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Effects of plating factors on morphology and appearance of electrogalvanized steel sheets

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Abstract: Because the lightness, the gloss and the press-formability of electrogalvanized steel sheets change depending on the morphology of deposited Zn, control of this factor is essential to improving these properties. The effects of plating factors on the morphology of deposited Zn were systematically discussed both from the crystallographic viewpoint of epitaxy between Zn and steel and from the electrochemical viewpoint of the overpotential for Zn deposition. Plating factors include crystal orientation of steel substrate, current density, flow rate, temperature, addition of inorganic compounds to the solution and pre-adsorption of organic compounds. These plating factors affect the overpotential for Zn deposition and epitaxy between Zn and steel. The crystal orientation index of the Zn basal plane and the platelet crystal size of Zn are decreased with increasing the overpotential for Zn deposition. They are also decreased with decreasing the epitaxy between Zn and steel, even when the overpotential is kept constant. When the overpotential for Zn deposition is increased, the surface roughness of deposited Zn increases because of an increase in the inclination of the Zn basal plane to the steel substrate. When the epitaxy between Zn and steel is decreased without changing the overpotential, the surface roughness is reduced due to the decrease in platelet crystal size of Zn, although the inclination of the Zn basal plane is somewhat increased. The lightness of deposited Zn is enhanced with decreasing the surface roughness of Zn.

Key words: lightness; zinc; electrodeposition; overpotential; morphology; epitaxy

1 Introduction

Electrogalvanized steel sheets coated with transparent organic composite films, in the form of functional conversion-coated steel sheets, are used extensively in home electrical appliances due to their high level of resistance to corrosion and fingerprints. Because their lightness, gloss, and press-formability of electrogalvanized steel sheets change depending on the morphology of the deposited Zn, control of this factor is essential to improving these properties. For this reason, many studies have been made on the effects of electrolytic conditions on the morphology of deposited Zn[1-4].

During Zn electrodeposition on an α -Fe substrate, the initial Zn deposits epitaxially following Burger orientation relationship, described as $(110)_{Fe}/((0001)_{Zn},$ $[\overline{1}11]_{Fe}/([11\overline{2}0]_{Zn} [5-6])$. In practice, Zn deposits epitaxially at first, then shifts to random growth that depends on the electrolytic conditions. Therefore, approaching this challenge from both the crystallographic and electrochemical viewpoints is essential to controlling the morphology of the deposited Zn. In this work, the effects of plating factors such as the crystal orientations of the steel substrate, current density, temperature, flow rate, addition of inorganic compounds to the solution and the pre-adsorption of organic compounds on the morphology of deposited Zn were systematically investigated from both the crystallographic viewpoint (the epitaxy of the Zn/steel) and the electrochemical viewpoint (the overpotential for Zn deposition).

2 Experimental

The electrolytic solution was prepared by dissolving reagent-grade $ZnSO_4 \cdot 7H_2O(1.2 \text{ mol/L})$ and $Na_2SO_4(0.5 6 \text{ mol/L})$ in distilled and deionized water. Inorganic compounds were added in amounts of 8×10^{-5} mol/L in the form of sulfate (Sn) or oxoacidic salts (W, Mo). Polycrystalline steel sheets measuring 3 cm \times 3 cm with a

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crystal grain size of No. 7 ferrite, based on the Japanese Industrial Standard (JIS), were used as substrates. The preferred orientation plane of the substrates was the (110) plane of Fe; and the X-ray diffraction intensity ratio of the (110)_{Fe} to the total Fe planes was 0.70. Each substrate was polished with emery papers and buffed to mirror smoothness before electrode position. In some experiments, to investigate the effect of pre-adsorption of organic compounds on the morphology of the deposited Zn, the buffed substrate was immersed in the solution of 40 °C containing 0.1 g/L polyethylene glycol (PEG) with mean relative molecular mass of 1 540 and 6 000 for 1 min, then washed in deionized water at 40 °C for 3 min by ultrasonic cleaning prior to electrodeposition.

