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Effect of Electrodeposition Parameters on Chemical Composition, Cathodic Current Efficiency, Hardness and Morphology of Zn-Ni Alloy Coatings

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1- Introduction

Zn coating is widely used to protect the steel parts against corrosion. Despite the benefits of zinc coatings, the high electric potential difference between the zinc and the metal substrate leads to instant dissolution of the deposit, and therefore the zinc is deposited with other metals such as Ni, Fe, Cu or Sn. Among these alloy coatings, the Zn-Ni has attracted much attention due to its high ductility, as well as good resistance against corrosion and hydrogen embrittlement. In this paper, the effects of bath temperature, current density, pH and the bath Ni^{2+}/Zn^{2+} ratio on chemical composition, current efficiency, morphology, and hardness of the Zn-Ni coatings are studied.

2- Experimental

In this study St37 steel sheets with dimensions of 25×25×2 mm was used as substrate. The same sized 316L stainless steel was utilized as the non-consumable anode. Electrodeposition was performed by using a DC current rectifier. Bath composition and deposition condition have been presented in Table 1. Hardness tests from surface of the coatings were done by a Vickers microhardness testing machine. The applied load and dwell time were 10 g and 15 s, respectively. Morphology and chemical composition of the coatings was examined via a scanning electron microscope equipped with an energy-dispersive X-ray spectroscope.

Table 1 Bath composition and deposition condition for electrodeposition of Zn-Ni coatings

Bath composition	Zn-Ni coatings
$ZnSO_4.7H_2O$	30-170 g L^{-1}
$NiSO_4.7H_2O$	170 g L^{-1}
H_3BO_3	-
Na_2SO_4	80 g L^{-1}
$NaC_{12}H_{25}SO_4$ (SDS)	0.1 g L^{-1}
Deposition condition	
Current density	30-70 mA cm^{-2}
Temperature	40-80°C
pH	1-4
Stirring speed	250 rpm
Deposition time	20 min

3- Results and Discussion:

3-1 Effect of bath and deposition parameters on chemical composition of the coating

3-1-1 Effect of temperature

Samples were electrodeposited in a current density of 40 mA/cm^2, pH= 2.5, Ni^{2+}/Zn^{2+}=2 and in temperatures of 40, 50, 60, 70 and 80 ˚C. Fig. 1a shows the effect of temperature on the Ni content of the alloy coatings. Ni percentage of the coatings increases with raising the bath temperature, which can be due to thinning of the diffusive layer (decrement of polarization) and variation of the kinetic parameters.

3-1-2 Effect of Current density

Samples were electrodeposited at 50 ˚C, pH= 2.5, Ni^{2+}/Zn^{2+}=2 and in current densities of 30, 40, 50, 60 and 70 mA/cm^2. As shown in Fig. 1b, the coatings have higher Ni percentage at low current densities as compared to the higher ones. In a low current density sequestration mechanism follows a regular mechanism but with the increase of current density the mechanism shifts to an anomalous mechanism. This is due to the decrement of hydrogen reduction overpotential, which facilitate hydrogen evolution and increases the pH near the cathode surface. Therefore, a zinc hydroxide layer is formed on the cathode surface. This prevents reduction of the more noble metal ions, and thus Ni content of the coatings is decreased.

3-1-3 Effect of pH

Samples were electrodeposited at 50 ˚C, current density of 40 mA/cm^2, Ni^{2+}/Zn^{2+}=2 and pH of 1, 1.5, 2, 2.5 and 3. As shown in Fig. 1c, with an increase in pH, Ni percentage of the coatings decreases. The reason is attributed to HSM (Hydroxide Suppression Mechanism) theory. According to this theory, an increase in the pH causes to a higher concentration of OH^- in the electrode/electrolyte interface, and as a result formation of a zinc hydroxide layer on the cathode surface. Deposition of more active metal hydroxide prevents the electrical discharge of the more noble metal.

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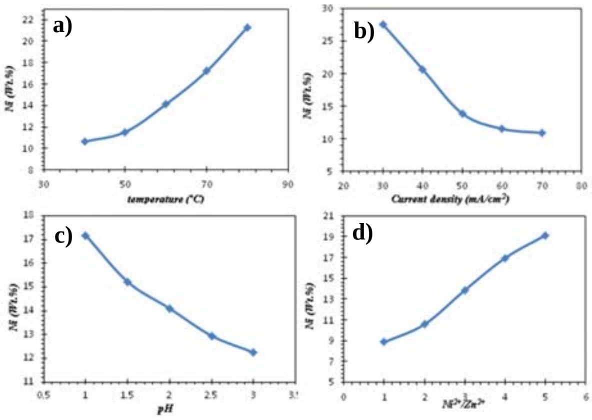

Fig. 1 Plot of Ni content vs. a) the electrodeposition bath temperature, b) the current density, c) the electrodeposition bath pH, d) Ni^{2+}/Zn^{2+} ratios in the electrodeposition bath

3-1-4 Effect of the Ni^{2+}/Zn^{2+} ratio

Samples were electroplated at 50 ˚C, pH= 2.5, current density of 40 mA/cm^2, and Ni^{2+}/Zn^{2+} ratios of 1, 2, 3, 4, and 5. The results are shown in Fig. 1d. As it can be seen, Ni content of the alloy coatings is increased by enhancing the Ni^{2+}/Zn^{2+} ratio, which is due to the competition of the Ni^{2+} and Zn^{2+} ions for reduction.

