Zn-Al₂O₃ Composites with High Aluminum Content and Nanostructured Al₂O₃/ZnO Prepared by Electrochemical Technique from Non-Suspended Solution

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ABSTRACT

Zn-Al₂O₃ composites were electrodeposited from a non-suspended solution containing ZnSO₄·7H₂O and Al₂(SO₄)₃·14–18H₂O using benzyldimethyltetradecylammonium chloride dehydrate (BDTAC) as the additive at an electrodeposition current of 50–500 A/m² with an air or a nitrogen bubbling. Initial layers with a thickness of approximately 1 μm were observed in the Zn-Al₂O₃ composite on copper substrates. Furthermore, the Zn-Al₂O₃ composite was composed of two different crystallographic areas, namely, nano-level size deposited grains with 20–60 nm in width and 100–200 nm in length, and closely packed fine particle deposits with a diameter of approximately 5 nm containing more than 26 atomic% aluminum. The nano-level size deposited grains and the closely packed fine particle deposits comprised nano-size ZnO and θ-Al₂O₃, respectively. The oxygen concentration in Zn-Al₂O₃ composite by the air bubbling was higher than that in Zn-Al₂O₃ composite by the nitrogen bubbling. In contrast, the zinc content ratio in Zn-Al₂O₃ composite by the air bubbling was lower than that in Zn-Al₂O₃ composite by the nitrogen bubbling. The aluminum concentration in closely packed fine particle deposits in Zn-Al₂O₃ composite by the air bubbling was almost the same value as that in Zn-Al₂O₃ composite by the nitrogen bubbling.

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1. Introduction

Composite electrodeposition is a very useful method for inducing a new functionality to metal matrices and improving their mechanical and chemical properties.^{1–6} Composite electrodeposits have been prepared by dispersing particles in the metal matrices. The co-deposition mechanism of particles was reported to be composed of two steps, namely, the adsorption of metal ions on the particles and the subsequent reduction of the adsorbed ions on cathode surfaces.⁷ Furthermore, several mechanisms have been proposed by considering the fluid dynamics and the path of the particles.^{8–10} The composite electrodeposition has been widely carried out by introducing particles into electrodeposition baths. However, the composite electrodeposition carried out from the bath containing particles has serious drawbacks, since the particles in the electrodeposition baths cause deterioration in the bath stability and hinder the electrolyte filtering, which maintains the film quality of electrodeposits. In addition, the particles in the electrodeposition baths tend to aggregate in the bath; this prevents the particles from uniformly distributing in the metal matrices. One of the solutions to this problem is to employ a composite electrodeposition process from a non-suspended solution without using any particles. A few studies have been carried out on the growth of ZnO films from aqueous solutions. ZnO films were prepared by carrying out the cathodic deposition from a simple aqueous solution of zinc nitrate electrolyte.^{11–13} Moreover, Peulon et al. reported that ZnO films were electrodeposited from aqueous zinc chloride solutions.^{14,15} Oue

et al. carried out the electrodeposition of the Zn-Al₂O₃ composite using a non-suspended solution containing quaternary ammonium salt additives.¹⁶ They reported that the Zn-Al₂O₃ composite with less than 11 mass% aluminum content (Al/(Al+Zn)).¹⁶ These reports indicate the possibility of electrodepositing compounds or composites from non-suspended solutions without introducing particles in the solutions.

In this study, Zn-Al₂O₃ composites are prepared from a non-suspended solution without introducing particles in the electrodeposition bath by employing an electrochemical technique using quaternary ammonium salt additives with air or nitrogen bubbling gas to agitate the solution in the electrodeposition baths. In particular, we focus on the nano-structure and composition of Zn-Al₂O₃ composites containing high aluminum content of over 20 mass% aluminum as Al/(Al+Zn), moreover the influence of bubbling gas to agitate the solution in the electrodeposition baths on the nano-structure and composition.

