Morphology Control of Zn-SiO$_2$ Composite Films Electrodeposited from Aqueous Solution Containing Quaternary Ammonium Cations

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Abstract. Zn-SiO$_2$ alloys were electrodeposited from acidic aqueous solution containing cationic surfactants such as diallyl-dimethyl-ammonium chloride, trimethyl-tetradecyl-ammonium chloride, trimethyl-stearyl-ammonium chloride and dimethyl-distearyl-ammonium chloride. Zn-SiO$_2$ alloy thin films were obtained at the wide current density range from 5 A/dm$^2$ to 100 A/dm$^2$. SiO$_2$ content in deposits was ca. 10 % at the maximum using the solution containing a surfactant with molecular weight range of 200 to 300.

1. Introduction

Electrodeposition of Zn alloy films on steel sheets has been investigated to achieve an excellent corrosion resistance rather than conventional hot-dip galvanized steel sheets [1-3]. Recently, much attention has also been paid to a Zn alloy films containing metal oxide particles electrodeposited on a steel sheet because of its excellent corrosion resistance properties and cost performance [4-6]. The co-deposition of Zn and metal oxide particles can be achieved using acidic aqueous solution containing cationic surfactants, which can adsorb on metal oxide particles. K. Kondo et al. reported that Zn-SiO$_2$ composite can be electrodeposited from the aqueous solution containing Sn$^{2+}$ ions [7]. They found that SiO$_2$ particles precipitated along the laterally growing macro-steps of Zn hexagonal crystals and randomly dispersed on the terrace of Zn hexagonal crystals. T. J. Tuaweri et al. reported that the electrodeposition behavior of Zn-SiO$_2$ composite from the aqueous solution containing N, N-dimethyl-dodecyl-amine [8]. They obtained Zn-33wt.%SiO$_2$ composite using SiO$_2$ particles with the diameter of 2 μm. M. Azizi et al. reported that the co-deposition process of Zn-SiO$_2$ composite from the aqueous solution containing gelatin [9]. They found that Zn-20mass%SiO$_2$ composite can be electrodeposited using the solution containing 50 g/L SiO$_2$ particles. However, the role of surfactants on the co-deposition process of Zn and SiO$_2$ is still in an unsettled issue.

In this paper, effect of surfactants molecular weight on the morphology of electrodeposited Zn-SiO$_2$ composite films was investigated using quaternary ammonium cations such as diallyl-dimethyl-ammonium chloride, trimethyl-tetradecyl-ammonium chloride, trimethyl-stearyl-ammonium chloride and dimethyl-distearyl-ammonium chloride.
2. Experimental Procedures

Electrolytic solutions were synthesized from the following chemicals (ZnSO$_4$$\cdot$7H$_2$O: 300 g/L, Na$_2$SO$_4$: 50 g/L, H$_2$SO$_4$: 25 g/L, SiO$_2$ particles: 50 g/L and cationic surfactants: 0.01 mol/L). Average size of SiO$_2$ particles is ca. 0.5 $\mu$m and that contains 6.0 at.% Ca$^{2+}$ ions. Molecular structures of cationic surfactants are shown in Fig. 1 (A: diallyl-dimethyl-ammonium chloride, B: trimethyl-tetradecyl-ammonium chloride, C: trimethyl-stearyl-ammonium chloride, D: dimethyl-distearil-ammonium chloride). The solution temperature was kept to 323K. A steel sheet and a gold wire were used as a cathode and an anode, while a Ag/AgCl electrode was used as a reference electrode. Optimum current density for electrodeposition of Zn-SiO$_2$ alloys was determined by a cathodic polarization curve measured over the wide range of cathode potential. Zn-SiO$_2$ alloys were galvanostatically electrodeposited over the wide range of current density from 5 A/dm$^2$ to 100 A/dm$^2$. Crystal phase, structure and chemical composition of electrodeposited Zn-SiO$_2$ alloys was investigated by using X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX).

