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Surface Characteristic and Corrosion Phenomena of X-ray Irradiated Pure Mg†

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Abstract

Magnesium (Mg) and its alloys are highly corrodible due to their low standard electrode potential (SEP). The conventional methods to improve corrosion resistance of Mg alloys are an anodic oxide film formation processing and chemical conversion treatment. However, these processes consume high energy. Besides, Mg products treated with these methods are hard to be recycled due to their large content of impurities. In this study, a unique Mg oxide (MgO) film, formed by a radical reaction between the pure Mg surface and radical species by X-ray irradiation, was fabricated on the Mg sample surface, and its corrosion phenomenon was evaluated. Pure Mg surface was modified by X-ray irradiation under atmospheric condition. XPS analysis indicated MgO film was formed on the surface of pure Mg after X-ray irradiation. Cross-sectional observation by TEM showed the MgO film was dense compared to the naturally formed oxide films with porous structures. The thickness of its surface modification film was increased with increase in the X-ray irradiation time. After salt water immersion test, the corrosion resistance of X-ray irradiated pure Mg for 24 hours was about four times higher than that of as-polished pure Mg sample. These results suggested X-ray irradiation of the Mg surface in a humid atmosphere was remarkably effective to improve the corrosion resistance of pure Mg by formation of the dense MgO films.

KEY WORDS: (Magnesium), (Corrosion phenomenon), (X-ray irradiation), (Dense MgO film)

1. Introduction

Magnesium (Mg) and its alloys exhibit an attractive combination of low density and high specific strength making them ideal candidates for light weight engineering applications [1-3]. However, Mg possesses a poor corrosion resistance attributed to their low standard electrode potential (SEP) of -2.36 V [3], which limit their applications [4-6]. Therefore, a suitable protective surface such as anodic oxide film or chemical conversion process is necessary. However, these processes are energy intensive. Besides, Mg treated by these surface modification processes are difficult to be recycled. From a viewpoint of recyclability, an alternative corrosion protection method is required. In the previous study [7-8], an electron beam irradiation method was employed as a new anti-corrosion technology because the surface modification layer contained no hazardous substances and increased the recycling efficiency. The corrosion resistance of Mg is improved by forming an electronic excitation field to change the potential of the sample. As a method for forming an electronic excitation field, X-ray

is much easier than the electron beam in a vacuum condition. When radiation is irradiated in a humid environment with moisture, the radical species such as hydroxyl radicals (OH·) and hydrogen radicals (H·) are generated by ionization of the water molecules [9]. These radical species cause a peculiar reaction such as an additional and abstraction reaction due to their high reactivity and energy instability. Therefore, it is used in various applications such as water treatment technologies and chemical etching techniques [10-12]. Thus, it is expected to form an oxide film, having a unique physical property and structure by reaction between radical species and Mg surface, after X-ray irradiation is applied to Mg sample in the atmosphere. In this study, the specific oxide film was formed on the Mg surface by X-ray irradiation, and its characteristics were evaluated by XPS and TEM analysis. In addition, the influence of oxide film on corrosion behavior of Mg was investigated by the salt water immersion test.
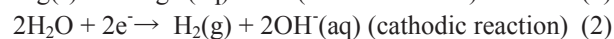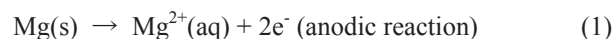
2. Experimental procedure

An electronic excitation field was formed on the pure Mg (Purity: 99.95 %) surface by the X-ray irradiation using the foreign material detecting device (Maximum ray intensity value: 10 kV). Before irradiation, the surface of each sample was polished using water-proof abrasive paper up to #4000 in tap water. Then, the mirror finish treatment was conducted by buffing process using diamond pastes. After polishing, the samples were irradiated by X-ray in different conditions, which are shown in **Table 1**. Changes in the chemical bonding state at the outermost surface of the Mg sample by X-ray irradiation were analyzed by X-ray photoelectron spectroscopy (XPS). Air-24h (X-ray irradiation in air for 24 hour), O-flow-24h (X-ray irradiation in oxygen atmosphere flow for 24 hour) and N-flow-24h (X-ray irradiation in nitrogen atmosphere flow for 24 hour) samples were used to investigate the effect of the X-ray irradiation atmosphere on the surface modification layer. In addition, pure Mg exposed in air for 24 hour (Exposed-24h) was also used as a comparative material. Mg Kα source (1.25 keV), which has sufficiently smaller energy than maximum ray intensity value of X-ray irradiation equipment, was used for XPS analysis. Furthermore, C1s peak of 284.6 eV was used for the correction of the binding energy change due to the electrically charging phenomenon [13].

