Formation of Corrosion-Resistant Films on Al–Zn–Mg Alloy by Steam Coating Using Acidic $\text{Zn}(\text{NO}_3)_2$ Aqueous Solutions*

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Corrosion-resistant films were fabricated on Al–Zn–Mg alloy by steam coating using an acidic aqueous solution of $\text{Zn}(\text{NO}_3)_2$ at different concentrations. X-ray diffraction patterns and Fourier transform-infrared spectrometer spectra demonstrated that nitrate-type Zn–Al layered double hydroxide (LDH) and ZnO films were formed on the Al–Zn–Mg surface by steam coating at temperatures of 373, 433, and 473 K, using $\text{Zn}(\text{NO}_3)_2$ aqueous solution at 1000 mM. At 513 K, $\gamma\text{-AlO}(\text{OH})$ films were formed on the Al–Zn–Mg surface by steam coating using 1 to 100 mM $\text{Zn}(\text{NO}_3)_2$ aqueous solution. The corrosion resistance of the films was investigated by potentiodynamic polarization curve measurements, which revealed that the $\gamma\text{-AlO}(\text{OH})$ films prepared by steam coating at 513 K using 1 mM of $\text{Zn}(\text{NO}_3)_2$ aqueous solution was the most effective treatment for suppression of pitting corrosion and anodic current density. [doi:10.2320/matertrans.L-M2018819]

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1. Introduction

Due to issues such as rising fuel consumption and the need to curb CO_2 emissions, car manufacturers in recent years have turned their attention more and more to the development of fuel cells and batteries as a source of energy rather than gasoline.¹⁾ This requires large-capacity batteries to drive the motor, which increase a car's weight by 15–20%.²⁾ To compensate for this increase in weight, there are calls for new materials that can lighten car bodies.³⁾ Al–Mg–Si alloys are lightweight materials whose high strength makes them a promising candidate for use in car bodies. In fact, they are already used in some vehicle components. However, in order to expand the use of aluminum alloys, some believe it will be necessary to find alloys stronger than Al–Mg–Si alloys. Al–Zn–Mg alloys have excellent strength of 600–650 MPa,⁴⁾ which is greater than that of high-strength Al–Mg–Si alloys. Thus, they are expected to be used widely, not just in cars but in airplanes as well. However, the presence of Cu and other additive elements needed to increase the strength of an alloy decrease their corrosion resistance,⁵⁾ making it necessary to find ways to improve this corrosion resistance.

Typical methods used for surface preparation of Al alloys include chemical conversion and anodic oxidation.^{6–10)} Anodic oxidation is a process in which voltage is applied to an aluminum anode in a dilute sulfuric acid or oxalic acid solution to produce an oxide film composed mainly of Al_2O_3 . As this reaction follows Faraday's principle, producing a thick film requires a great deal of electrical power. In addition, it has a heavy environmental footprint due to the use of dilute sulfuric acid and other harmful chemicals. Therefore, it is desirable to develop new surface preparation techniques for increasing the corrosion resistance of Al–Zn–Mg alloys.¹¹⁾

Steam coating is a process that causes metallic hydroxides and oxides to form on the surface of an alloy through the reaction of steam with the metal inside an airtight reaction vessel. Since it does not use harmful chemicals or, like

anodic oxidation, require a large amount of power, the environmental impact of steam coating is low.^{11,12)} This process can be used to make magnesium alloys highly corrosion-resistant, as it causes a thin film composed of a Mg–Al-based layered double hydroxide (LDH) and magnesium hydroxide to form on the surface.^{11,13,14)}

