Effect of Anions on Initial Stage of Localized Corrosion of Zn-55 mass% Al Alloy Coated Steels by Photon Rupture Method and Anodizing

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Photon rupture with a focused single pulse of pulsed YAG-laser irradiation was used to investigate abrupt destruction and repair of passive oxide films or localized corrosion on anodized Zn-55 mass% Al coated steels. The specimens were irradiated with a focused pulse of a pulsed Nd-YAG laser beam at a constant potential in borate solutions, pH = 9.2, with and without Cl^- , NO_3^- , and SO_4^{2-} ions and the current transients were monitored. The oxide films were reformed in the borate solution with NO_3^- and SO_4^{2-} ions after removal of the oxide film. The oxide film formation kinetics follows the inverse logarithmic law, according to Cabrera-Mott theory at the late stage after $t = 10$ ms. As the potential becomes nobler, the current increases. These behaviors can be explained by a preferential dissolution of the metal substrate, which is enhanced at nobler potentials and with the anions. In Cl^- containing solutions, localized corrosion of the coated layer occurs at high potentials, while film reformation occurs at low potentials.

Key words : Zn-55 mass% Al alloy coating, localized corrosion, photon rupture method

1. Introduction

Zinc and zinc based alloy coated steels are used for vehicles and in architecture because of their excellent corrosion protection characteristics in atmospheric environments. The corrosion protection of the coated layers are ascribe to cathodic protection by galvanic reaction between coated layer and substrate^{1), 2)}, and the formation of stable and compact corrosion products which have high corrosion resistance. Miyoshi et al.³⁾ have reported basic research on the corrosion resistance of pre-coated steel sheets for automobiles and the composition of corrosion products formed on the steels caused by atmospheric corrosion have been investigated in various exposure conditions^{4) - 7)}. Oesch et al.⁸⁾ have reported the effect of air pollutants such as SO_2 , NO_2 , NO , and O_3 on the corrosion of zinc and other light metals and Ramanauskas et al.⁹⁾ have reported the effect of corrosion products on the atmospheric corrosion of electrodeposited zinc and zinc alloy coatings.

There are problems in the application of electrochemical methods such as voltammetry, electrochemical impedance spectroscopy (EIS) in atmospheric corrosion study, due to the thin electrolyte layer are encountered. Recently, the EIS technique has been applied to measurements of atmospheric corrosion of Zn and Zn alloy^{10) - 16)}. El-Mahdy et al.¹⁷⁾ have reported electrochemical corrosion monitoring of galvanized steel under cyclic wet-dry conditions. Peiez et al.¹⁸⁾ have reported a EIS Study of the corrosion process on coated galvanized steel in a salt spray conditions.

Analysis of abruptly destroyed passive oxide films and

their repair is important to understand the localized corrosion of metals. Analysis of this behavior has been carried out by monitoring potential- and current-transients after mechanical stripping of the oxide films^{19) - 28)}. The mechanical film stripping poses problems in the film stripping rate, contamination from stripping tools, and stress and strain on the substrate. Recently, there are reports of film stripping by photon rupture (focused single pulse of pulsed YAG-laser irradiation) method, which resolves many of the problems caused by mechanical film stripping. The irradiation of a pulsed laser beam is able to strip oxide film at extremely high rates without contamination from film removing tools. Photon rupture stripping has applied to iron by Oltra et al.^{29), 30)} and by Itagaki et al.³¹⁾, to aluminum electrodes^{32), 33)} and to Zn-Al alloy coated steel by Sakairi et al.^{34) - 40)}.

In the present investigations, Zn-55 mass% Al alloy coated steel specimens covered with protective oxide film were irradiated with one pulse of a pulsed Nd-YAG laser beam at constant potential in sodium tetra-borate solutions with and without aggressive anions measuring the current transients to investigate the effect of aggressive anions to study initial stage of localized reformation of oxide film and localized corrosion.

2. Experimental

Specimen : Zinc-55 mass% aluminum coated steel (Nippon Steel Co.) sheets were cut into 10×13 mm coupons with a handle, and the edges were covered by silicone. The coated layer thickness was about $19 \mu\text{m}$.

