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Characteristics investigation of Ni-diamond composite electrodeposition

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ABSTRACT

Parameters of stirring rate and temperature were designed based on electrochemical testings of cathodic polarization, electrochemical impedance spectroscopy and defferential capacitance. At the same time electrochemical action of diamond particles in the bath was studied. Interface force per unit area between particle and cathode was calculated in order to analyse the mechanism of composite electrodeposition. And then Ni-diamond composite coatings with 1.47–15.6 wt.% particle content were prepared by composite electrodeposition technique in typical Watt's bath.

Result: of electrochemical measurements revealed that mass fraction of codeposited diamond particles at medium stirring rate is higher than those of high and low stirring rate. Technics experiments confirmed the foretaste well. It was proved that electrochemical testing is significant for parameter designment. It was also detected that fraction of coverage θ_{NF} which had effect on non-Faraday admittance could reflect more efficiently on particle content in coating compared with fraction of coverage θ_F which interfered with Faraday admittance. Interface force per unit area was found to be the key for particle to entry into coating since 3.57% particles were rooted in matrix metal at just 0.0252% coating thickness/particle size. Interim stirring designed according to interface force mechanism increased the weight percentage of diamond particles in coating. The mechenism could explain the effect of particle size on particle content in coating. Calculation results show that the interface force per unit area for Ni-diamond system was close to 3.3×10^3 N/m^2. Furthermore, composite electrodeposite process can be divided into three steps. Firstly, diamond particles adsorbing positive charges are direct transported toward cathodic surface due to stirring. Secondly, a tremendous amount of particles temporary attaching on cathode are scoured back into the bath by particles in the bath and flowing solution. A few particles root quickly in coating depending on interface pressure after formation of interface between particle and fresh nickel coating with the help of high electric field intensity of electric double layer. Finally, particles are buried slowly by fresh nickel coating.

1. Introduction

Composite electrodeposition is a method of codepositing particles into matrix in order to improve material property [1]. It can adapt physical and chemical properties of materials by controlling incorporated particle fraction in coating according to designment. Three important driving forces stimulate the research in this area since the first composite coating have been obtained in German in 1920: (i) the request of advanced materials with tailor-made properties, (ii) the need of a comprehensive model of the deposition process [2], and (iii) technological superiority of the simplicity to control, possibility to process complicated parts and the low initial capital investment [1]. Related products have been used in electronics, chemical industry, metallurgy, nuclear energy and aerospace fields.

The properties of composite coating depend on several variables, in particular on the incorporated particle fraction [1,3]. It is so complex that there have so many researches about the influence of experimental parameters on particle content in metal matrix such as temperature, stirring rate, current density, pH, particle size and concentration in bath [1,3]. It can be easy observed that the effect of the same parameter is different in different composite systems. Ranjan Sen et al. [6] found out that particle content in coating reaches the maximum at the middle

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stirring rate in Ni-CeO_2 system. Yingwu Yao et al. [7] and P.A.Gay et al. [8] obtained similar rules in their different composite systems. Differently, Si_3N_4 particle content in copper coating increased constantly when stirring rate increased from 240 rotation per minute (rpm) to 550 rpm [5]. Liping He et al. [11] studied the characteristics of Ni-HAP system and found out that an increase in temperature decreased the incorporated particle fraction. But Z. Abdel Hamid et al. [12] reported that the incorporated particle fraction reached the maximum value and then decreased with increasing temperature in Ni-polyethylene composite electrodeposition system. Although in the same composite system, disagreements between published results were also noted. For example, E. Garcia Lecina found that the wt.% of SiC particles in the nickel matrix increased at decreasing rate with particle bath concentration [1]. Differently, an increase in incorporated SiC particle fraction when the particle concentration in the bath increased from 15 to 35 g/L followed by a decrease between 35 and 45 g/L was observed by Zhu [13]. Another example, a zeta potential of about 7 mV at a pH value of 1.2 was obtained for SiC particles within the used nickel-phosphorus electrolyte in W. E. G. Hansal's research [4]. On the contrary, E. Garcia Lecina et al. found that the SiC particles suspended in the nickel electrolytes showed negative zeta potential values [1]. Thus the study about composite electrodeposition is complex and interesting.

