Electrodeposition Behavior of Zn-Polyethyleneimine Composite from Sulfate Solution and Its Micro Structure*

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Electrodeposition of Zn-polyethyleneimine composite was performed at 100–12000 A m⁻² and 4.8 × 10⁶ C m⁻² in agitated sulfate solutions containing 1.84 mol dm⁻³ of ZnSO₄ and 4 g dm⁻³ of polyethyleneimine at pH 1.8 and at 313 K: the composite’s deposition behavior and the relevant deposits’ micro-structure were investigated. The films obtained at current densities above 4000 A m⁻² from solutions containing polyethyleneimine exhibited gloss, and the gloss was highest for solutions containing polyethyleneimine with the highest molecular weight (70000). The preferred orientation of deposited Zn crystals changed from (0001) to (1120) and [1010] in the presence of polyethyleneimine, and the size of the platelet-shaped Zn crystals decreased as the polyethyleneimine molecular weight and current density increased. The deposition of Zn was polarized in the presence of polyethyleneimine, and the degree of polarization increased with the current density and with polyethyleneimine’s molecular weight. The C and N contents in deposited films increased as the polyethyleneimine molecular weight and current density increased, indicating an increase in the tendency of polyethyleneimine to be adsorbed onto the cathode. During deposition, polyethyleneimine buffered somewhat but the pH increase in the layer of the electrolyte solution in contact with the cathode. At this time, H⁺ ions are released from polyethyleneimine because of an increase in pH in the cathode’s vicinity, and consequently, the number of electron lone-pairs in N atoms of polyethyleneimine increased, resulting in an increase in the adsorption ability of polyethyleneimine onto the cathode.

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1. Introduction

Since the electrodeposition of a composite can produce deposits with properties like good abrasion resistance, good lubricating ability, and good corrosion resistance, this technique has been widely used to achieve the conversion of surface materials. Films have been reported to be co-deposited with oxides, carbides, nitrides, or diamond particle to increase strength; with molybdenum disulfide, liquid paraffin or polytetrafluoroethylene as lubricant; and with silica or alumina or chromat as agents that increase resistance to corrosion. In the electrodeposition of a composite, the solid fine particles, which are characterized by poor solubility, are generally suspended in an electrolyte acting as a dispersion material, and the dispersed particles are incorporated into the deposited films. However, since the fine particles are likely to aggregate during electrolysis and holding the electrolyte, it is difficult to co-deposit them in the form of fine and uniform with the matrix films. In addition, there is a problem on manufacturing process because the aggregated particles tend to sink, causing the formation of clogs in the filter and pipes of the electrolysis equipment. On the other hand, in the electrodeposition of less-noble metals like Zn from aqueous solution, the pH at cathode layer rises because of the evolution of hydrogen, which occurs as a side reaction of the metal deposition. Therefore, in the case of metal ions that undergo hydrolysis at low pH, a second form of the metal species is produced in the electrolysis solution, and the metal ions may end up being co-deposited with matrix films in the form of hydroxides or oxides. This deposition technique utilizing a hydrolysis reaction enable to deposition of composite from the non-suspension solution without the solid particles of poor solubility. However, few studies have been conducted on the deposition of organic composites from non-suspended solutions. When organic compounds can be co-deposited with matrix films, an increase in hardness and lubrication of the deposited films and the omission of pre-treatment for painting are expected as a result. For example, polyethyleneimine, the water-soluble product of ethyleneimine polymerization, is characterized by high cation density and reactivity because of the high number of primary and secondary amine groups within its structure. Therefore, during Zn deposition, the increase in pH occurring in the vicinity of the cathode causes polyethyleneimine to undergo deprotonation in the electrolyte solution layer in contact with the cathode, leading to an increase in the number of electron lone-pairs on the N atoms of the polymer; consequently, the adsorption ability of polyethyleneimine onto the cathode is expected to increase, resulting in the co-deposition of polyethyleneimine with metallic Zn. Hence, in this study, polyethyleneimine was selected as the organic co-depositing compound, and the electrodeposition of a Zn-polyethyleneimine composite was investigated. In particular, the co-deposition of polyethyleneimine with Zn was attempted, exploiting the increase in pH which occurs in the cathode layer of the electrolyte solution during Zn deposition. The micro-structure and properties of the deposited films were examined.