Anodizing : Specimens were anodized in a 0.1 kmol/m^3 $\text{Na}_2\text{B}_4\text{O}_7$ (pH = 9.2) and 0.1 kmol/m^3 H_3BO_3 / 0.05 kmol/m^3 $\text{Na}_2\text{B}_4\text{O}_7$ (pH = 8.7) solutions at 293 K with a constant current density of 10 A/m^2 .

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Laser Irradiation : After sealing in boiling distilled water for 120 s, the specimens were immersed in 0.1 kmol/m³ Na₂B₄O₇ with and without 0.01 kmol/m³ NaNO₃, Na₂SO₄, or NaCl solutions (pH = 9.2), and irradiated by one pulse of pulsed Nd-YAG laser (Sepctra Physics GCR-130) through a lens and quartz window at a constant potential, $E_a = -0.5$ to 1.0 V (vs. Ag/AgCl). Before reaching the lens, the laser beam was passed through a diaphragm to reduce the beam diameter to 1.5 mm. The laser beam was the second harmonic wave, with wave length 532 nm, wave duration was 8 ns and the frequency 10 s⁻¹, the laser power, P , was set to 30 mW. The current transients after laser irradiation were measured with a computer system through an digital storage oscilloscope. The laser irradiation time was also detected by a photo-detector³³.

The micro structure of the anodic oxide films and the coated layers were examined with ultramicrotomed sections by transmission electron microscopy (TEM ; H-700, Hitachi) and a scanning electron microscope (SEM ; JXA-8900M, JEOL) equipped with an energy-dispersive X-ray (EDX) analysis system. After the experiments, the specimen surfaces were examined by confocal scanning laser microscopy (CSLM ; 1SA21, LASERTEC Co.) and optical microscopy.

Polarization curves were measured by the potential sweep method, 0.33 mV/s in 0.1 kmol/m³ Na₂B₄O₇ with 0.01 kmol/m³ NaNO₃, Na₂SO₄ and NaCl solutions (pH = 9.2) to measure the pitting potential and determine the applied potential at the laser irradiation experiment.

3. Results

3.1 Anodizing and structure of the coated layer

Figure 1 shows change in potential with time during anodizing at 10 A/m² in 0.1 kmol/m³ Na₂B₄O₇ (pH = 9.2) and 0.1 kmol/m³ H₃BO₃/0.05 kmol/m³ Na₂B₄O₇ (pH = 8.7) solutions. The potential vs. time curve for electro-polished pure aluminum at 10 A/m² in 0.5 kmol/m³ H₃BO₃/0.1 kmol/m³ Na₂B₄O₇ (pH = 7.4).

Fig. 1 Change in potential with time during anodizing at 10 A/m² in a 0.1 kmol/m³ Na₂B₄O₇ (pH = 9.2) and 0.1 kmol/m³ H₃BO₃/0.05 kmol/m³ Na₂B₄O₇ (pH = 8.7) solutions. Dotted line : pure aluminum at 10 A/m² in 0.5 kmol/m³ H₃BO₃/0.1 kmol/m³ Na₂B₄O₇ (pH = 7.4).

kmol/m³ Na₂B₄O₇ (pH = 7.4) is also indicated as a dotted line in this figure. The potential increases with anodizing time in all conditions. The slope of coated specimens are gentler than that of pure aluminum. The slope of coated specimens becomes steeper with increasing pH. These results suggested that anodic oxide film formed at high pH is better for laser experience than that formed in at low pH.

Figure 2 shows a) SEM and b, c) TEM cross sectional photographs of the Zn-55 mass% Al alloy coated steel after anodized at 10 A/m² in 0.1 kmol/m³ Na₂B₄O₇ (pH = 9.2) up to 50 V. There are defects inside the coated layer and an intermediate layer of about 2 μ m thickness can be seen between coated layer and substrate. The anodic oxide film with amorphous structure can be seen on the coated layer and this oxide film thickness about 70 nm, the growth rate is about 1.4 nm/V, almost the same as on pure aluminum. This results suggested that composition of anodic oxide film formed on the coated layer is almost same as that of barrier type anodic oxide film formed on pure aluminum.

3.2 Polarization behavior

Figure 3 shows the anodic polarization curves, anodized samples (solid line) and without anodized samples (dotted line), of Zn-55mass% Al coated steels in 0.1 kmol/m³ Na₂B₄O₇ (pH = 9.2) solution with 0.01 kmol/m³ of NaNO₃, Na₂SO₄ and NaCl and in without these anions (thick solid

Fig. 2 Cross sectional photographs of the anodized specimen a) SEM, and TEM images, b) outer edge of coated layer and c) coated layer and steel interface.

