Structure and Polarization Properties of Zn–Nb Films Formed on Steel Sheet by Sputtering

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Zn–Nb films were formed on a steel sheet by helicon plasma sputtering in an argon gas atmosphere at 1.0 Pa, at RF power of 50 W and DC power of 50 mA. The structure and polarization properties of these films were studied using EPMA, X-ray diffraction and polarization curve measurements. Zn plate-like crystals in Zn–Nb films decreased with increasing Nb content, resulting in a smooth surface over the entire film at Nb content of 30 mass% and above. The preferred orientation plane of Zn plate-like crystals was (0002) at 0 mass% Nb, while the orientation indices of (10 $\bar{1}$ 1) and (10 $\bar{1}$ 0)Zn increased with rising Nb content. At 30–60 mass% Nb, the X-ray diffraction spectra showed a halo pattern characteristic of an amorphous structure. The corrosion current of Zn–Nb films, which was determined by polarization curves in 3% NaCl solution, decreased with increasing Nb content to reach a minimum value at 30–60 mass% Nb, corresponding to an amorphous structure.

KEY WORDS: Zn–Nb; sputtering; polarization property; amorphous structure.

1. Introduction

Zinc coating on steel sheet is produced by hot dip galvanizing or electroplating. Electroplating has been applied to the production of pure Zn and Zn–Ni alloy coated steel sheets, and Zn–Cr electroplating^{1–3)} has also been studied due to its excellent corrosion resistance. Substances of environmental concern and more noble metals than Fe which are difficult to recycle need to be avoided when designing highly corrosion-resistant Zn alloy films. It is known from the investigation of Zn alloy films produced by hot dip galvanizing and dry process coating that less noble metals than Zn, such as Mg, Al and Ti improve the corrosion resistance of the Zn alloy films.^{4–10)} These metals are not regarded as environmental pollutants. Nb is a less noble metal and is expected to improve the corrosion resistance of Zn alloy films. However, there have been very few studies on the corrosion properties of Zn–Nb alloy films. Since the melting point of Nb is 2 743 K, much higher than that of Zn, 1 180 K, it would be difficult to produce Zn–Nb alloy coating by hot dip galvanizing. Therefore, in this study, Zn–Nb alloy films were formed on steel sheets by sputtering, and the structure and polarization properties of the films were investigated.

2. Experimental

Commercial polycrystalline low carbon Al-killed steel sheet (14×14 mm² with a thickness of 1 mm) was used as

the substrate. Each substrate was polished with emery papers (Nos. 600, 1 500 and 2 000) and buffed to mirror smoothness. The substrate was then degreased in acetone by ultrasonic cleaning prior to sputtering. **Figure 1** shows the apparatus for helicon plasma sputtering used in this study. Zn plate (99.99 mass%) and Nb plate (99.9 mass%) with a thickness of 1 mm were given a fan-like shape with a radius of 3.81 cm as shown in Fig. 1 and used as targets for sputtering. The area ratio of Zn to Nb in the target was varied to obtain the Zn–Nb alloy films with different compositions. Two substrates were placed parallel to the target at a distance of 18 cm. During sputtering, temperature of the substrate was about 373 K. After the chamber had been evacuated to 4×10^{−4} Pa using a rotary pump and a turbomolecular pump, Ar gas was introduced into the chamber until pressure reached 1.0 Pa. Zn–Nb alloy films were formed on two substrates simultaneously by sputtering for 2 h at RF power of 50 W and DC power of 50 mA.

