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# Microstructure and properties of Ni–Co/nano-$Al_2O_3$ composite coatings by pulse reversal current electrodeposition

L.M. Chang [a,b], M.Z. An [a,*], H.F. Guo [a], S.Y. Shi [b]

[a] Department of Applied Chemistry, Harbin Institute of Technology, Harbin 150001, PR China
[b] Analysis and Measure Center, Jilin Normal University, Siping 136000, PR China

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## Abstract

Ni–Co/nano-$Al_2O_3$ (Ni–Co/$Al_2O_3$) composite coatings were prepared under pulse reversal current (PRC) and direct current (dc) methods respectively. The microstructure of coatings was characterized by means of XRD, SEM and TEM. Both the Ni–Co alloy and composite coatings exhibit single phase of Ni matrix with face-centered cubic (fcc) crystal structure, and the crystal orientation of the Ni–Co/$Al_2O_3$ composite coating was transformed from crystal face (2 0 0) to (1 1 1) compared with alloy coatings. The hardness, anti-wear property and macro-residual stress were also investigated. The results showed that the microstructure and performance of the coatings were greatly affected by $Al_2O_3$ content and the electrodeposition methods. With the increasing of $Al_2O_3$ content, the hardness and wear resistance of the composite coatings enhanced. The PRC composite coatings exhibited compact surface, high hardness, better wear resistance and lower macro-residual stress compared with that of the dc composite coatings.


*Keywords:* Pulse reversal electrodeposition; Ni–Co/nano-$Al_2O_3$ composite coating; Microstructure; Hardness; Wear

## 1. Introduction

Ni–Co alloy coatings are expected to apply to automobile, aerospace and other industrial fields owing to their high hardness, anti-wear and anti-corrosion resistance. However, the development of science and technology requires to improve the coatings performance to a higher level, and the co-deposition technique has been considered as an effective way to improve the performance of the coatings due to the excellent physical and mechanical properties of the composite coatings [1–4]. In recent years, many researchers have investigated extensively the preparation of composite coatings by electrodeposition, which mainly focus on electrodeposition coatings prepared by direct current (dc) or pulse current (PC) electrodeposition methods [5,6]. Our recent research shows that Ni–Co alloy coatings prepared by pulse reverse current (PRC) electrodeposition method are compacter than those by dc and PC methods. Since PRC not only provides the higher peak current density and eliminates the concentration polarization, but also possesses the positive pulse and reverse pulse characters, Furthermore, the nanoparticles exhibit better prospects of application to the composite coatings because of their higher hardness, high temperature resistance, small-size effects and other special characters [7–12], thus the Ni–Co/$Al_2O_3$ composite coatings deposited by PRC method are expected to show better properties.

In this paper, Ni–Co/$Al_2O_3$ composite coatings were prepared by PRC and dc methods, and their microstructure and properties were also investigated. The results showed that PRC could improve considerably the performance of Ni–Co/$Al_2O_3$ composite coatings.

## 2. Experimental

Polished mild steel sheets of 17 mm × 6 mm × 6 mm and nickel of 60 mm × 60 mm were used as cathode and anode respectively, and vertically maintained at 5 cm. Before electrodeposition, the samples were degreased, activated in 10 wt.% HCl, and then rinsed with distilled water.

The electrolyte composition and plating parameters were listed in Table 1. The solutions were prepared using distilled

* Corresponding author. Tel.: +86 451 86413721; fax: +86 451 86221048.
*E-mail address:* aaaa2139@163.com (M.Z. An).

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Table 1
The electrolyte composition and the plating parameters

| Electrolyte composition | | The plating parameters | | | |
|---|---|---|---|---|---|
| | | dc | | PRC | |
| $NiSO_4 \cdot 6H_2O$ | 250 g/L | Current density | 2 A/dm$^2$ | $i_{a,p}$ | 2.22 A/dm$^2$ |
| $NiCl_2 \cdot 6H_2O$ | 45 g/L | Total plating time | 3 h | $r_p$ | 0.3 |
| $CoSO_4 \cdot 7H_2O$ | 3 g/L | Temperature | 43 °C | $t_{p,on} + t_{p,off}$ | 3 ms |
| $Al_2O_3$ | 0–80 g/L | Stirring speed | 250 r/min | $i_{a,r}$ | 0.22 A/dm$^2$ |
| $H_3BO_3$ | 30 g/L | | | $r_r$ | 0.1 |
| pH | 4.3 | | | $t_{r,on} + t_{r,off}$ | 3 ms |
| Surfactant (LCM) | 0.05 g/L | | | Total plating time | 3 h |
| | | | | Temperature | 43 °C |
| | | | | Stirring speed | 250 r/min |

$i_{a,p}$, $i_{a,r}$ refers to the positive and reverse pulse average current densities, respectively; $r_p$, $r_r$ refers to the positive and reverse pulse duty cycles, respectively; LCM is abbreviation of dodecyl phenyl sodium sulfonate.

