplated without and with 10gL-1 of methanol

Figure 2 (a) suggests that Ni-Al_2O_3-plated coating is related to the Watt's solution without adding any organic solvent with a bright surface with a few dark spots. The dark spots were detected by EDX analysis of the alumina nanoparticles trapped in the nickel matrix. From the SEM micrographs, it is clear that the deposited alumina in the nanocomposite coatings increased by adding methanol. Figure 3 shows the effect of methanol addition on the difference between alumina adsorption in the coatings and zeta potential of nanoparticles in Watt's solution with and without methanol. Percentage of alumina nanoparticles, participation in Ni matrix coatings can be increased by up to 11Vol. % by adding 10 gL^{-1} methanol to the electrolyte (Figure 3); this increase is twice greater than the nanocomposite coatings plated in Watt's solution without additives (4.6vol. %).

On the basis of the investigation of Lee et al. [11]_the maximum amount of incorporated Al_2O_3 corresponded to steady-state equilibrium, where the number of co-deposited Al_2O_3 nanoparticles equals the number of Al_2O_3 nanoparticles approaching the surface of cathode. When the Al_2O_3 suspended near the cathode exceeded the maximum amount of deposited of Al_2O_3 at equilibrium, suspended Al_2O_3 nanoparticles agglomerated in the plating bath, and the amount of particles incorporated into the Ni matrix reduced [12]. Besides, the agglomerates themselves can resist incorporating other Al_2O_3 nanoparticles into the Ni matrix. This phenomena is called shield effect [13].

The zeta potential of alumina nanoparticles in the Watt's solution without additives and the Watt's solution containing methanol is also shown in Figure 3. The zeta potential of nanoparticles in Watts's solution without additives presents the absolute value of 4.1 mV. This value is too low according to the research results [14, 15]. Because these studies have shown that the zeta potential is a key value for the nanoparticles' suspension and to prevent their agglomeration in the plating electrolytes.

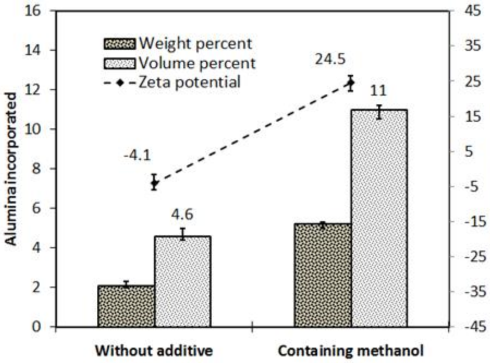

Fig. 3. The effect of methanol on zeta potential of Al2O3 nanoparticles in watts solution and Al2O3 incorporated in electroplated Ni-Al2O3 nanocomposite coatings measured by EDX analysis.

Chen et al. [15] mentioned the reason was surface charge modification of the nanoparticles by absorbing ions and molecules and thus increasing the electrophoretic motion of the suspended nanoparticles. According to Gul et al. [14] and Chen et al. [15] if no surfactant is added to Watt's solution, the potential of nanoparticles in the electrolyte will be very low or close to zero (absolute value less than 8 mV), and thus the lowest particle absorption occurs in the coatings. This result has been replicated in the present study. In other words, when the potential of the nanoparticles is significantly less than that of other specimens (4.1 mV here), the amount of nanoparticles in the coating is the lowest (Figures 3). The low and close to zero zeta potential increases the nanoparticles' agglomeration and reduces the absorption of nanoparticles in the coating because it can be stated that the hydrated or double layer formed around the nanoparticles is not thick enough to keep the nanoparticles separated and could modify the sustainable dispersion of the nanoparticles [16]. Because one of the properties of the hydrated and double layer formed around the nanoparticles is to prevent their agglomeration and modify the dispersion of nanoparticles in the electrolyte [17].

4. Conclusions

Nickel-alumina metal matrix nanocomposite (MMC) coatings were successfully pulse electrodeposited from a Watt's type bath containing methanol organic solvent and alumina nanoparticles on steel surface for high content reinforced nanocomposite coating. The morphology, the amount of participated alumina nanoparticles and the zeta potentials of the nanoparticles in electroplating bath were studied. The following can be concluded.

1) Zeta potential of alumina nanoparticles was increased from -4.1 mV to 24.5 mV affected by adding of methanol organic solvent to Watt's solution.
2) With addition of methanol to Watt's solution, alumina content in the electroplated nanocomposite coatings was significantly increased.
3) Increasing of alumina content from 4.6 vol. % to 11 vol. % may be due to the reduction of the possibility of elastic collisions of nanoparticles in the electrolyte-cathode interface, the reduced shield effect, and the decreased possibility of agglomeration in the electrolyte.

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