The alloy films formed were dissolved with hydrofluoric acid and the concentrations of Zn and Nb were determined by ICP to calculate the alloy composition and the coating weight. The morphology of the Zn–Nb films were observed SEM, and the distribution of Zn and Nb was visualized by EPMA. Analysis by X-ray diffraction was also carried out. The crystal orientation of Zn was determined using Willson and Rogers' method¹¹⁾ with an X-ray diffraction intensity of (0002) to the (11 $\bar{2}$ 2) planes. The polarization curves from less noble to more noble direction were obtained using the potential sweep rate of 1.0 mV s^{−1} in oxygen-saturated 3%

NaCl solution at 40°C. A saturated Ag/AgCl reference electrode (0.199 V vs. NHE, 25°C) was used for measurement. Then, the potentials were plotted with reference to NHE. The corrosion current density and the corrosion potential of Zn–Nb films were obtained by Tafel's plot extrapolation method.

The Zn–Nb films were formed simultaneously on two substrates. One was subjected to composition analysis by ICP and the other to polarization measurement. Then relationship between Zn–Nb alloy composition and the corrosion current density or the corrosion potential were investigated.

Fig. 1. Apparatus for helicon plasma sputtering.

Fig. 2. Effect of Nb/(Nb+Zn) ratio in target on the Nb content and the coating weight of Zn–Nb films.

3. Results and Discussion

3.1. Composition of Zn–Nb Films

Figure 2 shows the relationship between the Nb area ratio of the target and the Nb content and the coating weight of Zn–Nb films formed by sputtering. The Nb content in the films increased with increasing Nb area ratio of the target, indicating that Zn–Nb alloy films of various composition can be produced by changing the area ratio of the target. The Nb content in the films was considerably smaller than that in the target, suggesting that Nb was less likely to be deposited than Zn. In fact, the maximum sputtering ratios of Zn and Nb were reported to be 16 atoms ion⁻¹ and 1.87 atoms ion⁻¹, respectively.¹²⁾ Since Nb was less likely to be deposited, the coating weight of the Zn–Nb films decreased with increasing Nb area ratio of the target.

3.2. Structure of Zn–Nb Films

Figure 3 shows the SEM and EPMA images of Zn–Nb films with various compositions. Platelet crystals and smooth areas were observed in Zn–Nb films. With increasing Nb content of the film, smooth areas increased, resulting in a smooth surface all over film at Nb content exceeding 30 mass%. As can be seen from the characteristic X-ray images of Zn and Nb, the Zn content was higher in the platelet crystals than in the smooth areas. Zn and Nb were homogeneously distributed over the smooth areas. The platelet crystals became perpendicular to the substrate with increasing Nb content of the film as shown in Fig. 3(d).

Figure 4 shows the X-ray diffraction patterns of Zn–Nb films. X-ray diffraction analysis was carried out changing

Fig. 3. EPMA images of Zn–Nb films with various compositions.

Fig. 4. X-ray diffraction patterns of Zn-Nb films with various compositions.

Fig. 5. X-ray diffraction pattern of Zn-48mass%Nb film with coating weight of 2.4 g/m².

2θ from 30° to 130° . Figure 4 highlights the result in the low diffraction angle region where the intensity of Zn was very strong. The Zn diffraction peaks of the (0002), (10 $\bar{1}$ 0) and (10 $\bar{1}$ 1) were observed in Nb-free Zn film as shown in Fig. 4(a). The intensities of these diffraction peaks decreased with increasing Nb content in the film, and the peaks disappeared when the Nb content exceeded 30 mass%. On the other hand, no diffraction peak for Nb was observed, even when Nb content exceeded 50 mass%. The X-ray diffraction pattern of Zn-48mass%Nb with a coating weight of 2.4 g/m² is shown in Fig. 5. This X-ray diffraction spectrum showed a clear halo pattern characteristic of an amorphous structure. In addition, Zn-48mass%Nb resulted in a smooth surface in all over the film. The disappearance of X-ray diffraction peaks when Nb content exceeded 30 mass% (Fig. 4) appears to be attributable to a change in film structure to the amorphous type. It has been reported that the alloys which form intermetallic compounds are more likely to become amorphous.¹³⁾ With Zn-Nb alloys, many intermetallic compounds, such as NbZn, NbZn_{1.5}, NbZn₂, NbZn₃, NbZn₇ and NbZn₁₅ have been reported,¹⁴⁾ suggesting that Zn-Nb alloys become amorphous over a wide range of composition.

