Corrosion resistance of Mg(OH)₂/Mg–Al layered double hydroxide composite film formed directly on combustion-resistant magnesium alloy AMCa602 by steam coating

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Abstract

Films of the $\text{Mg}(\text{OH})_2/\text{Mg-Al}$ layered double hydroxide composite were formed on the combustion-resistant magnesium alloy AMCa602 by steam coating and characterized by X-ray diffraction, Fourier-transform infrared spectroscopy, and scanning electron microscopy. The corrosion-resistance performances of the films in a 5 wt% NaCl solution were investigated using electrochemical measurements. The corrosion current density of the sample that was steam-coated at 433 K for 6 h using the aqueous solution containing 200 mM $\text{Al}(\text{NO}_3)_3$ decreased significantly more than that of the bare AMCa602. The correlations between the Mg–Al LDH content in the films, $\text{Al}(\text{NO}_3)_3$ concentration in the aqueous solutions, and corrosion current densities were investigated.

Keywords: Combustion-resistant magnesium alloy, corrosion, Mg–Al layered double hydroxide, magnesium hydroxide, composite film, steam coating

1. Introduction

A reduction in material weight in the fields of transportation, such as lighter automobiles, ships, and trains, is one of the most important approaches to mitigate global warming induced by CO₂ emission. Magnesium alloys are the lightest among practical alloys, and they have superior physical and mechanical properties such as high stiffness, high weight ratios, good castability, good vibration and shock absorption, and high damping capacity [1-5]. Thus, magnesium alloys are expected to be used in transportation components and parts. However, magnesium alloys have two significant disadvantages—their combustible nature and low corrosion resistance—which have restricted their usage to the transportation industries. To combat their flammability, combustion-resistant magnesium alloys were developed by adding calcium [6-8]. The addition induces the oxidation reaction of Ca, resulting in the formation of calcium oxide on the magnesium alloy before Mg ignites [9], which leads to an increase in the ignition temperature from 200 to 300 K. Through the development of the combustion-resistant subgroup, the combustible nature of magnesium alloys has been considerably constrained.

On the other hand, the corrosion resistance of the combustion-resistant magnesium alloys is still low. It is thus essential to develop a surface-treatment technology that is suitable for these alloys to improve their ability to withstand corrosion. Although various surface-treatment methods such as application of an anodized film, a chemical-conversion film, and a polymer film on magnesium alloys have been developed [10-19], there are few reports on the surface treatment of combustion-resistant magnesium alloys. Xia et al. reported that the corrosion resistance of the Mg–4.0Zn–0.2Ca alloy was improved by a micro-arc oxidation treatment from an

alkaline aqueous solution containing NaOH, Na₄SiO₄, and NaF to form a coating that was mainly composed of MgO and MgF₂ [20]. However, the F atoms in this coating carried the risk of environmental pollution. In addition, the liquid waste produced by the anodic oxidation required treatment before disposal. Therefore, an environmentally friendly surface treatment to improve the low corrosion resistance of the combustion-resistant magnesium alloys is highly desirable.

Recently, some chemical-conversion methods have used the Mg–Al layered double hydroxide (LDH) as a protective film to significantly improve the corrosion resistance of magnesium alloys [21–29]. The LDHs have layered structures composed of positively and negatively charged substances and a general molecular formula of $[M_{1-x}^{2+}M'_x{}^{3+}(\text{OH})_2]^{x+}[A_{x/n}{}^{n-}] \cdot m\text{H}_2\text{O}$ [30], where M^{2+} and M'^{3+} represent divalent and trivalent cations, respectively, of two different metals, A^{n-} is an anion such as CO_3^{2-} , SO_4^{2-} , or OH^- , and x has a value between 0.2 and 0.33 [30]. The LDHs have anion exchange capability between chloride ions and the corrosion inhibitor, which allows them to work as self-healing protective coatings [31–33]. In addition, the LDH coating could be an effective agent for delaying the corrosion reaction because they can trap corrosion-relevant anions such as chloride ions in their interlayer [34,35]. Lin et al. demonstrated that the carbonate-based Mg–Al LDH had Cl^- anion-exchangeability in a corrosive environment, allowing the layer to protect the Mg alloy against corrosion [34]. Tedim et al. showed that Zn–Al LDH intercalated with nitrate anions could trap Cl^- in a corrosive environment in the interlayer of the LDH, and the addition of the LDH to a polymer layer drastically reduced the permeability of corrosive chloride anions through the protective coatings. Thus, LDHs are promising materials for improving corrosion resistance [35].

