Effect of Preadsorption of Organic Additives on the Appearance and Morphology of Electrogalvanized Steel Sheets

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Zn electrodeposition was performed galvanostatically on steel sheets at 1 500 A/m² in an agitated sulfate solution at 40°C to investigate the effect of preadsorption of organic additives on the lightness and morphology of Zn. The organic additives employed were classified into two types: 1) polyethylene glycol (PEG), gelatin, and stearyl dimethylbenzyl ammonium chloride (SDBAC) (Type I), which exhibit a polarization effect for Zn deposition; and 2) saccharin and sodium lauryl sulfate (Type II), which exhibit no polarization effect for Zn deposition. The platelet crystals of deposited Zn were reduced in size with preadsorption of all the organic additives considered. The observed decrease in the size of Zn platelet crystals with preadsorption is attributed to both an increase in the overpotential for Zn deposition and a decrease in the epitaxial growth of Zn on steel substrates. The preferred orientation of the (0001) Zn basal plane significantly decreased because of an increase in Zn deposition overpotential owing to preadsorption of PEG and gelatin, and the orientation slightly decreased with saccharin and sodium lauryl sulfate in spite of the absence of a polarization effect on Zn deposition. The surface roughness of deposited Zn decreased with preadsorption of organic additives with the exception of SDBAC. This is due to a decrease in the size of Zn platelet crystals. The lightness of deposited Zn was increased by preadsorption of organic additives with the exception of SDBAC. Because Zn deposited nonuniformly with preadsorption of SDBAC, the surface roughness of Zn increased and the lightness decreased.

KEY WORDS: Zn; electrodeposition; preadsorption; morphology; crystal orientation; overpotential; lightness; surface roughness; organic additive; epitaxial growth.

1. Introduction

Electrogalvanized steel sheets coated with transparent organic composite films are used extensively as conversion-coated steel sheets for home electrical appliances owing to their excellent resistance to corrosion and fingerprints. Because the lightness, gloss, surface roughness and press formability of electrogalvanized steel sheets change depending on the morphology of the deposited Zn, the control of the Zn morphology is essential for improving these properties. The addition of organic compounds into the electrolyte is known to markedly alter the morphology of the deposited Zn, but direct addition makes it difficult to control the concentration of organic compounds in solution and sometimes has a harmful effect on the adhesive properties of the deposited Zn. Therefore, controlling the morphology of deposited Zn by preadsorption of organic additives was attempted from the standpoint of applying additives in a commercial production line. Employing a pretreatment solution containing organic additives alone prior to electrodeposition resulted in the preadsorption of organic additives, such that no organic additives were included in the electrolyte. Zn electrodeposition was then performed in an electrolyte solution free from organic additives.

The authors used polyethylene glycol (PEG) as the organic additive in a previous study because of its stable straight-chain structure in electrolytic solution, and the effect of PEG preadsorption on the appearance and morphology of deposited Zn was reported. It was reported that the preadsorption of PEG decreased the size of platelet crystals of deposited Zn and increased the lightness. However, the effect of preadsorption is expected to depend on the type of organic additives used. The effect of preadsorption of organic additives other than PEG on the morphology of deposited Zn is unknown. Therefore, in this study, five organic additives possessing different molecular structures, radicals for adsorption, and adsorption capabiliites were selected, and the effect of preadsorption of organic additives on the lightness and morphology of deposited Zn was investigated. Relationships among the lightness, morphology, crystal orientation, and surface roughness of deposited Zn are discussed.

