Introduction

Some electrodeposited zinc based alloys have metastable phases which are different from thermal equilibrium phases. For electrodeposited Zn–Fe alloy, single \( \eta \) phase is observed in the range below 17 mass% Fe, which is much higher than the solid solubility of Fe in thermally equilibrium \( \eta \) phase. \( G \) like phase is observed over about 20 mass% Fe and \( \gamma \) phase which contains Zn atom exist in Fe rich region. However, some alloy phases (\( \delta \), \( \epsilon \), \( \zeta \), \( \eta \) phase, \( \gamma \)-Mn phase) are not observed. For electrodeposited Zn–Ni alloy, \( \eta \) phase and \( G \) phase are found in the Zn rich region but \( \delta \) phase in the thermal equilibrium Zn–Ni binary alloy are not observed.\(^2\)

For electrodeposited Zn–Ni alloy, \( \eta \) phase and \( \gamma \) phase are found in the Zn rich region but \( \delta \) phase in the thermal equilibrium Zn–Ni binary alloy exists as a non-equilibrium phase having a similar crystal structure to the thermal equilibrium phase and the \( \gamma \) phase of the electrodeposited ZnNi alloy exists is transformed to the thermal equilibrium phase by the heating in the temperature range above 180°C.\(^6\) Moreover, \( \gamma \)' phase which does not exist as a thermal equilibrium phase is found in electrodeposited Zn–Cr alloy.\(^7\)

Electrodeposited Zn–Mn alloys exhibit good corrosion resistance\(^8\)--\(^10\) as those alloys mentioned above. Although these results on the alloy phases appeared in the electrodeposited Zn system alloys\(^1\)--\(^7\) suggest that some metastable alloy phases may be realized in the electrodeposited Zn–Mn alloys, both the crystal structure of the electrodeposited Zn–Mn alloy and the change caused by the heating are not studied. Therefore, we investigated the structure and its change by heating of the electrodeposited Zn–Mn alloy using X-ray diffraction, SEM and SIMS.

Experimental

2.1. Sample Preparation of Electrodeposited Zn–Mn Alloy

The Zn–Mn alloys were electrodeposited on cold rolled steel sheet using a laboratory circulation cell. The sheet sheets as substrates were electrolytically degreased in an alkaline bath and were electrolytically pickled in H\(_2\)SO\(_4\) solution subsequently. The sheets were rinsed with water after each electrolysis. The sheets were 70\( \times \)185 mm in size and 0.8 mm in thickness. The coating was electrodeposited in a citrate bath which contains zinc sulfate, manganese sulfate and sodium citrate. The electrodeposited Zn–Mn alloy coatings with various compositions from 0.01 to 100 mass% Mn were obtained by controlling the plating conditions, i.e. current density and pH. The coating was electrodeposited in a citrate bath which contains zinc sulfate, manganese sulfate and sodium citrate.
posited Zn–Mn alloy were observed by SEM (Scanning Electron Microscope, JEOL JSM840A). The SEM observation for the intersection of the coating was performed using the specimen fractured in liquid N₂.

A depth profile of the electrodeposited Zn–42mass%Mn alloy was determined by SIMS (Secondary Ion Mass Spectrometry, CAMECA IMS-3F). The specimen was rinsed in an acetone ultra sonic bath. The analyzed area was 60 μm², Mn⁺, Zn⁺ and Fe⁺ secondary ions were measured using O₂⁻ primary ion of 8 kV acceleration voltage.

The crystal structure of the as-deposited and the heated alloys was examined using X-ray diffractometer (Rigaku, RAX10) with a receiving monochrometer. Cu Kα radiation was used at 2kV A power.

3. Results and Discussion

3.1. Morphology and Depth Profile of Electrodeposited Zn–Mn Alloy Coatings

The SEM images for the surface of the electrodeposited Zn-Mn alloy coatings, containing various Mn content, are shown in Fig. 1. Fine grains of submicrometre size are observed for the electrodeposited Zn–24mass%Mn alloy. Granular crystals, composed from fine grains, are observed for the electrodeposited Zn–62mass%Mn alloy. Both of the fine grains and the granular crystals are observed for the electrodeposited Zn–42mass%Mn alloy.