![Molecular structures of cationic surfactants](image)

Figure 1. Molecular structures of cationic surfactants (A: diallyl-dimethyl-ammonium chloride, B: trimethyl-tetradecyl-ammonium chloride, C: trimethyl-stearyl-ammonium chloride, D: dimethyl-distearil-ammonium chloride).

3. Results and Discussion

3-1. Effect of current density on the electrodeposition of Zn-SiO$_2$

Cathodic polarization curves for Zn-SiO$_2$ alloy deposition from acidic aqueous solutions with and without cationic surfactant-A are shown in Fig. 2. At the potential of ca. -0.5 V, H$^+$ ions began to be reduced. With increasing the current density up to 1 A/dm$^2$, the potential polarized to less-noble direction in the solution containing cationic surfactant-A. In this potential range, the pH in the vicinity of the cathode will increase up to around 6 due to the diffusion limit of H$^+$ ions, then Zn(OH)$_2$ forms in the vicinity of cathode [10-12]. Subsequently the cathode potential reaches to the equilibrium potential of Zn (-0.96 V vs. Ag/AgCl), cationic SiO$_2$ particles will adsorb on cathode surface. Electrodeposition of Zn-SiO$_2$ will proceed due to the following reaction.

$$\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2$$

$$\text{Zn(OH)}_2 + \text{SiO}_2 + 2e^- \rightarrow \text{Zn-SiO}_2 + 2\text{OH}^-$$

Furthermore, with increase in the current density more than 100 A/dm$^2$, the cathode potential polarized significantly to less-noble region rather than -3.0 V due to the diffusion limit of Zn$^{2+}$ ions. Consequently, optimum current density range for Zn-SiO$_2$ alloy deposition was determined to be the range from 5 A/dm$^2$ to 100 A/dm$^2$. 
Figure 2. Cathodic polarization curve for electrodeposition of Zn-SiO$_2$ from acidic aqueous solutions with and without cationic surfactant-A.

SEM images of electrodeposited Zn-SiO$_2$ thin films obtained from an acidic aqueous solution without cationic surfactants under the different current density (5, 20, 100 A/dm$^2$) are shown in Fig.3. As shown in this figures, electrodeposits are mainly composed from Zn small crystals with the shape of hexagonal plates. With increase in current density, the size of Zn crystals also increased up to around 5 $\mu$m in the diameter.

Figure 3. SEM images of electrodeposited Zn-SiO$_2$ thin films obtained from an acidic aqueous solution without cationic surfactants under the different current density (5, 20, 100 A/dm$^2$).

XRD patterns of electrodeposited Zn-SiO$_2$ thin films obtained from an acidic aqueous solution without cationic surfactants under the different current density (5, 20, 100 A/dm$^2$) are shown in Fig.4. It is well known that the electrodeposited crystal growth behavior depends on the deposition overpotential. Usually, with decrease in the deposition overpotential, the electrodeposited crystal growth rate will decrease. If the electrodeposited crystal growth rate is small, the electrodeposits are composed from preferentially oriented crystal plane with most close-packing in atomic arrangement. While, the deposition overpotential will decrease in decreasing current density. Therefore, this electrodeposited crystal growth behavior results in the following phenomenon. The electrodeposits obtained at the current density of 5 A/dm$^2$ are composed from Zn crystals with the preferentially oriented crystal plane in (002), which is most close-packed in atomic arrangement. On the other hand, the electrodeposits obtained at the current density of 100 A/dm$^2$ are composed from Zn crystals with the preferentially oriented crystal plane in (101), which is not close-packed.
Figure 4. XRD patterns of electrodeposited Zn-SiO$_2$ thin films obtained from an acidic aqueous solution without cationic surfactants under the different current density (5, 20, 100 A/dm$^2$).