LDHs (chemical formula: $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2][\text{A}^{n-}_{x/n} \cdot m\text{H}_2\text{O}]$) possess a layered structure of alternately laminated base layers composed of divalent and trivalent cations and intermediate layers composed of water molecules and anions.¹⁵⁾ The base layers themselves are positively charged, as some of their divalent metal hydroxides are double hydroxides that are replaced by trivalent cations. This attracts anions between the layers to compensate for their positive charge, thus creating a layered structure. LDHs are also non-stoichiometric compounds, and the x symbol in their chemical formula represents the compensation value for this positive charge, varying from 0.2 to 0.33. LDHs can exchange the anions present between their layers, such as F^- , Cl^- , Br^- , CO_3^{2-} , NO_3^- , and SO_4^{2-} , with different anions, through a phenomenon called *intercalation*. Intercalation occurs more easily as the charge density or valence increases; anions with high charge densities or valences are thus easily exchanged and captured between layers.¹⁶⁾ As such, it is possible to increase the corrosion resistance of an aluminum alloy, causing a film that contains LDHs to form on it and using intercalation in the LDHs.^{12,14)} For example, Zhang *et al.* coated an Al alloy with a fine LDH film and demonstrated that it was possible to form highly corrosion-resistant film with a corrosion current density on the order of 10^{-9} A/cm^2 .¹⁷⁾ This means that it should be possible to cause a thin film composed of LDHs and aluminum hydroxide to form on an Al–Zn–Mg alloy containing divalent and trivalent cations, just as it would on a Mg alloy, by applying a steam coating process to the alloy. As the formation of LDH in the film can enable chloride ions to be captured between LDH layers, which promote corrosion, this is expected to delay the corrosion reaction.¹²⁾

The objectives of this study were to apply a steam coating process to an Al–Zn–Mg alloy under various conditions,

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using a $\text{Zn}(\text{NO}_3)_2$ solution as the steam source, and to evaluate the corrosion resistance of the films thereby produced to devise a highly corrosion-resistant film. Specifically, $\text{Zn}(\text{NO}_3)_2$ solution was used as a steam source in the steam coating process in order to promote the formation of LDHs in the films produced. Then, the relationships between the processing conditions and various characteristics of the films were examined, including their corrosion resistance.

2. Experimental Methods

An Al–Zn–Mg alloy (hereafter referred to as A7075) was used for the substrates. Its chemical composition is shown in Table 1. The specimens were made by cutting the alloy into $20 \times 20 \times 3$ mm pieces, whose surfaces were polished with #2000 waterproof sandpaper. They were then ultrasonically cleaned at 42 kHz for 5 min in ethanol (99.5% purity) to remove any substances adhering to their surfaces, after which they were dried by a stream of nitrogen gas (99.5% purity). The dried substrates were then VUV/ozone-cleaned and hydrophilized by exposing them to vacuum ultraviolet light ($\lambda = 172$ nm) for 10 min. Ultrapure water (resistivity of $18.2 \text{ M}\Omega \cdot \text{cm}$) was used as a steam source. A water film was formed on the surface of the substrates by dripping $100 \mu\text{L}$ of $\text{Zn}(\text{NO}_3)_2$ aqueous solution at concentrations of 1–1000 mM on them. The pH of this solution was adjusted to 1 with HNO_3 . 20 mL of ultrapure water was poured into an autoclave. The substrates with water film were placed into a specimen holder wrapped with Teflon tape, placed in the autoclave, and vacuum-sealed. The airtight autoclave was placed in an electric furnace, where it was heated and held at various prescribed temperatures (from 393 K to 513 K) for 6 h to produce films. After the films were produced, the specimens were ultrasonically cleaned in ethanol for 5 min and dried with nitrogen gas.

The crystalline phase of the obtained films was identified from XRD patterns measured by the $2\theta/\theta$ method with a $\text{CuK}\alpha$ X-ray diffraction device (XRD: Rigaku SmartLab, 40 kV, 30 mA). An FE-SEM EDS (JEOL JSM-IT300HR, 30 kV) was used to observe and perform chemical analyses of surfaces and cross-sections. The cross sections were prepared by using a Cross-Section Polisher (CP: JEOL IB-09010CP) operating under a 6 kV accelerating voltage for 6 h. The chemical bonding state of the films was examined by FT-IR (Shimadzu IRPrestige-21) to analyze their attenuated total reflection (ATR) spectra. Polarization measurement was used to evaluate their corrosion resistance. The A7075 substrates, coated with films produced by steam-coating, were used as the working electrodes; Pt mesh as the counter electrode; and Ag/AgCl electrode as the reference electrode. The corrosion potential of the specimens was measured by submerging them for 30 min in 5 mass% NaCl aqueous solution that had been deaerated with nitrogen gas for 20 min. After that,

polarization curves were obtained using a potential sweep velocity of 0.5 mV/s and a potential sweep range from -100 mV to $+800 \text{ mV}$ vs. corrosion potential. Hereafter, all potentials were described against Ag/AgCl.

