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Electrodeposition of nanocrystalline Zn–Ni coatings with single gamma phase from an alkaline bath

Zhongbao Feng, Qingyang Li, Jinqiu Zhang, Peixia Yang, Hailin Song, Maozhong An *

State Key Laboratory of Urban Water Resource and Environment, School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, China

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ABSTRACT

Nanocrystalline Zn–Ni (grain size about 26 nm) alloy coatings were electrodeposited on carbon steel substrates in alkaline bath with 5,5′-dimethylhydantoin (DMH) as the complexing agent. The coatings with 13 wt.%–16 wt.% Ni content and the electrolyte with high current efficiency (>85%) were achieved at the optimized parameters, i.e., $Ni^{2+}/(Zn^{2+} + Ni^{2+})$ ratio 0.32, current density 2 $A \cdot dm^{-2}$, temperature 50 °C and agitation speed 1000 rpm. The electrochemical behavior of the bath has been studied by cyclic voltammetry (CV), chronopotentiometry (CE) and cathodic polarization. Results show that the deposition of Zn–Ni alloys occurs at moderate overpotential and the rotation speed and bath temperature have a strong effect on cathodic polarization curves. The effects of $Ni^{2+}/(Zn^{2+} + Ni^{2+})$ ratio, current density, temperature and agitation speed on Ni content and cathode current efficiency were investigated. Studies indicate that the phase structure, grain size, microhardness and corrosion resistance of deposits are directly dependent on Ni content in deposits. The phase structure of deposits changes from a mixture of η-phase and γ-phase to single γ-phase with (411) plane orientation. Furthermore, the grain size decreases with the increase of Zn content in deposits and the increase in current density can also lead to the decrease in grain size. The increase in microhardness of deposits is strongly affected by the increase of Ni content in deposits rather than the Hall–Petch relationship. Zn–Ni alloy coatings with about 13 wt.% Ni content present best corrosion resistance and the bath has a good stability.

1. Introduction

Electrodeposited zinc is often used as the sacrificial coatings to protect steel substrates against corrosion. However, its corrosion resistance is insufficient at high temperature and severe environments. According to the literature [1,2], zinc alloy coatings can provide higher corrosion resistance compared to pure zinc coatings. This is obtained by alloying zinc with Fe group metals such as Fe, Co and Ni. In recent years, the interest in Zn–Ni alloys has been increasing as a substitute for cadmium coatings [3,4] due to its eco-friendly properties [5,6]. In addition, Zn–Ni alloy coatings have attracted considerable attention in the aerospace and energy generation owing to its excellent corrosion resistance at high temperature and severe oxidizing conditions [7]. The properties and characteristics of Zn–Ni coatings are mainly determined by their microstructure and phase composition [8]. It is reported that the corrosion resistance of Zn–Ni alloy coatings with 8 to 14 wt.% of nickel and single gamma phase structure is five times higher than that of pure Zn coatings [9]. Hammami et al. [10] have demonstrated the increase in corrosion resistance with deposits electrodeposited under chronopotentiometry conditions (18.32 mA/cm^2 and 36.63 mA/cm^2). Mosavat et al. [11] have revealed that the Ni content was a major factor to the corrosion resistance of deposits.

Zn–Ni alloys are commonly electrodeposited from acid, alkaline cyanide and alkaline noncyanide (zincate type [12] and weak alkaline type) baths. The acid bath is the first commercial electrolyte [13], which displays a high cathode current efficiency but poor throwing power. In contrast, the alkaline bath can be used for steel parts of complex shape and exhibits more uniform Ni content in deposits. It is noted that the commercial alkaline bath used for Zn–Ni alloy deposition contains cyanide, which is toxic and carcinogenic to human health, and a low current efficiency [14,15] (60%–80%) is obtained in the zincate type alkaline bath. Therefore, it is necessary but difficult to develop an eco-friendly alkaline bath with high current efficiency.