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2. Experimental

The composition of the solution and electrolysis conditions are reported in Table 1. The electrolytic solution was prepared by dissolving fixed amounts of high-grade \( \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} \) (1.84 mol dm\(^{-3}\)) in distilled, deionized water. The pH was adjusted to 1.8 with sulfuric acid. Polyethyleneimine polymers characterized by 2000 or 7000 molecular weight were added into the solution, with a total amount of 4 g dm\(^{-3}\). The relative ratio of primary:secondary:tertiary amine groups per unit weight of polyethyleneimine is 38.5%:38.5%:23% for the polymer characterized by a molecular weight of 2000 and 25%:50%:25% for that characterized by a molecular weight of 7000. Sheets of Fe measuring 2 cm × 3 cm and of Pb measuring 5 cm × 2.5 cm were used as cathode and anode, respectively. Before the electrodeposition process was conducted, the Fe substrate was polished using emery papers, buffed and acid cleaned, electrolytically degreased, and acid cleaned. Electrodeposition was conducted in solutions agitated at 800 rpm using a stirrer under coulostatic (4.8 \( \text{C} \cdot \text{m}^{-2}\)) and galvanostatic (10–12000 \( \text{A} \cdot \text{m}^{-2}\)) conditions at 313 K. The deposits were dissolved off the cathode using nitric acid. Zn was quantitatively analyzed using inductively coupled plasma spectroscopy, and the current efficiency and the partial current density for Zn deposition were calculated. The partial current densities for Zn deposition and H\(_2\) evolution were determined by multiplying the total current density by each current efficiency value. The current efficiency for H\(_2\) evolution was calculated by subtracting the current efficiency value for Zn deposition from 100%. The cathodic potentials during deposition were measured against a saturated Ag/AgCl reference electrode (0.199 V vs. NHE at 298 K). In the polarization curves presented in this article, the potentials are plotted with reference to the NHE.

The concentration of polyethyleneimine in the deposited films was evaluated by rf-GDOES under the following analysis conditions: diameter of 2 mm \( \varnothing \), argon pressure of 600 Pa, pulse frequency of 2000 Hz, and duty cycle of 0.125. The surfaces of the deposits were analyzed using scanning electron microscopy (SEM), and the gloss was measured at an incidence angle of 20° using a digital variable gloss meter (Suga Test Instrument Co.). The crystal orientation of the deposited Zn was determined using the method developed by Willson and Rogers\[22,23]\ an X-ray diffraction intensity of 0002 to the 1122 reflection was used. An Sb micro-electrode\[24,25]\ was fabricated to measure the change in pH in the vicinity of the cathode during Zn-polyethyleneimine composite deposition accompanied by hydrogen evolution. Under a galvanostatic condition of 300 A m\(^{-2}\) in unagitated solutions, the potential of the Sb electrode attached to a micrometer was measured at various distances between the cathode and the Sb electrode. The distance between the capillary of the reference electrode and the Sb microelectrode was approximately 2 mm in the horizontal direction of the cathode, and the distance between the capillary of the reference electrode and the cathode was identical to that between the Sb microelectrode and the cathode. Using a pH–potential calibration curve constructed in advance, the pH profile near the cathode was determined during electrolysis. To study the deprotonation behavior of polyethyleneimine in the electrolytic solutions, pH titrations were performed with NaOH. In particular, a 2.0 mol dm\(^{-3}\) NaOH solution was added to solutions containing 0.0098 mol dm\(^{-3}\) \( \text{ZnSO}_4 \) and/or 2 g dm\(^{-3}\) polyethyleneimine with a molecular weight of 70000 using a burette. The hardness of the surface of the deposited films was measured using a micro Vickers hardness meter at a load of 0.05 kg for 15 s. The polarization curve of deposited films to evaluate the corrosion resistance were collected by polarizing from a less-noble potential than the corrosion potential toward the anodic-potential direction using a potential sweep method at 1.0 mV s\(^{-1}\) in an oxygen-saturated 3 mass% NaCl solution at 313 K.

