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Citation	Transactions of JWRI. 2011, 40(1), p. 9-14
Version Type	VoR
URL	https://doi.org/10.18910/8437
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Electron Excitation Effect of Pure Mg Surface on initial Corrosion Phenomenon†

FUNATSU Keisuke *, TAKEI Rei *, UMEDA Junko **, KONDOH Katsuyoshi ***

Abstract

Magnesium (Mg) has the lowest negative standard electrode potential (-2.363V) among industrial metals. This means that corrosion phenomena easily occur when Mg specimens contact with other metals because a galvanic cell is formed at the interface between two materials due to their large potential difference. The conventional method to improve corrosion resistance of Mg alloys is anodic oxide film formation and/or chemical conversion treatment. However, these methods are expensive and chemically treated Mg products are hard to recycle. In this study, a new corrosion protection method by electron excitation to change the surface potential of pure Mg was investigated. The surface potential variation of pure Mg was measured by using Scanning Kelvin Probe Force Microscopy (SKPFM) to determine the anodic/cathodic area at the interface between different phases in the local galvanic cell. The electronically excited area by electron beam irradiation of a Scanning Electron Microscope (SEM) showed a lower surface potential than that of the as-polished original surface. SEM observation results indicated corrosion resistance at the electronically excited area of a pure Mg specimen was improved. This observation is also supported by salt water immersion tests and Atomic Force Microscope (AFM) analysis results as they indicate fewer corrosion products at the electronically excited area.

KEY WORDS: (Magnesium), (Surface Potential), (SKPFM), (Galvanic corrosion)

1. Introduction

Magnesium (Mg) alloys have high specific strength and stiffness due to their low density of 1.7 g/cm^3. Plus, they possess other spectacular capabilities namely, vibrational absorption, the dimensional stability and electromagnetic wave shielding[1)]. Hence, they are used in industrial components such as transport products and mobile electronic devices. These low density Mg alloys are expected to improve fuel efficiency and to reduce CO_2 gas emission the automobiles[1-3)]. However, one of the disadvantages of the conventional Mg alloys is poor corrosion resistance[1)]. Pure Mg has a lower standard electrode potential (SEP) of -2.363V compared with other pure metals such as Fe, Ni and Cu. This means that when an electric potential difference occurs due to contact with other metals, Mg easily tends to become the anodic side of a galvanic cell[4)]. The greater difference of SEP, the more severe corrosion occurs[5-6)]. Therefore, in order to use Mg alloys as structural components, a suitable protecting surface coating treatment such as anodic oxide film formation and chemical conversion process is necessary. These methods improve the corrosion resistance of Mg by forming a barrier layer on the surface of Mg alloys. However, these methods are expensive and Mg treated by these methods is difficult to recycle. Thus, an alternative corrosion protection method in order to make Mg easy to recycle is needed. In this method, corrosion is expected to be prevented even without creating any protecting surface. As generally known, Mg is easy to corrode because of the existence of potential differences with other metals. Thus, corrosion phenomena in Mg could be obstructed by decreasing the potential difference between Mg and other metals. This study focused on how the electrochemical behavior of a pure Mg surface was influenced by the electronic state of the sample surface. In this way, a new corrosion protection method by changing surface potential of pure Mg through electron excitation was investigated. The surface potential change was observed experimentally and its influence on corrosion phenomena was investigated.

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Transactions of JWRI is published by Joining and Welding Research Institute, Osaka University, Ibaraki, Osaka 567-0047, Japan

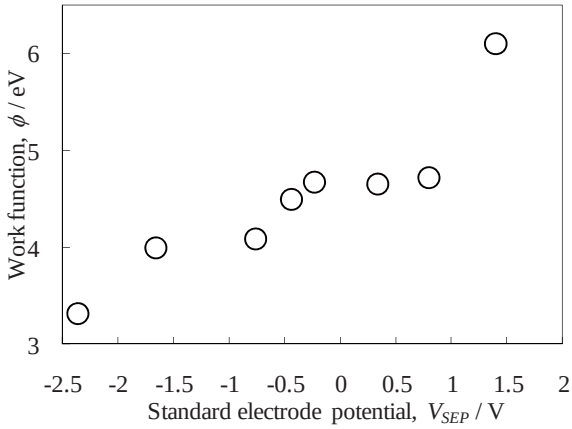


Fig.1 Relationship between standard electrode potential and work function of pure metals.

