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Elucidation of the Noise in Corrosion of Aluminum Foil

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Al foil used was 99.9 and 99.99 %. Test solution used was NaCl solution. The noise was determined using controlled potential electrolysis at -200 and -700 mV vs. NHE. The current fluctuation was caused by breakdown and repaired process of aluminum oxide film. The current fluctuation value of noise was proportion to degree of growth. The number of noise was proportion to the number of pit. The examining of current flutulation value and number of noise could be evaluated corrosion. A 99.99 % Al foil was the mostly crystal of {100} plane, and showed three-dimensional, as azimuth pit with along the direction of this place piled up. A 99.9 % Al foil was polycrystal, and in order of (311) > (222) > (200) > (111) plane. The azimuth pit did not occurred as the dissolution was occurred from each plane.

Keywords *: aluminum, pitting corrosion, electrochemical noise, NaCl solution*

1. Introduction

The localized corrosion generated by a deterministic chaotic process, whereas uniform corrosion is random process. Electrochemical noise can be considered as chaotic process. The measurements of electrochemical noise, spontaneous fluctuations of corrosion potential and/or current generated by corrosion reaction include: monitoring of current under potentiostatic control, potential under galvanostatic control, and potential and current fluctuations for freely corroding electrodes. In the literature, some different approaches have been proposed for performing electrochemical noise data analysis: statical analysis, spectral analysis, wavelet transform-based analysis and chaos theory-based methods.[1)-17)] The potential and current fluctuation during pitting corrosion is caused by breakdown and repair process aluminum oxide film in sodium chloride aqueous solution.[18)-20)]

In this study, the number of pit in the aluminum oxide film on current fluctuation during pitting was analyzed quantitatively by the experimental results.

2. Experimental

Fig. 1 shows the diagram of apparatus. Test solutions used 0.1~10% NaCl aqueous solutions. The working electrode (test peace) used 99.9% (thickness; 90 μm, impurity: Cu, 29; Si, 38; Mg, 3 ppm) and 99.99 % (thickness; 104 μm, impurity: Cu; 40; Si, 13; Fe, 8 and Mg, 7 ppm) Al foils and it exposed 1 x 1 cm. The counter electrode was platinum plate having exposed area of 2.5 x 4.0 cm. The reference electrode was saturated Ag/AgCl electrode. The noise was recorded using the transit converter TCFL-800 (Rika Denshi). The test piece was cleaned 2 mol/dm^3 NaOH solution for 1 min and rinsed in distilled water before the rest potential measurement. The pretreatment was not carried out in the measurement of the noise. The acrylic resin cell used was 3 x 4 x 5 cm, a 50 cm^3 of NaCl solution filled the cell. NaCl solution was presaturated with N_2 gas before the measurement, and it flowed over the NaCl solution at rate of 0.2 dm^3/min during the measurement.

3. Results and discussion

3.1 Rest potential

The rest potential of 99.9 % Al foil in a 0.5 % NaCl aqueous solution is shown in Fig. 1. The potential was changed very intensely, and shifted gradually noble direction as the immersion time proceeded. It was concluded that the breakdown of aluminum oxide film on surface by chloride ion and repair of oxide film caused. The repair of oxide film was more increased than the breakdown. The quantity of aluminum oxide film on the surface increased. The rest potential of 99.99 % Al foil had same tendency.