2. Experimental

The solution composition and electrolysis conditions for
Zn deposition are listed in Table 1. The electrolytic solution was prepared by dissolving reagent-grade ZnSO₄·7H₂O (1.2 mol/L) and Na₂SO₄ (0.56 mol/L) in distilled and deionized water. The pH was adjusted to 2.0 with sulfuric acid. Polycrystalline steel sheets that conformed to the Japanese Industrial Standard (JISG 3141) measuring 3 × 3 cm² were used as cathode 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 plane to the total Fe planes was 0.70. Each substrate was polished with emery papers (No. 320–2000) and buffed to mirror smoothness before electrodeposition. The buffed substrates were immersed in solutions containing 1.0 g/L of various organic additives for 1 min at 40°C and then washed in deionized water at 40°C for 1 min by ultrasonic cleaning prior to electrodeposition. As shown in Fig. 1. Zn electrodeposition was performed in solutions agitated at 400 rpm using a stirrer under coulostatic conditions at 40°C. Each substrate was polished with emery papers (No. 320–2000) and buffed to mirror smoothness before electrodeposition. The buffed substrates were immersed in solutions containing 1.0 g/L of various organic additives for 1 min at 40°C and then washed in deionized water at 40°C for 1 min by ultrasonic cleaning prior to electrodeposition. As shown in Fig. 1.

Table 1. Electrolysis conditions.

| Parameter          | Value          |
|--------------------|----------------|
| ZnSO₄·7H₂O (mol/L) | 1.2            |
| Na₂SO₄ (mol/L)     | 0.56           |
| pH                 | 2              |
| Current density (A/m²) | 1500          |
| Amount of charge (C/m²) | 1.6×10⁶–2.6×10⁶ |
| Operating conditions |                |
| Cathode            | Fe (3×3 cm²)   |
| Anode              | Pt (8×12 cm²)  |
| Stirrer (rpm)      | 400            |

Fig. 1. A schematic of the electrodeposition procedure.

X-ray diffraction peak of the 0002 reflection. The surface roughness of Zn was evaluated by centerline average roughness Ra (JIS B 0601) by using a SURFCON1500DX-3DF (Tokyo Seimitsu Co.). The lightness of Zn was measured by the 0-d method (JIS-Z-8722, for diffuse illumination/0° viewing angle) by using a colorimeter (CM-512m3; Konica Minolta Co.). The surface crystal orientations of Zn deposited at an initial stage and that of the Fe substrate were investigated by an electron back-scattering pattern (EBSP). Prior to EBSP, the Fe substrate was polished using emery paper and buffed. This was then electropolished in a solution containing 11.8 mol/L ethanol, 3.64 mol/L glycerol, and 0.75 mol/L of perchloric acid at 12 V and 6.7 C/cm².

3. Results

3.1. Effect of Preadsorption on the Cathode Potential

Figure 2 shows the structural formula of various organic additives used for preadsorption in this study. PEG (a) and gelatin (b) both have a straight-chain structure. Oxygen atoms in PEG and gelatin act as radicals for adsorption by utilizing their lone pairs of electrons. Stearyl dimethylbenzyl ammonium chloride (c) is a cationic surfactant, and nitrogen atoms act as radicals for adsorption. Saccharin (d) seems to adsorb by utilizing its oxygen and nitrogen atoms. Sodium lauryl sulfate (e) is an anionic surfactant, and hydrophilic groups (–O–SO₃Na) act as radicals for adsorption.

Figure 3 shows the time dependence of the cathode potential during Zn deposition with preadsorption of the various organic additives considered. The shift of the cathode potential in the less noble direction indicates an increase in the overpotential for deposition. Without preadsorption (1), Zn was deposited at potentials 35 mV less noble than its equilibrium potential (~0.76 V vs. NHE) and the cathode potential barely showed a change with time. With preadsorption by PEG (2), the cathode potential shifted 60–70 mV in the less noble direction during the initial stage of deposition, and approached the potential observed in the absence of preadsorption with time. In other words, the
overpotential for Zn deposition was found to increase over a period of approximately 120 s even without direct addition of PEG into the electrolyte. At 120 s, the coating mass of deposited Zn was 55 g/m², which indicated that the polarization effect of preadsorption was maintained despite continued Zn deposition. With preadsorption of gelatin (3) and SDBAC (4), the polarization effect of Zn deposition was observed during the initial stage as it was with PEG preadsorption. The duration of the polarization effect was shorter with gelatin than that with PEG. For direct addition of PEG, gelatin, and SDBAC into the electrolyte, these additives were reported to have demonstrated the polarization effect for Zn deposition, and the polarization effect was largest with SDBAC and smallest with gelatin.13,15) Preadsorption of PEG, gelatin, and SDBAC showed an equivalent trend in the polarization effect for Zn deposition. On the other hand, with preadsorption of saccharin (5) and sodium lauryl sulfate (6), the cathode potentials were almost the same as that without preadsorption, showing no polarization effect for Zn deposition.

