HOKKAIDO UNIVERSITY

Title	Electrochemical noise analysis of galvanic corrosion of anodized aluminum in chloride environments
Author(s)	Sakairi, Masatoshi; 坂入, 正敏; Shimoyama, Ukiya et al.
Citation	Electrochemistry 電気化学および工業物理化学, 74(6), 458-462
Issue Date	2006-06
Doc URL	https://hdl.handle.net/2115/14554
Type	journal article
File Information	sakairi.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

Electrochemical Noise Analysis of Galvanic Corrosion of Anodized Aluminum in Chloride Environments

SAKAIRI Masatoshi, SHIMOYAMA Ukiya and TAKAHASHI Hideaki

Research Group of Interface Control Engineering Molecular Chemistry,

Graduate School of Engineering, Hokkaido University

Kita-13, Nishi-8, Kita-ku, Sapporo, 060-8628. Japan

Key words : electrochemical noise, anodizing, galvanic corrosion, aluminum, localized corrosion

ABSTRACT

A new type of electrochemical noise analysis technique with First Fourier Transformation, FFT, was applied to galvanic corrosion of barrier and porous type anodic oxide films formed on aluminum in 0.5 kmol/m^3 H_3BO_4 / 0.05 kmol/m^3 $Na_2B_4O_7$ solutions with 0.01 kmol/m^3 NaCl. During localized corrosion, the current and potential were changed, with fluctuations and the potential and the current fluctuations show good correlation. The slope of the PSD spectra of both types of anodized specimens are about minus one (-1), just after localized corrosion started. This technique allows observation of electrochemical impedance changes during localized corrosion. The impedance spectra are independent of signal frequency and the impedance of porous types anodic oxide film specimens decrease with immersion time and increases with anodizing time.

1. **Introduction**

Aluminum and its alloys are widely used, because of their high strength - weight ratio and high corrosion resistance. Aluminum and its alloys are sometimes joined to other metals in specific applications. Galvanic corrosion may occur in such situations and this is a very severe problem to the durability of some systems.

Aluminum and its alloys are usually used after surface treatment processing, such as anodizing and painting. There are two types of anodic oxide films, a porous type and a barrier type that can be formed on aluminum[1-4]. The barrier type anodic oxide film has an amorphous structure[5] and the thickness depends on the anodizing potential or voltage. The porous type anodic oxide film has an outer porous layer and an inner barrier layer[6]. The porous layer thickness increases linearly with anodizing time and the barrier layer thickness is dependent on anodizing solution and current density. Barrier type anodic oxide films are commonly used in electrolytic capacitors, and porous type anodic oxide films as insulators to create 2D or 3D structures [7-14] or molds [15-17]. However, the extent of the effect of the anodizing surface treatment on the galvanic corrosion of aluminum and its alloys joined to other dissimilar alloys has not been established.

Recently, an electrochemical noise analysis technique has been applied in a number of corroding environments[18-23]. Bertocci et al. [18,19] has reported a electrochemical noise technique employing a corrosion couple and FFT (First Fourier Transformation). Traditional electrochemical impedance techniques are not suitable to measure the impedance during galvanic corrosion, but, this new noise technique can obtain the impedance even with localized corrosion, because the impedance is calculated using a power spectrum density (PSD) of the current and potential. The purpose of this study is to apply the new electrochemical noise technique to galvanic corrosion of anodized aluminum and to examine the effect of anodic oxide film structure and thickness on the electrochemical impedance during galvanic corrosion.

2. Experimental

Specimen: Electro capacitor grade pure aluminum foils, 99.99 mass %, 0.4 mm thick, were cut into 20 x 20 mm^2 specimens with a handle. The specimens were degreased in an ethanol ultrasonic bath, electro-polished in a mixture of 70 mass % perchloric acid and acetic acid, volume ratio 1:4, at a constant voltage of 28 V, at 286 K. After electro-polishing, the specimens were rinsed in doubly distilled water and acetone.

Anodizing: Porous type anodic oxide films were formed by anodizing at 293 K in 0.22 $kmol/m^3$ oxalic acid solution with a constant current density, i_a = 100 A/m^2, for different time periods, t_a. Barrier type anodic oxide films were formed by anodizing at 293 K in a neutral 0.5 $kmol/m^3$ H_3BO_4 / 0.05 $kmol/m^3$ $Na_2B_4O_7$ solution with a constant applied current density of i_a = 10 A/m^2 initially and then the samples were anodized until the increasing potential reached a set value, after which the potential was kept constant for 1800 s. After anodizing, the edges and parts of the specimens were sealed with silicone resin and an area of 1 cm^2 was left exposed.

