

***On-demand* release of corrosion-inhibiting molecules from layered double hydroxide film formed on magnesium alloy**

T. Ishizaki*, K. Teshima** and N. Saito*

* National Institute of Advanced Industrial Science and Technology (AIST), Materials Research Institute for Sustainable Development, 463-8560 Nagoya, Japan, t.ishizaki@aist.go.jp

** Department of Environmental Science and Technology, Faculty of Engineering, Shinshu University, Nagano 380-8553, Japan, teshima@shinshu-u.ac.jp

ABSTRACT

Mg-Al layered double hydroxide (LDH) film and Mg-Al LDH film intercalated with 8-hydroxyquinoline-5-sulfonic molecules (HQS) was formed directly on magnesium alloy AZ31 by *in situ* growth method using a hydrothermal treatment. The crystal structures and d-spacing of the LDH were estimated by XRD measurement. FE-SEM studies revealed that all the samples exhibit nanosheets that are aligned at fairly inclined angles with respect to the surface. Some rosette-like structures can be observed on the HQS molecules contained LDH surface. Potentiodynamic polarization curve measurements revealed that the corrosion resistance of the HQS intercalated LDH film coated magnesium alloy was greatly improved compared with the untreated magnesium alloy and the LDH film coated magnesium alloy.

Keywords: Magnesium alloy, Anticorrosion, Self-healing, Thin film, Layered double hydroxide (LDH), inhibiting molecule

1 INTRODUCTION

Recently, the most widespread approach for corrosion protection of metallic substrate is the application of protective polymer coatings [1-3]. The main role of an anticorrosion coating is to protect the metal, acting as an effective barrier against corrosive species present in the environment. Once corrosion started, the polymer coating no longer protects the defective region and the corrosion reaction is advanced at the defect. Thus, it is necessary to impart self-healing functionalities to coatings, i.e., the ability to repair the defects in an autonomous way and provide long-term protection. In nature, a damage inflicted to an organism evokes a healing response. Such examples have inspired material designers to combine traditional engineering approaches with biological self-healing mechanism. Many academic and industrial researchers are currently exploring new strategies to obtain self-repairing materials. Triggered release performance of corrosion inhibitors as a result of exposure to a corrosive species or after corrosion initiates is an important function for this goal. Chromate systems possess the active corrosion-

inhibition property [4]. However, chromate corrosion protection is being eliminated due to its high toxicity and carcinogenicity. Thus, it is necessary to develop a new system with self-repairing function as replacements for chromate systems. However, if the inhibiting species are directly incorporated into coatings, detrimental interactions may occur between the matrix and active species, namely the loss of the inhibition performance and/or coating degradation. A promising strategy to overcome this issue is the encapsulation of inhibitors within inert host structures of nanometer scales. The nanostructured materials will store the inhibitors while the coating is able to maintain the protective property of the coating. On breakdown of the protective properties, active species are released to inhibit the corrosion processes. Layered double hydroxides (LDHs) are anion exchange systems consisting of stacks of positively charged. Thus, the LDHs are promising candidate materials for this goal because they could incorporate anion corrosion-inhibiting molecules.

Magnesium is one of the lightest engineering materials. Thus, it is expected that magnesium and its alloys are applied to aerospace, aircraft, automobile, and railway [5-8]. However, they have a defect which is extremely low corrosion resistance. It is considerably difficult to completely suppress the corrosion reaction on the magnesium and its alloy surfaces. Thus, it is necessary to develop anticorrosion film with the self-repairing functionalities for magnesium and magnesium alloys. In this study, we tried to directly fabricate inhibitor molecule intercalated layered double hydroxide film on magnesium alloy and report the corrosion resistant performances of the LDH film coated Mg alloy.