3.2. Surface Morphologies of Deposited Zn

Figure 4 shows the surface morphologies of Zn deposited with a coating mass of 5 g/m² with preadsorption of the various organic additives considered. Platelet crystals of Zn were observed in all deposits. The number of Zn platelet crystals increased and the size significantly decreased for all preadsorption additives considered. In all cases of preadsorption, the platelet crystals of deposited Zn greatly inclined in the direction perpendicular to the steel substrate and grew in random directions. With preadsorption of SDBAC (d), at the right side area of Fig. 4(d), the platelet crystals were particularly small, and random in size.

Figure 5 shows the surface morphologies of Zn deposited with a coating mass of 20 g/m² with preadsorption of the various organic additives considered. In all cases, the Zn platelet crystals were larger and more definite than those deposited at 5 g/m². The size of the Zn platelet crystals was smaller with all preadsorption additives than that without these additives.

Figure 6 shows the surface morphologies of Zn deposited with a coating mass of 40 g/m² with preadsorption of the various organic additives considered. For depositions of 40 g/m², the Zn platelet crystal layers became somewhat irregular and the edges were not linear; however, the size of the Zn platelet crystals was smaller in all cases involving preadsorption than that without preadsorption. It is known that the platelet crystals of deposited Zn reduce in size with increasing deposition overpotential and with decreased epitaxy between the deposited Zn and steel substrate.16,17) This is because the nucleation rate of Zn prevails over the growth rate by increasing the Zn deposition overpotential,16) and also because Zn crystals grow in random directions by decreasing the Zn/steel epitaxy. Therefore, it was considered that the decrease in the size of Zn platelet crystals deposited with preadsorption of PEG, gelatin, and SDBAC was caused by an increase in Zn deposition overpotential (Fig. 3) and a decrease in the Zn/steel epitaxy. It is further considered that, with preadsorption of saccharin and sodium lauryl sulfate, the size of Zn platelet crystals decreased owing to a decrease in the Zn/steel epitaxy despite no change in the overpotential observed for Zn deposition in this case (Fig. 3). The decrease in Zn epitaxial growth with preadsorption of organic additives is ascribed to the observed increase in the Zn deposition overpotential and the suppression of Zn normal growth due to organic additives being adsorbed on the growth sites of Zn. The resulting decrease in the size of Zn
platelet crystals due to preadsorption even at depositions of 40 g/m² seems to be caused by both decrease in platelet crystal size at the initial stage of Zn deposition and the continuous adsorption effect of organic additives during the middle period of deposition. In contrast, without preadsorption, the deposited Zn platelets are partially parallel to the steel substrate and possess a smooth surface. With preadsorption of saccharin and sodium lauryl sulfate, the deposited Zn platelets became small, but were observed to be parallel to the steel substrate at many sites. It has been reported that the deposited Zn platelets are parallel to the substrate when the preferred orientation of Zn crystals is the {0001} basal plane of the hcp structure. The morphology of Zn deposited with preadsorption of saccharin and sodium lauryl sulfate suggests a preferred orientation of the {0001} plane.

Figure 7 shows the effect of preadsorption of organic additives on the crystallite size of deposited Zn. Zn crystallite sizes are observed to increase with coating mass during the initial stage of deposition and become almost constant for a deposition mass above 20 g/m² irrespective of whether preadsorption was performed or not. The Zn crystallite size with preadsorption was smaller for all organic additives considered than that without preadsorption at all coating masses, which showed a continuous effect of preadsorption despite increases in the coating mass. Differences in Zn crystallite-size reductions among the organic additives considered were negligible. The measured Zn crystallite size was approximately 40–100 nm, and the grain size of Zn platelet crystals was several micrometers, as shown in Figs.
4, 5, and 6. It is reported that hexagonal platelets of deposited Zn are composed of many particles having a size of several tens of nanometers. In this study, the crystallite size determined using the half-width of X-ray diffraction peaks appears to correspond to the size of each particle forming the hexagonal platelets of Zn. The grain size of Zn platelet crystals decreases with crystallite size, demonstrating a good correlation between the size of platelet crystals and the crystallite size. The observed decrease in crystallite size owing to preadsorption is ascribed to both increase in the Zn deposition overpotential and decrease in the Zn/steel epitaxy.