We have developed an environmentally friendly method of surface treatment, referred to as steam coating, for the magnesium alloy AZ31 [36,37]. A steam-coated film was formed directly on AZ31, which was then used as the Mg and Al sources of the film composed of $\text{Mg}(\text{OH})_2$ and Mg–Al LDH, and it showed good corrosion resistance in 5 wt% NaCl solution at temperature of 273–308 K. This method of direct growth of the film on a substrate can considerably improve the adherence and mechanical stability of the resulting film over films formed by other methods such as spin-coating and dip-coating [38]. An effective means to further improve the corrosion resistance of the film composed of $\text{Mg}(\text{OH})_2$ and Mg–Al LDH is to increase the Mg–Al LDH content in the film because the Mg–Al LDH can trap corrosion-relevant anions, thus delaying the corrosion reaction. Therefore, it is necessary to develop a technology to control the Mg–Al LDH content in the film.

In this paper, we report a method to prepare a film composed of the $\text{Mg}(\text{OH})_2$ and Mg–Al LDH on a combustion-resistant alloy, AMCa602, and a method of controlling the Mg–Al LDH content in the film by steam coating. In addition, the correlation between the Mg–Al LDH content in the film and the corrosion resistance was also investigated.

2. Experimental procedures

Specimens of the magnesium alloy AMCa602 (composition: 5.92 wt% Al, 0.36 wt% Mn, 1.99 wt% Ca, <0.01 wt% Si, <0.01 wt% Cu, <0.005 wt% Ni, <0.005 wt% Fe, balance Mg), with a size of $20 \times 20 \times 1.5$ mm, were used as substrates. The AMCa602 alloy was supplied by Fuji Light Metal Co., Ltd. The substrates were ultrasonically cleaned in absolute ethanol for 10 min. After the cleaning, the substrates were dried

with inert Ar gas. The cleaned AMCa602 substrates were placed on a substrate stage in a Teflon-lined autoclave with a 100-mL capacity, and 20 mL of ultrapure water containing 0, 2, 20, or 200 mM $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added to the bottom of the autoclave to produce steam. The distance between the water surface and the substrate stage was around 3 cm. The autoclave was heated to a temperature of 433 K and held at this temperature for 6 h; it was then cooled naturally to room temperature. After the steam treatment, the samples were ultrasonically cleaned in ethanol for 10 min and dried with Ar gas.

The surface morphologies and cross sections of the prepared films were observed using scanning electron microscopy (SEM; JSM-6010LA, JEOL) at 10–15 keV. The film thickness was estimated from the cross-sectional SEM images. The cross-sections of the films were prepared using a cross-section polisher (IB-09010CP, JEOL). The composition of the prepared films was determined using energy-dispersive X-ray (SEM-EDX) analysis. The crystal phase of the obtained film was examined using glancing-angle X-ray diffraction (GAXRD; Ultima IV, Rigaku) at a glancing angle of 2° with Cu K_α radiation (40 kV, 40 mA), within the range of $2\theta = 5\text{--}80^\circ$ and at a scanning rate of 4° min^{-1} . Information on chemical bonding of the samples was obtained by Fourier-transform infrared (FT-IR) spectroscopy (IR Prestige-21, Shimadzu Co.) with KBr pellets. The spectra were recorded within the range of $400\text{--}4000 \text{ cm}^{-1}$, with 20 scans at a resolution of 4 cm^{-1} .

The corrosion resistance was estimated by electrochemical measurements and immersion tests in a 5.0 wt% NaCl aqueous solution. All electrochemical measurements were performed in the NaCl solution at room temperature using a computer-controlled potentiostat (VersaSTAT3, Princeton Applied Research) with a resolution of 6 pA for

current-density measurements. The film-coated AMCa602 and a platinum mesh were used as the working and counter electrodes, respectively. The area of the working electrode exposed to the electrolytic solution as cathode surface was 1.0 cm². A commercial Ag/AgCl/sat.-KCl electrode was used as the reference electrode for all experiments. Each sample was immersed in the NaCl solution for 30 min, allowing the system to be stabilized, and potentiodynamic polarization curves were measured with respect to the open circuit potential (OCP) from -100 to +800 mV at a scanning rate of 0.5 mV s⁻¹. For samples prepared from different concentrations of the Al(NO₃)₃ solution, each polarization curve was measured three times. The values of the corrosion potential, E_{corr} , and corrosion current density, j_{corr} , were determined from the experimental potentiodynamic curves using the program CorrView (CorrView International) to obtain the fitting parameters. Immersion tests in the 5.0 wt% NaCl solution were also performed at 308 K for 72 h to estimate the corrosion resistance of the film-coated AMCa602. The NaCl solution was refreshed every time the samples were extracted from the solution; this procedure was repeated until the predetermined immersion time was reached.