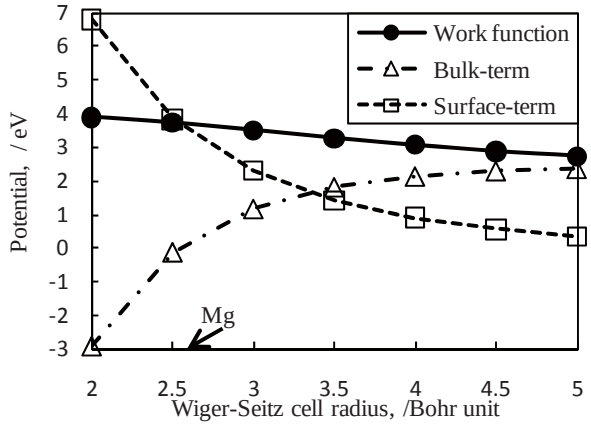
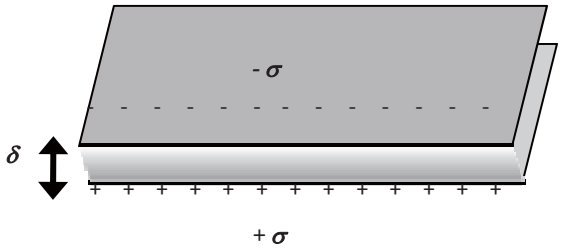


Fig.2 Portions of bulk-derived term and surface-derived term in work function as a function of Wigner-Seitz cell radius.



δ:Electrical double layer thickness
σ:Charge density

Fig.3 Schematic model of electrical double layer capacitor.

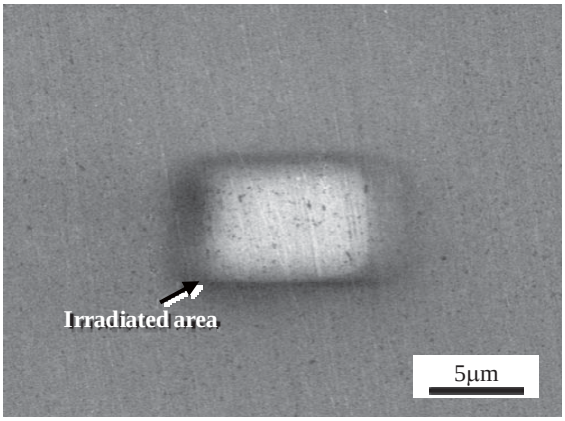


Fig.4 SEM image of pure Mg surface with electronically irradiated area.

2. Experimental

2.1 Chemical potential at the metal surface

The chemical potential of the metal can be expressed by using the work function (ϕ). It is the minimum energy needed to remove an electron from a solid surface into vacuum. It can be represented by using the equation[7-8] below, where χ represents the Pauling's electronegativity [9].

$$\phi = 2.27\chi + 0.34 \quad (1)$$

The relationship between the work function obtained by using the above equation and SEP[10] is shown in **Fig. 1**. It shows correlation between the work function and SEP. On the other hand, according to the Jellium model[11], the work function consists of a bulk term (Φ_{BR}) which has material-specific value and a surface term (Φ_{SF}) which depends on surface charge density. This model involves interaction between electrons and positive charge ion cores. In this model the positive charges are replaced by a uniform positive background charge density. Electronic interactions are taken to be of the coulomb type and expressed in the simplest possible way. **Figure 2** shows the portions of bulk-derived term and surface-derived term in the work function as a function of Wigner-Seitz cell radius[12]. Wigner-Seitz cell radius of Mg is about 2.65[12]. Hence, the work function of Mg is mostly determined by the surface term. The surface term can be represented as the work function of a capacitor model as shown in the following equation:

$$\Phi_{SF} = \frac{\delta \sigma e}{4\pi\varepsilon} \quad (2)$$

This equation suggests that change of charge density at the Mg surface causes surface potential change.

2.2 The method of electron excitation

In this study, electrons at the metal's surface were excited by scanning electron microscope (SEM, JEOL JSM-6500F). The outermost surface of the metal sample is covered with an insulator layer such as organic contamination and oxide film[13]. When electrons are irradiated to the insulator layer, the electrons are trapped in defects at the insulation. After that, the electric double layer of the surface changes[14]. This electric double layer can be regarded as a parallel plate capacitor when the size of electron excited area is much larger than that of

electrical double layer thickness. The thickness of the naturally formed oxide film was reported to be less than 100 nm[13]. In this study the size of electron excited area was about 55,000,000 nm^2 which was far greater the than electrical double layer thickness. Therefore, surface potential change value (V_{SPC}) obtained by the charge amount and the dielectric constant, is shown in the following equation (3) [14]. **Figure 3** shows a Schematic model of the electrical double layer capacitor.

$$V_{SPC} = \frac{\delta \Delta \sigma}{4 \varepsilon \pi} \tag{3}$$

The SEM image at the sample surface after electron beam irradiation is shown in **Fig. 4**, and indicates that the surface of the sample was charged-up due to electron irradiation.