The entry process of particle into coating not only relates with hydrodynamics, features of solid interface, adsorption, electrode process and so on, but also it is a dynamic procedure. So there have many different opinions on mechanisms of composite electrodeposition. N.Guglielmi et al. [14] reported two-step adsorption theory. The first step is physical adsorption. It is reversible and flimsy. The second step is electrochemical adsorption. It is irreversible and strong. Electrochemical adsorption is rate-determining step in the whole reaction. Liping He et al. [11] showed that HAP particles adsorbing Ni^{2+} migrated to cathodic surface with the action of electric field and then embedded by metal coating. U.Medeliene et al. [15] analysed that the entry of particle into coating depends heavily on the hydrophilic-hydrophobic balance among electrode surface, particle and solution and the interaction force between cathode and particle. It is possible for particles staying on cathodic surface to be embedded by elelctrodeposited metal. This is consistent with the model described by Yeh et al. [16]. Valdes et al. [17] proposed the complete entry model from the aspect of electrochemistry that all particles can be immediate irreversible captured by electrode as long as the distance between electrode and particle is less than critical distance.

Electrochemical technology is mostly used to test properties of composite coating in most studies of composite electrodeposition. For example wear resistance, corrosion resistance [5,6,18–21] and electrocatalytic performance for hydrogen evolution reaction [10] etc. It is unusual to be used to study the composite electrodeposite process. Generally, particles adsorb on electrode surface before it can be captured into deposite metal during composite electrodeposition. This is bound to make both surface condition of electrode and convective state of solution near the electrode change in this situation. It is well know that polarization methods such as cathodic polarization can reflect the relationship between electrode reaction speed and electrode potential. Electric double layer of electrode-solution interface which helps to detect even the slightest changes on the interface can be quantified by electrochemical impedance spectroscopy (EIS) using electrical equivalent circuit [20]. Differential capacitance curve can also obtain many impontant informance about the interface. For example surface residual charge etc. Thus it is advanced and feasible for electrochemical method to study the process of composite electrodeposition. Furthermore, material properties are determined by its structure. Coating structure relies on different composite system and different operating parameters. It is interesting to research the internal logic between parameters and incorporated particle fraction by electrochemical method.

Xiangzhu He et al. [21] have reported that Ni-diamond composite coating has a completely different structure from pure nickel coating and the presence of diamond particles in coating provides better corrosion resistance than pure nickel coating in 5 wt% NaOH, 5 wt% NaCl and 5 wt% H_2SO_4. In this study, Ni-diamond composite coatings with 1.47–15.6 wt% incorporated diamond particle fraction were prepared by composite electrodeposition using typical Watt's solution. The actions of stirring and diamond particle on both coating and solution were investigated according to different electrochemical methods. Results of electrochemical testing confirmed each other with results of technical experiments and then particle percentage in coating could be controlled more efficiently. Finally, Ni-diamond composite electrodeposite mechanism were discussed from a new perspective.

2. Experimental

2.1. Deposition of Ni and Ni-diamond coatings on carbon steel sheets

Carbon steel sheets with 10 × 10 × 0.2 mm in size are used as carrier. The steel sheets were mechanically polished with #1200 and #2000 emery paper and then suspended in a degreasing bath with Na_2CO_3 30 g/L, Na_3PO_4 30 g/L, NaOH 40 g/L at 70 °C. After that, the sheets were chemically etched in dilute sulfuric acid at room temperature in order to expose the contamination-free surface.

During deposition, steel plate was used as the cathode; a pure Ni plate was used as the anode. The bath for electrodeposition is a standard Watt's solution. The analytical reagent grade chemicals are added into the distilled water to form the electrolytic solution. Bath composition and its operating condition are listed in Table 1. The suspension bath was stirred by a mechanical stirrer at a stable rotational speed. Commercially available diamond power with the diameter of 10, 30, 45 and 223 μm was used in this study. It was etched with H_2SO_4 10 vol.% for several hours and then a sequence of cleanings was performed with surfactant prior to being added to the composite plating solution. The temperature was controlled by a water jacket. After plating, deposits were washed with deionized water and dried with air.

The weight ratio of diamond particle in the composite coatings was measured by weighing. The weight of the composite coatings was weighed after the coatings had been artificially stripped. The weight of diamond particle in the coatings was weighed after Ni in the composite coatings had been etched in 1:1HNO_3 solution. And then the weight ratio of diamond particle in the composite coatings was obtained. Weighing was carried out using a BS210S electronic balance (Sartorius, Germany). The error is about ±0.2 mg.

Table 1
Bath composition and operating conditions.

Component	Bath
$NiSO_4 \cdot 12H_2O$	0.81 mol dm^{-3}
$NiCl_2 \cdot 6H_2O$	0.084 mol dm^{-3}
H_3BO_3	0.566 mol dm^{-3}
Diamond Particle	150 g dm^{-3} (0 g dm^{-3} for Ni system)
Stirring Rate	300-520 rpm
Current Density	1–5 A dm^{-2}
Temperature	40–80 °C