3. Results

3.1 Appearance of deposited films

Figure 1 shows images of the films deposited at various current densities from polyethyleneimine-free solution and from solutions containing polyethyleneimine of different molecular weights. The film deposited from polyethyleneimine-free solution exhibited the characteristic gray appearance of deposited Zn regardless of current density. On the contrary, the films obtained from solutions containing polyethyleneimine have the appearance of glossy deposits when current densities above 4000 A m\(^{-2}\) were utilized for the deposition process. Focusing on the difference of molecular weight between polyethyleneimine, the gloss was most evident when polyethyleneimine with a larger molecular weight (70000) was utilized. However, when polyethyleneimine characterized by a molecular weight of 70000 was utilized, light-gray surface irregularities were sometimes observed in the deposited films. When polyethyleneimine whose molecular weight was 2000 was utilized, the glossy deposits were not clear, and the number of light-gray irregularities increased. On the other hand, although the film deposited from solution containing polyethyleneimine of both molecular weights (70000 and 2000) displayed a lower

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Solution composition and electrolysis conditions.</th>
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<tr>
<td>ZnSO(_4) ( \cdot 7\text{H}_2\text{O} ) (mol ( \cdot ) dm(^{-3}))</td>
<td>1.84</td>
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<tr>
<td>Polyethyleneimine (g ( \cdot ) dm(^{-3}))</td>
<td>4.0</td>
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<tr>
<td>(Molecular weight 2000, 70000)</td>
<td>pH</td>
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<td>Current density (A ( \cdot ) m(^{-2}))</td>
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level of gloss than that obtained from solutions containing polyethyleneimine with a single molecular weight of 70000, that exhibited a uniform appearance, and that lacked the aforementioned light-gray irregularities.

Figure 2 shows the gloss of films deposited at various current densities from solutions containing polyethyleneimine of different molecular weights. The gloss of films deposited was highest when the film had been obtained from solution comprising polyethyleneimine whose molecular weight was 70000, followed by that obtained from solution containing polyethyleneimine characterized by both molecular weights (70000 and 2000), and it was lowest in the case of the film obtained from solution containing polyethyleneimine whose molecular weight was 2000. For all polyethyleneimine, the gloss of films deposited at 8000 A·m⁻² was the highest. In the case of the solution containing polyethyleneimine of both molecular weights (70000 and 2000), the difference in gloss between the deposits obtained at 8000 and 12000 A·m⁻² was small, indicating that gloss level had a small current density dependence in this current density region.

3.2 Deposition behavior of the Zn-polyethyleneimine composite

Figure 3 shows the partial polarization curves for Zn deposition (a) and H₂ evolution (b) from polyethyleneimine-free solution and from solutions containing polyethyleneimine of different molecular weights. As shown in Fig. 3(a), in which the partial polarization curve for Zn deposition is reported, in the presence of polyethyleneimine, polarization occurred even at current densities below 1000 A·m⁻²; furthermore, the degree of polarization in the presence of polyethyleneimine increased at higher current densities (above 1000 A·m⁻²). Focusing on the effect of polyethyleneimine of different molecular weights at current densities above 1000 A·m⁻², evidence indicated that the polarization for Zn deposition was largest when deposition took place starting from solution containing polyethyleneimine whose molecular weight was 70000. Additionally, evidence indicated that the behavior of solution containing polyethyleneimine of both molecular weights (70000 and 2000) was almost identical to that of solution containing polyethyleneimine whose molecular weight was 2000. On the other hand, the partial polarization curve for hydrogen evolution was rarely affected by the presence of polyethyleneimine at current densities below 1000 A·m⁻². However, polarization increased significantly in the presence of polyethyleneimine at current densities above 1000 A·m⁻². The degree of polarization was largest in the case of
polyethyleneimine. At current densities below 4000 A·m⁻², the density increased, whether in the absence or presence of the maximum before starting to decrease as the current density increased with the current density; it then reached a decrease in current density of Zn deposition associated with the presence of polyethyleneimine than in its absence. The decrease in current efficiency for Zn deposition associated with the presence of polyethyleneimine at current densities below 1000 A·m⁻² is due to the fact that hydrogen evolution was not suppressed by polyethyleneimine, whereas Zn deposition was suppressed in the low-current-density region (Figs. 3(a) and (b)).