3. Results and Discussion

Figure 1 shows GAXRD patterns of the films formed on AMCa602 at 433 K over a 6-h period from aqueous solutions containing (a) 0, (b) 2, (c) 20, and (d) 200 mM Al(NO₃)₃·9H₂O in 20 mL of ultrapure water. A weak peak attributable to the Mg-alloy substrate is visible at approximately $2\theta = 34^\circ$ in all the patterns. A diffraction peak corresponding to the (101) reflection at approximately $2\theta = 38^\circ$, which has the highest intensity according to JCPDS No. 44-1482, appears slightly weaker with an increase in

the $\text{Al}(\text{NO}_3)_3$ concentration. In addition, several peaks at approximately $2\theta = 18, 33, 51, 58, 62, 68,$ and 72° , assigned to the (001), (100), (102), (110), (111), (200), and (201) diffraction peaks of brucite-type $\text{Mg}(\text{OH})_2$, are also clearly observable in all of the GAXRD patterns, indicating the formation of hexagonal $\text{Mg}(\text{OH})_2$. In addition to these peaks, one or two peaks attributable to the hydrotalcite (HT)-like structure, which are assigned to $\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2(\text{NO}_3)_x \cdot n\text{H}_2\text{O}$ intercalated with nitrate anions, can be distinguished [39]. The diffraction peaks are indexed according to the $3R$ symmetry. The two peaks at around $2\theta = 11^\circ$ and 22° are assigned to the (003) and (006) reflections, respectively, of $\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2(\text{NO}_3)_x \cdot n\text{H}_2\text{O}$ [40-42]. This means that the treated surfaces were crystallized with a preferential hexagonal orientation along the (003) plane, which is a characteristic feature of the spontaneous texture axis of $\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2(\text{NO}_3)_x \cdot n\text{H}_2\text{O}$. These XRD patterns indicate that all the films were composed of crystalline $\text{Mg}(\text{OH})_2$ and Mg–Al LDH, independent of the $\text{Al}(\text{NO}_3)_3$ concentration in the aqueous solutions.

Figure 2(a–c) show the appearances of the samples after steam coating at 433 K for 6 h using aqueous solutions containing $\text{Al}(\text{NO}_3)_3$ at concentrations of (a) 2, (b) 20, and (c) 200 mM. All the substrates were uniformly covered with films, independent of the $\text{Al}(\text{NO}_3)_3$ concentration, although the film colors changed depending on the $\text{Al}(\text{NO}_3)_3$ concentration. Figure 2(d–f) show SEM images of the samples after steam coating at 433 K for 6 h using aqueous solutions with $\text{Al}(\text{NO}_3)_3$ concentrations of (d) 2, (e) 20, and (f) 200 mM. For the sample prepared with the aqueous solution containing 2 mM $\text{Al}(\text{NO}_3)_3$, a relatively smooth surface was formed on AMCa602 even though some minute pores measuring several hundred nanometers in diameter could be observed on this surface. The surface of the sample prepared from the aqueous solution containing

20 mM $\text{Al}(\text{NO}_3)_3$ was rough and exhibited a small number of nanosheets that were slightly inclined with respect to the surface. As shown in Figure 3, elemental mapping by EDX revealed that traces of elemental Mg, Al, and O could be detected primarily where the nanosheets existed, indicating the presence of Mg–Al LDH. In addition, aggregated particles are clearly discernible in the images, and the nanosheets were formed on the aggregated particles. Most of these particles could have formed during steam treatment and condensed on the substrate. The sample prepared from the aqueous solution containing 200 mM $\text{Al}(\text{NO}_3)_3$ was smooth and dense compared to that from the aqueous solution containing 20 mM $\text{Al}(\text{NO}_3)_3$. Formation of the small nanosheets that were slightly inclined with respect to the surface was observed, and no traces of cracks could be found on the film.

Figure 4 shows the FT-IR spectra of the samples after steam coating at 433 K for 6 h using aqueous solutions containing $\text{Al}(\text{NO}_3)_3$ at concentrations of (a) 2, (b) 20, and (c) 200 mM. The most dominant spectral feature is the intense sharp peak observed at 3696.9 cm^{-1} . It has been reported that pure $\text{Mg}(\text{OH})_2$ exhibits a single band at 3698 cm^{-1} owing to the high basicity of its O–H groups [43]. The peak at 3696.9 cm^{-1} is well defined in the spectra for all the samples, which is in good agreement with the XRD patterns. The shoulder band at 781 cm^{-1} could be ascribed to the Al–OH translational mode [44]. Some bands at approximately $1370\text{--}1520\text{ cm}^{-1}$ are attributed to the symmetric and asymmetric stretching modes of CO_3^{2-} in the interlayer [44,45]. Another peak at approximately 1385 cm^{-1} is attributed to the ν_3 vibrational mode of NO_3^- with D_{3h} symmetry in the interlayer [46]. These peaks and bands are present in the spectra of all the samples that had peaks attributable to Mg–Al LDH in the XRD patterns. Another band at approximately $1630\text{--}1650\text{ cm}^{-1}$ is assigned to the bending mode of water

