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Morphology Control of Zn-SiO₂ Composite Films Electrodeposited from Aqueous Solution Containing Quaternary Ammonium Cations

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Abstract. Zn-SiO₂ 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-SiO₂ alloy thin films were obtained at the wide current density range from 5 A/dm² to 100 A/dm². SiO₂ 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-SiO₂ composite can be electrodeposited from the aqueous solution containing Sn²⁺ ions [7]. They found that SiO₂ 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-SiO₂ composite from the aqueous solution containing N, N-dimethyl-dodecyl-amine [8]. They obtained Zn-33wt.%SiO₂ composite using SiO₂ particles with the diameter of 2 μm. M. Azizi *et al.* reported that the co-deposition process of Zn-SiO₂ composite from the aqueous solution containing gelatin [9]. They found that Zn-20mass%SiO₂ composite can be electrodeposited using the solution containing 50 g/L SiO₂ particles. However, the role of surfactants on the co-deposition process of Zn and SiO₂ is still in an unsettled issue.

In this paper, effect of surfactants molecular weight on the morphology of electrodeposited Zn-SiO₂ 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 ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$: 300 g/L, Na_2SO_4 : 50 g/L, H_2SO_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 μm 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-distearyl-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-SiO₂ alloys was determined by a cathodic polarization curve measured over the wide range of cathode potential. Zn-SiO₂ alloys were galvanostatically electrodeposited over the wide range of current density from 5 A/dm² to 100 A/dm². Crystal phase, structure and chemical composition of electrodeposited Zn-SiO₂ alloys was investigated by using X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX).

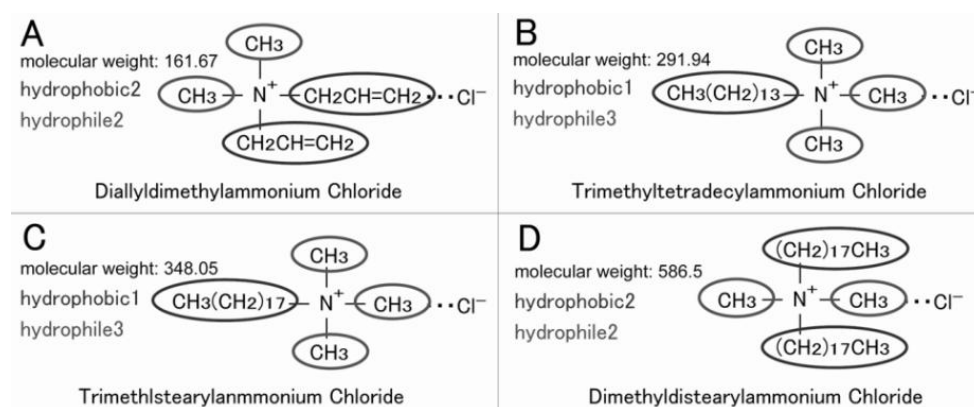
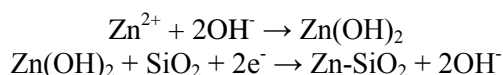


Figure 1. Molecular structures of cationic surfactants (A: diallyl-dimethyl-ammonium chloride, B: trimethyl-tetradecyl-ammonium chloride, C: trimethyl-stearyl-ammonium chloride, D: dimethyl-distearyl-ammonium chloride).

3. Results and Discussion

3-1. Effect of current density on the electrodeposition of Zn-SiO₂

Cathodic polarization curves for Zn-SiO₂ 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/dm², 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 $\text{Zn}(\text{OH})_2$ forms in the vicinity of cathode [10-12]. Subsequently the cathode potential reaches to the equilibrium potential of Zn (-0.96 Vvs.Ag/AgCl), cationic SiO_2 particles will adsorb on cathode surface. Electrodeposition of Zn-SiO₂ will proceed due to the following reaction.



Furthermore, with increase in the current density more than 100 A/dm², 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-SiO₂ alloy deposition was determined to be the range from 5 A/dm² to 100 A/dm².