Effect of bath and deposition parameters on morphology of the coatings

3-2-1 Effect of temperature

Fig. 2 shows the SEM micrographs from surface of the Zn-Ni coatings electrodeposited at 40, 60, and 80ºC. It is obvious that the electrodeposition temperature has a dramatic effect on the surface morphology of the Zn-Ni coatings. The surface roughness is increased and the morphology is coarsen by raising the bath temperature.

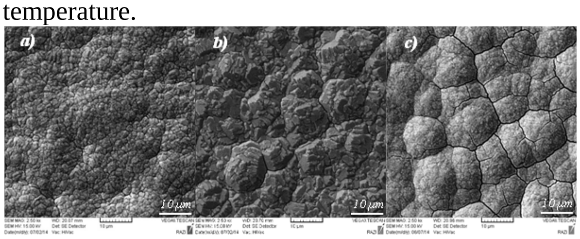

Fig. 2 Morphology of the Ni-Zn coatings deposited at a) 40, b) 60, and c) 80 ˚C

3-2-2 Effect of current density

SEM micrographs from surface of the Zn-Ni coatings electrodeposited at 20, 40, and 60 mA/cm^2 are shown in Fig. 3. The size of the coating grains decreases but the surface becomes rougher with increasing the current density.

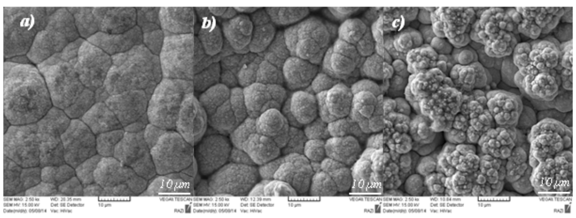

Fig. 3 Morphology of the Ni-Zn coatings deposited at current densities of a) 20; b) 40; and c) 60 mA/cm^2

3-2-3 Effect of pH

Fig. 4 shows the SEM micrographs of the Zn-Ni coatings deposited at pH values of 1, 2, and 4. At low pH values, there is not enough time for hydrogen molecules to exit from the cathode surface due to the high reduction rate of hydrogen ions. Therefore, hydrogen molecules are confined within the coating, resulting in rough, non-uniform, and porous film. The hydrogen reduction rate decreases and reduction reaction of zinc ions facilitates with increasing the pH to 4. Hence, the amount of Zn in the coating increases and the formation of the hydroxide causes roughness, unevenness and porosity on the surface.

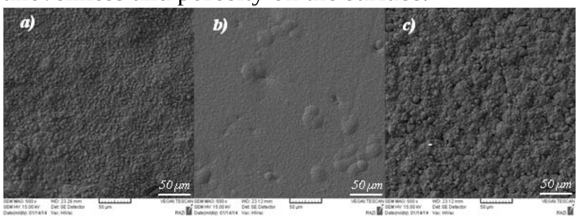

Fig. 4 Morphology of the Ni-Zn coatings deposited at pH of a) 1; b) 2; and c) 3

3-2-4 Effect of Ni^{2+}/Zn^{2+} ratio

Fig. 5 shows the SEM micrographs of the Zn-Ni coatings obtained from baths with the Ni^{2+}/Zn^{2+} ratios of 1, 2 and 5. At small Ni^{2+}/Zn^{2+} ratio the surface morphology is fine grained, which can be because of the high reduction overpotential of H^+ on the surface of the substrate. The reduction overpotential of Zn^{2+} increases, while that of Ni^{2+} and H^+ decreases with raising the Ni^{2+}/Zn^{2+} ratio of the bath. Consequently, the reduction reactions of Ni^{2+} and H^+ take place with a higher speed than the Zn^{2+}.

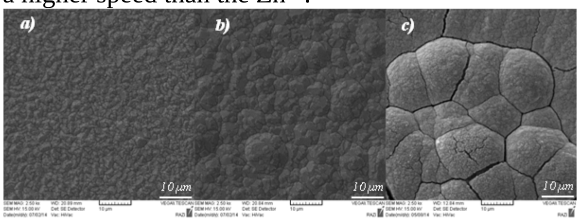

Fig. 5 Morphology of the Ni-Zn coatings deposited from baths with Ni^{2+}/Zn^{2+} ratios of a) 1; b) 2; and c) 5

4- Conclusions

1- Increasing the temperature and Ni^{2+}/Zn^{2+} ratio, as well as decreasing the pH and current density enhance the Ni content of the alloy coatings.

2- The coatings electrodeposited at high pH and current density don't have a good quality (although the current efficiency is high) and can end up in the burning of the surface.

3- Increasing the temperature and the Ni^{2+}/Zn^{2+} ratio, and decreasing the current density and pH leads to harder coatings.

4- Over 70 ˚C temperatures cause brittleness and crack on the coating due to the subsequent hydrogen evolution and residual stress.

5- Coatings obtained at pH=2 have dense and uniform surfaces.

6- Increasing the current density causes fine-grained morphologies, although the obtained coatings have rough surfaces.