The thickness of the surface modification film was also investigated by sputtering using an Ar ion gun. XPS analysis was carried out after every 60 minutes of sputtering until the O^{2-} spectrum disappeared. Film thickness was calculated by the etching time and etching rate. In order to obtain the etching rate, the film thickness of Air-24h was measured directly by TEM observation.

The traditional salt water immersion test was carried out to study the influence of the surface modification film formed by the X-ray irradiation on the corrosion behavior of Mg samples. The test conditions were shown in **Table 2**. The solution was agitated with magnetic rotator at 420 rpms and deaerated with Ar gas flow of 1 L/min during the experiment. Throughout the immersion tests, pH changes of the test solution were monitored with a pH meter. The reactions between Mg and deaerated aqueous solution are expressed in the chemical formulas as below [14];

Table 2 Salt water immersion test condition for corrosion phenomenon evaluation of Mg specimens.

Concentration	Solution temperature	Testing time	Initial pH
mass%	K	min	
3.0	303	15	7.10 ± 0.15

$$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^- \text{ (anodic reaction)} \quad (1)$$
$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \text{ (cathodic reaction)} \quad (2)$$
$$Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s) \quad (3)$$

When Mg matrix dissolves into the test solution, hydroxide ions (OH^-) are released according to the above formulas. Consequently, the more Mg dissolves into the solution, the higher solution pH value can be expected. After the corrosion test, the corrosion rate of Mg sample was calculated by the change of pH values.

3. Results and discussion

When the moisture in the atmosphere is irradiated by X-rays, reactive radical species such as OH· and H· are generated by ionization of water [15]. OH· has highest SEP (2.80 V) and a powerful oxidizing power in active oxygen [15]. Thus, OH· rapidly changes to H_2O by depriving electrons and hydrogen ions from the surroundings as shown in the following reaction equation [16];

$$OH\cdot + H^+ + e^- \rightarrow H_2O \quad (4)$$

On the other hand, H· has a lower SEP (-2.94 V) than Mg [15]. Thus, H· also rapidly changes to H_2O by depriving hydrogen ions from the surroundings as shown in the below reaction equation [16];

$$H\cdot + OH^- \rightarrow H_2O + e^- \quad (5)$$

When the radicals, such as H· and OH·, are generated on the natural oxide film of Mg, it is expected that the surface modification occurs by oxidation-reduction reaction between the radicals and Mg surface.

Table 1 X-ray irradiation conditions used for surface modification in this study.

Sample name	Tube current	Irradiation time	Gas flow rate	Humidity	Atmosphere
	mA	h	L/min	%	
Air-1mA	1.0	-	-	95 – 100	Air
Air-2mA	2.0	-	-	95 – 100	Air
Air-3mA	3.0	-	-	95 – 100	Air
Air-4mA	4.0	-	-	95 – 100	Air
Air-6h	4.0	6	-	95 – 100	Air
Air-12h	4.0	12	-	95 – 100	Air
Air-24h	4.0	24	-	95 – 100	Air
O-flow-24h	4.0	24	1.0-1.5	0	Oxygen
N-flow-24h	4.0	24	1.0-1.5	0	Nitrogen