2.3 Principle of SKPFM and surface potential

The surface potential was measured by Scanning Kelvin Probe Force Microscope (SKPFM, Shimadzu SPM-9600). This has been used to determine the anodic/cathodic area at the interface of different phases in the galvanic cell. Electron-excited pure Mg samples under different conditions were used to investigate V_{SPC} and the galvanic corrosion phenomena at the interface. The surface potential is measured as the contact potential difference (V_{CPD}) between the sample specimen and the cantilever probe coated with PtIr5 by SKPFM. The V_{CPD} value was obtained by subtracting the work function of the sample metal ϕ_{sample} from PtIr5 ϕ_{PtIr5} and then dividing by elementary electric charge, as shown in the following equation:

$$V_{CPD} = (\phi_{\mathrm{ptIr5}} - \phi_{\mathrm{Mg}}) / e \tag{4}$$

The variation tendency of this surface potential is different from SEP. Correlation between work function and SEP (Fig. 1) indicates that the work function of low SEP metals generally have small values. According to the above equation a smaller work function results in higher V_{CPD} values. Hence, surely low SEP metals (i.e. Mg and Al) have higher V_{CPD}. The surface potential difference value (V_{SPD}) between Mg and other metals is calculated as shown below.

$$\begin{aligned} V_{SPD} &= V_{Mg} - V_{Metal} \\ &= (\phi_{\mathrm{Metal}} - \phi_{\mathrm{Mg}}) / e \\ &= (\phi_{\mathrm{ptIr5}} - \phi_{\mathrm{Mg}}) / e - (\phi_{\mathrm{ptIr5}} - \phi_{\mathrm{Metal}}) / e \end{aligned} \tag{5}$$

In addition, the difference of SEP is also defined using the following equation, where V_{Metal} and V_{Mg} are SEP of contacted metal and Mg, respectively.

$$\Delta V_{SEP} = V_{Metal} - V_{Mg} \tag{6}$$

The values of theoretical V_{SPD} and ΔV_{SEP} are calculated by eq. (5) and eq. (6) shown in **Table 1**[15]. It shows the correlation between V_{SPD} and ΔV_{SEP}. Therefore, the local differences of surface potential could indicate the galvanic corrosion. This study evaluated the corrosion resistance quantitatively by measuring V_{SPD}.

2.4 Identification method of the electron excitation region

When some phases of pure metals or the interfacial phase of Mg and Fe are scanned, the interfacial phase can be identified by the optical microscope equipped with the SKPFM. The magnification of this optical microscope is 84 to 525 times. However the electron excited area is so small at about 55μm^2, that the area can't be observed by this optical microscope. The X-Y 2 dimensional coordinate was fixed on the mirror polished surface of the specimen by the identification schematically illustrated in **Fig. 5**. In this way, the relative position of the electron excited area can be identified in the coordinates. Some indentations were produced quite a distance away from the electron excited area as shown in Fig. 5. After that, the relative position of each area against the four indentations was captured as an SEM image. Therefore,

Table 1 Values of ΔV_{SEP} and theoretical V_{SPD} of each pure metal.

Contacted metal	Al	Zn	Fe	Ni	Cu	Ag	Au
ΔV_{SEP} (V)	0.7	1.6	1.92	2.13	2.7	3.16	3.76
V_{SPD} (V)	0.681	0.7718	1.1804	1.362	1.3393	1.4074	2.7921