Fig. 3 Anodic polarization curves of Zn-55mass% Al coated steels, anodized samples (solid line) and without anodized samples (dotted line), in $0.1 \text{ kmol/m}^3 \text{ Na}_2\text{B}_4\text{O}_7$ ($\text{pH} = 9.2$) solution with $0.01 \text{ kmol/m}^3 \text{ Na}_2\text{SO}_4$, Na_2NO_3 , and NaCl and in without these anions.

line). The current increases with electrochemical noise, current fluctuations, with rising potential especially in the Cl^- containing solution. Each of the current fluctuations in the figure is related to each events of the initial stage of pitting or localized corrosion. The pitting or localized corrosion potentials in Cl^- containing solution are lower than that in SO_4^{2-} and NO_3^- containing solutions. These potentials of the anodized samples are higher than those without anodizing in the same solution.

Figure 4 shows a) top views, b) CSLM contrast images of after removal of corrosion products and c) schematic drawing of cross section without anodized samples after polarization in solutions. The samples are covered by corrosion products, which have about $20 \mu\text{m}$ height, and some

Fig. 4 Top views, a), CSLM contrast images of after removal of corrosion products, b), and schematic drawing of cross section, c), without anodized samples after polarization in $0.1 \text{ kmol/m}^3 \text{ Na}_2\text{B}_4\text{O}_7$ ($\text{pH} = 9.2$) solution with $0.01 \text{ kmol/m}^3 \text{ Na}_2\text{SO}_4$, Na_2NO_3 , and NaCl.

parts are covered with red rusts in NaCl solution. This red rusts indicates that no coated layer remains under these areas. After removal of the corrosion products, there are many pits or locally dissolved areas. A total dissolved area in NaCl solution is bigger than that with other aggressive anions (SO_4^{2-} and NO_3^-).

3.3 Film removal by the photon rupture method

Figure 5 shows the change in current, I , with time, t , obtained at $E_a = 0.5 \text{ V}$ in $0.1 \text{ kmol/m}^3 \text{ Na}_2\text{B}_4\text{O}_7$ solutions with and without $0.01 \text{ kmol/m}^3 \text{ Na}_2\text{SO}_4$, Na_2NO_3 , and NaCl after laser irradiation. By laser irradiation, the current increases instantaneously through a maximum, I_p , at about 0.4 ms , the decreases exponentially with time except with NaCl. In the $\text{Na}_2\text{B}_4\text{O}_7$ solutions, the current reaches a value as low as that before the laser irradiation about 600 ms after laser irradiation. While in the solutions with Cl^- and at high potentials, the current remained high after 0.4 ms . In the $0.1 \text{ kmol/m}^3 \text{ Na}_2\text{B}_4\text{O}_7$ solution, the slopes of the $\log I$ vs. $\log t$ curves are about -0.3 immediately after the peak, and after $t = 10 \text{ ms}$, it is -1 . This result suggests that the film formation kinetics follow the inverse logarithmic law, according to Cabrera-Mott theory at the late stage after $t = 10 \text{ ms}$. We will discuss detail of film formation kinetics later. The slope after the peak is slightly smaller in the Na_2SO_4 and NaNO_3 solutions. Immediately after the peak current, after $t = 0.4 \text{ ms}$, the oxide film formation is accompanied by film dissolution. In Cl^- containing solution, localized corrosion took place at the irradiated area at high potential.

Figure 6 shows the CSLM images of specimen surface polarized for 2 s after laser irradiation at $E_a = 0.5 \text{ V}$ in a) $0.1 \text{ kmol/m}^3 \text{ Na}_2\text{B}_4\text{O}_7$, and with 0.01 kmol/m^3 b) Na_2SO_4 . The areas where film was removed is a rough surface of pentagon due to the diaphragm about $200 \mu\text{m}$ diameter, and the surface appears to have been rapidly melted and solidified. It is considered that the anodic oxide film on the Zn-55

Fig. 5 Change in current with time obtained after laser irradiation in $0.1 \text{ kmol/m}^3 \text{ Na}_2\text{B}_4\text{O}_7$ solution and $\text{Na}_2\text{B}_4\text{O}_7$ with $0.01 \text{ kmol/m}^3 \text{ Na}_2\text{SO}_4$, Na_2NO_3 , and NaCl solutions at $E_a = 0.5 \text{ V}$.