molecules in the interlayer. A shoulder band at 3080 cm^{-1} shows the presence of water molecules, which allowed hydrogen bonding between water and CO_3^{2-} in the interlayer [45]. These results indicate that all the films were composed of crystalline $\text{Mg}(\text{OH})_2$, carbonate-based Mg–Al LDH ($\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2(\text{CO}_3)_{x/2} \cdot n\text{H}_2\text{O}$), and nitrate-based Mg–Al LDH ($\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2(\text{NO}_3)_x \cdot n\text{H}_2\text{O}$).

Figure 5(a) shows the cross-sectional SEM image of the film prepared at 433 K for 6 h from the aqueous solution containing 200 mM $\text{Al}(\text{NO}_3)_3$. Elemental mapping images of the film for Mg, Al, and O are also exhibited in Fig. 5(b), (c), and (d), respectively. The film had a thickness of about $197\text{ }\mu\text{m}$, as shown in Fig. 5(a). The thicknesses of the films prepared at 433 K for 6 h from the aqueous solution containing 0, 2, and 20 mM $\text{Al}(\text{NO}_3)_3$ were estimated to be about 53, 308, and $193\text{ }\mu\text{m}$, respectively, from the cross-sectional SEM images. The films formed from the aqueous solution containing $\text{Al}(\text{NO}_3)_3$ were much thicker than that formed from ultrapure water, which implies that the presence of $\text{Al}(\text{NO}_3)_3$ in the closed reaction vessel promoted film growth. The elemental mapping images in Fig. 5(b–d) reveal that the film included mostly Mg and O, indicating that the film comprised primarily $\text{Mg}(\text{OH})_2$. This result agrees well with the XRD patterns and FT-IR spectra obtained for the samples. A small trace of Al was also observed, providing evidence that Mg–Al LDH existed locally in the film. From the results of XRD, FT-IR, and SEM-EDX, it is concluded that steam coating enabled the formation of $\text{Mg}(\text{OH})_2$ and Mg–Al LDH on AMCa602 as well as AZ31.

Based on these results, a formation mechanism of the film could be proposed. First, the aqueous solution containing $\text{Al}(\text{NO}_3)_3$ was heated in the electric oven. Steam that contained Al^{3+} and NO_3^- ions was generated, and the closed reaction vessel was saturated with the steam. When the steam made contact with the magnesium alloy

AMCa602, Mg metal could be easily dissolved into Mg^{2+} ions owing to the high temperature and pressure. It was likely that the $\text{Mg}(\text{OH})_2$ crystallites grew via a dissolution–precipitation mechanism, resulting in the formation of $\text{Mg}(\text{OH})_2$ on AMCa602. Nordlien et al. hypothesized that amorphous platelets of $\text{Mg}(\text{OH})_2$ are initially formed by the precipitation of Mg^{2+} or other soluble magnesium species [47]. In addition, the Mg^{2+} , Al^{3+} , and NO_3^- ions might have reacted with the steam, resulting in the formation of the nitrate-based Mg–Al LDH. Moreover, the carbonate ions could have been generated from CO_2 in the enclosed autoclave atmosphere before the steam treatment. By using the carbonate ions, carbonate-based Mg–Al LDH could have been formed. Thus, in this process, $\text{Mg}(\text{OH})_2$, nitrate- and carbonate-based Mg–Al LDHs could have been formed on AMCa602. If these reactions occurred at the AMCa602 surface, they could have progressed at the interface between AMCa602 and the formed film because the steam could have continued to penetrate the formed film owing to the difference in pressure and its high kinetic energy. Thus, a film composed of $\text{Mg}(\text{OH})_2$ and Mg–Al LDH could have been formed directly on AMCa602. When the film was not dense at the beginning, the steam could have easily passed through the film, thus leading to the formation of a thick film. In contrast, it would have been difficult for the steam to easily penetrate a dense film. Thus, the differences in the film thickness is considered to have accrued depending on the preparation conditions.