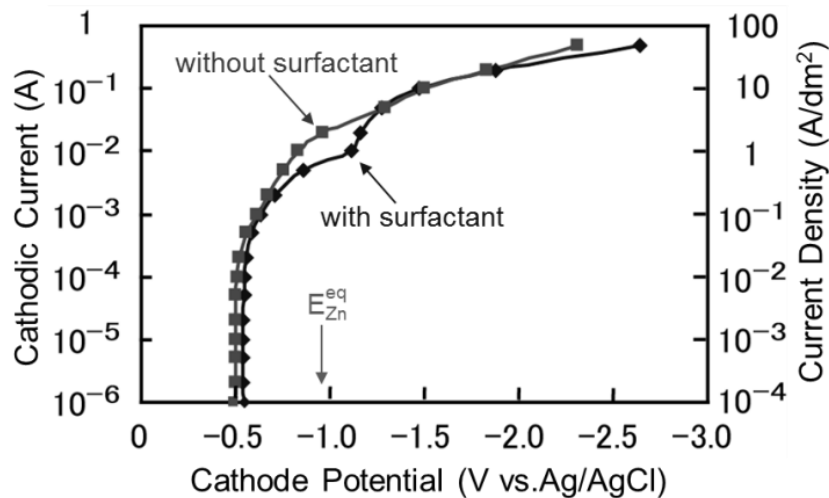


Figure 2. Cathodic polarization curve for electrodeposition of Zn-SiO₂ from acidic aqueous solutions with and without cationic surfactant-A.

SEM images of electrodeposited Zn-SiO₂ thin films obtained from an acidic aqueous solution without cationic surfactants under the different current density (5, 20, 100 A/dm²) 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 μm in the diameter.

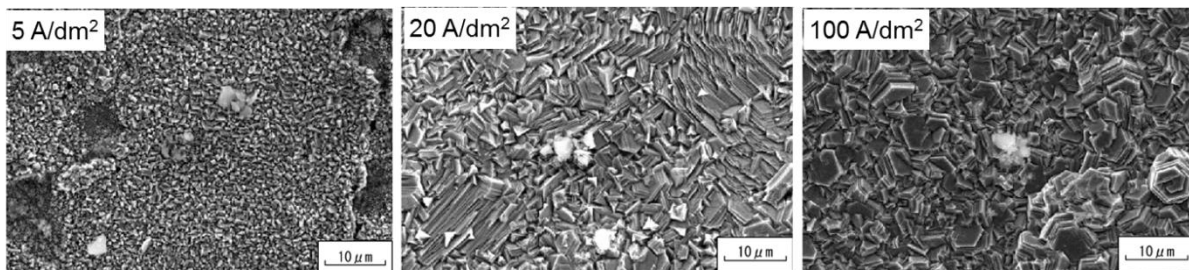


Figure 3. SEM images of electrodeposited Zn-SiO₂ thin films obtained from an acidic aqueous solution without cationic surfactants under the different current density (5, 20, 100 A/dm²).

XRD patterns of electrodeposited Zn-SiO₂ thin films obtained from an acidic aqueous solution without cationic surfactants under the different current density (5, 20, 100 A/dm²) 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/dm² 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/dm² are composed from Zn crystals with the preferentially oriented crystal plane in (101), which is not close-packed.

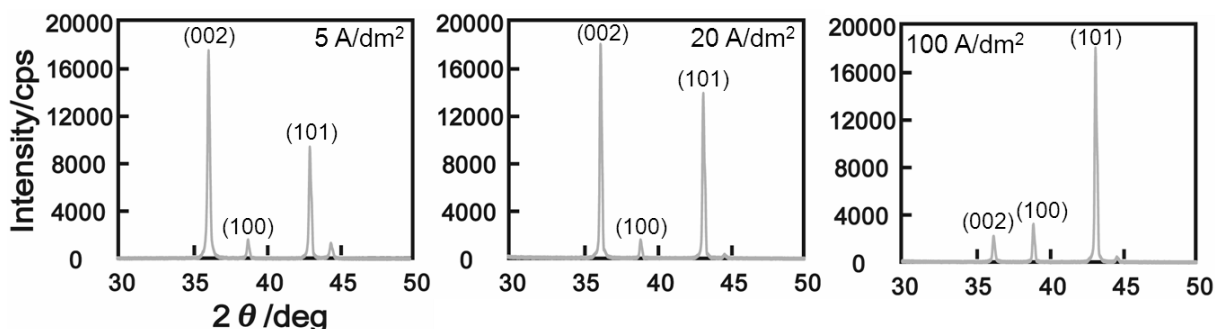


Figure 4. XRD patterns of electrodeposited Zn-SiO₂ thin films obtained from an acidic aqueous solution without cationic surfactants under the different current density (5, 20, 100 A/dm²).