2 EXPERIMENTAL PROCEDURE

All chemicals were of reagent grade and used without any pretreatment. Aqueous ammonium solution containing NH_4NO_3 , NaOH and $\text{Al}(\text{NO}_3)_3$ was used for the fabrication of Mg-Al system layered double hydroxide (LDH) films. This ammonium solution was obtained by dissolving 0.1 M NH_4NO_3 and $\text{Al}(\text{NO}_3)_3$ with concentrations of 0 to 50 mM. The dissolution process was carried out at room temperature by stirring the solution mixture for a few

minutes. 8-hydroxyquinoline-5-sulfonic acid (HQS) was used as an inhibiting molecule. To intercalate the HQS molecules into the Mg-Al system LDH film, the HQS was added into the mixed solution. The solution pH was adjusted to ranging from 5.0 to 8 by adding 1 M NaOH. In some cases, 10 mM $Zn(NO_3)_2$ was also adding to the above-mentioned mixed solutions. Magnesium alloy AZ31 (composition: 2.98% Al, 0.88% Zn, 0.38% Mn, 0.0135% Si, 0.001% Cu, 0.002% Ni, 0.0027% Fe, and the rest is Mg) with a thickness of 1.5 mm was used as the substrate. The substrate had a size of 10 X 10 mm square. The substrates were ultrasonically cleaned in ethanol for 10 min. After the cleaning, the substrates were dried with inert Ar gas. The cleaned magnesium alloy substrates were introduced in a Teflon-lined autoclave with a 50 ml capacity. The autoclave was filled with the aqueous ammonium solution mixture to fill 40% of its capacity. The autoclave was maintained at temperatures of 80–150 °C for 6 h and subsequently left to cool to room temperature. After the samples were subjected to the treatments, the substrate was ultrasonically cleaned in ethanol for 10 min and dried with Ar gas.

The surface morphologies of the obtained samples were observed by FE-SEM (S-4300, Hitachi High-Technologies Corp.). The crystal structure of the samples was examined by XRD (Rigaku, RINT2200V) at a glancing angle of 1°. The XRD data were recorded on a powder diffractometer with $CuK\alpha$ radiation (40 kV, 40 mA) within the range of 3° and 90° at a scanning rate of $2\theta = 4^\circ (\text{min}^{-1})$. The XRD peaks were assigned to the appropriate phases on the basis of the JCPDS data. The XPS measurements were performed using $Mg-K\alpha$ (1253.6 eV) radiation at 12 mA and 20 kV. All binding energies in the spectra were obtained and the calibrations of the charge up were conducted against C 1s peak (284.6 eV) as a reference. The corrosion resistant performances of the LDH films were examined using electrochemical measurements. All electrochemical measurements were performed in 5.0 wt% NaCl aqueous solution, pH 6.2, at room temperature, using a computer-controlled potentiostat (Princeton Applied Research, VersaSTAT3) under open circuit conditions. The LDH film coated magnesium alloy AZ31 and a platinum plate were used as the working and counter electrodes, respectively. The working electrode was set in a homemade holder made of Teflon. The holder composed of two parts. One is screw type cap with a circular window with an area of 0.785 cm^2 and another is body. In the body, a conductive brass connected with coated copper wire was embedded. The working electrode was directly set on the brass. To protect the penetration of the electrolytic solution in the holder, O-ring with an inner diameter of 10mm was placed to overlap the position of the circular window on the working electrode. The screw type cap was then closed tightly. The window was exposed to the electrolytic solution. A saturated calomel electrode (SCE) was used as the reference electrode. The reference electrode was set in the close vicinity of the circular window. The LDH film coated magnesium alloy substrate was immersed in the NaCl

solution for 30 min, allowing the system to be stabilized, and potentiodynamic polarization curves were subsequently measured with respect to the OCP at a scanning rate of 0.5 mV/s from -400 to +800 mV.

3 RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of the LDH film coated magnesium alloys obtained from the aqueous solutions containing NH_4NO_3 , NaOH and (a) 0 mM-Al, (b) 10 mM-Al, and (c) 50 mM-Al, respectively. Two clear peaks at around $2\theta = 11^\circ$, and 22° are assigned to the [003] and [006] reflections of the Mg-Al LDH films. This means that the treated surfaces were well crystallized with a preferential hexagonal orientation along the [003] plane, which is a characteristic feature of the spontaneous texture axis of the LDH film. Their peak intensities became strong with an increase in the Al concentrations in the solutions. This indicates that many crystallites originating from Mg-Al LDH were contained in the film. Another peaks at around $2\theta = 35^\circ$ are attributed to the AZ31 substrate.