2. Experimental

Copper sheets of 10 mm × 5 mm in size were used as substrates. The substrates were immersed in a degreasing solution of 10.0 g/dm³ NaOH and 8.0 g/dm³ trisodium citrate at 60°C for 5 min and subsequently in an activation solution containing 10 volume% sulfuric acid at 25°C for 1 min. ZnSO₄·7H₂O (0.52 mol/dm³) and Al₂(SO₄)₃·14–18H₂O (0.079 mol/dm³) were dissolved in pure water. Quaternary ammonium salts of benzyldimethyltetradecylammonium

chloride dehydrate (BDTAC, 1.0 g/dm^3) were introduced to the solution as additives. $\text{Zn-Al}_2\text{O}_3$ composites were electrodeposited using a platinum sheet as the anode at a pH of 2.5 and 60°C , after bubbling the electrodeposition bath solution with air or N_2 for 1 h. An electrodeposition current density of $50\text{--}500 \text{ A/m}^2$ was employed. The crystallographic structure of $\text{Zn-Al}_2\text{O}_3$ composites were evaluated using transmission electron microscopy (TEM) and selected-area electron diffraction (SAED). Moreover, the composition of the $\text{Zn-Al}_2\text{O}_3$ composites was examined using energy dispersive x-ray spectroscopy (EDS).

3. Results and Discussion

Figure 1 shows the cross sectional TEM image of the $\text{Zn-Al}_2\text{O}_3$ composites electrodeposited from the baths with the air bubbling and the N_2 bubbling at the electrodeposition current density of 500 A/m^2 . The discussions below show the results about $\text{Zn-Al}_2\text{O}_3$ composites electrodeposited at the electrodeposition current density of 500 A/m^2 , because $\text{Zn-Al}_2\text{O}_3$ composites electrodeposited at the electrodeposition current density of 500 A/m^2 included the highest aluminum content among the $\text{Zn-Al}_2\text{O}_3$ composites. Two layers consisted of layers with the thickness of approximately $1 \mu\text{m}$ on the copper substrates and upper layers were observed. The layers with the thickness of approximately $1 \mu\text{m}$ on the copper substrates were likely to grow initially. Thus, the layers are called as the initial layers. The thickness of the initial layers was measured using the scale in the microphotograph. The initial layers exhibited a higher concentration of nano-level size deposited grains. The nano-level size deposited grains were grown into dendritic structures from the initial layers to the upper layers.

The TEM photographs revealed the formation of two different types of deposits in the $\text{Zn-Al}_2\text{O}_3$ composite, namely, the nano-level size deposited grains (ex. “N” area inserted in Fig. 2(a)) and the closely packed fine particle deposits (ex. “P” area inserted in

Fig. 2(a)). The deposited grains and the closely packed fine particle deposits were observed on the $\text{Zn-Al}_2\text{O}_3$ composites by the air bubbling and N_2 bubbling baths (Figs. 2(a) and (d)). Furthermore, the bright field and the dark field images indicate that the deposited grains consist of crystals with several orientations. The deposited grains were $20\text{--}60 \text{ nm}$ in width and $100\text{--}200 \text{ nm}$ in length. The other parts except the deposited grains were composed of fine particles with an approximate size of $5\text{--}10 \text{ nm}$ (Figs. 2(c) and (f)).

The composition of the deposited grains and the closely packed fine particle areas was investigated by EDS. Figures 3 and 4 show the SAED images and the EDS spectra of the $\text{Zn-Al}_2\text{O}_3$ composites by the air bubbling and the N_2 bubbling baths, respectively. The deposited grains were found to be mainly composed of zinc and oxygen. Furthermore, the closely packed fine particles areas were mainly composed of aluminum, zinc, and oxygen. Table 1 and 2 show the composition of the deposited grains and closely packed fine particle deposits in the $\text{Zn-Al}_2\text{O}_3$ composites by the air bubbling and the N_2 bubbling baths, respectively. The deposited grains composed of oxygen and zinc on the $\text{Zn-Al}_2\text{O}_3$ composite by the air bubbling and the N_2 bubbling baths. The oxygen concentration, 40.8 atomic%, in the deposited grains in the $\text{Zn-Al}_2\text{O}_3$ composite by the air bubbling bath was much higher than that, 15.7 atomic%, in the $\text{Zn-Al}_2\text{O}_3$ composite by the N_2 bubbling bath. In contrast, the zinc concentration in the deposited grains in the $\text{Zn-Al}_2\text{O}_3$ composite by the air bubbling bath was lower than that in the