3. Results and Discussion

3.1 Effect of different processing temperatures

3.1.1 Crystalline structure of the films

Figure 1 shows the XRD patterns for the films produced using a 1000 mM dropping solution at different processing temperatures. In the XRD patterns of the specimens produced at 393 K and 433 K, XRD lines are observed at $2\theta = 9.9^\circ$, 19.9° , 34.3° , and 60.1° ; these peaks match the XRD lines assigned to 003, 006, 012, and 110 reflections of nitric acid-type Zn–Al-based LDHs (chemical formula: $[\text{Zn}_2\text{Al}(\text{OH})_6] \cdot [\text{NO}_3 \cdot 1.9\text{H}_2\text{O}]$), respectively. At 473 K and 513 K, XRD lines are observed at $2\theta = 19.6^\circ$, 20.7° , and 41.3° ; these peaks are ascribed to MgZn_2 reflections 100, 002, 101, and 201, respectively. At 473 K, XRD lines are observed at $2\theta = 31.8^\circ$, 34.4° , 36.3° , 47.6° , and 62.9° ; these peaks are ascribed to 100, 002, 101, 102, and 103 reflections of ZnO, respectively. These results demonstrate that at processing temperatures of 473 K and higher, ZnO and precipitated MgZn_2 are created without forming LDHs, but at processing temperatures of 433 K and lower the formation of LDHs is possible.

3.1.2 Surface structure of the films

Figure 2 shows SEM images of the surface of the films produced at various processing temperatures. The formation of an LDH-derived platy structure is observed on the surface of the films produced at 393 K and 433 K,¹⁸⁾ in which it can be seen that many gaps exist, as the arrows in Fig. 2 indicate. Meanwhile, no LDH-derived platy structure is observed in the films produced at 473 K and 513 K. This is consistent with the results of the XRD. Moreover, while it has been

Fig. 1 XRD patterns of the films prepared on A7075 substrates by steam coating using $100 \mu\text{L}$ of $\text{Zn}(\text{NO}_3)_2$ aqueous solutions at the concentration of 1000 mM for 6 h at the temperatures of (a) 393 K, (b) 433 K, (c) 473 K, and (d) 513 K.

Table 1 Chemical composition of Al–Zn–Mg alloys used in this study.

(mass %)								
Zn	Mg	Cu	Cr	Fe	Si	Mn	Ti	Al
5.7	2.5	1.7	0.2	0.19	0.07	0.03	0.02	Bal.

Fig. 2 SEM images of the films prepared on A7075 substrates by steam coating using 100 μl of $\text{Zn}(\text{NO}_3)_2$ aqueous solutions at the concentration of 1000 mM for 6 h at the temperatures of (a) 393 K, (b) 433 K, (c) 473 K, and (d) 513 K.

Table 2 Chemical composition of the films prepared on A7075 substrates by steam coating using 100 μl of $\text{Zn}(\text{NO}_3)_2$ aqueous solutions at the concentration of 1000 mM for 6 h at different temperatures.

(at.%)					
Sample	C	N	O	Al	Zn
393 K	0.42	1.76	49.50	24.98	23.34
433 K	0.30	7.01	55.29	8.97	28.43
473 K	0.37	6.41	61.52	17.00	14.70
513 K	0.39	6.50	62.76	16.50	13.86

reported that pores do exist on the surface of the anodic oxide film formed on most aluminum alloys,¹⁹⁾ pores were not confirmed to exist on the surface of the films produced at 473 K and 513 K, which were thin films covered with tiny particles. These results show that the application of steam coating at temperatures of 473 K and higher caused a thin film to form on the surface of the specimens. The results of the SEM-EDS chemical analysis of the films are shown in Table 2. It can be seen that the composition ratio of Zn in the surface of the films produced at 393 K and 433 K, in which LDHs were formed, is higher than in those produced at 473 K and 513 K. This is considered to be because Zn–Al-based LDHs are formed as films, resulting in films with increased Zn content.