In order to investigate the deposition behavior of the Zn-polyethyleneimine composite, the pH of the cathode layer of the electrolyte solution was measured using an Sb microelectrode during deposition from unagitated solutions containing Zn²⁺ ions alone or polyethyleneimine and Zn²⁺ ions. Figure 5 shows the pH profiles in the vicinity of the cathode during the deposition of Zn-polyethyleneimine or Zn at 300 A·m⁻² from solutions containing polyethyleneimine of different molecular weights or no polyethyleneimine at all. In a solution containing only Zn²⁺ ions, the pH in the cathode layer of the electrolyte solution increased up to a value of 5.6, which is significantly higher than that of the rest of the solution; on the other hand, in a solution containing polyethyleneimine, the pH increased to either 4.8 or 5.2, depending on the polymer’s molecular weight. During deposition from a solution containing Zn²⁺ ions, the pH of the cathode layer of the electrolyte solution increases because of hydrogen evolution, which causes the formation of metal oxides by way of hydrolysis. The critical pH value for Zn(OH)₂ formation is calculated to be 5.5 on the basis of the solubility product of Zn(OH)₂ (2 × 10⁻¹⁷ at 298 K)

polyethyleneimine whose molecular weight was 70000, showing an observation which can also be applied to the case of Zn deposition.}

Figure 4 shows the current efficiency for Zn deposition determined from polyethyleneimine-free solution and from solutions containing polyethyleneimine of different molecular weights. At low current density, the current efficiency for Zn deposition increased with the current density; it then reached the maximum before starting to decrease as the current density increased, whether in the absence or presence of polyethyleneimine. At current densities below 4000 A·m⁻², the current efficiency for Zn deposition was lower in the presence of polyethyleneimine than in its absence. The degree of decrease in current efficiency was largest in the presence of polyethyleneimine whose molecular weight was 70000. The decrease in current efficiency for Zn deposition after a maximum value is attributed to the diffusion limitation of Zn²⁺ ions. As can be evinced in Fig. 3(a), Zn deposition actually approaches its diffusion-limited current density at current densities above 4000 A·m⁻². In the current density region where Zn deposition proceeds under the diffusion limit of Zn²⁺ ions (above 4000 A·m⁻²), polyethyleneimine was observed to have hardly any effect on the current efficiency for Zn deposition. The decrease in current efficiency for Zn deposition associated with the presence of polyethyleneimine at current densities below 1000 A·m⁻² is due to the fact that hydrogen evolution was not suppressed by polyethyleneimine, whereas Zn deposition was suppressed in the low-current-density region (Figs. 3(a) and (b)).

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layer of the electrolyte solution seems to increase to the critical value for \( \text{Zn(OH)}_2 \) formation. On the contrary, in a solution containing polyethyleneimine, the increase in pH of the cathode layer of the electrolyte solution remained somewhat suppressed below that critical value as a consequence of the pH buffering action of polyethyleneimine.

To further investigate the pH buffering activity of polyethyleneimine, pH titration curves were measured using NaOH solution. Figure 6 shows the pH changes observed when a 2 mol dm\(^{-3}\) NaOH solution was added to a solution containing \( \text{Zn}^{2+} \) ions (a) and to one containing \( \text{Zn}^{2+} \) ions together with polyethyleneimine (b). Upon the addition of a NaOH solution to a solution containing only \( \text{Zn}^{2+} \) ions (a), the pH increased gradually at first; once the pH reached approximately a value of 3, it increased abruptly up to a value of 5.5, at which the formation of \( \text{Zn(OH)}_2 \) began. On the contrary, upon the addition of a NaOH solution to a solution containing polyethyleneimine and \( \text{Zn}^{2+} \) ions (b), the pH abruptly increased up to a value of approximately 3; above a pH value of about 4, however, the increase was only moderate.