Fig. 6 CSLM images of specimen surfaces after polarizing for 2 s following laser irradiation at $E_a = 0.5$ V. a) $0.1 \text{ kmol/m}^3 \text{ Na}_2\text{B}_4\text{O}_7$, b) $0.1 \text{ kmol/m}^3 \text{ Na}_2\text{B}_4\text{O}_7$ with $0.01 \text{ kmol/m}^3 \text{ Na}_2\text{SO}_4$.

Fig. 7 CSLM image a) before removal of corrosion products and b) after removal of corrosion products; specimen surfaces after polarized for 2 s after laser irradiation in $0.1 \text{ kmol/m}^3 \text{ Na}_2\text{B}_4\text{O}_7$ with $0.01 \text{ kmol/m}^3 \text{ NaCl}$ at $E_a = 0.5$ V.

mass% Al alloy is removed by the high pressure produced by laser ablation. There are no corrosion products at area where the film has been removed.

Figure 7 shows CSLM images a) before corrosion products were removed and b) after corrosion products were removed from the specimen surface polarized for 2 s after laser irradiation in $0.1 \text{ kmol/m}^3 \text{ Na}_2\text{B}_4\text{O}_7$ with $0.01 \text{ kmol/m}^3 \text{ NaCl}$ at $E_a = 0.5$ V. The white precipitates observed at the laser irradiated area were produced by the preferential dissolution of the alloy layer. After removal of the oxide film, pentagon shaped and many pits can be seen at the laser irradiated area.

Figure 8 shows the current transient after laser irradiation in $0.1 \text{ kmol/m}^3 \text{ Na}_2\text{B}_4\text{O}_7$ with $0.01 \text{ kmol/m}^3 \text{ NaNO}_3$ at $E_a = -0.5, 0$ and 0.5 V. At every E_a , the curves show a 0.4

Fig. 8 Change in current with time obtained after laser irradiation at $E_a = -0.5, 0$ and 0.5 V in $0.1 \text{ kmol/m}^3 \text{ Na}_2\text{B}_4\text{O}_7$ with $0.01 \text{ kmol/m}^3 \text{ NaNO}_3$.

ms induction time before an abrupt increase maximum current, I_p . At $E_a = -0.5$ V, the slope of the curve is about -0.3 at the initial stage up to 10 ms, and at the late stage after 10 ms, it is about -1 . This suggests that the oxide film formation kinetics follows an inverse logarithmic law. As the E_a becomes nobler, the I and I_p increase and the slopes at the initial stage up to 10 ms become slightly smaller. Above $E_a = 0$ V, the I decreases after $t = 0.4$ ms and the rate of decreasing becomes slower after $t = 100$ ms. This behavior can be explained by a preferential dissolution of the metal substrate, which is enhanced by NO_3^- ions and nobler potential.

3.4 Effect of anions on reformation and localized corrosion

Figure 9 shows the relationship between the slope of the $\log I$ vs. $\log t$ plots at the late stage after 10 ms and E_a in $0.1 \text{ kmol/m}^3 \text{ Na}_2\text{B}_4\text{O}_7$ with and without $0.01 \text{ kmol/m}^3 \text{ Na}_2\text{SO}_4$, NaNO_3 and NaCl . The slope in the $0.1 \text{ kmol/m}^3 \text{ Na}_2\text{B}_4\text{O}_7$ solution does not change with E_a , however, at lower E_a , it is steeper with the aggressive anions. Above $E_a = 0$ V, the slope in the NaNO_3 solution is steeper than that of the NaCl and Na_2SO_4 solutions.