In order to verify whether the radical reaction occurs by the X-ray irradiation, the presence of radical species in the air atmosphere during X-ray irradiation was detected using a spectrometer. Air-1mA, Air-2mA, Air-3mA and Air-4mA samples were used for analysis. **Figure 1** shows the measurement results of the spectrum by the spectrometer. The peak appeared at around 309 nm corresponds to the OH· [17] during X-ray irradiation. The relationship between the spectrum intensity of the OH· and X-ray irradiation intensity is shown in **Fig. 2**. The spectral intensity of the OH· increased linearly with increasing the tube current value. This means that the moisture in atmosphere was ionized by the X-ray irradiation. Therefore, it is predicted that the Mg surface is modified by oxidation-reduction reaction of the radical species generated by ionization of water during X-ray irradiation in air atmosphere.
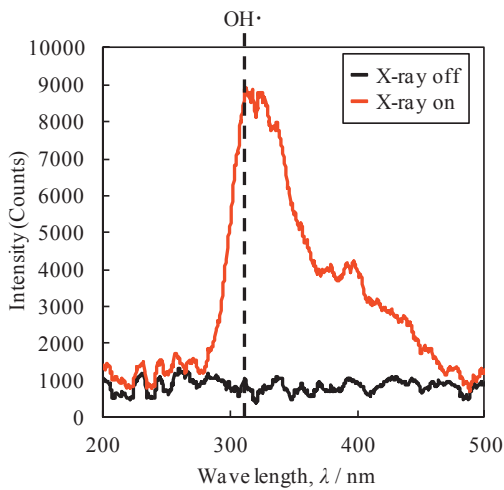

Fig. 1 Spectra of Mg surface treated with and without X-ray irradiation in a humid atmosphere.
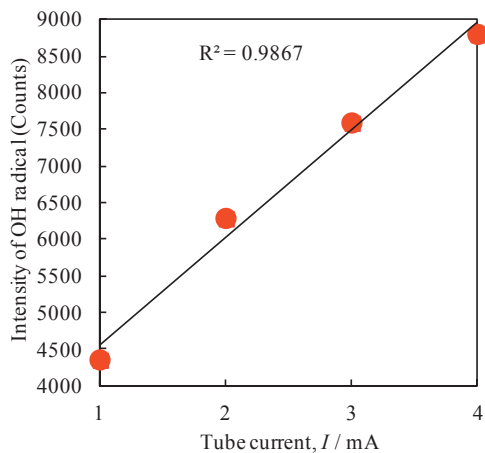

Fig. 2 Dependence of emission intensity of OH radical on X-ray irradiation intensity.

In order to investigate the effect of the radical reaction by X-ray irradiation on the surface of the Mg sample, the structure and morphology of the oxide film on the Mg of Air-24h were compared with the naturally formed oxide film by exposure in atmosphere. **Figure 3** shows the observation results by scanning electron microscopy (SEM) and energy dispersed X-ray spectrometer (EDS) for each sample. In general, the naturally formed oxide film of Mg has a porous structure as shown in Fig.3 (a) [18]. Comparatively, the X-ray irradiated sample showed a smooth organizational structure. In addition, according to the elemental analysis results by EDS, the Mg and O atomic ratio of pure Mg exposed in atmosphere material was approximately 1:2. In the Air-24h sample, the Mg and O atomic ratio was detected as 1:1. These results mean that the oxide film structure of the X-ray irradiated pure Mg is different from the naturally formed oxide film. It suggests that the sample surface was altered by the oxidation-reduction reaction between Mg and radical species during the X-ray irradiation. When this surface modification is a reaction with OH· as shown in equation (3), it is considered that the reaction occurs at the Mg surface as shown in the following equations;

$$Mg(OH)_2 + 2H\cdot \rightarrow Mg + 2H_2O \qquad (6)$$
$$Mg + 2OH\cdot \rightarrow MgO + 2H_2O \qquad (7)$$
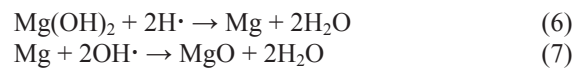
Gibbs free energies of these reactions are -110 kJ/mol and -924 kJ/mol, respectively, and thermodynamically stable [15].

By examining the binding state of the Mg and O at the outermost sample surface using XPS, the above hypothesis was validated. **Figure 4** shows the XPS O1s and Mg 2p spectra of Exposed-24h and X-ray-24h.