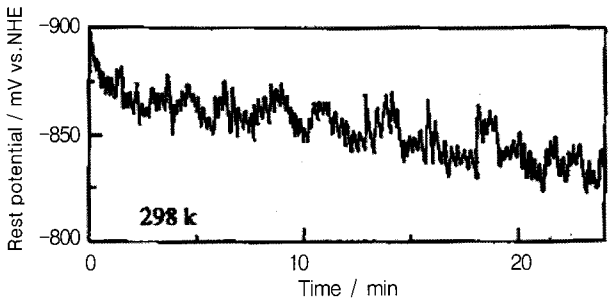

Fig. 1. Rest potential of 99.9 % Al foil in a 0.5 % NaCl aqueous solution

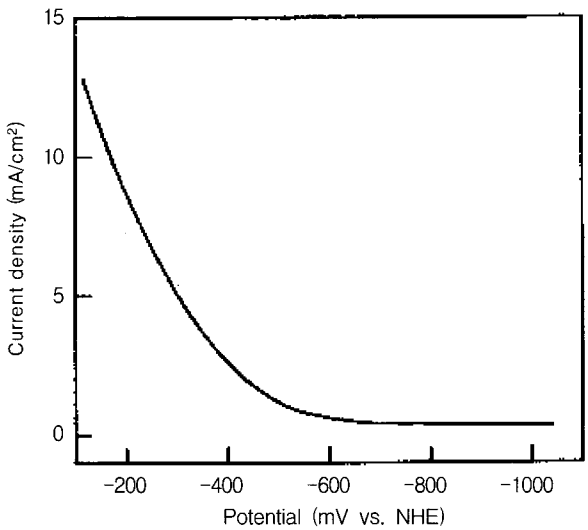

Fig. 2. Polarization curve of 99.9 % aluminum foil in 0.5 % NaCl solution

3.2 V-I curve

The polarization curve of 99.9 % aluminum foil in a 0.5 % NaCl solution is shown in Fig. 2. The current was decreased with decreasing of potential, and was slightly flowed under 600 mV vs. NHE.

3.3 Noise

The noise of corrosion was observed during controlled potential electrolysis at -200 and -700 mV vs. NHE. The noise for 40 min after electrolyte is shown Fig. 3 and 4. When the controlled potential electrolysis was carried out at -200 mV vs. NHE, the large number of noise in which the current fluctuation value was small appeared. The largest current fluctuation value increased, thereafter it was almost constant with the elapsed time. When the controlled potential electrolysis was carried out at -700 mV vs. NHE, the periodic noise was simply appeared.