The complexing agents are the key factors to obtain a stable alkaline Zn–Ni bath. Conrad et al. [16] have used sodium acetate as a complexing ligand to stabilize the Zn^{2+} and Ni^{2+} in weak alkaline bath. Müller et al. [12] have investigated four amine alkaline baths. Their results showed that all of those amines were good complexing agents and a homogeneous composition of Zn–Ni alloy can be obtained. Up to now, 5,5′-dimethylhydantoin(DMH) is often used as a complexing ligand in Au [17] or Ag [18] deposition. To the best of our knowledge, there is no report on the application of DMH used as a complexing ligand in Zn–Ni alloy deposition.

* Corresponding author. Tel./fax: +86 451 86418616.
E-mail address: mzan@hit.edu.cn (M. An).

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Table 1
The bath composition and process parameters of the bath.

Bath composition and process parameters	Optimum values
$ZnSO_4 \cdot 7H_2O$ (g/L)	70
$NiSO_4 \cdot 6H_2O$ (g/L)	30
DMH (g/L)	140
$Na_4P_2O_7 \cdot 10H_2O$ (g/L)	40
K_2CO_3 (g/L)	95
Additives (g/L)	0.04
PH	9–10
Cathode density ($A \cdot dm^{-2}$)	1, 2, 3, 4, 5
Temperature (°C)	20, 30, 40, 50, 60
Agitation speed (rpm)	0, 200, 600, 1000, 1400

Nanocrystalline Zn–Ni alloy coatings are usually obtained by using different plating modes [19] (PC, RPC, etc.) or adding additives. Alfantez et al. [20] produced nanocrystalline Zn–Ni coatings from a chloride-based electrolyte and Tehrani et al. [21] presented nanocrystalline single γ-Zn_3Ni phase by cyclic voltammetry at a scan rate of 10 V/s. Their coatings were both obtained from acid bath. By comparison, it is difficult to obtain nanocrystalline Zn–Ni alloy coatings from alkaline bath and there are a few reports about it. Li et al. [22] prepared nanocrystalline Zn–Ni alloy coatings with the grain size in the range of 14 nm to 33 nm in alkaline bath using a laboratory-made additive. Mosavat et al. [23] also obtained nanocrystalline Zn–Ni alloy coatings with average grain size ranging from 13 nm to 68 nm containing saccharin as additive from alkaline bath. However, these works were complicated and the coatings had some disadvantages, e.g.: low microhardness. Brooks et al. [24] electrodeposited nanocrystalline γ-phase Zn–Ni alloy coatings from a chloride-based bath and their results indicated that the hardening of the coatings was independent on grain size.

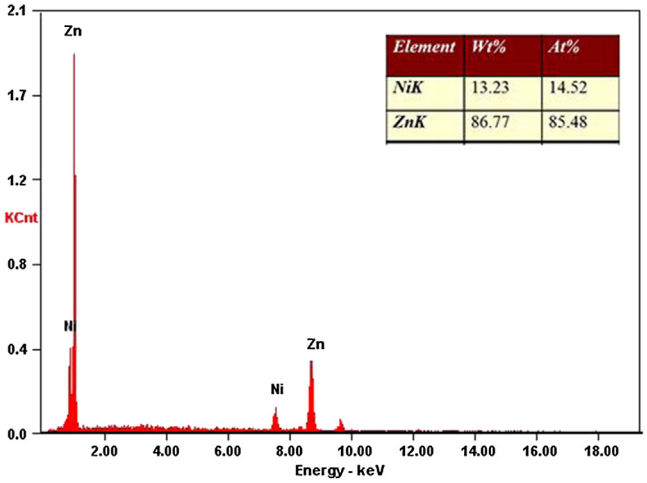

Fig. 2. EDS of Zn–Ni alloy deposits at the optimized parameters.