(a) Naturally formed oxide film

(b) X-ray irradiated Mg surface
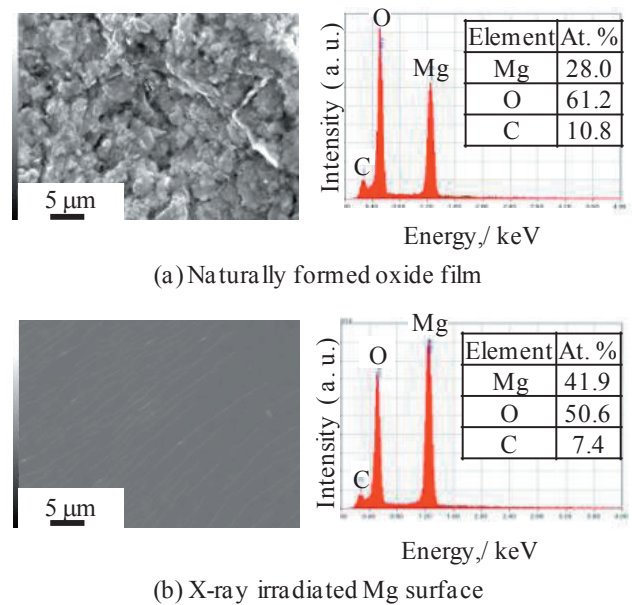
Fig. 3 SEM image and EDS analysis results of naturally formed oxide film of pure Mg (a) and X-ray irradiated pure Mg surface (b).

The spectrum corresponding to the binding energy of MgO (50.6 eV) [19] was detected only in Air-24h. On the other hand, in the other samples, the binding energy spectra corresponding to the oxide and hydroxide state (51.6 eV) [20] originated from the natural oxide films was confirmed. Furthermore, in the O1s binding energy spectrum shown in Fig. 4 (b), OH- peak [21] of the material exposed in atmosphere was eliminated, because a significant increase of the peak corresponding to the state O^{2-} [21] oxide was detected. These results indicate that Mg sample surface was modified to single phase of MgO by X-ray irradiation under the atmospheric environment with moisture. In addition, this surface modification never occurred in O-flow-24h. It means that the surface modification to from the single phase MgO needs moisture. Therefore, it is considered that the surface modification occurred due to the oxidation reaction of the radical species by ionization of water.

MgO film formed by the X-ray irradiation Air-24h was observed by TEM as shown in **Fig. 5**. In order to investigate the structural differences, naturally formed oxide film was also observed. The cross-sectional observation result of pure Mg after atmospheric exposure treatment for one month is shown in **Fig. 6**. In general, when the metal sample surface was covered by an insulating material such as a dense oxidation film, the corrosion rate of the sample decreases with increasing its film thickness [22]. For example, Aluminum and Titanium have high corrosion resistance despite of their