3.3. Crystal Orientation of Deposited Zn

The crystal orientation of deposited Zn was examined to evaluate the effect of preadsorption of organic additives on the coating morphology. Figure 8 shows the crystal orientation of Zn deposited with and without preadsorption of PEG. Without preadsorption of PEG, as shown in Fig. 8(a), the preferred orientation of deposited Zn was the \{0001\} plane regardless of the coating mass. This agreed well with the surface morphologies shown in Figs. 4, 5, and 6. With preadsorption of PEG, as shown in Fig. 8(b), the orientation of the \{0001\} plane was diminished relative to that without preadsorption for all coating masses. The preferred orientation plane was \{0001\} during the initial stage of deposition, but the orientation of the \{0001\} plane significantly decreased, and those of \{10\} and \{10\} planes increased at coating masses above 20 g/m². The orientation of the \{10\} and \{12\} planes, which were scarcely observed without preadsorption, were observed to a small degree.

Figure 9 shows the crystal orientation of Zn deposited with preadsorption of gelatin and SDBAC. With preadsorption of gelatin, as shown in Fig. 9(c), orientation of the \{0001\} plane significantly decreased compared with that without preadsorption. This trend agrees with that observed with preadsorption of PEG, as shown in Fig. 8(b). With preadsorption of SDBAC, as shown in Fig. 8(d), the orientation of the \{0001\} plane decreased compared with that without preadsorption; however, the degree of decrease in the \{0001\} plane orientation was not as significant as that observed with preadsorption of PEG.

Figure 10 shows the crystal orientation of Zn deposited with preadsorption of saccharin and sodium lauryl sulfate. With both additives, the preferred orientation plane of deposited Zn was \{0001\}, showing the same preferred orientation as that without preadsorption [Fig. 8(a)]. However, the orientation index of the \{0001\} plane decreased a bit compared with that without preadsorption.

It is known that the crystal orientation of Zn deposited on steel sheets depends on the Zn deposition overpotential and also on the extent of Zn/steel epitaxy. Pangarov calculated the relative values of two-dimensional nucleation work for various crystal planes. Assuming that two-dimensional nuclei with the smallest nucleation work were formed at a given crystallization overpotential, he examined the overpotential dependence of the preferred orientation of various metals deposited from aqueous solutions. According to Pangarov, the preferred orientations of hcp Zn are shifted from the \{0001\} plane to the \{10\} \{11\}, \{12\}, and \{10\} planes (in that order) with increasing Zn deposition overpotential. It is considered that the remarkable decrease in the \{0001\} Zn plane orientation by preadsorption of PEG and gelatin, as shown in Figs. 8 and 9, was caused by the increase in the overpotential for Zn deposition (Fig. 3).

On the other hand, during Zn deposition on an α-Fe substrate, the initial Zn deposits grow epitaxially according to Burgers’ orientation relationship described as \{110\} \{110\} \{11\} \{11\} Zn, \{1\} \{1\} \{1\} \{1\} Fe. Because the preferred orientation of the steel substrate used in this study is \{110\}, the crystal orientation plane of epitaxially deposited Zn should be \{0001\}. It is considered that, to some extent, the decrease in the \{0001\} Zn plane orientation for preadsorption of saccharin and sodium lauryl sulfate, as shown in