### 3.3 Structure of the deposited films

Figure 7 shows the Rf-GDOES depth profiles of films deposited at 1000 and 8000 A m\(^{-2}\) from solutions containing polyethyleneimine of different molecular weights. C and N atoms scarcely co-deposited in films obtained from polyethyleneimine-free solution (Figs. 7(a) and (b)), whereas they were evidently present in films deposited from solutions containing polyethyleneimine (Figs. 7(c)–(f)), indicating that the deposited compound resulted from the co-deposition of polyethyleneimine. The contents of C and N in films deposited at 8000 A m\(^{-2}\) (Figs. 7(d) and (f)) were larger than those in films deposited at 1000 A m\(^{-2}\) (Figs. 7(c) and (e)), indicating that the adsorption ability of polyethyleneimine onto the cathode increased with the current density. On the other hand, the contents of C and N in films deposited from solution containing polyethyleneimine whose molecular weight was 70000 (Figs. 7(e) and (f)) were larger than those obtained from solution containing polyethyleneimine whose molecular weight was 2000 (Figs. 7(c) and (d)), indicating that the adsorption ability of polyethyleneimine onto the cathode increased with the molecular weight of the polymer. All of the films deposited from the solutions containing polyethyleneimine showed a large C content at the interface between the Fe substrate and the deposited films. This observation indicates that C significantly co-deposites in films during the initial stage of the deposition, or the adsorption ability of polyethyleneimine onto the Fe substrate is large.

Figure 8 shows the SEM images of the surfaces of films deposited at 1000 and 8000 A m\(^{-2}\) from polyethyleneimine-free solution or from solutions containing polyethyleneimine of different molecular weights. The films deposited at 1000 (a) and 8000 A m\(^{-2}\) (e) from polyethyleneimine-free solution were characterized by large, hexagonal, platelet-shaped Zn crystals layered in parallel to the surface of the substrate. When the preferred orientation of deposited Zn is the [0001] basal plane of the hcp structure, the platelet-shaped crystals of Zn become parallel to the substrate surface. Therefore, on the basis of the surface morphology, the preferred orientation of Zn deposited from a polyethyleneimine-free solution seems to be the [0001] plane. On the other hand, the morphology of deposited Zn changed significantly in the presence of polyethyleneimine in the solution. The films deposited at 1000 A m\(^{-2}\) from solution containing only polyethyleneimine whose molecular weight was 70000 (c) and solution containing polyethyleneimine of both 2000 and 70000 molecular weights (d) were characterized by layers of platelet-shaped Zn crystals displaying a significant inclination from the surface of the substrate. As the current density increased to 8000 A m\(^{-2}\), the platelet-shaped crystals of Zn became fine, irrespective of the molecular weight of polyethyleneimine [Figs. 8(f), (g) and (h)]. The platelet-shaped crystals of Zn deposited from solution containing polyethyleneimine whose molecular weight was 70000 (g) were finer than those obtained from solution containing polyethyleneimine whose molecular weight was 2000 (f).
The platelet-shaped crystals of Zn deposited from solution containing polyethyleneimine of both molecular weights (h) displayed sizes which were between those obtained from solution containing polyethyleneimine whose molecular weight was 70000 only (g) and those obtained from solution containing polyethyleneimine whose molecular weight was 2000 only (f).

Figure 9 shows the crystal orientations of Zn deposited at 1000 and 8000 A·m$^{-2}$ from polyethyleneimine-free solution and from solutions containing polyethyleneimine of different molecular weights. The preferred crystal orientation of Zn deposited from a polyethyleneimine-free solution was the \{0001\} plane, regardless of current density, or in other words, other orientations, besides the \{0001\} plane, were scarcely observed in this case. This evidence is in agreement with the crystal orientation expected on the basis of the surface morphology shown in Fig. 8. On the contrary, the preferred crystal orientation of Zn deposited from solutions containing