3-2. Effect of surfactant molecular weight on the electrodeposition of Zn-SiO₂

Figure 5 shows effect of surfactant molecular weight on SiO₂ content in deposits obtained from acidic aqueous solution with and without cationic surfactants under the current density of 100 A/dm². 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. SiO₂ 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 SiO₂ 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 SiO₂ content in deposits obtained from the solution containing the surfactants with molecular weight higher than 400. As shown in **Fig.5**, SiO₂ content in deposits will be ca. 10 % at the maximum using the solution containing a surfactant with molecular weight range of 200 to 300.

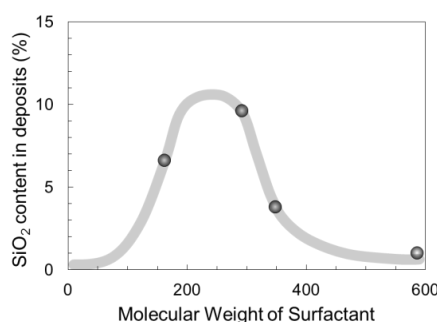


Figure 5. Effect of surfactant molecular weight on SiO₂ content in deposits obtained from acidic aqueous solution with and without cationic surfactants under the current density of 100 A/dm². The molecular weights of each surfactant are as followings; surfactant-A: 161.67, surfactant-B: 291.94, surfactant-C: 348.05, surfactant-D: 586.5.

SEM images of electrodeposited Zn-SiO₂ thin films obtained from acidic aqueous solution with and without cationic surfactants under the current density of 100 A/dm² 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.

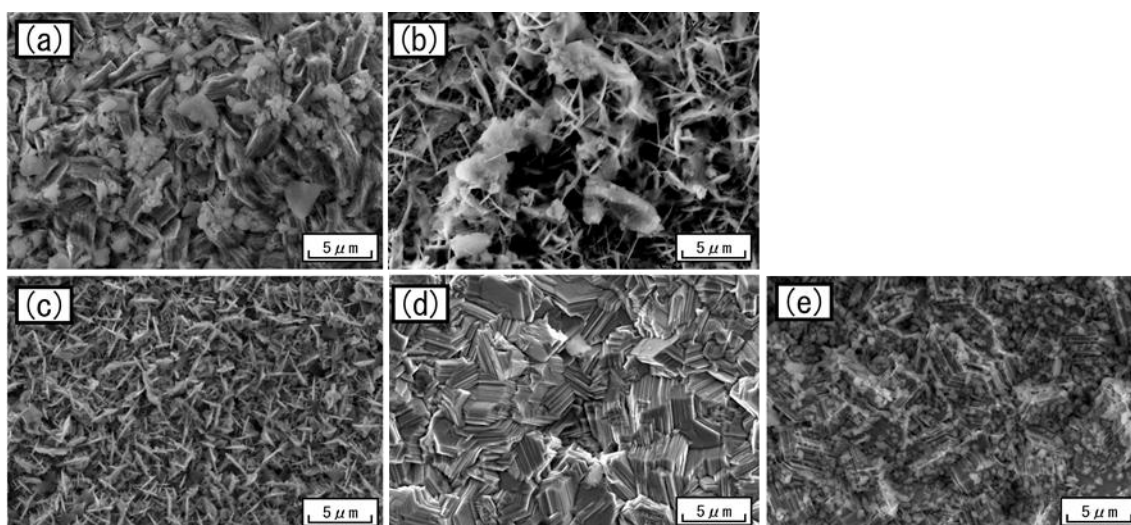


Figure 6. SEM images of electrodeposited Zn-SiO₂ thin films obtained from acidic aqueous solution with and without cationic surfactants under the current density of 100 A/dm². (a): surfactant-A, (b): surfactant-B, (c): surfactant-C, (d): surfactant-D, (e): without surfactant.

XRD patterns of electrodeposited Zn-SiO₂ thin films obtained from acidic aqueous solution with and without cationic surfactants under the current density of 100 A/dm² 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/dm², which results in large deposition overpotential.

