Effect of Brightener and Solution Temperature on the Electrodeposition Behavior of Zn-Ni alloy from Alkaline Zincate Solution

裵，聖和

氏　　名　：BAE SEONGHWA

論 文 名　：Effect of Brightener and Solution Temperature on the Electrodeposition Behavior of
　　　　　　Zn-Ni alloy from Alkaline Zincate Solution
　　　　　　(アルカリジンケート浴からの Zn-Ni 合金電析挙動に及ぼす光沢剤と浴温の影響)

区　　分　：甲

論 文 内 容 の 要 旨

Electrodeposited Zn–Ni alloy coatings are used for automobile parts, electric household products, and building materials owing to their superior corrosion resistance. Zn–Ni alloys are usually deposited in a sulfate or chloride solution; however, considering the throwing power on small parts, the use of a zincate solution is preferable. The brightening agents are usually added to zincate solutions for the electrodeposition of Zn-Ni alloys, unlike for sulfate and chloride solutions. In contrast, the solution temperature is an extremely important factor in electrodeposition, but the effect of solution temperature on the electrodeposition behavior of Zn-Ni alloys from zincate solutions has rarely been reported. Therefore, in this study, Zn-Ni alloy electrodeposition was performed in zincate solutions at different solution temperatures using IME as a brightener, and the respective and synergistic effects of IME and solution temperature on the electrodeposition behavior were discussed based on the partial polarization curves of Zn and Ni depositions and hydrogen evolution, appearance, and microstructure of the electrodeposited films.

In Chapter 1, with respect to the background of this study as mentioned above, the previous studies on the deposition behavior of Zn-Ni alloys, and the mechanism of brightening agents, and the purpose and structure of this thesis were described.

In Chapter 2, the effect of the reaction product of epichlorohydrin and imidazole (IME) on the deposition behavior of Zn–Ni alloys was investigated using polarization curves for the Zn and Ni depositions and hydrogen evolution. The IME was used as the brightener. The transition current density at which the deposition behavior shifted from the normal type to anomalous was 50–100 $A \cdot m^{-2}$ in the IME-free solution; it became 10–20 $A \cdot m^{-2}$ with the addition of the IME, indicating that the IME greatly decreased the transition current density. The transition current density corresponds to the current density at which the potential of the total polarization curve significantly shifts from the more noble region than the equilibrium potential of Zn to the less noble region. With the addition of the IME, the decrease in transition current density was attributed to the suppression of hydrogen evolution, and the current efficiency for the alloy deposition in the high-current-density region decreased due to the suppression of both the Zn and Ni depositions. The Ni content of the deposited films decreased with the IME, indicating that Ni deposition was more suppressed by the IME than Zn deposition. With increasing current density, the crystals of the films deposited from the IME-containing solution became smooth and showed significant brightness. The oxidation reaction of the films deposited from the IME-containing solution was suppressed. Consequently, the corrosion potential shifted to the noble direction with the IME.

In Chapter 3, the effect of solution temperature on the deposition behavior of Zn–Ni alloys from alkaline zincate solutions was investigated. The transition current density at which the deposition behavior shifted from the normal to anomalous co-deposition was almost identical at solution temperatures of 293 and 313 K but clearly increased at 333 K. The transition current density appeared to increase due to the enhancement of H2 evolution and Ni deposition at 333 K. The current efficiency for alloy deposition also increased with

increasing solution temperature in both the normal (10–50 A・m^{-2}) and anomalous (500 A・m^{-2}) co-deposition regions. In the normal co-deposition region, Ni deposition and H$_2$ evolution mainly occurred, and the promoting effect of increase in the solution temperature on the Ni deposition was greater than that on the H2 evolution, resulting in an increase in current efficiency alongside solution temperature. In the anomalous co-deposition region at 500 A・m^{-2}, Zn deposition and H$_2$ evolution mainly occurred, and Zn deposition appeared to proceed under a mixed rate-determining process comprising the charge transfer and diffusion of Zn ions. Since the diffusion of Zn ions is promoted by increasing the solution temperature, the current efficiency also seems to increase. Furthermore, the Ni content in the deposited films increased with the solution temperature at all current densities. In the region where the charge transfer process is rate-limiting, Ni deposition accelerates to a greater degree compared with Zn deposition alongside increasing solution temperature, as a result, Ni content in the deposited films seems to increase. In addition, the γ-phase of the deposited films increased with an increasing solution temperature.

In Chapter 4, the synergistic effect of IEM and solution temperature on the deposition behavior of Zn–Ni alloy from alkaline zincate solutions was investigated. The transition current density, at which the deposition behavior shifted from the normal to anomalous type decreased with the addition of IME at 293 K but did not change regardless of IME addition at 313 K and 333 K. This indicates that the inhibitory effect of IME on the hydrogen evolution decreases with increasing the solution temperature. The suppression effect of IME on the Zn and Ni depositions during the alloy deposition was observed at 293 K, while at 313 K and 333 K, the suppression effect was decreased on the Zn deposition, though maintained on the Ni deposition. Therefore, Ni content in the deposits significantly decreased with IME as the temperature increased. The current efficiency for Zn deposition significantly decreased with IME at 293 K, while decreasing insignificantly at 313 K and 333 K. The C content in the deposits was the highest at 293 K, and decreased with the increasing solution temperature, indicating that the adsorption ability of IME on the cathode decreases with the increasing temperature. As a result, the suppression effect of IME on the Zn deposition seems to decrease with increasing the temperature. The gloss of the deposited films was the highest at 293 K, attributed to the adsorption ability of IME being large at 293 K and deposited films with fine crystals becoming smooth.

In Chapter 5, the effect of IME addition on the corrosion resistance of the deposited Zn-Ni alloy films was investigated using immersion tests in a 3 mass% aqueous NaCl solution, which is a typical environment containing chloride ions. In the deposited Zn-Ni alloy films without 24 h immersion in the 3 mass% aqueous NaCl solution, the anodic reaction was suppressed with IME and the corrosion potential shifted to noble direction. Even in the films on which the corrosion products were formed after 24 h immersion in the 3 mass% aqueous NaCl solution, the anodic reaction was suppressed by IME addition and the corrosion potential shifted to the noble side. The corrosion products which were zinc chloride hydroxide (Zn5(OH)$_8$Cl$_2$・H$_2$O), were formed after 24 h immersion in the 3 mass% NaCl solution of Zn-Ni alloy films deposited with and without IME. The plate-like crystals of zinc chloride hydroxide formed on the Zn-Ni alloy films, which was obtained from the solution containing 5 ml·dm^{-3} of IME, were fine and uniform over the entire surface. In the films on which the corrosion products were formed after 24 h immersion in the 3 mass% aqueous NaCl solution, the suppression of anodic reaction with IME is attributed to the formation of uniform corrosion products (zinc chloride hydroxide) on the surface, in addition to the co-deposition of C.