![Graph](image-url)
3.4. Surface Roughness and Lightness of Deposited Zn

Figure 11 shows the effect of preadsorption of organic additives on the surface roughness of deposited Zn. The surface roughness of deposited Zn increased with coating mass, irrespective of whether preadsorption was performed. With preadsorption of all organic additives except SDBAC, the surface roughness of Zn was smaller than that without preadsorption over all coating masses. The smaller surface roughness observed with preadsorption may be attributed to the decrease in the size of Zn platelet crystals. With preadsorption of organic additives, the surface roughness of Zn should be larger than that without preadsorption from the perspective of crystal orientation only because of the decrease in the {0001} plane orientation or increase in the inclination of Zn platelet crystals to the steel substrate. The smaller surface roughness is due to the fact that the surface roughness of the Zn coatings was more greatly affected by the decrease in the size of platelet crystals than by the crystal orientation. Among the organic additives considered, the surface roughness was smaller with preadsorption of gelatin and saccharin. On the other hand, with preadsorption of SDBAC, the surface roughness was larger than that without preadsorption. With preadsorption of SDBAC, the polarization of Zn deposition was largest (Fig. 3), and the inclination of Zn platelet crystals to the steel substrate was almost all nonuniformly (Fig. 4). The surface roughness of Zn increased with preadsorption of SDBAC because of the rise in nonuniformity of Zn deposition despite the corresponding decrease in the size of Zn platelet crystals.

Figure 12 shows the effect of preadsorption of the organic additives considered on the lightness of the deposited Zn. The lightness gradually increased with an increase in the coating mass and became almost constant above 20 g/m² irrespective of whether preadsorption was performed. With preadsorption of organic additives except SDBAC, the lightness of Zn was higher than that without preadsorption for almost all coating masses. When the preferred orientation of the deposited Zn is the {0001} plane, Zn platelet crystals are likely to be parallel to the substrate, resulting in a smooth surface. Consequently, the intensity of diffuse reflection is strong in the case of Zn deposited with preferred {0001} plane orientation, resulting in an increase in the lightness of Zn. However, in this study, the lightness increased with preadsorption despite the decrease in {0001} plane orientation. This suggests that the size of Zn platelet crystals has a greater effect on the lightness than crystal orientation. In other words, the lightness increased with preadsorption because of the decrease in surface roughness due to a decrease in size of Zn platelet crystals. Particularly at coating masses of approximately 40 g/m², the preadsorption significantly enhanced the lightness of deposited Zn. Even at coating masses of approximately 60 g/m², the effect of preadsorption on the lightness of Zn coatings was still observed. It is notable that the effect of preadsorption on the enhancement of lightness of Zn was seen even when Zn deposition proceeded. Among organic additives, the lightness was highest with preadsorption of saccharin. With preadsorption of SDBAC, the lightness was somewhat lower than that without preadsorption. This is attributed to the increase in surface roughness due to the increase in nonuniformity of Zn deposition.

3.5. Morphology and Crystal Orientation at the Initial Stage of Zn Deposition

Zn deposition was performed on electropolished steel sheets, and the morphology and crystal orientation at the initial stage of deposition were investigated to clearly evaluate the effect of preadsorption of organic additives. Figure 13 shows the surface morphologies of Zn deposited at 1 g/m² with and without preadsorption of gelatin. Without preadsorption, as shown in Fig. 13(a), Zn deposition was observed over almost the entire surface, while Zn deposition greatly differed for every crystal grain of the steel substrate with preadsorption of gelatin, as shown in Fig. 13(b). With preadsorption of gelatin (Fig. 13(b)), Zn barely deposited on
the upper half area of the SEM image.

**Figure 14** shows the SEM and crystal orientation mapping images of Zn deposited at 1 g/m² on the cathode without preadsorption. Zn deposited over almost the entire surface, and the preferred orientation was the \{0001\} plane.

**Figure 15** shows the SEM and crystal orientation mapping images of Zn deposited at 1 g/m² on the cathode preadsorbed by gelatin. Zn deposited locally, and therefore the steel substrate was partially exposed. Zn deposition was suppressed with the preadsorption of gelatin, and as a result, Zn deposition was nonuniform at the initial stage. Zn deposition greatly differed for every crystal grain of the steel substrate, as shown in Fig. 13. This suggests that adsorption of gelatin onto the steel substrate depends on the orientations of crystal grains of the steel.