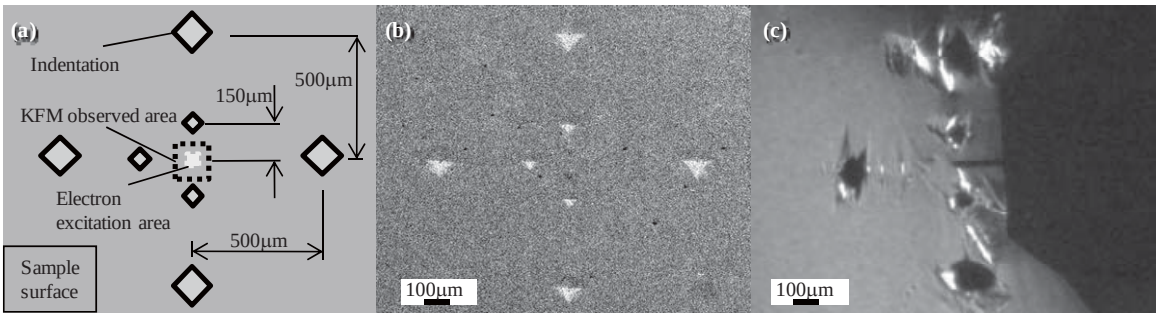


Fig. 5 Arrangement of indentations schematic illustration (a), SEM image (b) and optical micro scope image(c).

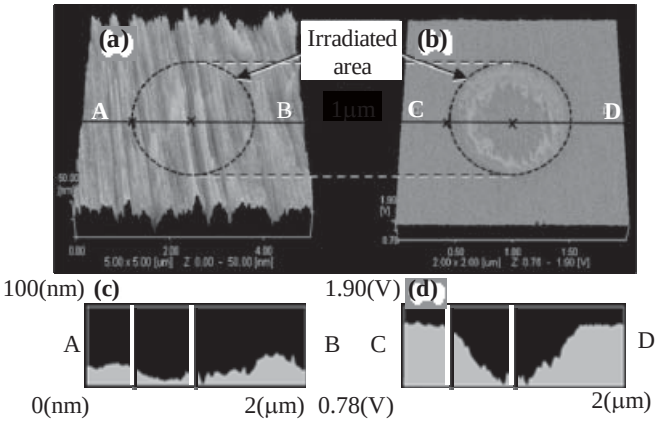


Fig. 6 Topography (a) and surface potential map (b) around electronically irradiated area . Cross section view of height changes (c) and surface potential (d) at line was measured along A-B and C-D line.

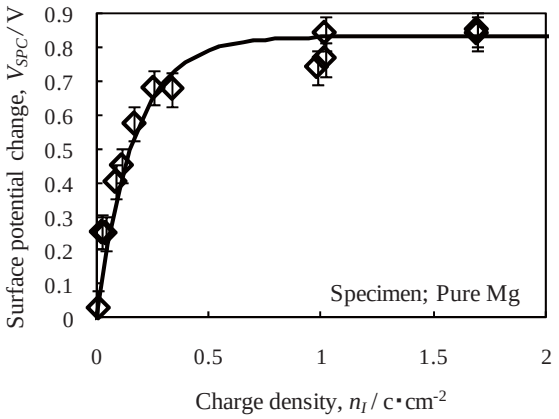


Fig.7 Relationship between surface potential change of pure Mg specimen and irradiation charge density.

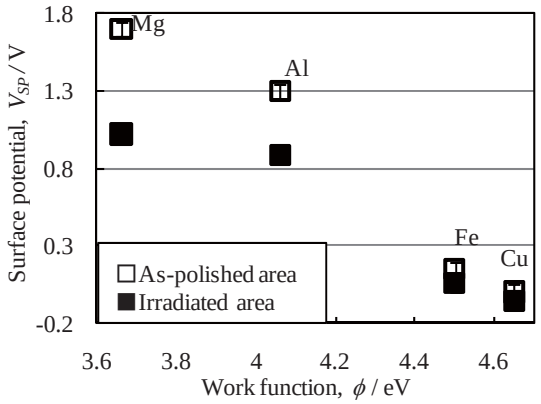


Fig.8 Relationship between surface potential change and work function of each pure metal specimen with and without electron irradiation.

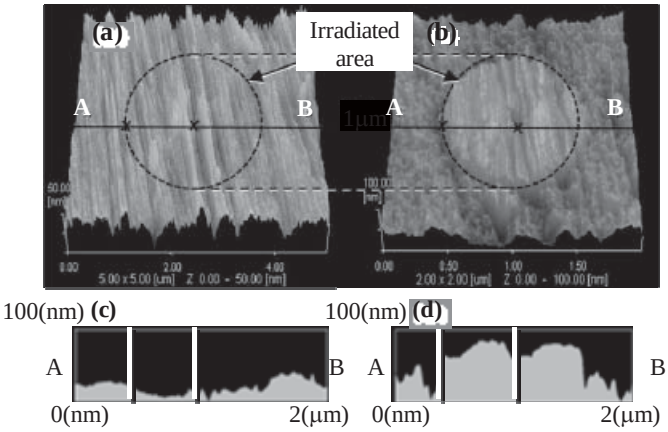


Fig.9 Topography around electronically irradiated area before (a) and after (b) salt water immersion test. Cross section view of height at line by SKPFM A-B line before (c) and after (d) salt water immersion test.

from the above mention method, it could be concluded that the electron excited area can be fixed through the relative position of excited area. The square area that covers the electron excited area and as-polished area is chosen in order to observe the interfacial V_{SPC} between excited area and as-polished area.