3.1.3 Thickness and cross-sectional structure of the films

Figure 3 shows cross-sectional SEM images of the films produced at various processing temperatures, as well as EDS mapping images for Al and O in these films. The thickness of the films was calculated from the EDS mapping images for O. The films produced at processing temperatures of 393 K, 433 K, 473 K, and 513 K have approximate thicknesses of 2.6 μm , 3.6 μm , 1.6 μm , and 1.5 μm , respectively. At above 433 K, the thickness decreases as the processing temperature increases. While the thickness increases from 393 K to 433 K due to vertical growth of LDHs on the surfaces of the substrates, at the processing temperatures of 473 K and 513 K there appears to be no LDH growth and instead films composed of tiny particles are formed. Aluminum is also concentrated on the surface layer of the films at 393 K and 433 K, which suggests that a larger amount of LDHs is formed on the surface layer of those films.

3.1.4 Chemical bonding state of the films

Figure 4 shows the FT-IR spectra of the specimens produced at various processing temperatures. In the FT-IR spectra of the films produced at 393 K and 433 K, in which LDHs were present, absorption peaks ascribed to NO_3^- are observed near 820 cm^{-1} , 1350 cm^{-1} , and 1410 cm^{-1} , and absorption peaks ascribed to OH^- are observed near 3695 cm^{-1} and 1620 cm^{-1} .^{20,21)} This shows that the films contain NO_3^- and OH^- , with nitrate ions and water molecules located between LDH layers. The reason that NO_3^- exists between LDH layers in the films is that $\text{Zn}(\text{NO}_3)_2$ was used in the solution dripped on the substrate surface in the application of the steam coating process. As the anions in the LDHs can be exchanged based on charge density, it is theorized that LDHs with nitrate ions between the layers can attract chloride ions, which causes pitting corrosion. In addition, the absorption peaks observed near 420 cm^{-1} and 600 cm^{-1} are ascribed to Al–O lattice vibration and to the symmetric stretching vibration of octahedral AlO_6 , respectively.²²⁾ Furthermore, the absorption peak observed near 550 cm^{-1} is ascribed to the lattice vibration of Zn or Al and OH.²³⁾ These findings further demonstrate the formation of Zn–Al-based LDHs and agree with the XRD patterns. In contrast, absorption peaks due to NO_3^- and OH^- are not present in the films produced at processing temperatures of 473 K and 513 K because LDHs are not present in these films.

3.1.5 Corrosion resistance of the films

To test the corrosion resistance of the film-coated A7075 specimens, polarization measurements were taken in

Fig. 3 Cross-sectional SEM images of the films prepared on A7075 substrates by steam coating using 100 μl of $\text{Zn}(\text{NO}_3)_2$ aqueous solutions at the concentration of 1000 mM for 6 h at the temperatures of (a) 393 K, (b) 433 K, (c) 473 K, and (d) 513 K.

Fig. 4 FT-IR spectra of the films prepared on A7075 substrates by steam coating using 100 μ l of Zn(NO₃)₂ aqueous solutions at the concentration of 1000 mM for 6 h at the temperatures of (a) 393 K, (b) 433 K, (c) 473 K, and (d) 513 K.

Fig. 5 Polarization curves of (a) bare A7075 and (b–e) film coated A7075 substrates in 5 mass% NaCl aqueous solution. The films were prepared by steam coating for 6 h at the temperatures of (b) 393 K, (c) 433 K, (d) 473 K, and (e) 513 K.

5 mass% NaCl aqueous solution. Figure 5 shows the polarization curves obtained from the A7075 specimens coated with film at various processing temperatures and from unprocessed A7075. The corrosion potential, E_{corr} , of unprocessed A7075 is -0.71 V. When the potential was swept beyond E_{corr} in the anodic direction, the current density increases sharply at around -0.62 V, then started to level off near -0.4 V, approaching a constant value. Dissolution of the surface of the substrate and the formation of a protective coating could be the main reasons, respectively. The increase in current density reduced when the potential was increased, likely because aluminum actively dissolves and approaches its diffusion limit for dissolution.

