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Effect of magnetic field on electroplating Ni/nano-Al_2O_3 composite coating

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The influence of static horizontal magnetic field on the electrocodeposition process of Ni/nano-Al_2O_3 composite coating has been studied in a modified Watts electrolyte through stationary and dynamic electrochemical investigations. The results showed that the mass transport process and charge transfer process were enhanced by applying magnetic field. The results of SEM and XRD showed that the nickel grains were refined by adding nano-particles and (220) crystal orientation was strengthened by increasing magnetic flux density (MFD). Alumina particles content and deposit rate increased with increasing MFD due to the magneto hydrodynamic effect (MHD effect). However, the current efficiency decreased with particle content increased.

1. Introduction

Recent years, nano-composite coating has got much attention for its excellent mechanical properties such as wear resistance, corrosion resistance and lubrication [1–5]. However, it has been not so easy to elevate the content of nano-particles in deposit and control the distribution of nano-particles by traditional way up to now.

It is well known that the application of magnetic field into electrodeposition process will be helpful to get fine and orientated grains and much work has been done on metal or alloy electrodeposition [6–8]. However, the effect of magnetic field on the composite coating including inert particles has been reported relatively less. Dash et al. [9] firstly applied magnetic field into the preparation of Cu-Al_2O_3 composite coatings and found magnetic field not only was helpful to the particles suspension in solution but also to improve the particles incorporated content in coatings. Yamada and Asai [10,11] investigated the effect of particle size (micrometer scale) and magnetic flux density (MFD) on the distribution of alumina particles in the coatings prepared in parallel magnetic field (regard to current). They found that the alumina particles in Ni matrix distributed in a honeycomb pattern or aligned along the grooves scratched on the cathode with the MFD up to 2 T. Peipmann et al. [12] demonstrated that the perpendicular magnetic field could improve the current efficiency and incorporation nanoscale alumina content regardless of reduction reaction of hydrogen, the improvement might be due to convection induced by MHD effect [13]. Unexpected fact of the experiment results showed that the nanoscale alumina particles reached a maximum value with MFD increased [14], which might be the result of competitive deposition between Ni^{2+} and charged Al_2O_3 particles [15]. Investigations showed that the properties of composite coating such as microhardness, wear resistance and corrosion resistance were enhanced by applying magnetic field during electrodeposition [14]. The enhancement might due to the refinement and growth orientation of metal crystals induced by magnetic field.

Our previous work found the nanosize alumina particles dispersed in network form in 10 T parallel (B//J) magnetic field [16]. This paper with the goal to investigate the influence of magnetic field on electrocodeposition process using electrochemical technology and study the microstructure and texture of composite coatings. Therefore, linear sweep voltammetry and AC impedance techniques were used to examine the mass transfer process and electrochemical reaction process. The structure and texture of coatings were analyzed by scanning electron microscopy (SEM), transmission electron microscope (TEM) and X-ray diffraction (XRD), respectively.

2. Experimental

The compositions of the solution and codeposition condition are listed in Table 1. All of the experiment reagents are analytical grade. $NiCl_2 \cdot 6H_2O$ worked as activator of anodic reaction. The Cl^- was adsorbed on the anode to prevent pure nickel passivity. Boric acid not only adjusted the pH value of electrolyte but also enhanced polarization and modified the layers, and it did not

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Table 1
The composition of the bath solution and codeposition condition.

Composition	Content/g L^{-1}
Nickel sulfate	200
Nickel chloride	20
Boric acid	30
α-Alumina (30 nm)	5
Arabin	1
Codeposition condition	
Temperature	40 ± 0.5 °C
pH	3.6 ± 0.1
Current density	2 A dm^{-2}
Plating time	30 min
Magnetic flux density	0–0.7 T

influence the ζ potential of particles [17]. The nano-alumina particles are commercial (99.99%, average size: 30 nm, Hang Zhou, China).

In this work, CHI 660C electrochemical workstation (Chenhua, CHI, China) and a typical three-electrode glasses cell were used for electrochemical experiments. The experiments were carried out in a modified Watts type bath at room temperature (23 °C). A 232 type saturation calomel electrode (SCE, RUOSULL, Shanghai, China) filled with saturation KCl electrolyte was used as reference electrode. Pure copper plane (diameter of 10 mm) and platinum chip (diameter of 15 mm) was used as working electrode and counter electrode, respectively. The electrochemical impedance spectra (EIS) measurements were done under −600 mV vs. SCE with perturbation amplitude of 10 mV and a frequency ranged from 100 kHz to 10 mHz. The EIS data was analyzed by the software which was attached to the machine. Potentiodynamic polarization were obtained by sweeping the potential from 0 V to −1.0 V (vs. SCE), with a scan rate of 1 mV/s after stabilizing the open-circuit potential.