2.5 Immersion test conditions

In order to understand the corrosion behavior of the specimen, an immersion test was carried out in 5 mass % NaCl aqueous solutions having initial pH value of approximately 6.0 at 30 °C. During the test, the solution was agitated at 420 rpm with a magnetic rotator and deaerated with 1.5 L / min Ar gas flow. To quantitatively evaluate the changes, the topography variation was measured by Atomic Force Microscope (AFM). Subsequently, the microstructure and phases were investigated with SEM and energy dispersive X-ray spectrometry (EDS), respectively.

3. Results

3.1 Surface potential measurement results

Figure 6 shows the surface potential map and topography around the electron excited area measured by SKPFM. It shows that electron irradiation didn't cause topographic changes. On the other hand, it also indicated that the surface potential of the sample surface at electron excited area decreased because of electron irradiation. The surface potential decline means that the excited area became cathodic. Therefore, it is expected that the electron excited area shows higher corrosion resistance than the as-polished area. **Figure 7** shows the surface potential variations of electron-excited pure Mg specimen under different conditions measured by SKPFM. It shows the following two different trends. First, when small amounts of electron beam were irradiated, the value of V_{SPC} increased as the density of electron beam irradiation increased. This means that electron irradiation caused the charge density of the pure Mg surface to increase. On the other hand, when large amounts of electron beam were

Table 2 Changes in height of dispersoids at interface before and after salt water immersion test.

	Height (nm)		Height changes (nm)
	Before corrosion	After corrosion	
As-polished area	20.2	28.4	8.2
Irradiated area	20.3	65.2	44.9

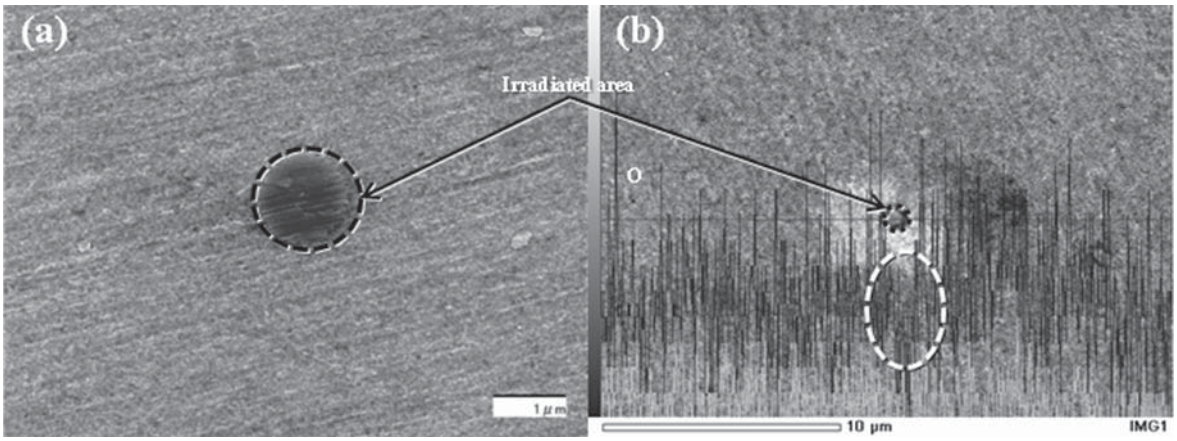


Fig. 10 SEM image of Mg (a) and EDS analysis result (b) including electronically irradiated area after salt water immersion test.