Zinc electrodeposition was conducted in solutions agitated at 400 r/min by a stirrer under coulostatic $(6.8 \times 10^4 \text{ or } 2.1 \times 10^5 \text{ C/m}^2)$ and galvanostatic (1 500 A/m²) conditions at 40 °C. Platinum mesh measuring 8 cm×12 cm was used as the anode. In some experiments, to investigate the effect of current density, temperature and flow rate, Zn deposition was performed using a circulation-type electrolytic cell in which the electrolyte was circulated between a platinum anode and steel cathode placed in parallel. The cathode potentials were measured using a saturated Ag/AgCl reference electrode (0.199 V vs. NHE, 25 °C). The potentials were shown in reference to the NHE.

The surface orientations of the steel substrate were determined by the ECP after electropolishing. The morphology of the deposited Zn was examined by SEM. The crystal orientation of deposited Zn was determined by the method of Willson and Rogers using the X-ray diffraction intensities from the (0002) to $(11\overline{2}2)$ planes of Zn[7]. The lightness of Zn was measured colorimetrically using the 0-d method (JIS-Z-8722).

3 Results and discussion

3.1 Epitaxial growth behavior of Zn deposited on steel sheet

Fig.1 shows SEM images of electrodeposited Zn with a thickness of 2.8 μ m and the steel substrate after dissolving the Zn layer. Both micrographs were taken form the same area. The deposited Zn consisted of a stack of thin hexagonal platelet crystals, and a clear change in the stacking direction was observed at the steel grain boundaries. More specifically, the crystals of deposited Zn tended to grow in identical directions on each crystal grain of the steel sheet. In this work, when Zn was deposited aligning the layered platelet crystals on each crystal grain of the steel sheet, it was clear that Zn grew epitaxially on the steel sheet.

Fig.2 shows the morphologies of Zn deposited on each crystal grain of the polycrystalline steel sheet. The



Fig.1 Surface morphologies of steel substrate (a) and electrodeposited Zn (b) (5 k A/m^2)

morphology of the deposited Zn was classified into the following two types based on the crystal orientations of the steel substrate. 1) Zn was deposited epitaxially and the thin platelet crystals were regularly layered on each crystal grain of the (211), (554) and (221) planes of Fe substrate. 2) Zn grew randomly on the (111) and (100) planes of Fe substrate. The degree of Zn epitaxial growth depends on the crystal orientation of the steel sheet and Zn grows more epitaxially on that close to the $(101)_{Fe}$ plane. This result suggests that Zn epitaxial growth occurs more easily on the crystal grains of the steel substrate where the angles between the Zn basal plane and steel surface plane are small. In other words, Zn can continue to deposit epitaxially, according to Burger orientation relationship[8], i.e., $(110)_{Fe}/(0001)_{Zn}$, $[\bar{1}11]_{Fe}/[1120]_{Zn}$, with decreasing the inclination of the Zn basal plane to the steel surface plane.

3.2 Morphologies and lightness of Zn deposited under various electrolytic conditions

Fig.3 shows the morphologies of Zn deposited at different current densities, flow rates and bath temperatures. At 5 kA/m², Zn was deposited in large grains due to arrangement of the layered thin platelet crystals on each crystal grain of the steel sheet. However, with increasing the current density to 20 kA/m², these crystals became random in their growth direction and small in size, as evident from Figs. 3(a) and (b). As can



Fig.2 morphologies of Zn deposited on each crystal grain of polycrystalline steel sheet (5 kA/m², coating density of Zn 20 g/m²): (a) $(100)_{Fe}$; (b) $(211)_{Fe}$; (c) $(111)_{Fe}$; (d) $(554)_{Fe}$; (e) $(221)_{Fe}$

be seen from Figs.3(c)-(f), with decreasing the flow rate and solution temperature, Zn deposited randomly in small grains in approximate proportion to the increase in current density.

Fig.4 shows the crystal orientations of Zn deposited at various current densities, flow rates and solution temperatures. With a decrease in the current density, the orientation indices of (0002) and $(10\bar{1}3)_{Zn}$ increased markedly, while those of $(10\bar{1}1)$ and $(10\bar{1}1)_{Zn}$ correspondingly decreased. When the flow rate and solution temperature were raised, the orientation indices of (0002) and $(10\bar{1}3)_{Zn}$ increased but those of $(10\bar{1}1)$ and $(10\bar{1}0)_{Zn}$ decreased. This tendency can be explained in terms of the overpotential for Zn deposition. The plating conditions which permitted an increase in the overpotential for Zn deposition caused a decrease in the orientation indices of the (0002) and $(10\bar{1}3)_{Zn}$ and a corresponding increase in those of $(10\bar{1}1)$ and $(10\bar{1}0)_{Zn}$.