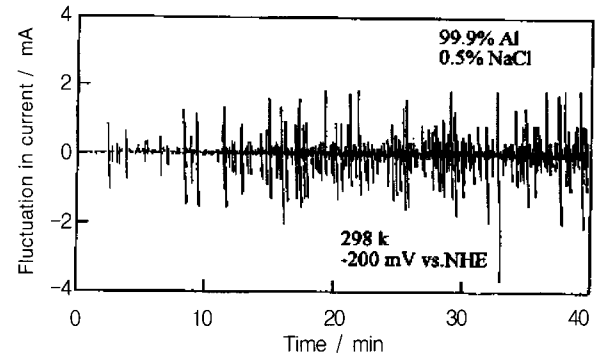

Fig. 3. Noise for 40 min after electrolyte Scan rate:50 mV/s

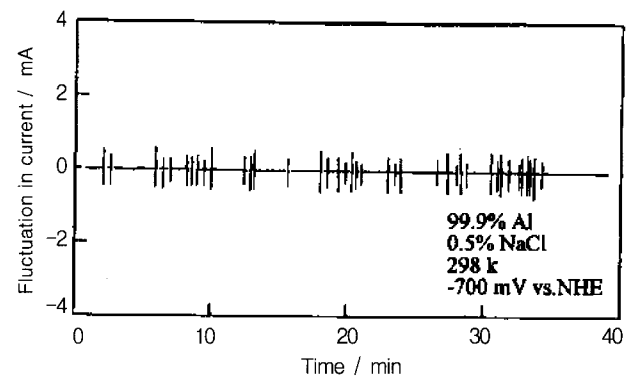

Fig. 4. Noise for 40 min after electrolysis

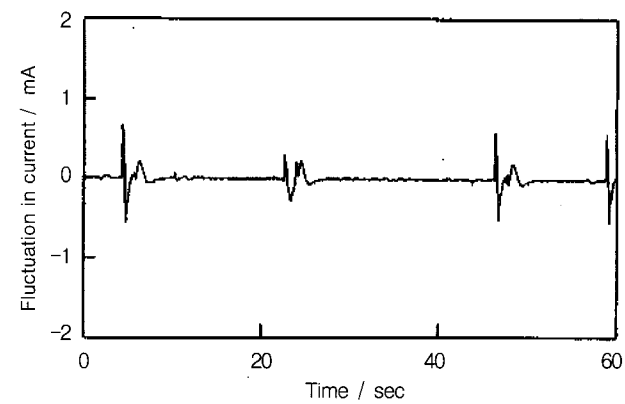

Fig. 5. Noise of 99.9 % Al foil for 1 min after electrolysis

The current fluctuation value had little or no change with the elapsed time. The noise of 99.9 % Al foil for 1 min after electrolyte is shown Fig. 5. The fluctuation current decreased after the increasing, thereafter it decreased after the increasing again. Using 99.99 % Al foil, other NaCl concentrations and potentials, noise had same pattern. It was concluded that the noise of corrosion appeared by the same mechanism. This waveform was caught at one

noise, and 1/2 of the lengths of upper and lower end was made to be the current fluctuation value. The noise was decided the current fluctuation value over 0.2 mA in this study. The effect of NaCl concentration on the current fluctuation within 5 min after the electrolysis is shown in Fig. 6. The current fluctuation after the electrolysis increased rapidly until 1% NaCl concentration, thereafter it increased slowly in the range of 1 ~ 3% concentration. When the controlled potential electrolysis was carried out at -700 mV vs. NHE, the noise in which the current fluctuation value had little or no difference with both 99.9 and 99.99 % Al foils. When the controlled potential electrolysis carried out at -200 mV, the difference of the current fluctuation after the electrolytes increased with increasing of NaCl concentration. The impurity in 99.9 % aluminum had larger effects as -200 mV vs. NHE of electrolysis was high corrosiveness. The electrolysis carried out at -700 mV in 15 min, the number of the noise is shown in Fig. 7. The number of the noise increased with elapsed time. However, a proportion of increasing was partially decreased. It was considered that it is based on the periodicity of the noise generation. To keep the same conditions, the number of pit over the about 40 μm diameters on aluminum surface is shown in Fig. 8. The number of pit was similarly increased with the noise number with elapsed time, a proportion of increasing partially decreased. The relationship between noise and pit could not be considered the perfectly one-to-one. It was estimated that pit number and noise number was correlated, as a proportion of increasing was similar against elapsed time. The quantitatively generation of pit was not possible to know by examining noise number. The corrosiveness could be compared with the different system. The diameter of typical size was measured when noise determined. The current fluctuation and diameter of pit