The intersection of the electrodeposited Zn–Mn alloy coating is illustrated in Fig. 2. Only fine grains are observed in each coating containing various Mn content.

Additionally, a sharp-edged structure which is artificially formed during the fracture in liquid N₂ is observed. Although the granular crystals are seen at the surface of the electrodeposited Zn–Mn alloys in the range of Mn content beyond 42mass%Mn, the granules are closely packed and fine grains exist. Therefore, each coating exhibits a homogeneous structure.

The SIMS depth profile of Mn, Zn and Fe for electrodeposited Zn–42mass%Mn alloy coated steel is shown in Fig. 3. The secondary ion intensities of Mn⁺ and Zn⁺ are almost constant in the coating layer, except at the surface. The enhancement of the intensity at the surface results from the surface oxidation or contamination, since secondary ion yield of the metals is vastly increased by oxidation. Therefore, the depth profile shows that the coating has an uniform dis-
The intensity of Mn secondary ion which results from Mn added in the steel is relatively high even in the steel substrate, because the secondary ion yield of Mn is much higher than that of Fe.12)  

### 3.2. Crystal Structure of the Electrodeposited Zn–Mn Alloy

#### 3.2.1. Crystal Structure of As-deposited Zn–Mn Alloy

The X-ray diffraction patterns are displayed in Fig. 4 for the electrodeposited Zn–Mn alloy containing various Mn content. The alloy phases which appeared in each diffraction pattern of the coatings were identified as follows: the h phase having hcp structure (lattice constants: \(a = 2.67\) Å and \(c = 4.95\) Å) exists in the electrodeposited Zn–0.01 mass% Mn alloy. The \(\Gamma\) phase having Cu₃Zn₄ type structure (lattice constants: \(a = 9.14\) Å) and the \(\varepsilon\) phase having hcp structure exist in the electrodeposited Zn–14 mass% Mn alloy. Only the \(\varepsilon\) phase exists in the electrodeposited Zn–24 mass% Mn alloy. The \(\varepsilon\) phase and the \(\gamma\)-Mn phase having bct structure exist in the electrodeposited Zn–42 mass% Mn alloy. Single \(\gamma\)-Mn phase exist in the electrodeposited Zn–62 mass% Mn alloy. The lattice constant of \(\varepsilon\) phase was \(a = 2.74–2.77\) Å and \(c = 4.45–4.46\) Å, and the lattice constants for \(\gamma\)-Mn phase differs in the range of \(a = 2.67–2.69\) Å and \(c = 3.53–3.78\) Å which depend on the Mn content. The \(\alpha\)-Mn phase having \(\alpha\)-Mn type structure (lattice constants: \(a = 8.91\) Å) exist in the electrodeposited 100 mass% Mn. The results indicate that the electrodeposited Zn–Mn alloy is composed of either a single phase or two phases from the phases as seen in thermal equilibrium Zn–Mn binary alloys.

A phase diagram for the Zn–Mn binary alloys13) is shown in Fig. 5. The phase diagram displays that the following phases are stable at room temperature. The \(\eta\)-Zn has solid solution in the range of less than 0.14 mass% Zn. \(\zeta\) phase of CoZn₁₃ type structure and the \(\delta\) phase of hexagonal structure exist in Zn rich region. \(\Gamma\) phase which exists at around 85 mass% Zn, the \(\alpha\) phase of Cu₃Au type structure is stable around 80 mass% Zn. The beta-Mn phase of bcc structure and the \(\alpha\)-Mn phase of \(\alpha\)-Mn type structure are stable in Mn rich regions.