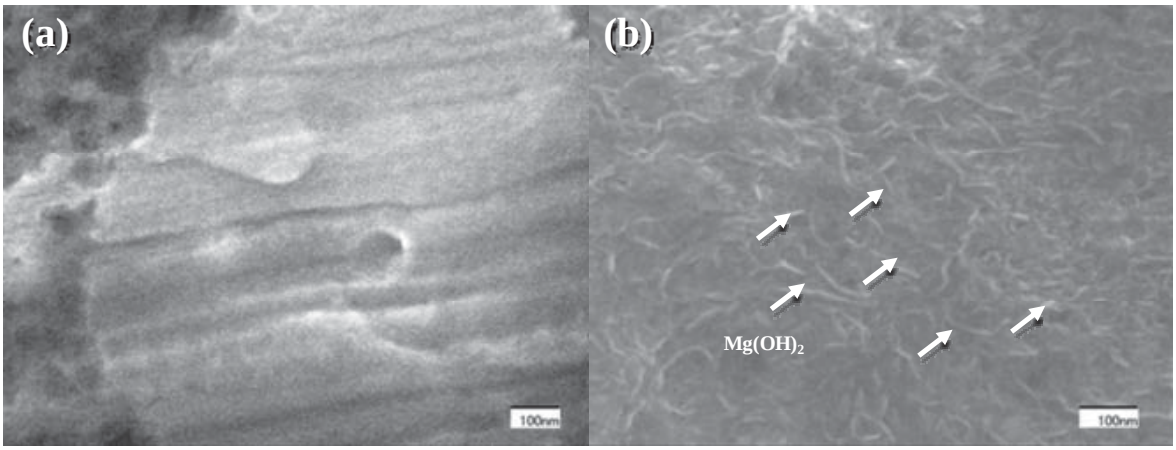


Fig. 11 High magnification SEM image of Figure 9 nearby electronically excited area (a) and as-polished area (b).

irradiated, the V_{SPC} becomes saturated. The saturation occurred here because the defects at the insulation were filled with the irradiated electrons. This indicates that electon irradiation causes variation in surface charge density. Therefore, the surface potential of Mg can be controlled by electron irradiation until the saturation of electron charge density. In order to ensure that the surface potential decline was due to the charging of the metal surface, the V_{SPC} of electron irradiated pure Al, pure Fe and pure Cu were also measured. The results are shown in **Fig. 8**. Surface potential decreased in all specimens. Therefore, it could be understood that the decline of surface potential through electron excitation was due to electrical modification of metal surfaces. The V_{SPC} of metal with a large work function was small and vice the versa. The difference of V_{SPC} value in each specimen was due to differences in surface condition.

3.2 Salt water immersion test results

Figure 9 indicates topographic mapping result of an electron excited area and a nearby area by AFM. **Table 2** shows the height variation after the corrosion test. It increases to about 50 nm compared with the one before the corrosion test. This indicates that unlike as-polished areas, the corrosion at electron excited areas was inhibited. Mg reaction with deaerated aqueous solution is expressed in the chemical formulas below[16].

$$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^{-} \text{ (anodic reaction)}$$

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \text{ (cathodic reaction)} \quad (7)$$

$$Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s) \text{ (corrosion product)}$$

In corroded areas, corrosion product can be found. **Figure 10** shows SEM observation and EDS analysis result of the area which covers electron excited area after salt water immersion test. SEM image of electron excited area indicated another phase compared with that of as-polished area. Besides, EDS elemental analysis showed (Fig. 10 (b)) low O concentration in the area. In order to investigate the difference between electron excited areas and as-polished areas in more detail, high magnification SEM images at a nearby electron excited area (a) and an as-polished area (b) are shown in **Fig. 11**. The corrosion product was insignificant in Fig. 11 (a), and the electron excited area suppressed dissolution of Mg. This means that electron excitation can improve pure Mg corrosion resistance.

4. Conclusion

Mg is easy to corrode because of it has low SEP. This becomes significant when Mg is in contact with other metals. In this study, a new method of corrosion protection using the surface potential change of pure Mg was investigated. The surface potential of pure Mg was changed by electron excitation. The correlation between surface potential variation and galvanic corrosion behavior was investigated by SKPFM and SEM observation. The results obtained in the present study are summarized as follows;

(1) The electron excited area at a pure Mg surface was formed by irradiation of electron beam using SEM. The specimen showed a lower surface potential than that of the as-polished area. The value of V_{SPC} increased with the increasing amounts of the electron irradiation. Hence, it was found that the value of V_{SPC} can be controlled by amounts of the electron irradiation.

(2) Salt water immersion tests were conducted in order to investigate the effect of V_{SPC} on corrosion phenomena. They revealed that electron excited areas showed excellent corrosion resistance. That was because the electron excited area had less corrosion product than that of an as-polished area. It confirmed that electron excitation improves corrosion resistance of pure Mg.

Acknowledgement

This study was financially supported by the light metal educational foundation, Inc.

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