As shown in Fig. 3, the number of platelet crystal decreased with increasing Nb content in the film, resulting in a smooth surface over the entire film at Nb content exceeding 30 mass%. The intensities of X-ray diffraction peaks decreased with increasing Nb content in the film, indicating that Zn-Nb film became amorphous at Nb content exceeding 30 mass%, as illustrated in Fig. 4. From these results,

Fig. 6. Relationship between Nb content and the crystal orientation of Zn-Nb films.

the smooth area and the platelet crystals of Zn-Nb films appear to correspond to the amorphous phase and Zn crystals, respectively. Both the smooth areas and the platelet crystals were present in Zn-7.6mass%Nb and Zn-13mass%Nb films, suggesting that these films are composed of the amorphous phase and Zn crystals.

Figure 6 shows the crystal orientation indices of Zn in Zn-Nb films. The preferred orientation of (0002)Zn plane was observed in the Nb-free Zn film. However, in Zn-3.5mass%Nb film, the crystal orientation index of (0002)Zn is significantly smaller than that of Nb-free Zn film and those of (10 $\bar{1}$ 1) and (10 $\bar{1}$ 0)Zn are larger. On further increasing the Nb content in the films, the crystal orientation index of (10 $\bar{1}$ 0)Zn increased. When the preferred orientation of Zn crystal is the (10 $\bar{1}$ 0) plane, (0002), the Zn basal plane of the hcp structure, is vertical to the substrate: in other words, the hexagonal Zn platelets are perpendicular to the steel substrate. In Zn-13mass%Nb film, the platelet crystals were perpendicular to the substrate, as shown in Fig. 3, which agrees with the assumption that the platelet crystals are Zn in an oriented (10 $\bar{1}$ 0) plane.

With regard to the crystal orientation of films produced by PVD, a gas-adsorptive inhibition model has been reported.^{15,16)} According to this model, when the concentration of adsorptive inhibitors such as argon gas is low, films grow perpendicularly to a plane with high surface energy, resulting in the preferred orientation of the plane with low surface energy. On increasing the concentration of the adsorptive inhibitor, the inhibitor is preferentially adsorbed onto the plane with high surface energy, thus suppressing any growth vertical to that plane, resulting in the preferred orientation of a plane with high surface energy. Assuming Nb to be the adsorptive inhibitor in the growth of Zn films in this study, Nb-free Zn film more rapidly grows perpendicularly to high energy surface, the (10 $\bar{1}$ 0)Zn plane, due to the low concentration of adsorptive inhibitor, resulting in the preferred orientation of low energy surface, the (0002)Zn plane. On increasing the Nb content of the film, the Nb is adsorbed onto high energy surface, the (10 $\bar{1}$ 0)Zn plane and inhibits growth vertical to the (10 $\bar{1}$ 0)Zn plane, finally resulting in the preferred orientation of the (10 $\bar{1}$ 0)Zn plane. As described above, the crystal orientation of Zn can be explained by an adsorptive inhibition model based on the assumption that Nb acts as an adsorptive inhibitor in the same way as argon gas.

The X-ray diffraction patterns of (0002) and (10 $\bar{1}$ 0)Zn plane were shifted to the small 2θ and large 2θ directions,

Fig. 7. Relationship between Nb content and the spacing of Zn lattice planes.