Pitting corrosion occurs on aluminum alloys starting from weak points in a passive film.²⁴⁾ The dissolution reaction of Al on the surface of the substrates occurs as in eq. (1) below, where AlCl₃, an aluminum salt, is eluted and concentrated.²⁵⁾

The hydrolysis of this AlCl₃ can lead to the growth of pitting corrosion with a decreasing pH value.²⁵⁾

Furthermore, a cathodic reaction like the one in eq. (4) occurs at the counter electrode, resulting in the production of OH[−].²⁵⁾

In order to improve corrosion resistance, it is necessary to prevent the occurrence of pitting corrosion. Since chloride ions are responsible for pitting corrosion, reducing the concentration of chloride ions in the vicinity of electrodes can be an effective way to increase corrosion resistance.

Since the films produced at 393 K and 433 K contain LDHs, it may be possible to decrease the concentration of

Cl[−] in the vicinity of the electrodes. The polarization curves of A7075 coated with these films (Figs. 5(b) and 5(c)) show that their corrosion potential became nobler compared to the unprocessed specimen. However, as the potential was swept away from the corrosion potential in the anodic direction, the current density increased sharply near the corrosion potential, suggesting that the dissolution of aluminum progressed rapidly. This could be due to that films containing LDHs have many gaps, and the dissolution of aluminum occurred from these gaps in the films. Photographs taken of the specimens after polarization testing (Figs. 6(a) and 6(b)) suggest that pitting corrosion occurred on them as well, as the formation of holes may result from pitting corrosion can be seen. The polarization curves of A7075 coated with film, produced at 473 K and 513 K (Figs. 5(d) and 5(e)), show that while their corrosion potential is only slightly less noble than the unprocessed specimens, their cathodic and anodic current densities are both suppressed; this effect is particularly pronounced in the film produced at 513 K. As the potential was swept away from the corrosion potential in the anodic direction, its current density increased sharply when the potential was near -0.65 V. This sharp increase in current density can be caused by pitting corrosion, as evidenced by the formation of holes visible in Figs. 6(c) and 6(d). As the potential is swept past -0.4 V in the anodic direction, their current densities start to increase less, approaching a constant value lower than that of the unprocessed specimen. We attribute this to a decrease in the speed of the active dissolution of aluminum caused by the coating of film. Based on these results, the film produced at 513 K appears to exhibit the best corrosion resistance.

3.2 Effect of Zn(NO₃)₂ concentration

As mentioned in section 3.1, the specimen produced at 513 K was found to have the best corrosion resistance. For this reason, the processing temperature was kept constant at

Fig. 6 Photographs of sample surfaces prepared by steam coating for 6 h at the temperatures of (a) 393 K, (b) 433 K, (c) 473 K, and (d) 513 K after polarization curve measurements.

Fig. 7 XRD patterns of the films prepared on A7075 substrates by steam coating for 6 h at the temperature of 513 K using 100 µl of $\text{Zn}(\text{NO}_3)_2$ aqueous solutions at the concentrations of (a) 1 mM, (b) 10 mM, (c) 100 mM, (d) 1000 mM.

513 K for the next set of experiments, where the supplied concentration of $\text{Zn}(\text{NO}_3)_2$ aqueous solution was varied.

3.2.1 Crystalline structure of the films

Figure 7 shows XRD patterns of the films produced at a processing temperature of 513 K using $\text{Zn}(\text{NO}_3)_2$ aqueous solution at various concentrations. XRD lines are observed in the XRD patterns of every specimen at $2\theta = 19.6, 20.7, 22.2$, and 41.3° ; these peaks match the XRD lines ascribed to MgZn_2 reflections 100, 002, 101, and 201, respectively. At concentrations of 1 mM, 10 mM and 100 mM, XRD lines are observed at $2\theta = 14.5^\circ, 28.2^\circ$, and 48.9° , respectively; these peaks are ascribed to 020, 120, and 051 reflections of $\gamma\text{-AlO}(\text{OH})$. In addition, the strength of the peak derived from 020 reflection of $\gamma\text{-AlO}(\text{OH})$ decreases at a higher concentration of $\text{Zn}(\text{NO}_3)_2$, and at 1000 mM, this peak is not observed at all. Also, the presence of LDH-derived peaks is not observed at 513 K, regardless of the $\text{Zn}(\text{NO}_3)_2$ concentrations. This demonstrates that LDHs cannot form at 513 K and also that the amount of $\gamma\text{-AlO}(\text{OH})$ produced increases as the concentration of $\text{Zn}(\text{NO}_3)_2$ supplied to the surface decreases.