\begin{figure}[h]
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\includegraphics[width=\textwidth]{fig7.png}
\caption{Rf-GDOES depth profiles of films deposited at 1000 and 8000 A·m$^{-2}$ from polyethyleneimine (PEI)-free solution and from solutions containing PEI of different molecular weights (M.W.). (a) PEI-free at 1000 A·m$^{-2}$, (b) PEI-free at 8000 A·m$^{-2}$, (c) in the presence of 2000 M.W. PEI at 1000 A·m$^{-2}$, (d) in the presence of 2000 M.W. PEI at 8000 A·m$^{-2}$, (e) in the presence of 70000 M.W. PEI at 1000 A·m$^{-2}$, and (f) in the presence of 70000 M.W. PEI at 8000 A·m$^{-2}$.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig8.png}
\caption{SEM images of the surface of films deposited at 1000 and 8000 A·m$^{-2}$ from polyethyleneimine (PEI)-free solution and from solutions containing PEI of different molecular weights (M.W.). (a) PEI-free at 1000 A·m$^{-2}$, (b) PEI-free at 8000 A·m$^{-2}$, (c) with 2000 M.W. PEI, (d) with 70000 M.W. PEI, (e) with both 2000 and 70000 M.W. PEI, (f) PEI-free, (g) with 2000 M.W. PEI, (h) with both 2000 and 70000 M.W. PEI.}
\end{figure}
polyethyleneimine changed to the \{11\bar{2}0\} and \{10\bar{1}0\} planes. In the presence of polyethyleneimine whose molecular weights were 2000 (only) and 70000 (only), the preferred orientations of Zn crystals deposited at 1000 and 8000 A·m⁻² were the \{11\bar{2}0\} and \{10\bar{1}0\} planes, respectively. In the presence of polyethyleneimine of both molecular weights (2000 and 70000), the preferred orientation of Zn crystals was the \{11\bar{2}0\} plane, irrespective of current density. The two crystal orientations of \{11\bar{2}0\} and \{10\bar{1}0\} correspond to situations whereby the basal plane (the \{0001\} plane) of hcp Zn becomes perpendicular to the surface of the Fe substrate. Comparing the surface morphology of deposited Zn as reported in Fig. 8 with the crystal orientation of Zn depicted in Fig. 9, accounting for the fact that the preferred crystal orientation of Zn became \{11\bar{2}0\} and \{10\bar{1}0\} following the addition of polyethyleneimine to the electrolyte solution and that, in this case, the platelet-shaped Zn crystals were perpendicular to the Fe substrate surface, inference can be made that the crystal orientation of deposited Zn corresponded to that expected from the macro-morphology of the surfaces of platelet-shaped crystals.

Figure 10 shows the hardness of films deposited at 1000 and 8000 A·m⁻² from polyethyleneimine-free solution and from solutions containing polyethyleneimine of different molecular weights. The hardness of the deposited films significantly increased as a consequence of the presence of polyethyleneimine in the electrolyte solution. The degree of increase in hardness of films deposited from solution containing polyethyleneimine whose molecular weight was 70000 was remarkably larger than that with solution containing polyethyleneimine whose molecular weight was 2000. This result stems from the fact that the C and N contents of films deposited from solution comprising polyethyleneimine whose molecular weight was 70000 were larger than those obtained from solution comprising polyethyleneimine whose molecular weight was 2000 (Fig. 7). On the other hand, hardly any effect was observed of the current density on the hardness of the films when the electrolyte solution contained polyethyleneimine whose molecular weight was 2000. By contrast, in the case of solution containing either a mixture of the two polyethyleneimine samples or polyethyleneimine of 70000 molecular weight alone, the hardness of the films deposited at 1000 A·m⁻² was larger than that obtained when deposition was carried out at 8000 A·m⁻². Considering that the C and N contents of films deposited at 1000 A·m⁻² were smaller than those of films deposited at 8000 A·m⁻² (Fig. 7), the larger hardness of films deposited at 1000 A·m⁻² cannot be explained by the difference in C and N contents between films. The hardness of films deposited at 1000 A·m⁻² in solution containing polyethyleneimine whose molecular weight was 70000 only or polyethyleneimine of both molecular weights was largest. In both cases, the film surfaces consisted of regularly layered platelet-shaped Zn crystals displaying a substantial inclination from the surface of the substrate (Figs. 8(c) and (d)). This surface morphology appears to contribute to an increase in hardness of the film.