Fig. 8. Polarization curves of Zn-Nb films of various compositions in 3% NaCl solution. [Nb content in film (mass%), (a): 0, (b): 2.9, (c): 7.2, (d): 13, (e): 23, (f): 32, (g): 53.]

respectively, with increasing Nb content in the film, as shown in Fig. 4. The relationship between the Nb content in the film and the spacings of (0002) and (10 $\bar{1}$ 0)Zn lattice planes was therefore investigated. The results are shown in Fig. 7. The spacing of the (0002) and (10 $\bar{1}$ 0)Zn lattice planes based on JCPDS are also described for reference in Fig. 7. In Nb-free Zn film, the spacing of the (0002)Zn lattice planes was slightly smaller than the JCPDS value, while that of (10 $\bar{1}$ 0)Zn lattice planes was larger than the JCPDS value. In short, the crystal of Zn films produced by sputtering was slightly reduced in the direction of *c*-axis of the hcp structure. The spacing of (0002)Zn lattice planes became identical to that of the JCPDS value in Zn-3.5mass%Nb film and increased with increasing Nb content in the film. On the other hand, the spacing of (10 $\bar{1}$ 0)Zn lattice planes decreased with increasing Nb content in the film. Although phase diagrams show no region for the formation of a solid solution of Nb in Zn,¹⁴⁾ it can be presumed from the observed changes in spacing of the (0002) and (10 $\bar{1}$ 0)Zn lattice planes that a solid solution of Nb in Zn is formed.

3.3. Polarization Property of Zn-Nb Films

Figure 8 shows the polarization curves of Zn-Nb film in 3% NaCl solution. There were no differences in polarization curves between Nb-free Zn film and Zn-2.9mass%Nb film, while the polarization curves were shifted to the noble direction with increasing Nb content exceeding 7.2 mass%. At an Nb content exceeding 7.2 mass%, anodic current den-

Fig. 9. Relationship between Nb content and the corrosion current density of Zn-Nb films in 3% NaCl solution.

Fig. 10. Relationship between Nb content and the corrosion potential of Zn-Nb films in 3% NaCl solution.

sities of Zn-Nb films reached the maximum and then decreased. This trend suggests the formation of passivated films.

Figure 9 shows the corrosion current densities of Zn-Nb films determined from the polarization curves. The corrosion current density gradually decreased with increasing Nb content in the film, and leveled off at Nb content above 30 mass%. This result corresponds to the change in structure of Zn-Nb films from platelet crystals to amorphous. Zn platelet crystals appear to dissolve readily. It is known that amorphous films show excellent corrosion resistance due to their homogeneous structure free from grain boundaries, dislocations, or heterogeneity of composition.¹⁷⁾ The Zn-Nb films produced by sputtering in this study also showed optimal corrosion resistance when they have an amorphous structure.

Figure 10 shows the corrosion potential of the steel sheet with Zn-Nb films determined from the polarization curves. The corrosion potentials were shifted to more noble direction with increasing Nb content in the film, and leveled off at Nb content above 30 mass% in an amorphous structure. The corrosion potentials of Zn-Nb films were less noble than that of steel sheet at all Nb contents, indicating that Zn-Nb films act as a sacrificial anode that protect the steel sheet.

4. Conclusions

The structure and polarization properties of Zn-Nb films formed on steel sheet by sputtering were investigated using SEM, EPMA, X-ray diffraction and electrochemical techniques. The following results were obtained. The number of Zn plate-like crystals in Zn-Nb films decreased with in-

creasing Nb content, resulting in a smooth surface over the entire film at Nb content of 30 mass% and above. The preferred orientation plane of Zn plate-like crystals was (0002) at 0 mass% Nb, while the orientation indices of (10 $\bar{1}$ 1) and (10 $\bar{1}$ 0)Zn increased with increasing Nb content. This variation of orientation can be explained by the adsorptive inhibition model, assuming that Nb acts as an adsorptive inhibitor. At 30–60 mass% Nb, the X-ray diffraction spectra showed a halo pattern characteristic of an amorphous structure. The corrosion current of Zn–Nb films, which was determined by polarization curves in 3% NaCl solution, decreased with increasing Nb content to reach their minimum value at 30–60 mass% Nb in an amorphous structure.

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