However, the phases of the electrodeposited Zn–Mn alloys were different from the phases shown in the diagram, although the alloys were deposited in the room temperature. Namely, the \(\delta\) phase, the \(\zeta\) phase, the \(\alpha\) phase and the beta-Mn phase do not appear, and the \(\varepsilon\) phase and the \(\gamma\)-Mn phase which are high temperature phases appeared. It is reported that the \(\gamma\)-Mn phase as the thermal equilibrium phase have fcc structure and that face centered tetragonal structure which is equivalent to the bct structure is realized in quenched materials.14) A similar structure appears in the electrodeposited Zn–Mn alloy system. The disappearance of the thermal equilibrium phases and the appearance of the high temperature phases are reported in the other alloys prepared by the electrodeposition.1–7) The difference between the thermal equilibrium phases and the phases by electrodeposition may be attributed to high internal energy caused by a high over potential and high fast deposition rate with the present conditions of the electrolysis.8) Thus the high temperature phase of \(\varepsilon\) phase and \(\gamma\)-Mn phase are supposed to be stabilized in the electrodeposited Zn–Mn alloys.

#### 3.2.2. Crystal Structure of \(\gamma\)-Mn Phase and \(\varepsilon\) Phase in Electrodeposited Zn–Mn Alloy

Figure 6 shows the lattice constant of \(\gamma\)-Mn phase which is observed in the electrodeposited Zn–Mn alloy as a function of Mn content. The lattice constant for the electrodeposited pure Mn is close to that for the thermal equilibrium phase. The c axis of the \(\gamma\)-Mn phase for the electrodeposi-
ed Zn–Mn alloy increases with decreasing Mn content, while the a axis remains almost constant.

Figure 7(a) shows a unit cell of the γ-Mn type structure, (b) atomic arrangement in (011) plane for equilibrium γ-Mn phase, (c) atomic arrangement in (011) plane for distorted γ-Mn phase by dilution of Zn.

but the distance between AB atoms can be kept constant until AB atoms contact.

The modification of the lattice of the γ-Mn alloy, keeping the symmetry of the bct structure is allowed until AC=AB. When Zn is alloyed to the γ-Mn phase beyond the limit, the γ-Mn phase transits to another alloy phase, i.e. ε phase. The atomic arrangement for the maximum limit is shown in Fig. 7(c). The obtained maximum of c axis is 3.78 Å corresponding to that for an ideal lattice as shown in Fig. 7(c).

On the other hand, the lattice constant of the ε phase was almost constant in the range where the phase was observed. The concentrations of the ε phases observed in the coatings with various Mn content may stay almost constant, because the single ε phase exists in the very narrow range and the ε phase co-exists with the other phase, namely γ-Mn phase in the Mn rich region or Π phase in the Mn poor region. Therefore, the lattice constant of the ε phase is almost constant.

Ratio of ε phase and γ-Mn phase is estimated using relative intensities defined as γ ratio. The γ ratio is \( I_{γ(101)}/(I_{γ(101)}+I_{ε(101)}) \), where \( I_{γ(101)} \) and \( I_{ε(101)} \) are intensities of the (101) reflection for each phase. The phase composition evaluated by the γ ratio is shown in Fig. 8. A single γ-Mn phase exists above the range of 50 mass% Mn. The ε phase and the γ-Mn phase coexist in the range between 24 and 50 mass% Mn. The γ-Mn phase is not observed below the range of 24 mass% Mn.

3.2.3. Phase Transformation of ε-Mn Phase and γ-Mn Phase in Electrodeposited Zn–Mn Alloy by Heating

Even after heating at 170°C in the air which corresponds to the actual painting process, the crystal structures of the ε phase and the γ-Mn phase in the electrodeposited Zn–Mn alloy were not changed.

By increasing the temperature to over 250°C, changes in the crystal structure are observed. The diffraction patterns of Zn–14mass%Mn heated at 250°C, Zn–42mass%Mn and Zn–62mass%Mn heated at 300°C are displayed in Fig. 9(a), 9(b) and 9(c), respectively. The phase transformation of the electrodeposited Zn–Mn alloys caused by the heating are summarized in Fig. 10.