Figure 11 shows the polarization curves in 3 mass% NaCl solution for films deposited at 8000 A·m⁻² from polyethyleneimine-free solution and from solutions containing polyethyleneimine of different molecular weights. The anodic polarization curve for Zn dissolution shifted in the noble direction when the solution contained polyethyleneimine; this shift causes the corrosion potential to also shift in the noble direction. On the other hand, the cathode current density for the reduction of dissolved oxygen increased in the presence of polyethyleneimine. The changes observed in the polarization curves for the anodic and cathodic reactions...
associated with the presence of polyethyleneimine in solution appear to be due to the co-deposition of C and N in the deposited films and to change in the surface roughness of the films.

4. Discussion

Herein are discussed the electrodeposition behavior of the Zn-polyethyleneimine composite and the relationship between the micro-structure and appearance of deposited films. From the data summarized in Figs. 5 and 6, it is evident that polyethyleneimine has a suppressing effect on the increase in pH in an acid solution. The structure of polyethyleneimine in an acid solution is expected to be that reported in Fig. 12; when the pH increases in solution, H⁺ ions are released from primary and secondary amine groups of polyethyleneimine, resulting in a suppression of pH increase. The N atoms of polyethyleneimine which have stripped H⁺ ions possess a lone pair of electrons which increases the tendency of the polymer to be adsorbed onto the cathode. Since hydrogen evolution occurs as a side reaction during Zn deposition, the pH in the layer of the electrolyte solution in contact with the cathode increases. The pH of the cathode layer of the electrolyte solution increases as the current density increases, which is a consequence of an increase in the rate of hydrogen evolution. From another perspective, as the current density increases, the tendency of H⁺ ions to be released from polyethyleneimine also increases, resulting in an increase in lone-pair electrons on polyethyleneimine, which may, in turn, promote adsorption of the polymer onto the cathode. In fact, the contents of C and N in films deposited at 8000 A·m⁻² were larger than those at 1000 A·m⁻² (Fig. 7), indicating that the adsorption ability of polyethyleneimine increases with the current density. In the presence of polyethyleneimine in the electrolyte solution, the polarization associated with Zn deposition was larger in the high-current-density region than in the low-current-density region (Fig. 3(a)), an effect is attributed to the increase in adsorption ability of polyethyleneimine resulting from an increase in current density. Focusing on the difference in molecular weight of the polyethyleneimine, the C and N contents of films deposited from solution containing polyethyleneimine whose molecular weight was 70000 were larger than those of films deposited from solution containing polyethyleneimine whose molecular weight was 2000 (Fig. 7). Additionally, the polarization effect for Zn deposition in solution containing polyethyleneimine whose molecular weight was 70000 was larger than that for the deposition from solution containing polyethyleneimine whose molecular weight was 2000 (Fig. 3(a)). These results indicate that the cathode adsorption ability of polyethyleneimine increases with the polymer’s molecular weight. As mentioned above, the relative ratio of primary:secondary:tertiary amine per unit weight of polyethyleneimine is 38.5%:38.5%:23% for the polymer whose molecular weight is 2000 and 25%:50%:25% for the polymer whose molecular weight is 70000, showing that the sum of the relative ratios of primary and secondary amine groups in the polymer of 2000 molecular weight is identical to that in the polymer of 70000 molecular weight (75%). In this study, the polyethyleneimine with a larger molecular weight also displayed a higher tendency to be adsorbed onto the cathode, which is attributed to an increase in the number of adsorption sites per molecule as the polymer’s molecular weight increases.