Fig.5 shows the lightness of Zn deposited at various current densities, temperatures and flow rates. The lightness of the deposited Zn was enhanced with decreasing the current density, and increasing the temperature and flow rate, indicating that, within the range studied, the lightness was enhanced with decreased overpotential for Zn deposition. Because the preferred orientation of the $(0001)_{Zn}$ plane increases with

decreasing the overpotential for Zn deposition, the platelet crystals of Zn are likely to be parallel to the substrate, producing a visibly smooth surface. As a result, the intensity of diffuse reflectance on deposited Zn increases, and the lightness of Zn is enhanced.

3.3 Morphologies and lightness of Zn deposited from solutions containing small amounts of Mo, W or Sn

Fig.6 shows SEM images of Zn deposited from solutions containing 8×10^{-5} mol/L of Mo, W or Sn as an additive. Zn deposited from additive-free solution (Fig.6(a)) showed regularly layered platelet crystals, whereas deposits from Mo or W-containing solution (Figs.(b) and (c)) consisted of some irregular platelet crystals. In solutions containing Sn (Fig.6(d)), the deposited Zn showed an absence of platelet crystals, but consisted of blocks with smooth surfaces.

Table 1 lists the cathode potential during Zn deposition, the orientation and the lightness of Zn deposited from solutions containing 8×10^{-5} mol/L of Mo, W or Sn as an additive. The cathode potential in solutions containing Mo or W was almost identical to that in the additive-free solution, showing that Mo and W had no effect on the overpotential for Zn deposition. In Sn-containing solutions, the cathode potential shifted in



Fig.3 Morphologies of Zn deposited at different current densities, flow rates and bath temperatures: (a) 5 kA/m²; (b) 20 kA/m²; (c) 1 m/s; (d) 2 m/s; (e) 50 °C; (f) 70 °C



Fig.4 Crystal orientations of Zn deposited at various current densities, flow rates and bath temperatures



Fig.5 Lightness of Zn deposited at various current densities, temperatures and flow rates



Fig.6 SEM images of Zn deposited from solutions containing 8×10^{-5} mol/L of Mo, W or Sn as additive: (a) Additive-free; (b) 8×10^{-5} mol/L of Mo; (c) 8×10^{-5} mol/L of W; (d) 8×10^{-5} mol/L of Sn

the noble direction, indicating a decrease in the overpotential for Zn deposition. The current efficiency of Zn deposition decreased with addition of Sn. Consequently, the total polarization curve shifted in the noble direction as a result of an increase in hydrogen evolution, leading to a decrease in the overpotential for

Zn deposition.

Zn deposited at a coating density of 64 g/m² from additive-free solution showed hardly any orientation of the (0001) and ($10\overline{1}3$) planes, as shown in Table 1. However, the orientation of the (0001) and ($10\overline{1}3$) planes of Zn was increased by addition of Mo, W or Sn. The

Table 1 Cathode potential during Zn deposition, orientation and lightness of Zn deposited from solutions containing 8×10^{-5} mol/L of Mo, W or Sn as additive

Additive	Capthode potential (vs NHE)/V	Orientation index		Lightnag
		(0002)	(1013)	Lightness
Additive-free	-0.828	0.3	1.7	75.5
Мо	-0.830	1.0	1.4	80.0
W	-0.826	3.0	2.7	80.5
Sn	-0.798	0.4	5.5	89.0

increase in orientation of the $(10\overline{13})$ plane of Zn with addition of Sn is ascribed to a decrease in the overpotential for deposition, which can be explained in terms of Pangarov's calculation. However, the orientation for the (0001) plane of Zn increased with addition of Mo and W, despite the fact that these additives did not change the overpotential for deposition. This cannot be explained by Pangarov's calculation[8]. Mo and W are assumed to adsorb onto cathodes in the form of oxygen-containing anions such as MOQ_4^{2-} and WO_4^{2-} , which act as catalysts for hydrogen evolution. The adsorption of MOQ_4^{2-} and WO_4^{2-} appears to have some effect on increasing the orientation of $(0001)_{Zn}$.