The corrosion resistance of the film formed on the magnesium alloy AMCa602 was estimated by potentiodynamic polarization curve measurements. Figure 6 shows the potentiodynamic polarization curves of samples that were prepared at 433 K for 6 h from the aqueous solutions containing 0, 2, 20, and 200 mM $\text{Al}(\text{NO}_3)_3$. As a control, the potentiodynamic polarization curve of untreated AMCa602 is also shown in Fig. 6. The

corrosion potentials (E_{corr}) and corrosion current densities (j_{corr}) for the untreated AMCa602 and the samples prepared at various conditions are listed in Table 1. The Tafel slopes (b_a : anodic; b_c : cathodic) obtained from the polarization curve for each sample are also shown in Table 1. The E_{corr} and j_{corr} values for the untreated AMCa602 were estimated to be -1.524 V vs. Ag/AgCl/sat.-KCl and 4.214×10^{-5} A cm $^{-2}$, respectively. In the cathodic branch for the untreated AMCa602, hydrogen evolution dominated at potentials that were more negative than E_{corr} (i.e., negative potentials with magnitudes above 1.524 V), resulting in an increase in the cathodic current densities. The anodic branch of the curve for the untreated AMCa602 can be divided into two regions: (i) The first region starting from E_{corr} (low anodic overpotential, -1.524 V) showed abrupt linear increase of the logarithm of the current density with the shift toward positive voltage in the potential. In this region, the dominant dissolution reaction of Mg to Mg $^{+}$ or Mg $^{2+}$ ions could have occurred [48]. (ii) As the potential moved toward more positive values than -1.4 V vs. Ag/AgCl/sat.-KCl (i.e., negative potentials with magnitudes below 1.4 V and positive potentials), a current plateau was observed, where the electrode surface was covered with a film identified as Mg(OH) $_2$ [49]. It has been reported that the anodic branch of the polarization curves for AZ31 could be divided into three regions [49]. This indicates that the overpotential for the dissolution reaction of Mg to Mg $^{+}$ or Mg $^{2+}$ ions for AMCa602 was lower than that of AZ31. The facilitation of the dissolution reaction might have resulted from the addition of Ca to magnesium alloy because Ca is more reactive than Mg.

Figure 7 shows potentiodynamic polarization curves for all measurements of the untreated AMCa602 and the samples that were prepared at 433 K for 6 h from the aqueous solutions containing 0, 2, 20, and 200 mM Al(NO $_3$) $_3$. The current densities in

the anodic and cathodic branches for all the film-coated samples were suppressed compared to the untreated AMCa602, as shown in Fig. 6, and reproducibly low, as shown in Fig. 7, indicating that all films led to the improvement of the corrosion resistance of AMCa602. Independent of the $\text{Al}(\text{NO}_3)_3$ concentrations in the aqueous solutions, E_{corr} shifted toward positive values. At potentials that were more positive than E_{corr} , long passive regions could be clearly observed on the curve for the samples prepared from the aqueous solutions containing 0 and 200 mM $\text{Al}(\text{NO}_3)_3$, as shown in Fig. 6. The presence of a long, perfect passive region implies that the film effectively protected AMCa602 in a solution containing Cl^- ions. The j_{corr} values decreased with an increase in the $\text{Al}(\text{NO}_3)_3$ concentration, independent of the film thickness. In general, the thickness and density of the film are important factors for improving the corrosion resistance because they can inhibit the contact of a metal surface with the corrosive solution. In this case, the film prepared from the aqueous solution containing 2 mM $\text{Al}(\text{NO}_3)_3$ was the thickest among all of the samples. Thus, it can be expected that the film had the best corrosion resistance. However, j_{corr} of this film had the highest value because it was not dense, as explained earlier in the discussion on the formation mechanism. Although the thicknesses of the films prepared from the aqueous solutions containing 20 and 200 mM $\text{Al}(\text{NO}_3)_3$ were comparable, the j_{corr} values were significantly different, which indicates that the density of the films could be considerably different.

An increase in current densities at approximately 0.3 and 0 V vs. $\text{Ag}/\text{AgCl}/\text{sat.}-\text{KCl}$ was observed on the polarization curves for the samples prepared from the aqueous solutions containing 2 and 20 mM $\text{Al}(\text{NO}_3)_3$, respectively. These increases in the current densities might be an indication that the corrosive solution permeated the cracks or

pores in the film and initiated pitting corrosion as a result. Similar behavior has been reported even in aluminum alloys [50]; however, the increase in the current densities was suppressed and the current densities showed passive-like behavior with a shift in the potential towards positive values. This behavior suggests that the film might show self-healing functionality. It has been reported that the Zn–Al LDH film formed on an Al substrate showed the self-healing property, although the passive current density values after immersion in a corrosive electrolyte increased and recovered to the value before immersion in the corrosive electrolyte [51].