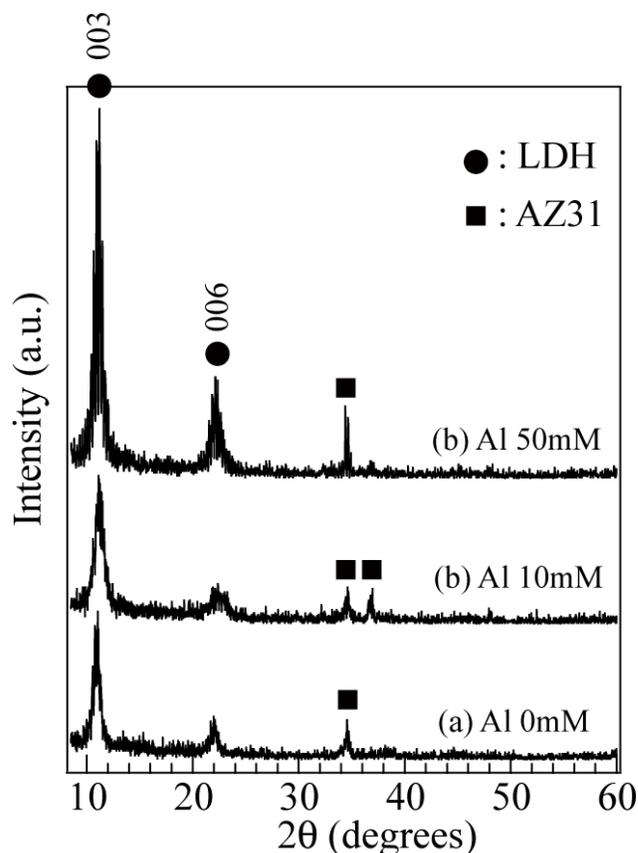


Figure 1: XRD profiles of the LDH film formed on the magnesium alloys obtained from the aqueous solutions containing NH_4NO_3 , NaOH and (a) 0 mM $Al(NO_3)_3$, (b) 10 mM $Al(NO_3)_3$, and (c) 50 mM $Al(NO_3)_3$.

Figure 2 shows XRD profiles of (a) the LDH film formed on the magnesium alloys and (b) HQS intercalated

LDH film formed on the magnesium alloys. On both profiles, two peaks attributable to the hydroxylite (HT)-like structure were clearly observed. The two peaks at around $2\theta = 11^\circ$, and 22° are assigned to the [003] and [006] reflections of the Mg-Al LDH films. The peak position of the HQS intercalated LDH film corresponds to a d-spacing of 0.82 nm, which is higher than the d-spacing of the NO_3^- anion intercalated LDH film (0.75 nm), indicating that the HQS molecules are intercalated. Another three peaks at around $2\theta = 32^\circ$, 34° , and 36° are attributed to the magnesium alloy substrate.

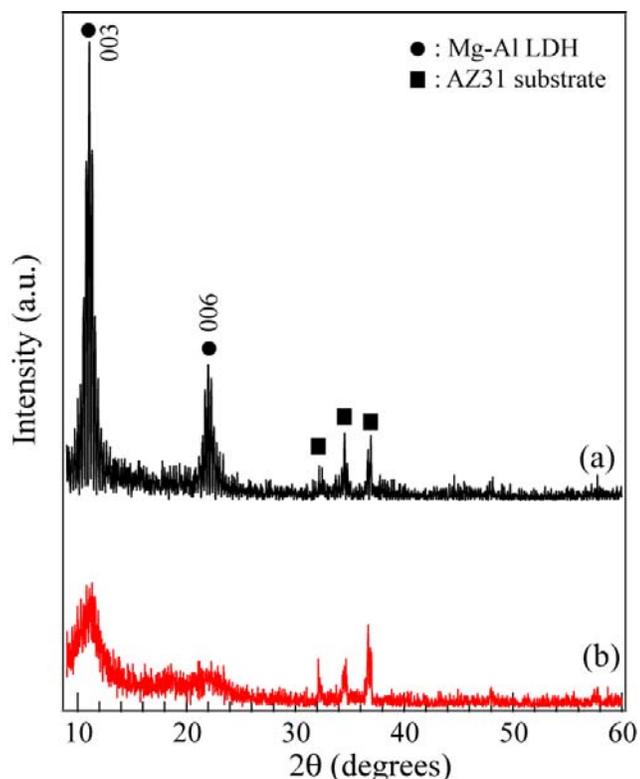


Figure 2: XRD profiles of (a) the LDH film formed on the magnesium alloys and (b) HQS intercalated LDH film formed on the magnesium alloys.