Figure 10 shows the relationship between the I_p and E_a in $0.1 \text{ kmol/m}^3 \text{ Na}_2\text{B}_4\text{O}_7$ with and without $0.01 \text{ kmol/m}^3 \text{ NaNO}_3$, Na_2SO_4 and NaCl . The I_p increases linearly as the E_a becomes nobler in all solutions. At the lower potential region, $E_a < 0$ V, the I_p is similar in all the solutions, however at $E_a > 0$ V, the I_p of with the NaCl solution higher than that of the other solutions. The Q , current was integrated between 0 and 1 s, with NaCl solutions was larger than that of the other solutions at all E_a . The Q was independent of E_a in $\text{Na}_2\text{B}_4\text{O}_7$ with and without $0.01 \text{ kmol/m}^3 \text{ NaNO}_3$, with $0.01 \text{ kmol/m}^3 \text{ NaCl}$ and Na_2SO_4 , the Q increased linearly with increasing E_a . These results suggest that the aggressive anions and especially chloride ions accelerate the dissolution of metals at the very initial stage after the oxide film was removed.

Fig. 9 Relationship between the slope of the $\log I$ vs. $\log t$ plots at the late stage after 10 ms and E_a in $0.1 \text{ kmol/m}^3 \text{ Na}_2\text{B}_4\text{O}_7$ with and without $0.01 \text{ kmol/m}^3 \text{ Na}_2\text{SO}_4$, Na_2NO_3 , and NaCl .

Fig. 10 Relationship between the I_p of the current transients and E_a in $0.1 \text{ kmol/m}^3 \text{ Na}_2\text{B}_4\text{O}_7$ with and without $0.01 \text{ kmol/m}^3 \text{ Na}_2\text{SO}_4$, Na_2NO_3 , and NaCl .

4. Discussion

4.1 Anodic oxide film removal mechanism

The coated layer may be considered almost all aluminum in this study, because the concentration of aluminum in the layer is very high. With transparent anodic oxide films on aluminum, almost all of the irradiated laser light reaches the metal-oxide interface, and assuming that the reflectivity of aluminum is about $\gamma = 0.819$ at $532 \text{ nm}^{41)}$, the adsorbed power density is expressed as $E_{ad} = 4(1 - \gamma)P/[\pi \cdot D^2 \cdot t_p]$, the E_{ad} in this experimental condition, $t_p = 8 \text{ ns}$, $D = 150 \mu\text{m}$, and $P = 3.0 \text{ mJ}$ ($30 \text{ mW}/10 \text{ Hz}$) then becomes $3.8 \times 10^{12} \text{ W/m}^2$.

According to Ready⁴²⁾, the approximate expression of the minimum laser power density for ablation is $E_{av} = 2 \cdot L \cdot \rho \cdot k^{0.5} \cdot t_p^{-0.5}$, where t_p is the pulse duration, L the latent heat required to vaporize the solid metal, k the thermal diffusivity and ρ the density of the metal, in this case, E_{av} becomes $0.65 \times 10^{12} \text{ W/m}^2$.

The value of E_{ad} in the present investigation is much larger than that of E_{av} , and this strongly suggests that laser ablation takes place beneath the laser irradiated area just after irradiation. The ablation of metal produces pressure at the film/substrate interface, and can be calculated from $p = E_{ad}/[\rho[L + C(T_v - T_0)]^{2/3}]^{43)}$, where C , T_0 , and T_v are the specific thermal capacity of metal, the initial, and the vaporization temperatures of the metal leading to a calculated $p = 10^8 \text{ Pa}$ for the coated layer. Simple calculation of volume changes of aluminum solid to gas, leads to an estimated pressure of about $2 \times 10^8 \text{ Pa}$ at the laser irradiated area. This pressure is much higher than film deformation pressure reported by Hoshino⁴⁴⁾ and it may be concluded that the anodic oxide film can be destruction and removed by the high pressure at the film/substrate interface produced by the laser ablation of the metal.

4.2 Reoxidation and localized dissolution

The current transient after laser irradiation follows the inverse logarithmic law, $I = -\log t + K$ at the late stage after $t = 10 \text{ ms}$. Fig. 11 shows schematic drawing of potential energy at metal oxide film interface. Cabrera and Mott equation⁴⁵⁾ for thin oxide film growing under high electric filed as follows.

$$i = 2q\alpha_s n_s v_s \exp[-(W_s - q\alpha_s E)/kT] \quad (1)$$

where q the charge of metal ions, n_s number of metal ions moving metal/oxide film interface, v_s frequency of metal ion at interface, W_s activation energy of metal ion move to metal to oxide film, α_s half width of activation energy, k Boltzmann constant, T temperature, E applied potential.