3-2. Effect of surfactant molecular weight on the electrodeposition of Zn-SiO$_2$

Figure 5 shows effect of surfactant molecular weight on SiO$_2$ content in deposits obtained from acidic aqueous solution with and without cationic surfactants under the current density of 100 A/dm$^2$. The molecular weights of each surfactant are as followings; surfactant-A: 161.67, surfactant-B: 291.94, surfactant-C: 348.05 and surfactant-D: 586.5. SiO$_2$ contents in deposits obtained from the solution containing each surfactant are as followings; surfactant-A: 6.6 %, surfactant-B: 9.6 %, surfactant-C: 3.8 % and surfactant-D: 1.0 %. It is well-known that adsorption behavior of surfactants depends on their molecular weight [3]. Usually, with increase in molecular weight, the adsorption capacity will increase. Therefore, this adsorption behavior results in decreasing SiO$_2$ content in deposits obtained from the solution containing the surfactants with molecular weight lower than 100. On the other hand, with increase in molecular weight, the solubility in aqueous solution will decrease [3]. Therefore, this solubility behavior results in decreasing SiO$_2$ content in deposits obtained from the solution containing the surfactants with molecular weight higher than 400. As shown in Fig.5, SiO$_2$ content in deposits will be ca. 10 % at the maximum using the solution containing a surfactant with molecular weight range of 200 to 300.

Figure 5. Effect of surfactant molecular weight on SiO$_2$ content in deposits obtained from acidic aqueous solution with and without cationic surfactants under the current density of 100 A/dm$^2$. The molecular weights of each surfactant are as followings; surfactant-A: 161.67, surfactant-B: 291.94, surfactant-C: 348.05, surfactant-D: 586.5.

SEM images of electrodeposited Zn-SiO$_2$ thin films obtained from acidic aqueous solution with and without cationic surfactants under the current density of 100 A/dm$^2$ are shown in Fig.6. As shown in these figures, morphology of the electrodeposits strongly depends on the molecular weight of surfactant. Electrodeposits obtained from the solution without and with surfactant D are composed from Zn crystals with the shape of hexagonal plates. On the other hand, electrodeposits obtained from the solution containing surfactant A, B and C are composed from Zn crystals with the shape of small thin leaves.
Figure 6. SEM images of electrodeposited Zn-SiO$_2$ thin films obtained from acidic aqueous solution with and without cationic surfactants under the current density of 100 A/dm$^2$. (a): surfactant-A, (b): surfactant-B, (c): surfactant-C, (d): surfactant-D, (e): without surfactant.

XRD patterns of electrodeposited Zn-SiO$_2$ thin films obtained from acidic aqueous solution with and without cationic surfactants under the current density of 100 A/dm$^2$ are shown in Fig.7. Electrodeposits obtained from the solution containing each surfactant are composed from Zn crystals with the preferentially oriented crystal plane in (101), which is not close-packed. Usually, with increase in the deposition overpotential, the electrodeposited crystal growth rate will also increase. Therefore, independently in the molecular weight of surfactants, non-close-packed (101) was preferentially oriented in the electrodeposits obtained at the current density of 100 A/dm$^2$, which results in large deposition overpotential.

Figure 7. XRD patterns of electrodeposited Zn-SiO$_2$ thin films obtained from acidic aqueous solution with and without cationic surfactants under the current density of 100 A/dm$^2$. (a): surfactant-A, (b): surfactant-B, (c): surfactant-C, (d): surfactant-D, (e): without surfactant.
4. Conclusions
Zn-SiO$_2$ alloy thin films were obtained at the wide current density range from 5 A/dm$^2$ to 100 A/dm$^2$. Electrodeposits obtained at current density of 5 A/dm$^2$ are composed from Zn crystals with preferential orientation in (002), while electrodeposits obtained at the current density of 100 A/dm$^2$ are composed from Zn crystals with preferential orientation in (101). SiO$_2$ content in deposits was ca. 10% at the maximum using the solution containing a surfactant with molecular weight range of 200 to 300.

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