The lightness of Zn deposited at a coating density of 20 g/m^2 was the maximal with Sn addition, and also increased with the addition Mo or W as shown in Table 1. The preferred orientation of Zn deposited from solutions containing 8×10^{-5} mol/L of Mo, W or Sn was the (0001) or (1013) plane, as shown in Table 1. The surface of the Zn platelet crystals is the (0001) basal plane of HCP, and the inclination of the (1013) to the (0001) plane is smaller than that of the other planes to (0001). Briefly, when the preferred orientation of deposited Zn is the (0001) or (1013) plane, Zn platelet crystals are likely to be parallel to the substrate, resulting in a smooth surface. Consequently, the intensity of diffusion reflection was strong in the case of deposited Zn with a preferred orientation of the (0001) or (1013) plane, resulting in an increase in the lightness of Zn. The increase in the lightness of the deposited Zn with the addition of Mo, W or Sn is ascribed to an increase in the orientation of the (0001) or (1013) plane. Notably, in the case of the Sn-containing solution, the lightness of Zn increased significantly as a result of the marked orientation of the (1013) plane.

3.4 Morphologies and lightness of Zn deposited with pre-adsorption of PEG

Although the crystal orientation of deposited Zn significantly changes with addition of organic compounds to the electrolyte, addition of these compounds to electrolyte has a harmful effect on the adhesive properties of deposited Zn, and their

concentration in the electrolyte is difficult to control. The authors therefore tried to control the morphology of deposited Zn by pre-adsorption of organic additives from the viewpoint of commercial production. With this strategy of employing pre-adsorption of organic additives, no organic additives were added to the electrolyte, but they were contained in the pre-treatment solution prior to electrodeposition. A steel substrate was immersed in a solution containing the organic additive alone, followed by washing in deionized water. Zn electrodeposition was then conducted in a solution without any organic additive. The morphology of deposited Zn was expected to change significantly because of a decrease in epitaxy of Zn/steel during Zn deposition due to several atomic layers of organic additive adsorbed onto the steel substrate prior to electrodeposition. This pre-adsorption method of organic additive has no harmful effect on the adhesive properties of deposited Zn because no organic compounds are added to the electrolyte.

Fig.7 shows the morphologies of Zn deposited after pre-adsorption of PEG with relative molecular mass of 6 000 and without. The platelet crystals of Zn deposited



Fig.7 Morphologies of Zn deposited after pre-adsorption of PEG with relative molecular mass of 6 000 (a) and without pre-adsorption (b)

with pre-adsorption of PEG grew in random directions and were small. The cathode potential for Zn deposition was slightly polarized by pre-adsorption of PEG, showing a slight increase in overpotential for Zn deposition due to the pre-adsorption. The decrease in size of platelet crystals of Zn due to pre-adsorption of PEG is attributed to both the increase in overpotential for Zn deposition and the decrease in epitaxy of Zn/steel.

Fig.8 shows the lightness of Zn deposited with preadsorption of PEG and without. The lightness of deposited Zn was enhanced by pre-adsorption of PEG at coating densities of Zn exceeding 20 g/m². Because the pre-adsorption of PEG created a smooth surface of deposited Zn due to a decrease in the size of the platelet crystals of Zn, the intensity of diffusion reflectance of Zn increased, resulting in the enhancement of lightness.



Fig.8 Lightness of Zn deposited with pre-adsorption of PEG and without

4 Conclusions

The effect of plating factors on the morphology, crystal orientation and lightness of deposited Zn was investigated. The plating factors were divided into the following two types from the viewpoint of the overpotential for Zn deposition and epitaxy of the Zn/steel. Type I includes current density, flow rate, solution temperature and addition of a small amount of inorganic additive such as Sn^{2+} to the electrolyte, which induce a change in the overpotential for Zn deposition, therefore, have a significant effect on the morphology, crystal orientation and lightness of the deposited Zn. Type II includes the pre-adsorption of an organic compound and a decrease in orientation index of the {110} plane of the steel substrate, which chiefly inhibit the epitaxial growth of Zn on the steel sheet but have little effect on the overpotential for Zn deposition, and accordingly cause variation in the crystal orientation and lightness of the deposited Zn.

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