We may rewrite Eq. (1) as

$$i = K_1 \exp(K_2 \times E) = K_1 \exp(K_2 \times E_s/d) \quad (2)$$

$$\log i = \log K_1 + (K_2 \times E_s)/(2.303 \times d) \quad (3)$$

where d film thickness, E_s electric field, $K_1 = 2q\alpha_s n_s v_s \exp(-W_s/kT)$, $K_2 = q\alpha_s E/kT$. We may rewrite Eq. (3) as

$$K - \log t = \log K_1 + (K_2 \times E_s)/(2.303 \times d) \quad (4)$$

$$d^{-1} = 2.303/[K_2 \times E_s \{(K - \log K_1) - \log t\}] \quad (5)$$

This means that the oxide film formation kinetics follows the inverse logarithmic law at the late stage after $t = 10 \text{ ms}$.

Figure 12 shows a schematic model of the film reformation and localized dissolution after the oxide film was removed. Stage I) ; The oxide film was removed by laser

Fig. 11 Schematic drawing of potential energy at metal oxide film interface.

Fig. 12 Schematic model of film reformation and localized dissolution of coated layer after the oxide film was removed.

irradiation which exposed the coated metal to the solution. Stage II); The coating metals are oxidized electrochemically to Zn^{2+} and Al^{3+} ions, and these ions react with water to form oxide or hydroxide film. Stage III-i); In the $Na_2B_4O_7$ solution with or without aggressive anions at low potentials, film is continuously reformed. The current transients show a sudden increase, a maximum, and a continuous decrease with a slope of about -1 . Stage III-ii); In the solutions with SO_4^{2-} and NO_3^- at high potentials, the anions adsorb on the metal surface and accelerate the dissolution of the metals so reducing film reformation rate. The rate of decrease in the current was slower than that of the $Na_2B_4O_7$ solution at low potentials. Stage III-iii); In the chloride ion containing solutions at high applied potentials, the aluminum dissolution by formation of aluminum-chloride complexes may compete with oxide film formation. The Zn also dissolves as zinc-aquo complexes, $Zn^{2+}(aq)$, after the layer is exposed to the solutions. Because of these reactions, the current did not decrease after the maximum and formed corrosion products at the area where film had been removed.

5. Conclusions

The photon rupture method was employed to the study initial stage of localized reformation of oxide film and local-

ized corrosion on Zn-55 mass% Al alloy coated steel specimens covered with protective anodic oxide films, and the following conclusions may be drawn.

- 1) Ultra-microtomy can be used with Zn-55 mass% Al alloy coated steel to prepare thin films for TEM observation. The coated layers have numerous internal micro and macro defects.
- 2) A protective anodic oxide film can be formed by anodizing coated steels in sodium borate solutions at pH = 9.2. After anodizing, the pitting potential of the coated steel becomes higher in the same solutions.
- 3) In sodium borate solution with and without Na_2SO_4 and $NaNO_3$, oxide films are reformed between -0.5 to 1 V vs. Ag/AgCl after removal of the anodic oxide film by photon rupture. The oxide film formation kinetics follows the inverse logarithmic law, according to Cabrera-Mott theory at the late stage after $t = 10$ ms. The SO_4^{2-} and NO_3^- ions accelerate dissolution of the coated layers.
- 4) Localized dissolution occurs at high potentials, while film reformation occurs at low potentials in Cl^- ions containing solutions.

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要 旨

フォトンラプチャー法, 集光したパルス YAG レーザー照射による皮膜の局部除去法をアノード酸化した Zn-55 mass% Al めっき鋼板の再不働態化及び局部腐食に適用した. Cl^- , NO_3^- および SO_4^{2-} を含む pH=9.2 の $\text{Na}_2\text{B}_4\text{O}_7$ の溶液に浸漬した試料に, 集光した 1 パルスの YAG レーザー光を照射し, 酸化皮膜を局部的に除去した際の電流の時間変化を測定した. NO_3^- および SO_4^{2-} 中においては, 照射後 10 ms 経過してから, Cabrera-Mott theory の機構による逆対数則に従って再不働態化した. 設定電位が高くなると, 溶解反応が加速されるため照射後の電流は大きくなった. Cl^- を含む溶液中においては, 電位が低いときは再不働態化するが, 電位が高くなると局部溶解が進行した.

キーワード Zn-55 mass% Al 合金めっき鋼板, 局部腐食, フォトンラプチャー法