In contrast, no evidence of pitting corrosion could be observed on the curve of the sample prepared from the aqueous solution containing 200 mM $\text{Al}(\text{NO}_3)_3$. The E_{corr} and j_{corr} values of this sample were estimated to be -1.007 V vs. Ag/AgCl/sat.-KCl and 9.560×10^{-11} A cm^{-2} , respectively, as shown in Table 1. The j_{corr} values that were closely related to the corrosion reaction were found to be the lowest current densities in all of the samples, indicating that the sample prepared from the 200 mM $\text{Al}(\text{NO}_3)_3$ solution had the best corrosion-resistance performance.

The correlations between Mg–Al LDH content in the films, $\text{Al}(\text{NO}_3)_3$ concentration in the aqueous solutions, and corrosion current densities are shown in Fig. 8. The Mg–Al LDH content in the films was roughly estimated from the ratio of the XRD intensity of the (003) plane of Mg–Al LDH, $I_{\text{LDH-003}}$, to the XRD intensity of the (101) plane of $\text{Mg}(\text{OH})_2$, $I_{\text{Mg}(\text{OH})_2\text{-101}}$. The peak intensities for these planes correspond to the strongest intensities shown in the standard powder diffraction data for $\text{Mg}(\text{OH})_2$ and Mg–Al LDH. The LDH content in the films is roughly defined as the peak intensity ratio, $I_{\text{LDH content}} = I_{\text{LDH-003}} / I_{\text{Mg}(\text{OH})_2\text{-101}}$. As the $\text{Al}(\text{NO}_3)_3$ concentration in the aqueous solutions increased, the $I_{\text{LDH content}}$ value increased, whereas the corrosion current density

value decreased, suggesting that the Mg–Al LDH content in the films could be strongly related to the corrosion current density. It has been reported that the carbonate-based Mg–Al LDH has anion-exchangeability, where Cl^- ions are absorbed from NaCl solution and CO_3^{2-} ions are exhausted [30]. In addition, the nitrate-based Mg–Al LDH can introduce Cl^- by exhausting NO_3^- and thus have anion-exchangeability that is higher than that of the carbonate-based Mg–Al LDH. Therefore, it can be considered that the Mg–Al LDH content in the films could considerably affect the corrosion current density that is strongly related to corrosion reaction rate.

Finally, the durability for the corrosion-resistance performance of the sample prepared from the aqueous solutions containing 200 mM $\text{Al}(\text{NO}_3)_3$ was investigated by immersing it in a 5 wt% NaCl aqueous solution. Figure 9 shows images of the sample surfaces (a) before and after immersion in 5 wt% NaCl aqueous solution for (b) 5, (c) 12, (d) 24, (e) 48, and (f) 72 h. The beige color of the film surfaces appeared to change slightly with the immersion. However, no corrosion product and no physical change in the appearance of the film were observed after the sample was immersed in the 5 wt% NaCl aqueous solution for up to 12 h. In contrast, the appearance changed after 24 h of immersion and some spotty contrasts were evident. These contrasts emerged because the film could have been damaged by the corrosive solution. An increase in the immersion time from 48 to 72 h was found to lead to the slight dissolution at the corners of the sample and the AMCa602 substrate owing to corrosion. Once the corrosion reaction started on the sample through a pit or minute pore, the corrosive medium could come into contact with AMCa602. Thus, the dissolution of the substrate at the corner was an indication of the progression of the corrosion reaction. Furthermore, as corrosion resistance is known to be closely related to the film thickness, it is possible that the film

thickness of the sample at the corner was thinner than that of other parts of the sample. This non-uniformity in the film thickness at the corners might have occurred because of differences in crystal growth at the edge of the substrate. Figure 10 shows SEM images of the sample surfaces (a) before and after immersion in the 5 wt% NaCl aqueous solution for (b) 24 h and (c) 72 h. With an increase in the immersion time, the surface morphology changed and nanosheets that were slightly inclined with respect to the surface were more likely to be noticed on the surface. Figure 10(d) and (e) show EDX spectra at the spots labeled (i) and (ii), respectively, in Fig. 10(c). The EDX spectrum in Fig. 10(d) revealed that at spot (i), two peaks attributable to Cl and Al were detected while the Na peak was undetectable, which support the earlier report that the Mg–Al LDH layer remained in the film and exhausted CO_3^{2-} and NO_3^- in exchange for Cl^- anions. On the other hand, Cl was not detectable at spot (ii), although Al was detected, indicating that the Mg–Al LDH layer remained. These results indicate that the nitrate or carbonate anions in the Mg–Al LDH layer were partially replaced with Cl^- anions.