Figure 1. Cross sectional TEM image of the $\text{Zn-Al}_2\text{O}_3$ composite electrodeposited from the baths with (a) the air bubbling and (b) the N_2 bubbling at the electrodeposition current density of 500 A/m^2 . The image at the right shows the magnified micrograph of the square area shown in the image at the left.

Figure 2. (a), (b), (c) $\text{Zn-Al}_2\text{O}_3$ composite by the air bubbling and (d), (e), (f) the N_2 bubbling baths at the electrodeposition current density of 500 A/m^2 . (a), (d) surface bright field, (b), (e) surface dark field TEM images, and (c), (f) magnified bright field TEM images corresponding to the closely packed fine particle area shown in the bright field images in (a), (d). “N” and “P” in (a) represent the deposited grain area and the closely packed fine particle area.

Figure 3. (Color online) SAED image and EDS spectra of the Zn-Al₂O₃ composite by the air bubbling bath at the electrodeposition current density of 500 A/m². (a) SAED image, (b) EDS spectrum from the closely packed fine particle area, and (c) EDS spectrum from the deposited grain area shown in the micrograph in (a).

Table 1. Composition of the two types of deposits in the Zn-Al₂O₃ composites by the air bubbling.

Element	Concentration (atomic%)	
	deposited grain	closely packed fine particle deposit
O	40.8	49.5
Al	0.0	26.6
Zn	59.2	17.8
S	0.0	6.1

Zn-Al₂O₃ composite by the N₂ bubbling bath. Furthermore, the closely packed fine particle deposits consisted of zinc, aluminum, oxygen, and sulfur in the Zn-Al₂O₃ composite by the air bubbling and the N₂ bubbling baths. The oxygen concentration in the closely packed fine particle deposits in the Zn-Al₂O₃ composite by the air bubbling bath was also higher than that in the Zn-Al₂O₃ composite by the N₂ bubbling bath. In contrast, the zinc concentration in the closely packed fine particle deposits in the Zn-Al₂O₃ composite by the air bubbling bath was lower than that in the Zn-Al₂O₃ composite by the N₂ bubbling bath. On the other hand, the aluminum content in the closely packed fine particle deposit in the Zn-Al₂O₃ composite by the air bubbling bath was almost the same as that in the Zn-Al₂O₃ composite by the N₂ bubbling bath. The aluminum content in the closely packed fine particle deposits was more than 26.6 atomic%. This value corresponds to more than 20.9 mass% according to Al/(Al+Zn) defined by Oue et al., furthermore was larger than approximately 11 mass% reported by Oue.¹⁶ These results indicate that the deposited grain was mainly composed of nano-level zinc oxides and zinc metal, whereas the closely packed fine particle deposit was mainly composed of nano-level aluminum oxides and zinc oxides. In addition, higher oxygen concentration in the Zn-Al₂O₃ composite by the air bubbling bath suggests that the composition of the Zn-Al₂O₃ composite is influenced by oxygen in the air bubbling for both the deposited grains and the closely packed fine particle deposits. The origin of sulfur was not clear at the present status.

Figure 4. (Color online) SAED image and EDS spectra of the Zn-Al₂O₃ composite by the N₂ bubbling bath at the electrodeposition current density of 500 A/m². (a) SAED image, (b) EDS spectrum from the closely packed fine particle area, and (c) EDS spectrum from the deposited grain area shown in the micrograph in (a).

Table 2. Composition of the two types of deposits in the Zn-Al₂O₃ composites by the N₂ bubbling.