For the electrodeposited Zn–Mn alloy with the ε phase and the Γ phase, the ε phase disappears and it becomes a single phase of the Γ phase, demonstrating that the ε phase is transformed to the stable Γ phase by the heating. The coatings with the single ε phase is unchanged by the heating below 300°C. The γ-Mn phase is transformed to the α-Mn phase or the β-Mn phase. For the alloys containing both of the ε phase and the γ-Mn phase, the α-Mn phase ap-
pears. These results demonstrate that the metastable γ-Mn phase is transformed to the thermally stable α-Mn phase and the β-Mn phase but that ε phase is unchanged.

4. Summary

The structure of the electrodeposited Zn–Mn alloys was investigated using the SEM observation, the SIMS depth profile and X-ray diffraction analysis. The followings were clarified by the analysis of these coatings.

1. The surface structure of the coatings changes from fine grain to granular grain which contains fine particles of submicrometer order as Mn content increases. The intergranular structure of each coating is homogenous, resulting in uniform depth profile.

2. Observed alloy phases of the coating are the η phase, the Γ phase, the ε phase, the γ-Mn phase and the α-Mn phase. The electrodeposited Zn–Mn alloy coatings are composed of either a single phase or two phases from these phases.

3. Single ε phase is observed at around 20 mass% or less Mn, the ε phase and the γ-Mn phase coexist in the range from 20 to 50 mass% of Mn and single γ-Mn phase exists over 50 mass% Mn. The phases are the thermally non-equilibrium alloy phase which is seen in the high temperature region in the binary alloy system. The ε phase and the γ-Mn phase in the coating which are stable for heating at 170°C. The γ-Mn phase is transformed to the β-Mn phase and the α-Mn phase by the heating beyond 250°C while the ε phase is unchanged.

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REFERENCES

1) E. Raub and K. Müller: Fundamentals of Metal Deposition, ed. by E. Raub and K. Müller, Elsevier, Amsterdam, (1967), 144.
2) Y. Shima, M. Terasaka, K. Nakaoka and T. Hara: Tetsu-to-Hagané, 72 (1986), 954.
3) A. Shibuya, N. Kurimoto, K. Korekawa and K. Noji: Tetsu-to-Hagané, 66 (1980), 771.
4) M. R. Lambert, R. G. Hart and H. E. Twonsend: SAE Tech. Paper Series 83187, (1983).
5) K. Kondo: Tetsu-to-Hagané, 77 (1991), 886.
6) S. Hashimoto, M. Nagoshi, S. Ando, T. Urakawa and M. Sagiyama: Proc. of the 4th Int. Conf. on Zinc and Zinc Alloy Coated Steel Sheet (Galvatech‘98), ed. by N. Masuko, ISIJ, Tokyo, (1998), 537.
7) S. Hashimoto, S. Ando, T. Urakawa and M. Sagiyama: J Jpn. Inst. Met., 62 (1998), 9.
8) T. Urakawa, M. Sagiyama, T. Adaniya and T. Hara: Tetsu-to-Hagané, 72 (1986), 968.
9) T. Hara, M. Sagiyama, T. Adaniya, T. Urakawa, Y. Fukuda and Y. Tsujiya: Nippon Kokan Tech. Rep., (1986), No. 114, 8.
10) T. Hara, M. Sagiyama, T. Urakawa, T. Adaniya, Y. Fukuda and Y. Tsujiya: Nippon Kokan Tech. Rep., (1987), No. 48, 29.
11) A. Benningham, Surf. Sci., 53 (1975), 596.
12) K. Tsunoyama, Y. Ohashi, T. Suzuki and K. Tsuruoka: Tetsu-to-Hagané, 60 (1974), 89.
13) E. A. Brandes: Smedlels Metals Reference book 6th ed., Butterworth & Co Ltd., London, (1983)
14) R. W. G. Wyckoff: Crystal Structures 2nd ed., John Wiley & Sons, New York, (1963), 52.