Figure 11(a) shows the XRD patterns of the film-coated AMCa602 before and after immersion in the 5 wt% NaCl aqueous solution for 24 to 72 h. The peak attributable to the (101) plane of the $\text{Mg}(\text{OH})_2$ crystallite decreased slightly in intensity with an increase in the immersion time, whereas that attributable to the (003) plane of the Mg–Al LDH crystallite increased in intensity with an increase in the immersion time. This indicates that even though the $\text{Mg}(\text{OH})_2$ film was slightly dissolved in the corrosive solution, the Mg–Al LDH crystallite remained intact. Figure 11(b) shows potentiodynamic polarization curves of the film-coated AMCa602 before and after the immersion in the 5 wt% NaCl aqueous solution for 24 and 72 h. The E_{corr} and j_{corr} values of the film-coated AMCa602 were -0.348 V vs. Ag/AgCl/sat.-KCl and 1.821×10^{-9} A

cm^{-2} , respectively, after the 24 h immersion and -0.065 V vs. Ag/AgCl/sat.-KCl and $1.326 \times 10^{-9} \text{ A cm}^{-2}$, respectively, after the 72 h immersion. E_{corr} of the film-coated AMCa602 shifted toward positive values with an increase in the immersion time, possibly owing to the change in the ratio of the number of anodic and cathodic sites on the surface, which could be induced by the dissolution of Mg(OH)_2 in the film. The j_{corr} value of the film-coated AMCa602 after immersion in the NaCl aqueous solution increased compared to that before the immersion, indicating an increase in the corrosion rate. This result agrees well with the results of the immersion tests. In contrast, the j_{corr} values of the film-coated AMCa602 after it was immersed in the NaCl aqueous solution for 24 and 72 h were almost comparable, independent of the increase in immersion time.

From the results of the XRD patterns, SEM observation, EDX spectra, and polarization curve measurements, the corrosion resistance mechanism of the film can be described as follows. At first, Mg(OH)_2 from the $\text{Mg(OH)}_2/\text{Mg-Al}$ LDH composite film that was formed earlier on AMCa602 could be dissolved to some extent through contact with the corrosive solution. With the dissolution of Mg(OH)_2 , the amount of the Mg-Al LDH with anion-exchangeability present on the film surface gradually increased, resulting in an increase in the intensity of the (003) reflection of Mg-Al LDH, as shown in Fig. 11(a). Owing to the presence of Mg-Al LDH on the film surface, Cl^- ions could be trapped in the Mg-Al LDH, as shown in the EDS analysis, leading to a film that could substantially delay corrosion. These results support the hypothesis that the Mg-Al content in the $\text{Mg(OH)}_2/\text{Mg-Al}$ LDH composite film would be an important factor for improving the corrosion resistance and durability of the film. In addition, the film was thick and had high density owing to the presence of the two phases, Mg(OH)_2 and Mg-Al LDH, with different sizes. All these factors could contribute to the improvement

of the corrosion resistance.

4. Conclusions

In conclusion, a film composed of $\text{Mg}(\text{OH})_2$ and Mg–Al LDH was formed on the combustion-resistant magnesium alloy AMCa602 by environmentally friendly steam coating. XRD and FT-IR studies confirmed that the film was composed of $\text{Mg}(\text{OH})_2$ and nitrate- and carbonate-based Mg–Al LDHs. The film thickness varied from approximately 52 to 308 μm depending on the $\text{Al}(\text{NO}_3)_3$ concentration. The formation mechanism of the film was proposed based on the results of XRD, FT-IR, SEM, and EDX measurements. The corrosion resistance of the films coating AMCa602 was estimated by potentiodynamic measurements and immersion tests in a 5 wt% NaCl aqueous solution. The film prepared by steam coating at 433 K for 6 h using the aqueous solution containing 200 mM $\text{Al}(\text{NO}_3)_3$ showed the highest corrosion resistance of all samples. The correlations between Mg–Al LDH content in the films, $\text{Al}(\text{NO}_3)_3$ concentration in the aqueous solutions, and corrosion current densities was investigated, and it was revealed that the Mg–Al LDH content in the films could be strongly related to the corrosion current density. The durability of the corrosion-resistant film was also investigated. As the demand for magnesium alloys continue to grow, the need for the development of a coating technology to improve the corrosion resistance increases. We believe that our steam-coating technique would be an effective method to improve the corrosion resistance of existing magnesium alloys and future generations of magnesium alloys.

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Figure captions

Figure 1. GAXRD patterns of films formed on AMCa602 at 433 K for 6 h from aqueous solutions with different $\text{Al}(\text{NO}_3)_3$ concentrations: (a) 0, (b) 2, (c) 20, and (d) 200 mM.

Figure 2. Appearances of samples after steam coating at 433 K for 6 h using aqueous solutions containing $\text{Al}(\text{NO}_3)_3$ at concentrations of (a) 2, (b) 20, and (c) 200 mM. SEM images of the samples after steam coating at 433 K for 6 h from aqueous solutions containing $\text{Al}(\text{NO}_3)_3$ at concentrations of (d) 2, (e) 20, and (f) 200 mM.