3.2.2 Surface structure of the films

Figure 8 shows SEM images of the surface of the films

Fig. 8 SEM images of the films prepared on A7075 substrates by steam coating for 6 h at the temperature of 513 K using 100 µl of $\text{Zn}(\text{NO}_3)_2$ aqueous solutions at the concentrations of (a) 1 mM, (b) 10 mM, (c) 100 mM, (d) 1000 mM.

Table 3 Chemical composition of the films prepared on A7075 substrates by steam coating for 6 h at the temperature of 513 K using 100 µl of $\text{Zn}(\text{NO}_3)_2$ aqueous solutions at different concentrations.

(at.%)					
Sample	C	N	O	Al	Zn
1 mM	0.17	0.03	61.47	38.19	0.14
10 mM	-	0.12	58.85	40.78	0.26
100 mM	0.31	6.30	63.15	18.94	11.30
1000 mM	0.39	6.50	62.76	16.50	13.86

produced at the processing temperature of 513 K using $\text{Zn}(\text{NO}_3)_2$ aqueous solution at various concentrations. Tiny particles formed on the surface of all of the films, which were thinly formed. In the films produced using $\text{Zn}(\text{NO}_3)_2$ concentrations of 1 mM, 10 mM, and 100 mM, the presence of rectangular euhedral crystals was confirmed, which are thought to be rhombic $\gamma\text{-AlO}(\text{OH})$ based on XRD identification.²⁶⁾ When using a concentration of 1000 mM $\text{Zn}(\text{NO}_3)_2$, the presence of euhedral crystals was not confirmed, and only tiny amorphous particles were observed. XRD identification showed that in this specimen, there was a peak derived from precipitated MgZn_2 ; however, as a precipitate, this MgZn_2 can be present in the alloy rather than in the film, which may be why these tiny particles are amorphous. Table 3 shows the results of FE-SEM-EDS

Fig. 9 Cross-sectional SEM images of the films prepared on A7075 substrates by steam coating for 6 h at the temperature of 513 K using 100 μl of $\text{Zn}(\text{NO}_3)_2$ aqueous solutions at the concentrations of (a) 1 mM, (b) 10 mM, (c) 100 mM, (d) 1000 mM.

chemical analysis. The Zn content increases with increasing concentration of $\text{Zn}(\text{NO}_3)_2$. The Zn content particularly increased at the concentrations of 100 and 1000 mM, thought to be due to the formation of large amounts of MgZn_2 .

3.2.3 Thickness and cross-sectional structure of the films

Figure 9 shows cross-sectional SEM images of the films produced at a processing temperature of 513 K using $\text{Zn}(\text{NO}_3)_2$ aqueous solution at various concentrations, as well as EDS mapping images for Al and O in those films. The films produced using $\text{Zn}(\text{NO}_3)_2$ concentrations of 1 mM, 10 mM, 100 mM, and 1000 mM have approximate thicknesses of 13.1 μm , 11.0 μm , 4.1 μm , and 1.5 μm respectively, with the thickness decreasing as the concentration of $\text{Zn}(\text{NO}_3)_2$ increased. The films produced using $\text{Zn}(\text{NO}_3)_2$ concentrations of 1 mM, 10 mM, 100 mM contain $\gamma\text{-AlO}(\text{OH})$ and, based on the observation that $\gamma\text{-AlO}(\text{OH})$ content increases with a lower concentration of $\text{Zn}(\text{NO}_3)_2$, the formation of $\gamma\text{-AlO}(\text{OH})$ may be responsible for the increase in thickness. The film produced using 1000 mM $\text{Zn}(\text{NO}_3)_2$ was thin, presumably because $\gamma\text{-AlO}(\text{OH})$ and LDH crystals were not produced. In addition, in the case of the films produced using 100 mM and 1000 mM $\text{Zn}(\text{NO}_3)_2$, the MgZn_2 -derived peak strength in their XRD patterns and their Zn content as calculated with FE-SEM-EDS are considered to be high because they had a thickness of less than 5 μm .