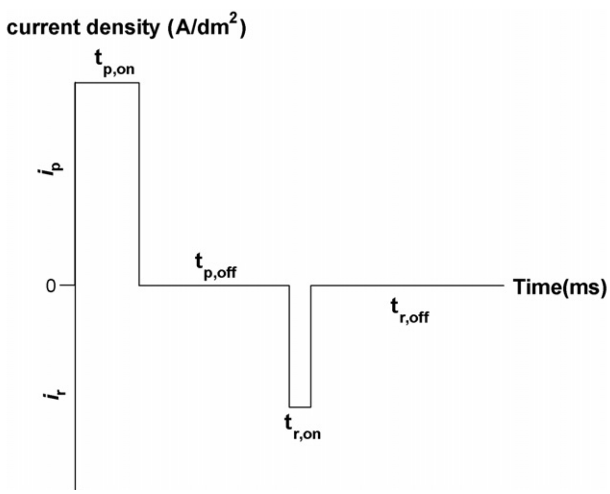


Fig. 1. Schematic diagram of the wave shape of PRC.

water and reagent grade chemicals. The Ni–Co/$Al_2O_3$ composite coatings were prepared with dc and PRC (Fig. 1) methods respectively. The diameter of $Al_2O_3$ particles was about 30 nm, and the thickness of the Ni–Co/$Al_2O_3$ composite coatings was about 60 μm. The Co, Ni and $Al_2O_3$ contents in the composite coatings were determined by X-ray fluorescence spectrometer (XRF, ADVANTPXP-381) and shown in Table 2, the Co content is almost same in composite coatings prepared by dc and PRC methods. The effect of $Al_2O_3$ on content of Co in composite coatiing is negletable, thus the effect of Co was not considered when analysizing composition and evaluation of properties of composite coatings.

Table 2
The contents of $Al_2O_3$, Co and Ni in composite coating (wt.%)

| | | | | | |
|---|---|---|---|---|---|
| dc | | | | | |
| $Al_2O_3$ | 0 | 2.3 | 4.1 | 4.7 | 5.4 |
| Co | 6.0 | 6.1 | 5.8 | 6.2 | 6.1 |
| Ni | 94.0 | 91.6 | 90.1 | 89.1 | 88.5 |
| PRC | | | | | |
| $Al_2O_3$ | 0 | 2.2 | 3.3 | 4.6 | 5.2 |
| Co | 6.1 | 6.2 | 6.1 | 5.9 | 6.3 |
| Ni | 93.9 | 93.8 | 90.6 | 89.5 | 88.5 |

The microhardness of the composite coating, which was an average value of the results of five tests, was measured by microhardness tester (l MHV-2000) at a load of 50 g. The anti-wear experiments were carried out on a homemade ring-on-block wear tester, the counter materials were GCr15 steel with a hardness of HRC60-62 and surface roughness of $R_a = 0.54$ μm. The tests were carried out using a load of 9.8 N at a sliding speed of 0.48 m/s in air (relative humidity 60%) for 20 min under unlubricated condition. Weight loss was measured with an electrical analytical balance (CP225D, 0.01 mg) and three measurements were taken on each sample. The microstructure and worn tracks of the composite coatings were observed with scanning electron microscope (SEM, Hitachi S-570, 10 kV, 10 mA) and transmittance electron microscope (TEM, H-800), and macro-residual stress of the composite coatings was measured by X-ray diffractometer (XRD, D/max-3C, 45 kV, 35 mA) with Cu Kα radiation equipped with stress measuring devices.

## 3. Results and discussion

### 3.1. Surface morphology

The SEM images of Ni–Co/$Al_2O_3$ composite coatings prepared by dc and PRC methods are shown in Fig. 2, respectively.

It is found that, compared with the dc coatings, the PRC composite coatings show a smooth surface with fine and compact crystal of Ni matrix, and the size of Ni grains of the PRC composite coating is smaller than that of dc composite coating. These changes may be attributed to the two facts as followed: on the one hand, $Al_2O_3$ nanoparticles distribute along the boundaries of Ni grains, which restricts the growth of Ni grains in the process of the electrodeposition and results in the fine and compact surface; On the other hand, in the pulse reversal current electrodeposition process, the alternative transformation of the current direction increases the electrochemical polarization of cathode, results in the decrease of the nucleation energy for the metallic grains on the electrode surface and further makes the nucleation rate increase. As a result, the number of nuclei increases.