Figure 3. Elemental mapping images of the sample surface after steam coating at 433 K for 6 h using an aqueous solution containing 20 mM $\text{Al}(\text{NO}_3)_3$: (a) O, (b) Mg, (c) Al, and (d) Ca.

Figure 4. FT-IR spectra of the samples after steam coating at 433 K for 6 h using aqueous solutions containing $\text{Al}(\text{NO}_3)_3$ at concentrations of (a) 2, (b) 20, and (c) 200 mM.

Figure 5. (a) Cross-sectional SEM image of the film prepared at 433 K for 6 h from the aqueous solution containing 200 mM $\text{Al}(\text{NO}_3)_3$. Elemental mapping images of the cross sections for (b) Mg, (c) Al, and (d) O.

Figure 6. Potentiodynamic polarization curves of sample that was untreated and samples that were treated at 433 K for 6 h using the aqueous solution containing 0, 2, 20, and

200 mM $\text{Al}(\text{NO}_3)_3$. The scanning rate was 0.5 mV s^{-1} .

Figure 7. Potentiodynamic polarization curves for all measurements of the untreated AMCa602 and the samples that were prepared at 433 K for 6 h from the aqueous solutions containing 0, 2, 20, and 200 mM $\text{Al}(\text{NO}_3)_3$. Each system shows 3 repeat polarization curves (labeled 1, 2 and 3) measured under identical conditions to demonstrate reproducibility.

Figure 8. Correlations between Mg–Al LDH content in the films, $\text{Al}(\text{NO}_3)_3$ concentration in the aqueous solutions, and corrosion current densities. The standard deviation of j_{corr} data for the samples obtained from the aqueous solution containing 0, 2, 20, and 200 mM $\text{Al}(\text{NO}_3)_3$ were 9.85×10^{-10} , 7.68×10^{-7} , 2.39×10^{-9} , and $2.17 \times 10^{-10} \text{ A cm}^{-2}$, respectively.

Figure 9. (a) Surface of the sample that was steam coated at 433 K for 6 h using the aqueous solution containing 200 mM $\text{Al}(\text{NO}_3)_3$ before immersion in a 5 wt% NaCl aqueous solution. Same surface after immersion in a 5 wt% NaCl aqueous solution for (b) 5, (c) 12, (d) 24, (e) 48, and (f) 72 h. All scale bars are 1 cm.

Figure 10. SEM images of the sample surface (a) before and after immersion in the 5 wt% NaCl aqueous solution for (b) 24 h and (c) 72 h. (d, e) EDX spectra at spots (i) and (ii) in (c).

Figure 11. (a) GAXRD patterns and (b) potentiodynamic polarization curves of the

film-coated AMCa602 before and after immersion in the 5 wt% NaCl aqueous solution for 24 to 72 h.

Figure 1, Ishizaki et al.

Figure 2, Ishizaki et al.

Figure 3, Ishizaki et al.

Figure 4, Ishizaki et al.

Figure 5, Ishizaki et al.

Figure 6, Ishizaki et al.

Figure 7, Ishizaki et al.

Figure 8, Ishizaki et al.

Figure 9, Ishizaki et al.

Figure 10, Ishizaki et al.

Figure 11, Ishizaki et al.

Table 1: Fitting results of potentiodynamic polarization curves of samples immersed in 5.0 wt% NaCl solution

	E_{corr} (V vs. Ag/AgCl. Sat.)	j_{corr}^* (A/cm ²)	Tafel slope (mV/decade)
Untreated AMCa602	-1.524	$4.21 \times 10^{-5} \pm 4.82 \times 10^{-5}$	b_a : 21.2 b_c : -178.7
Film coated AMCa602 prepared from ultrapure water	-0.385	$1.85 \times 10^{-9} \pm 9.85 \times 10^{-10}$	b_a : 198.7 b_c : -66.9
Film coated AMCa602 prepared from 2 mM Al(NO ₃) ₃	-0.322	$7.86 \times 10^{-8} \pm 7.68 \times 10^{-7}$	b_a : 278.1 b_c : -164.0
Film coated AMCa602 prepared from 20 mM Al(NO ₃) ₃	-0.316	$1.16 \times 10^{-9} \pm 2.39 \times 10^{-9}$	b_a : 235.4 b_c : -56.2
Film coated AMCa602 prepared from 200 mM Al(NO ₃) ₃	-1.007	$9.56 \times 10^{-11} \pm 2.17 \times 10^{-10}$	b_a : 288.6 b_c : -198.0

*The j_{corr} values include the standard deviation of 3 separate measurements.

Table of contents

Immersion in a 5 wt% NaCl solution