3.2.4 Corrosion resistance of the films

Figure 10 shows polarization curves obtained from A7075 specimens coated with film produced at a processing temperature of 513 K using $\text{Zn}(\text{NO}_3)_2$ aqueous solution at various concentrations, and from unprocessed A7075. Comparing polarization curves for film-coated A7075 and unprocessed A7075 shows that, regardless of the concentration of $\text{Zn}(\text{NO}_3)_2$ aqueous solution, the E_{corr} value of the former became far less noble due to the film coating. This change in E_{corr} may be due to a change in the ratio of formed film to A7075 alloy present in the brine interface. In the polarization curve of the 1 mM film, which contains the largest amount of $\gamma\text{-AlO}(\text{OH})$ (Fig. 10(b)), the anodic current density is suppressed the most, with no pitting corrosion occurring over the sweep range. This can be due to that the film was thinly formed. Meanwhile, in the case of the specimens produced at 10 mM and 100 mM concentrations, as the potential is swept away from the corrosion potential in the anodic direction, the current density increases sharply directly past the corrosion potential, suggesting that the

Fig. 10 Polarization curves of (a) bare A7075 and (b–e) film coated A7075 substrates in 5 mass% NaCl aqueous solution. The films were prepared by steam coating for 6 h at 513 K using 100 μl of $\text{Zn}(\text{NO}_3)_2$ aqueous solutions at the concentrations of (b) 1 mM, (c) 10 mM, (d) 100 mM, and (e) 1000 mM.

dissolution reaction of aluminum progresses rapidly. In the 1000 mM specimen, as the potential is swept away from the corrosion potential in the anodic direction, a passive region exists between the corrosion potential and -0.58 V, with current density increasing sharply near -0.58 V. This sharp increase in current density can be caused by active dissolution of aluminum. These results show that pitting corrosion and the active dissolution of aluminum are suppressed the most in the film produced using $\text{Zn}(\text{NO}_3)_2$ aqueous solution at 1 mM concentration, which contained the highest amount of $\gamma\text{-AlO}(\text{OH})$.

4. Summary

Dripping $\text{Zn}(\text{NO}_3)_2$ aqueous solution at a concentration of 1000 mM on an Al–Zn–Mg alloy and then applying the steam coating process at temperatures of 393 K and 433 K LDH resulted in the formation of LDH films. However, the LDH films had low corrosion resistance due to their low denseness. Dripping $\text{Zn}(\text{NO}_3)_2$ aqueous solution at the same

concentration when the steam coating process was applied at a processing temperature of 473 K caused ZnO film to form, and when the process was applied at 513 K an amorphous substance was formed. On the polarization curves of A7075 coated with film produced at 473 K and 513 K, the corrosion potential was slightly less noble than that of unprocessed specimens, but their cathodic and anodic current densities were suppressed. Meanwhile, applying the steam coating process with $\text{Zn}(\text{NO}_3)_2$ aqueous solution at concentrations of 1 to 100 mM caused the formation of $\gamma\text{-AlO}(\text{OH})$ film. In the polarization curve of the 1 mM film, the anodic current density was suppressed the most, with no pitting corrosion occurring over the sweep range. In contrast, in the specimens processed at 10 and 100 mM concentrations, as the potential was swept away from the corrosion potential in the anodic direction, current density increased sharply directly past the corrosion potential, and the dissolution reaction of aluminum progressed rapidly. Among the films produced in this study, it was demonstrated that pitting corrosion and the active dissolution of aluminum were suppressed the most in the film produced using $\text{Zn}(\text{NO}_3)_2$ aqueous solution at a concentration of 1 mM, and this film contained the highest amount of $\gamma\text{-AlO}(\text{OH})$.

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