Element	Concentration (atomic%)	
	deposited grain	closely packed fine particle deposit
O	15.7	20.6
Al	1.7	29.2
Zn	82.6	45.7
S	0.0	4.5

Figure 5. SAED patterns of (a) the deposited grain and (b) the closely packed fine particle deposit in the Zn-Al₂O₃ composite electrodeposited from the bath at the electrodeposition current density of 500 A/m². The analysis area is shown in the lower right corner. The SAED images and distance between spots can be seen in the inset.

As shown in Figs. 5(a) and (b), the SAED measurement results indicate that the deposited grains was composed of ZnO and zinc, moreover the closely packed fine particle deposit was made of θ -Al₂O₃. The growth of θ -Al₂O₃ can be interpreted as follows: at the initial stage, aluminum ions are converted to Al(OH)₃ near the cathode electrode by increasing the pH. It is then converted to θ -Al₂O₃ by dehydration.

Figure 6. (Color online) Zn 3p and Al 2p XPS spectrum from the Zn-Al₂O₃ composite electrodeposited from the air bubbling bath at current densities of 50, 100, 200 and 500 A/m².

Figure 6 shows XPS spectrum from the Zn-Al₂O₃ composites by the air bubbling bath at the electrodeposition current density of 50–500 A/m². Peaks from ZnO and metallic zinc are recognized on the Zn-Al₂O₃ composites electrodeposited at the current density of 50 A/m², although no aluminum related peaks are observed. This indicates that zinc is possible to be partially hydroxylated by the increase of pH. The hydrogen generation is suppressed at low electrodeposition current density, leading to reduce the increase of pH. Consequently, the production of Al(OH)₃ and Al₂O₃ is suppressed. The increase in current density over 100 A/m² provided Al₂O₃ growth. The increase in current density promotes the hydrogen generation near the cathodes. The hydrogen generation produces Al(OH)₃, then the dehydration of Al(OH)₃. As a result, the increase in current density at 100 and 200 A/m² provides Al₂O₃. Furthermore, the rate of ZnO and Al₂O₃ in the Zn-Al₂O₃ composite decreased with increasing the electrodeposition current density. The standard electrode potential of Al/Al³⁺ is −1.66 V, and is less noble than that of Zn/Zn²⁺, −0.763 V. Thus, Zn²⁺ rather than Al³⁺ is easier to be reduced in the electrodeposition bath. Therefore, Al³⁺ is hard to be deposited compared to Zn²⁺. However, the increase of pH near cathodes by the increase of electrodeposition current density induce the deposition of Al₂O₃ via Al(OH)₃.

4. Conclusions

Zn-Al₂O₃ composites were electrodeposited from the non-suspended solution containing quaternary ammonium salt additives without using any particles with the air bubbling or the N₂ bubbling. The dense dendrite layer with a thickness of approximately 1 μm

was formed at the initial stage of the Zn-Al₂O₃ composite growth. Furthermore, the TEM and SAED analyses indicated that the Zn-Al₂O₃ composites consisted of nano-level size deposited grains and closely packed fine particle deposits. The deposited grains were comprised of ZnO and zinc metal. In contrast, the closely packed fine particles with a diameter of approximately 5 nm included θ-Al₂O₃ with high aluminum content of more than 26 atomic%. In particular, the oxygen concentration in the deposited grains and the closely packed fine particle deposits in Zn-Al₂O₃ composites by the air bubbling bath was higher than that in Zn-Al₂O₃ composites by the N₂ bubbling bath. These findings indicate that the concentration of zinc oxides and aluminum oxides in Zn-Al₂O₃ composites by the air bubbling bath is higher than that of zinc oxides and aluminum oxides in Zn-Al₂O₃ composites by the N₂ bubbling bath. In contrast, the concentration of metallic zinc and aluminum in Zn-Al₂O₃ composites by the air bubbling bath is lower than that of metallic zinc and aluminum in Zn-Al₂O₃ composites by the N₂ bubbling bath. Also, the composition in the Zn-Al₂O₃ composites is influenced by the electrodeposition current density as well as the kind of bubbling gas. The rate of oxygen compounds such as ZnO and Al₂O₃ decreases, in contrast, the rate of metallic zinc and aluminum increases with increasing the electron current density.

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