In this paper, a new alkaline Zn–Ni alloy bath with DMH as the complexing agent was obtained. The effects of the $Ni^{2+}/(Zn^{2+} + Ni^{2+})$ ratio, cathode current density, temperature and agitation speed on Ni content and cathode current efficiency were studied. Simultaneously, electrochemical behavior was investigated by cyclic voltammetry (CV), chronopotentiometry (CE) and cathodic polarization. The influence of Ni content on phase structure, surface morphology, grain size, microhardness and corrosion resistance of deposits and the relationship between grain size and microhardness were also analyzed. Finally, the stability of the bath was studied.

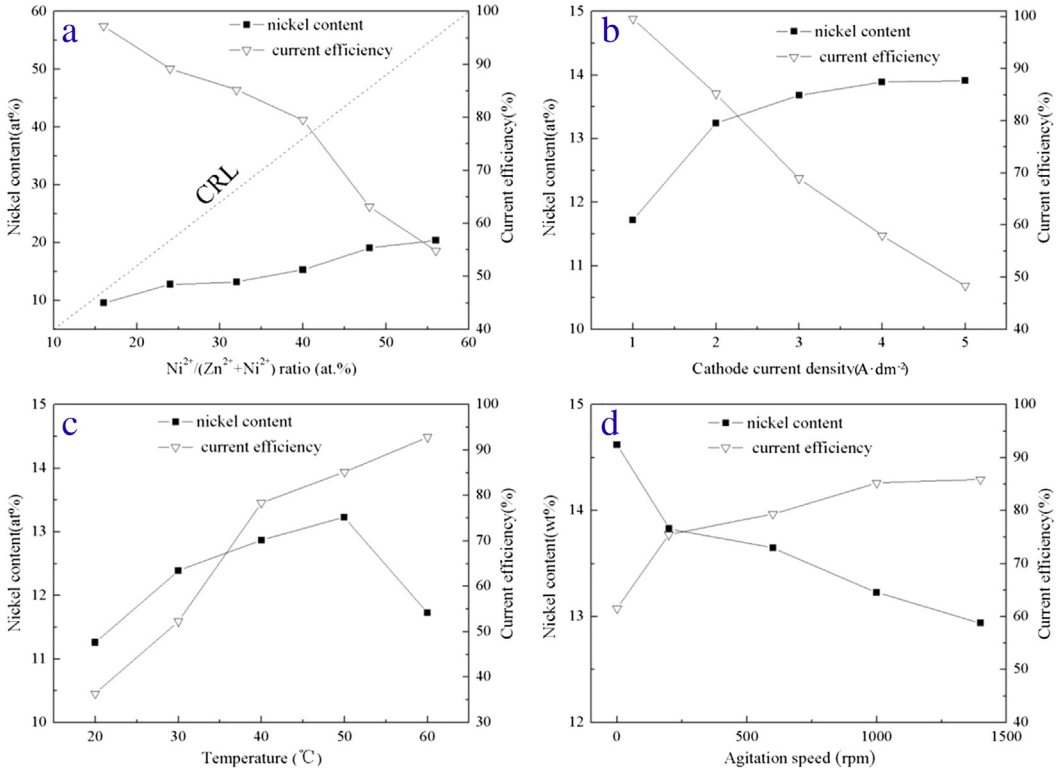

Fig. 1. Effects of bath composition and process parameters on Ni content and current efficiency: a) $Ni^{2+}/(Zn^{2+} + Ni^{2+})$ ratio, electrodeposition was carried out at 2 $A \cdot dm^{-2}$, 50 °C and 1000 rpm, b) cathode current density, electrodeposition was carried out at 50 °C and 1000 rpm from bath with $Ni^{2+}/(Zn^{2+} + Ni^{2+})$ ratio = 0.32, c) temperature, electrodeposition was carried out at 2 $A \cdot dm^{-2}$ and 1000 rpm from bath with $Ni^{2+}/(Zn^{2+} + Ni^{2+})$ ratio = 0.32, d) agitation speed, electrodeposition was carried out at 2 $A \cdot dm^{-2}$ and 50 °C from bath with $Ni^{2+}/(Zn^{2+} + Ni^{2+})$ ratio = 0.32.

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