The platelet-shaped crystals which constitute the Zn deposits became fine as the current density increased. This effect is due to both an increase in overpotential for the deposition and an increase in the tendency of polyethyleneimine to be adsorbed onto the cathode. In particular, as the overpotential for deposition increases, the crystals of deposited Zn become finer because the nucleation rate of Zn increases relatively to the crystal’s growth rate.26,27 Organic additives are known to suppress the growth of crystals of metals during their deposition by adsorbing onto the kink and step sites of the crystals. When the cathode adsorption ability of polyethyleneimine increases, the growth of crystalline Zn deposits is suppressed, resulting in finer crystals of Zn. The crystals of Zn deposited from solution containing
polylethyleneimine whose molecular weight was 70000 were finer than those obtained from solution containing polylethyleneimine whose molecular weight was 2000. This effect is attributed to the fact that an increase in the molecular weight of polylethyleneimine is associated with both an increase in cathode adsorption ability of the polylethyleneimine itself and an increase in the overpotential for deposition.

On the other hand, the orientation of deposited Zn crystals is reported to depend on the overpotential for deposition.\(^{26,27}\) Pangarov calculated the relative values of a two-dimensional nucleation work for various crystal planes.\(^{28,29}\) By 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 shifted from the \{0001\} plane to the \{1011\}, \{1120\}, and \{1010\} planes (in that order) as the Zn deposition overpotential increased progressively. In the present study, once polylethyleneimine was added to the electrolyte solution, the preferred orientation of deposited Zn crystals changed from \{0001\} to \{1010\} and \{1120\} planes, which was caused by an increase in the overpotential for deposition.

Comparing the gloss (Figs. 1 and 2) and surface morphologies (Fig. 9) of deposited films, it is concluded that the gloss of deposited films increases as the size of the platelet-shaped Zn crystals decreases. As either the molecular weight of polylethyleneimine or the current density increases, so does the gloss of deposited films, as a consequence of a decrease in size of Zn crystals. The gloss of films deposited from solution containing polylethyleneimine of both molecular weights (2000 and 70000) had a value in between those measured for films obtained from solutions containing polylethyleneimine of 2000 and 70000 molecular weight (alone). However, in solution containing polylethyleneimine of both molecular weights (2000 and 70000), the deposited films exhibited a more uniform appearance with fewer light-gray irregularities. The current density dependence of gloss overpotential increased progressively. In the present study, the preferred orientation of deposited Zn crystals changed from solution containing polyethyleneimine of both molecular weights than that for solution containing either polylethyleneimine of 2000 molecular weight or polyethyleneimine of 70000 molecular weight. The adsorption behavior of polylethyleneimine onto the cathode seems to be different between solution containing polyethyleneimine of both molecular weights and those containing polymer of just one molecular weight; however, further investigation is required in this case.

5. Conclusion

The electrodeposition behavior of the Zn-polylethyleneimine composite from a sulfate solution and the microstructure of the resulting deposits were investigated. The films deposited at current densities above 4000 A·m\(^{-2}\) in the solutions containing polylethyleneimine exhibited gloss, and the gloss was highest for solution containing polylethyleneimine whose molecular weight was higher (70000). The preferred orientation of deposited Zn changed from the \{0001\} plane, obtained in the case of polyethyleneimine-free solution, to \{1120\} and \{1010\}, obtained in the presence of polylethyleneimine in solution. Furthermore, the size of the observed platelet-shaped Zn crystals decreased as the molecular weight of polyethyleneimine and the current density increased. The deposition of Zn was polarized in the presence of polylethyleneimine in solution, and the degree of polarization became substantially larger in the higher current density region (above 4000 A·m\(^{-2}\)) in the presence of polylethyleneimine of higher molecular weight (70000). The C and N contents in the deposited films increased in response both to an increase in the molecular weight of polyethyleneimine and to an increase in current density, indicating in both cases an increase in the adsorption ability of polylethyleneimine onto the cathode. Polylethyleneimine in solution suppressed somewhat the increase of pH in the vicinity of the cathode during deposition, displaying a degree of pH buffering ability. During deposition, as a consequence of the increase in pH in the vicinity of the cathode, H\(^{+}\) ions are released from polylethyleneimine, leading, in turn, to an increase in the number of lone-pair electrons centered on the amine N atoms of polyethyleneimine. This process then resulted in an increase in the tendency of polylethyleneimine to be adsorbed onto the cathode.

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