low standard electrode potentials (-1.66 V, and -1.63 V, respectively) [23], because of these materials form protective coating films of dense surface oxides due to their strong affinity with oxygen [24-25].
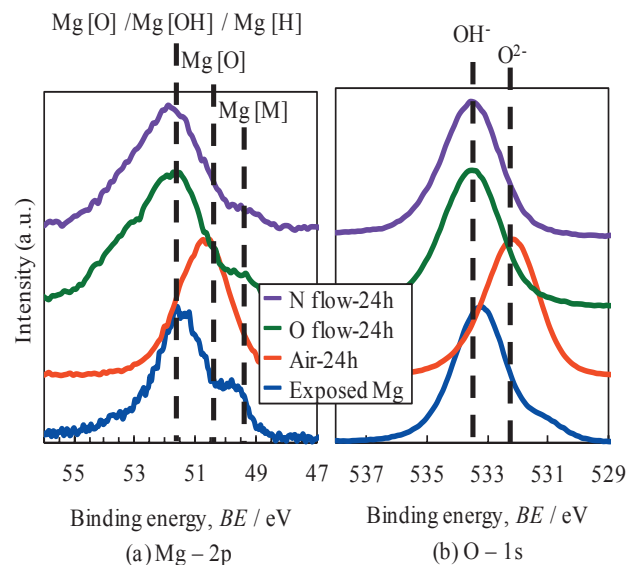
Fig. 4 Mg 2p (a) and O 1s (a) core level XPS spectra of each Mg specimen surface.
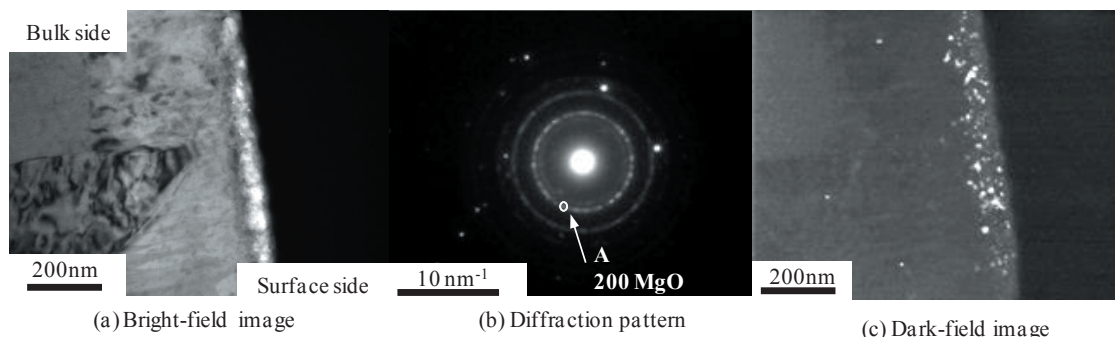
Fig. 5 TEM image of X-ray irradiated Mg surface (a), electron diffraction pattern of (a) area (b) and corresponding A area dark field image (c).
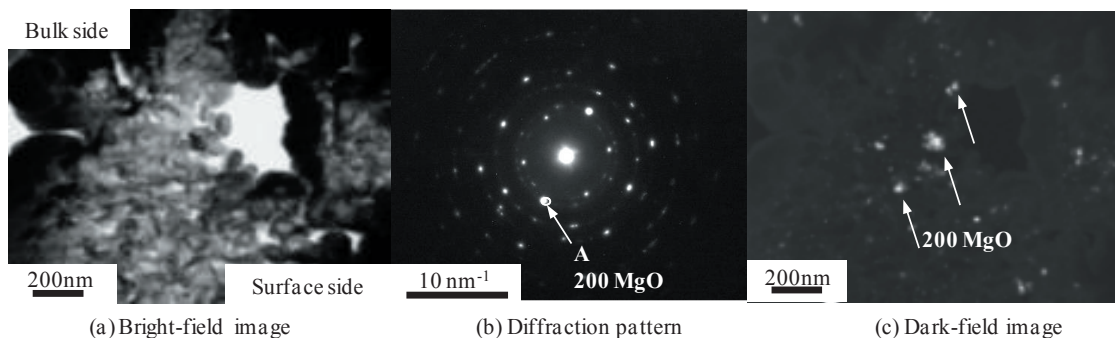
Fig. 6 TEM image of naturally formed MgO layer (a), electron diffraction pattern of (a) area (b) and corresponding A area dark field image (c).

However, a naturally formed oxide film of Mg has a porous structure comprising $Mg(OH)_2$ and MgH_2 besides MgO. Thus, in a corrosive environment, Mg is corroded due to the penetration of water to the inside oxide film [26-27]. According to the Fig. 6, the naturally formed oxide films including many pores of about one hundred nanometers, that is, a porous structure. On the other hand, the dense surface modification film of MgO with a thickness of about 80 nm was formed on the surface of Mg sample by X-ray irradiation. It means that the surface modified film produced by X-ray irradiation is a dense MgO film containing no $Mg(OH)_2$.

It, it is expected to improve corrosion resistance of Mg by producing dense surface film via the X-ray irradiation. To investigate the relationship between the film thickness and X-ray irradiation time, the thickness of surface modification film formed by X-ray irradiation was measured. The film thickness results measured by XPS analysis were shown in **Table 3**. The thickness of the MgO film was significantly increased by increasing X-ray irradiation time. It indicates that the reaction between the sample and radicals generated by the X-ray irradiation progressed. Thus, the corrosion resistance of Mg with thicker MgO films could be improved with the increase in the X-ray irradiation time.
Surface morphology changes of the pure Mg samples before and after the salt water immersion test are shown in **Fig. 7**.

Table 3 Film thickness of surface modification layer measured by XPS.