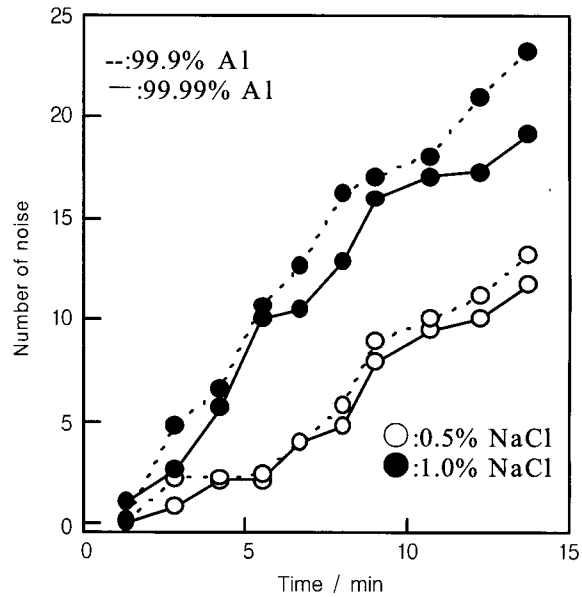

Fig. 7. Effect of electrolysis time on the number of noise

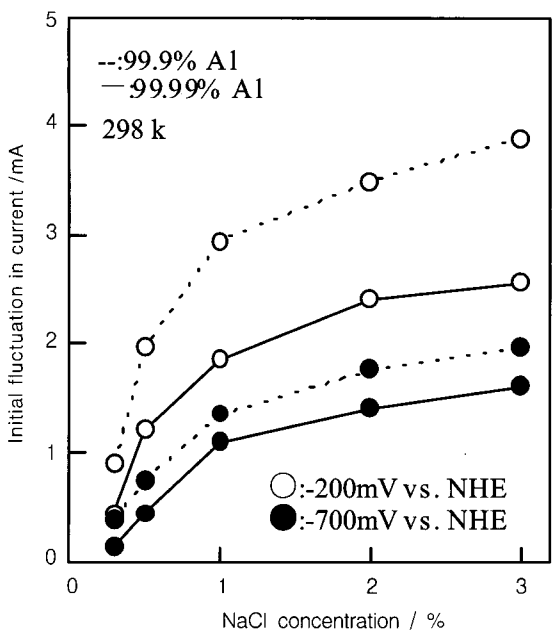

Fig. 6. Effects of NaCl concentration on the current fluctuation within 5 min after the electrolysis

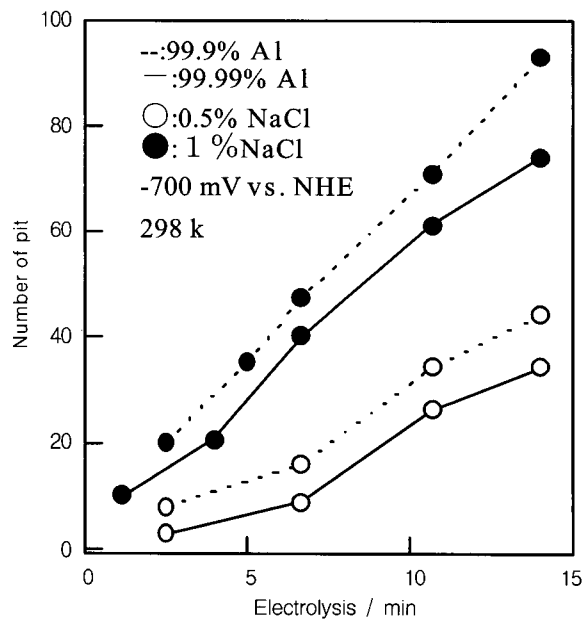

Fig. 8. Number of pit over the about 40 μm diameters on aluminum surface

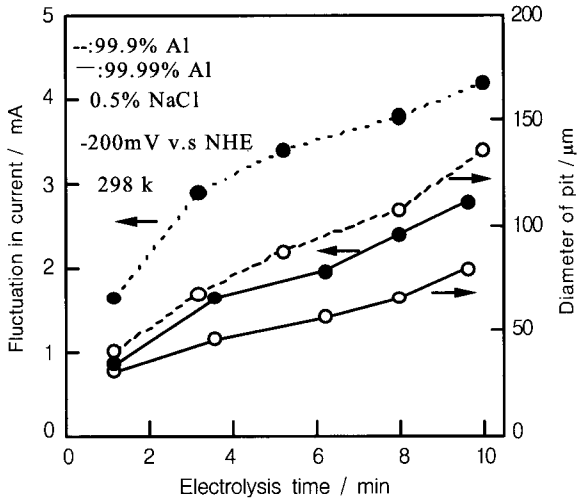

Fig. 9. Current fluctuation and diameter of pit at -200 mV and -700 mV

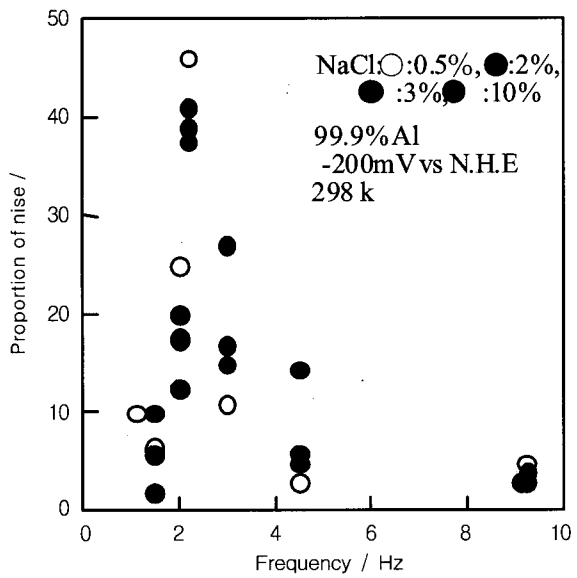

Fig. 10. The proportion of the frequency component which was included in the noise