Figures 3(a), (c), and (e) shows FE-SEM images of the sample surfaces obtained from the aqueous solutions containing NH_4NO_3 , NaOH and (a) 0 mM-Al, (c) 50 mM-Al, (e) 50 mM-Al and 1 mM-HQS, respectively. The temperature and time of the hydrothermal treatment were 100°C and 6 h, respectively. As shown in the fig. 3 (a), (c) and (e), there are some cracks on all the sample surfaces. Moreover, some white contrasts attributable to charge up can be observed in the fig. 3 (e). This could be due to the presence of the nonconductive HQS molecules in the film. Figure 3 (b), (d), and (f) shows the enlarged versions of the FE-SEM images of the fig. 3 (a), (c), and (e), respectively. As shown in fig. 3 (b), (d), and (f), all the samples exhibit nanosheets that are aligned at fairly inclined angles with respect to the surface. When the Al concentration was 0 mM, the nanosheets were locally formed on the surfaces. In contrast, the nanosheets were observed to be vertically

aligned over the entire substrate surface with an increase in the Al concentrations. The vertically aligned nanosheets became dense as the Al concentrations increased. The nanosheets exhibit an edge length in the range of approximately 100–700 nm and a thickness of 20–50 nm. Moreover, several individual crystals were found to have a length of approximately 1 μm . The FE-SEM observation results were consistent with the results of the XRD profiles. On the HQS molecules contained LDH surface, some rosette-like structures can be observed as shown in fig. 3 (f). The rosette-like structures somewhat appear to be laid on a carpet of vertically aligned nanosheets. The unique morphology of the LDH intercalated with HQS molecules might be created by the cooperation of LDH and HQS molecules.

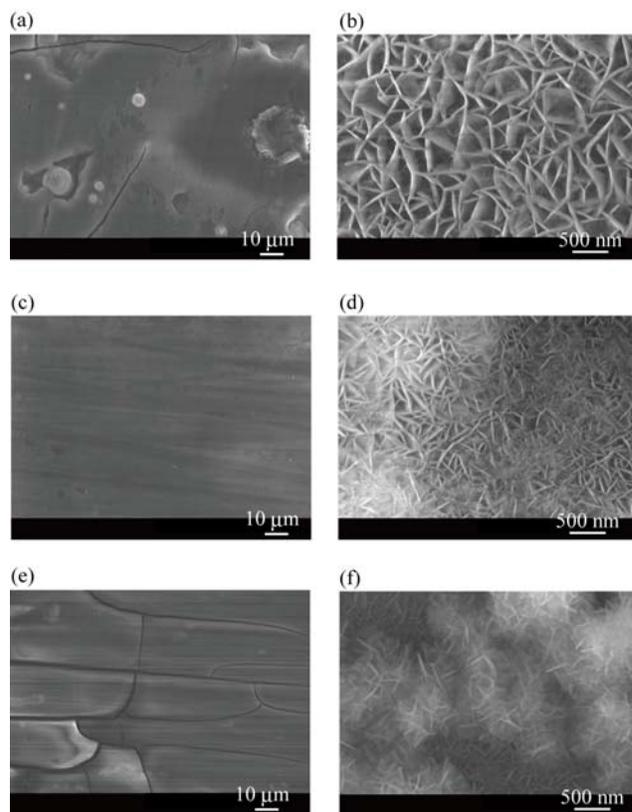


Figure 3: FE-SEM images of sample surfaces obtained from the aqueous solutions containing NH_4NO_3 , NaOH and (a) 0 mM-Al, (c) 50 mM-Al, (e) 50 mM-Al and 1 mM-HQS. (b), (d), and (f) shows the enlarged versions of the FE-SEM images of the fig. 3 (a), (c), and (e), respectively.