4. Discussion

As discussed above, preadsorption of organic additives caused an increase in overpotential for Zn deposition and a decrease in epitaxial growth between steel and Zn, which resulted in changes in the morphology, crystal orientation, and surface roughness of deposited Zn. On the basis of in situ electrochemical AFM observations, it has been reported that the growth of deposited Zn proceeded through an advancement of macrosteps of platelet crystals in the [2130] direction. The suppression of Zn normal lateral growth appears to have an effect on the morphology of deposited
Zn. The decrease in the size and the increase in the inclination of Zn platelet crystals by preadsorption are attributed to the suppression of Zn normal lateral growth due to the presence of organic additives adsorbed on Zn growth sites.

The effect of preadsorption of organic additives on the crystal lattice size of deposited Zn shown in Fig. 7 reveals that this effect is maintained even during consistent Zn deposition. This shows that organic additives initially preadsorbed on steel sheets successively adsorb onto the deposited Zn coating as well. Surfactants adsorbed on metal have been reported to desorb in aqueous solution.\(^{25,26}\) In this study, it can be presumed that organic additives preadsorbed on the steel sheets repeatedly adsorb and desorb on the cathode during Zn deposition. As a result, the effect of the preadsorption can be maintained even while Zn deposition proceeds. However, the time dependence of the cathode potential during Zn deposition shown in Fig. 3 suggests that the effect of preadsorption of PEG, gelatin, and SDBAC is larger at the initial stage of deposition and its effect decreases with increasing coating mass. It is possible that organic additives adsorbed on the cathode during deposition are partially incorporated into the deposits. On the other hand, it has been reported for Ni deposition that saccharin directly added into the electrolyte has only a small effect on the Ni deposition overpotential but promotes a decrease in the Ni crystal grain size due to the codeposition of S.\(^{27,28}\) In this study, with preadsorption of saccharin, S possibly codeposits with Zn and becomes the origin of the crystalline nucleus of the Zn. There is some ambiguity as to why the overpotential for Zn deposition and the Zn/steel epitaxy depend on the types of organic additives used for preadsorption. The higher-molecular-weight polymers, such as PEG and gelatin, have a larger number of radicals for adsorption. It is known that the number of radicals for adsorption in a given straight-chain molecule, and hence the adsorption capability of the polymer, also appear to exponentially increase with molecular weight, resulting in an increase in the overpotential for metal deposition.\(^{15}\) It is reported that cationic surfactant additives, such as SDBAC increase the overpotential for deposition with increasing lengths of the hydrophobic groups.\(^{15}\) These results suggest that the structure of organic additives used for preadsorption affect the Zn deposition overpotential and the Zn/steel epitaxy. Preadsorption of organic additives can be easily applied to the pretreatment process of a commercial electrogalvanizing line. Because this application suppresses the epitaxial growth of Zn and increases the lightness of the deposited Zn, the appearance of electrogalvanized steel sheets can be expected to be more stable because Zn deposition is barely affected by surface defects of the steel substrate.

5. Conclusion

The effect of preadsorption of organic additives on the lightness and morphology of deposited Zn was investigated. The organic additives used for preadsorption were classified into two groups: 1) polyethylene glycol (PEG), gelatin, and stearyl dimethylbenzyl ammonium chloride (SDBAC) (Type I), which have a polarization effect on Zn deposition; 2) saccharin and sodium lauryl sulfate (Type II), which have no polarization effect. The size of Zn platelet crystals were observed to decrease with preadsorption regardless of the organic additives employed, which is attributed to both an increase in the overpotential for Zn deposition and a decrease in the epitaxial growth of Zn owing to preadsorption of organic additives. The orientation of the \{001\} Zn basal plane significantly decreased with preadsorption of PEG, gelatin, and SDBAC, which have a polarization effect on Zn deposition, while the orientation decreased slightly with the preadsorption of saccharin and sodium lauryl sulfate, which have no polarization effect. The surface roughness of deposited Zn decreased with preadsorption of organic additives except for SDBAC. This is attributed to a decrease in the size of Zn platelet crystals with preadsorption. The lightness of deposited Zn was higher with preadsorption of organic additives except for SDBAC. With the preadsorption of SDBAC, Zn deposited nonuniformly, and the lightness of Zn decreased owing to an increase in the surface roughness.

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