Ni–Al_2O_3 films were prepared in two-electrode cell with an electrolyte volume of 150 mL. The working electrode is pure copper and the counter electrode is pure nickel. The electrolyte was agitated by nitrogen bubbles (99.99%) for 10 min before plating to clear up the oxygen in the liquid. Ultrasonic was used for particles dispersion for 40 min after electromagnetic stirring at 200 rpm for 5 min. The substrates were activated in a mixed acid solution for 2 min at room temperature prior to the deposition. After deposition, the thin film was cleaned by deionized water and alcohol for several times to remove the adsorbed alumina particles, and then dried in the air. After codeposition, the samples were cut and embedded in epoxy resin to observe the cross-sections.

The imposed magnetic field with a gap of 98 mm is produced by direct current and cooled by water, whose MFD can change from 0 T to 1 T. The perpendicular magnetic field was applied parallel to the working electrodes surface, i.e., perpendicular to the current lines to get the maximum MHD effect. The schematic diagram of the magneto-codeposition setup is shown in Fig. 1. The MFD was measured with a Hall producer.

Scanning electron microscopy (SEM) (JEOL, JSM-6700F, Japan) with energy dispersive X-ray (EDX) (EDAX, America) was used to study the surface morphology and content of the nano-Al_2O_3 particles on the membrane's surface and cross-section. Five different regions had been chosed at random on the surface and cross-section, respectively, and got the average value of 10 data. The alumina concentration was determined from the stoichiometric ratio of oxygen to aluminum in Al_2O_3. X-ray diffractometry (XRD) (D \ max-2200, Japan) was used to characterize the crystalline orientation of composite coatings. The size of alumina particles in the composite coatings was investigated by Transmission electron microscopy (TEM).

3. Results and discussion

3.1. Potentiodynamic polarization

The polarization currents were measured with different MFD as shown in Fig. 2. It is noted that the electrolytic currents are enhanced by applying perpendicular magnetic field during electrodepositing Ni–Al_2O_3 films. It has been well known that the MHD convection induced by Lorentz force could reduce the thickness of diffusion layer and concentration polarization, thus enhanced the mass transport process [12,18–20]. In other words, MHD effect leads to a convective movement of Ni^{2+}, nano-alumina particles, and other involved reagents to the electrode surface, and for the electrochemical systems limited by the mass transport it induced an increase of the electrolytic current. Bund et al. [7] thought that the enhanced phenomenon was ascribed to interplay of natural convection and forced convection induced by Lorentz force. As α-Al_2O_3 particle were surrounded by a thin layer of adsorbed Ni^{2+} and H_3O^+ ions after being immersed in Watts electrolyte [21], the more adsorption of nano-particles on the cathode, the more ions reached the cathode surface and reduction current increased.

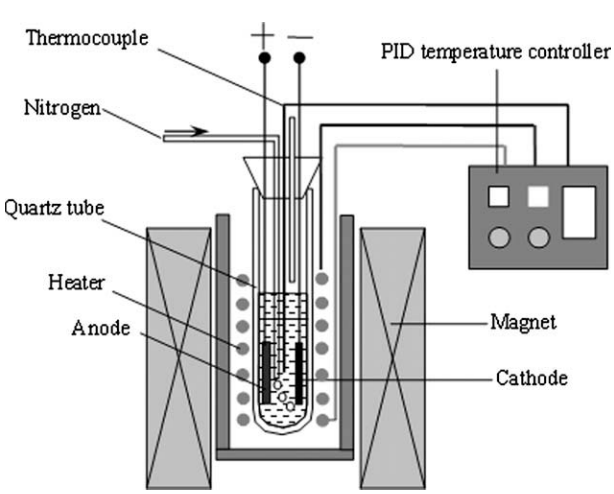

Fig. 1. Schematic diagram of the experimental setup for the Ni–Al_2O_3 composite deposition in magnetic field.

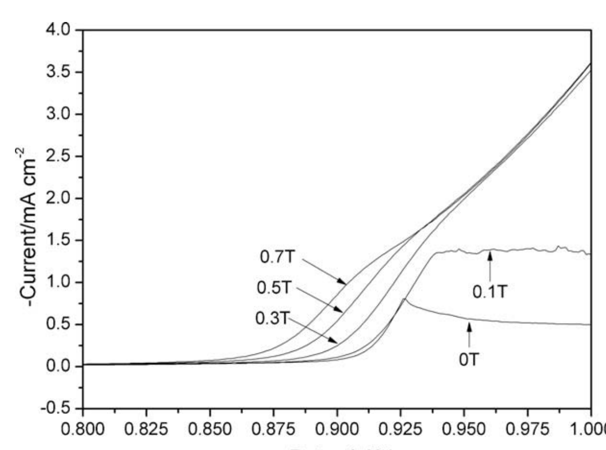

Fig. 2. Polarization curves for the Ni–Al_2O_3 codeposition in various magnetic fields.