The corrosion resistance performance was investigated using electrochemical measurements. Figure 4 shows the potentiodynamic polarization curves of (a) untreated, (b) LDH film coated, and (c) HQS intercalated LDH film coated magnesium alloy AZ31. The treatment time and temperature of the LDH film was 6 h and 100°C , respectively. The corrosion current density (j_{corr}) of the bare magnesium alloy substrate ($1.94 \times 10^{-4} \text{ A/cm}^2$) was almost identical to those of the LDH film coated (4.42×10^{-4}

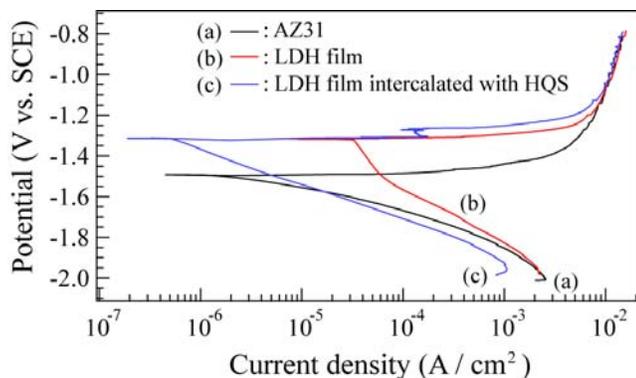


Figure 4: Potentiodynamic polarization curves of (a) the untreated, (b) LDH film coated, and (c) HQS intercalated LDH film coated magnesium alloy AZ31.

The scan rate was 0.5 mV/s.

A/cm^2) and HQS intercalated LDH film coated magnesium alloy substrate ($1.37 \times 10^{-4} \text{ A}/\text{cm}^2$). The corrosion potential (E_{corr}) of the magnesium alloy was -1502 mV . Hydrogen evolution dominates at more negative potentials than E_{corr} , resulting in an increase in the cathodic currents. On the other hand, E_{corr} of the LDH film coated and HQS intercalated LDH film coated magnesium alloy substrates are -1326 and -1324 mV , respectively, and are more positive than that of the bare magnesium alloy, indicating that the LDH film suppresses the anodic corrosive reaction. This indicates that the magnesium alloy substrate coated with the LDH film has a higher anticorrosion performance than the bare magnesium alloy. A substantial change in E_{corr} between the LDH film coated and LDH film intercalated with HQS molecules coated magnesium alloy was not detected. However, the current density behavior of anodic branch for LDH film intercalated with HQS molecules are different from that of the LDH film. Once the pitting corrosion occurred at c.a. -1320 mV for both curves, however, the increase in current density of the LDH film intercalated with HQS molecules is suppressed at a current density of c.a. $10^{-4} \text{ A}/\text{cm}^2$ and the current density values remained constant for a short time. This stagnation of the current density could be due to the presence of the protective layer that can be formed during immersion in the corrosive medium. The protective layer can be created by the *on demand* release of the HQS molecules from the LDH film. This indicates that the HQS released from the LDH film could provide an effective protection against corrosion of the magnesium alloy, and the LDH film can be considered as a potential nanocontainer to be used in protective coatings. However, an abrupt increase in the current density occur again at the potential of c.a. -1250 mV . This increase in the current density could be related to the pitting corrosion, indicating that the protective layer is broken by the attack of the corrosive medium. This degradation of the protective layer in short time is due to that the total abundance of the HQS molecules in the LDH film was low. Thus, the protective layer might be formed incompletely on the pitting region.

Potentiodynamic polarization measurement revealed that the corrosion resistance of the HQS intercalated LDH film coated magnesium alloy was improved compared with the untreated magnesium alloy and the LDH film coated magnesium alloy.

4 CONCLUSIONS

Mg-Al LDH film and Mg-Al LDH film intercalated with 8-hydroxyquinoline-5-sulfonic acid (HQS) was formed directly on magnesium alloy AZ31 by *in situ* growth method using a hydrothermal treatment. The crystal structures and d-spacing of the LDH were estimated by XRD measurement. FE-SEM observations revealed that all the samples exhibit nanosheets that are aligned at fairly inclined angles with respect to the substrate surface. Some rosette-like structures can be observed on the LDH film intercalated with the HQS molecules. Potentiodynamic polarization curve measurements revealed that the corrosion resistance of the LDH film coated and HQS intercalated LDH film coated magnesium alloy was greatly improved compared with the untreated magnesium alloy. Moreover, after pitting corrosion initiated once, the LDH film intercalated with the HQS molecules created a protective layer on the pitting region by *on demand* release of the HQS molecules from the LDH film intercalated with HQS molecules. The LDH film formed directly on the substrate is versatile structures with the potential ability to incorporate corrosion inhibiting molecules. We believe that the LDH film intercalated with corrosion inhibiting molecules would be a potential alternative materials for chromate systems with self-healing functionality.

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