at -200 mV is shown in Fig. 9. The diameter of pit increased to 140 μm in 99.9% Al foil and to about 80 μm in 99.99 % Al foil after 10 min at -200 mV vs. NHE. The current fluctuation values were also increased with the growth of pit. The diameter of pit increased to 50 μm in 99.9 % Al foil and to about 40 μm in 99.99 % Al foil after 20 min at -700 mV vs. NHE. The current fluctuation values were not changed. The growth of pit was inhibited.

Under this measurement condition, relation of the current fluctuation value in portion and the degree of growth of pit was not obtained quantitatively. An induced

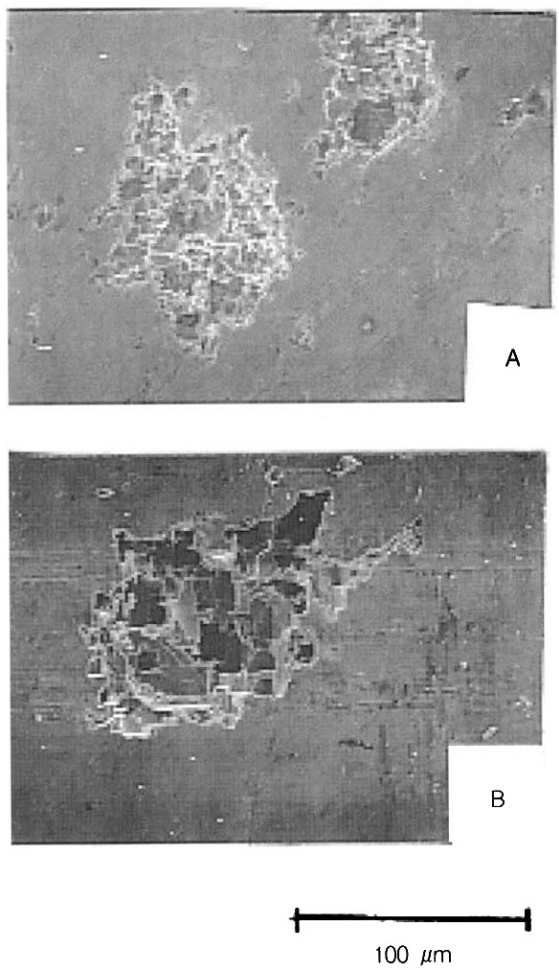

Fig. 11. Aluminum surface at the controlled potential electrolysis of -200 mV vs. NHE
A:99.9 % B:99.99 %

current fluctuation was proportional to the growth of specific pit. The correlation of diameter of pit was obtained to the current fluctuation value of noise. The proportion of the frequency component, which was included in the noise, is shown in Fig. 10. The proportion of 2.2 Hz was maximized and the similar distributed in 0 ~ 10 % NaCl solution. Velocity with which the reaction tacked place was the same.

The aluminum surface at the controlled potential electrolysis of -200 mV vs. NHE is shown in Fig. 11. A 99.99 % Al foil was the mestly crystal of {100} plane, and showed three-dimensional, as azimuth pit with along the direction of this place piled up. A 99.9 % Al foil was polycrystal, and in order of (311) > (222) > (200) > (111) plane. The azimuth pit did not occurred as the dissolution was occurred from each plane.

4. Conclusions

1) The current fluctuation was caused by breakdown and repaired process of aluminum oxide film.

2) The current fluctuation value of noise was proportion to degree of growth.

3) The number of noise was proportion to number of pit.

4) The examining of current flutulation value and number of noise could evaluate corrosion.

5) A 99.99 % Al foil was the mostly crystal of {100} plane, and showed three-dimensional, as azimuth pit with along the direction of this place piled up. A 99.9 % Al foil was polycrystal, and in order of (311) > (222) > (200) > (111) plane. The azimuth pits did not occurred as the dissolution was occurred from each plane.

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