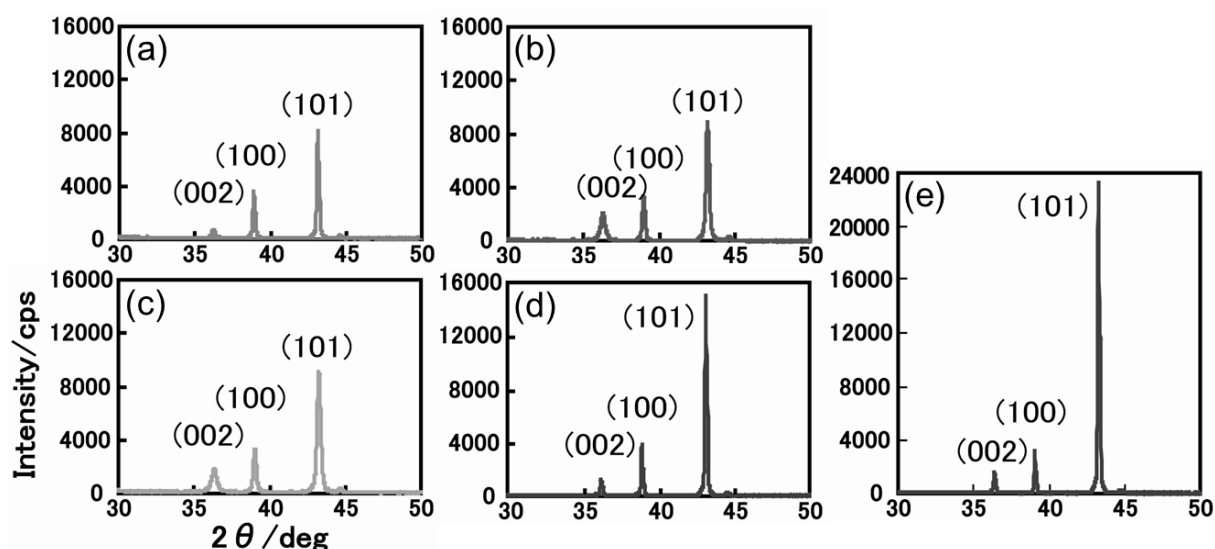


Figure 7. XRD patterns of electrodeposited Zn-SiO₂ thin films obtained from acidic aqueous solution with and without cationic surfactants under the current density of 100 A/dm². (a): surfactant-A, (b): surfactant-B, (c): surfactant-C, (d): surfactant-D, (e): without surfactant.

4. Conclusions

Zn-SiO₂ alloy thin films were obtained at the wide current density range from 5 A/dm² to 100 A/dm². Electrodeposits obtained at current density of 5 A/dm² are composed from Zn crystals with preferential orientation in (002), while electrodeposits obtained at the current density of 100 A/dm² are composed from Zn crystals with preferential orientation in (101). SiO₂ content in deposits was ca. 10 % at the maximum using the solution containing a surfactant with molecular weight range of 200 to 300.

References

- [1] Giridhar J, Ooij W J 1992 *Surf. Coat. Tech.* **52** 17
- [2] Hashimoto S, Abe M 1994 *Corrosion Science* **36** 2125
- [3] Tulio P C, Rodrigues S E B, Carlos I A 2007 *Surf. Coat. Tech.* **202** 91
- [4] Miranda F J F, Barcia O E, Diaz S L, Mattos O R, Wiart R 1996 *Electrochim. Acta* **41** 1041
- [5] Eliaz N, Venkatakrishna K, Hegde A C 2010 *Surf. Coat. Tech.* **205** 1969
- [6] Khan T R, Erbe A, Auinger M, Marlow F and Rohwerder M 2011 *Sci. Technol. Adv. Mater.* **12** 055005
- [7] Kondo K, Ohgishi A and Tanaka Z 2000 *J. Electrochem. Soc.* **147** 2611
- [8] Tuaweri T J, Wilcox G D 2006 *Surf. Coat. Tech.* **200** 5921
- [9] M. Azizi, W. Schneider, W. Plieth 2005 *J. Solid State Electrochem.* **9** 429
- [10] Ohgai T, Fukushima H, Akiyama T and Hirai Y 1997 *Metallurgical Review of MMIJ* **14** 24
- [11] Akiyama T, Kobayashi S, Ki J, Ohgai T, Fukushima H 2000 *J. Appl. Electrochem.* **30** 817
- [12] Nakano H, Ohgai T, Fukushima H, Akiyama T and Kammel R 2001 *METALL* **55** 676