Sample name	Irradiation tame	Thickness
	h	nm
Air 6 h	6	35.2
Air 12 h	12	52.8
Air 24 h	24	88.0

Corrosion area (black area) of the X-ray irradiated Mg sample was smaller than that of as-polished Mg. The ratio of the black area in the irradiated material for Air-24h, Air-12h and as-polished Mg samples were calculated as 11 %, 27 % and 49 % respectively using the image analysis software. It means corrosion area decreased with the increase in the X-ray irradiation time. **Figure 8** shows the corrosion rate of each sample calculated from the change in pH values of the aqueous solution after the test. Corrosion rate decreases with the increase in the X-ray irradiation time and the corrosion rate of Air-24h was reduced to about 1/4 of that of the as-polished Mg. These results showed corrosion rate decreased with increasing the MgO film thickness. Therefore, the improvement of corrosion resistance by increasing the X-ray irradiation time was strongly related to the growth of the MgO film formed on the sample surface. It is concluded that the dense MgO film was formed at the outermost surface of the sample by X-ray irradiation and effectively improved corrosion resistance of Mg.
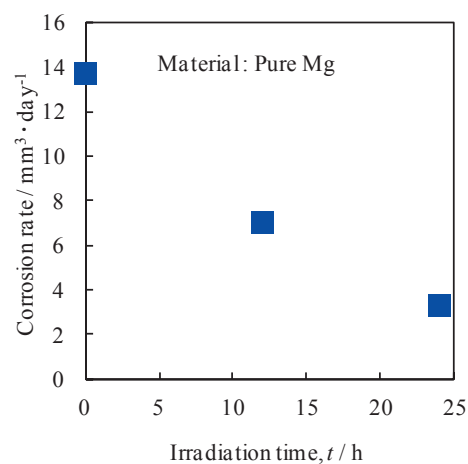
Fig. 8 Dependence of corrosion rate of pure Mg on X-ray irradiation time in atmosphere.
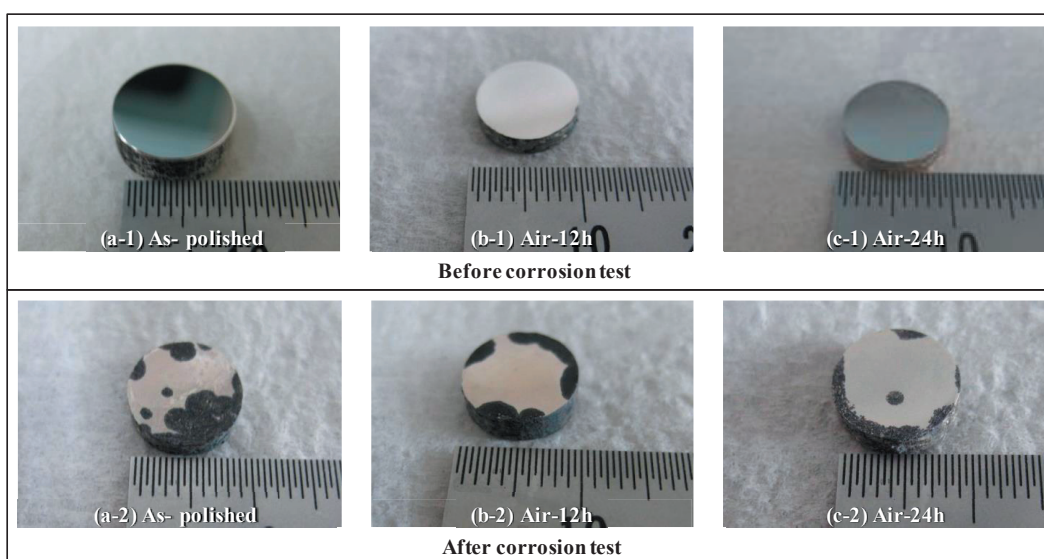
Fig. 7 Surface morphology changes in as-polished pure Mg (a), Air-12h (b) and Air-24h (C) before and after salt water immersion corrosion test.

4. Conclusions

In this study, the micro structure and corrosion behavior of the unique MgO film formed by the reaction between Mg and radicals generated by X-ray irradiation were analyzed. The results obtained were summarized as follows:

(1) Mg sample surface was modified to the single phase MgO by X-ray irradiation under the atmospheric environment with moisture. Cross-sectional observation by TEM showed the MgO film was dense compared to the naturally formed oxide films with porous structures. The thickness of the MgO film was significantly increased by increasing X-ray irradiation time.

(2) After salt water immersion test, the corrosion resistance of X-ray irradiated pure Mg was about four times higher than that of as-polished pure Mg sample. These results suggested that X-ray irradiation on the Mg surface in a humid atmosphere showed a remarkable effect to improve corrosion resistance of pure Mg due to the formation of the dense MgO films as corrosion protection.

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