Galvanic corrosion: Specimens were dipped in 0.5 $kmol/m^3$ H_3BO_4 / 0.05 $kmol/m^3$ $Na_2B_4O_7$ solutions with 0.01 $kmol/m^3$ NaCl, and connected to a 8 cm^2 Pt plate to form the galvanic couple. The galvanic current and specimen potential during the test were measured for a data acquisition time of 5 s. The records of the current and potential were processed by calculating the power spectrum density (PSD) with the FFT method using 1024 points. The electrochemical noise impedance was calculated from the current PSD and potential PSD values.

Characterization : After the galvanic corrosion tests, specimen surfaces were examined by a confocal scanning laser microscope (CSLM; 1SA21, LASERTEC Co.).

3. Results and Discussion

3.1 Galvanic corrosion

Figure 1 shows anodizing curves for both porous and barrier type anodic oxide films. Initially, both curves show an almost linear potential increases with time, after the porous type anodic oxide film reaches a maximum it decreases some what and settles to an almost constant potential for the remainder of the anodizing time. With the barrier type anodic oxide film the anodizing mode was changed from constant current to constant potential when the potential reached 50 V, and following that the current decreased rapidly with time. The anodizing curves of the porous type and barrier type anodic oxide films are different due to the existence of a porous layer with a thickness of about 1.5 μm.

Figure 2 shows the change in the potential (a), and current (b) with immersion time, t_i, during galvanic corrosion of Pt coupled to Al covered with barrier type anodic oxide film, E_a = 50 V, in 0.5kmol/m^3 H_3BO_3 / 0.05 kmol/m^3 $Na_2B_4O_7$ with 0.01 kmol/m^3 NaCl. During the incubation period (t_i < 45 ks), nether the current nor the potential change from their initial values, however, after 45 ks, there are sudden change as indicated by the electrochemical noise fluctuations, likely related to localized corrosion.

Figure 3 is a magnification of the potential and the current in Fig. 2 at just after the localized corrosion has started. The potential and current move in opposite directions, and show good correlation, the correlation coefficient is about 0.9. The current and potential fluctuations may be related to the generation, growth and extinction of instances of localized corrosion or pitting corrosion.

Figure 4 shows the change in the potential (a), and current (b) with immersion time, t_i, during galvanic corrosion of Pt coupled to Al covered with porous type anodic oxide film, t_a = 300 s, in 0.5kmol/m^3 H_3BO_3 / 0.05 kmol/m^3 $Na_2B_4O_7$ with 0.01 kmol/m^3 NaCl. During the incubation period (< 190 ks), neither current nor potential change from the initial values, however, after 190 ks, there

are sudden changes as indicated by the electrochemical noise fluctuation, related to localized corrosion.

The incubation periods were widely scattered because of localized corrosion is a stochastic process. However, for similar thickness of barrier layer the incubation periods of the porous type anodic oxide film specimens were always longer than that of the barrier type anodic oxide film specimens. This results suggests that the porous layer affects the incubation period of galvanic corrosion differently from the barrier layers.

Figure 5 shows a magnification of the potential and the current in Fig. 4 at just after the localized corrosion has started. Each small current fluctuation correlates well with the potential fluctuations, the correlation coefficient is about 0.9. The amplitude of the potential and current fluctuations of the porous type anodic oxide film specimens (Fig. 2) are smaller than that of the barrier type anodic oxide film specimens (Fig. 4). This suggests that the porous layer has good corrosion resistance after the incubation period. After the experiment, the specimen surfaces were observed by CSLM. When the experiment was terminated just after localized corrosion started a corrosion pit was observed. After the experiments showing Figs 2 and 4 there were many pits with corrosion products on the all specimens. These results strongly suggest that the current and potential changes are related to the initiation of localized corrosion. The electrochemical noise fluctuations would also be related to localized corrosion.

3.2 Power spectrum density of electrochemical noise

Figure 6 shows the PSD of the potential (a), current (b), and impedance (c) of Al covered with barrier type anodic oxide film E_a= 50 V in 0.5 kmol/m^3 H_3BO_4 / 0.05 kmol/m^3 $Na_2B_4O_7$ solution with 0.01 kmol/m^3 NaCl. The potential and current PSD decrease with increasing frequency with slopes slightly steeper than minus one (-1), the impedance spectra show no clear frequency dependence. The potential PSD and the impedance decreases slightly with immersion time.

Figure 7 shows the PSD of the potential(a), current (b), and impedance (c) of Al covered with porous type anodic oxide film, t_a = 300 s, in 0.5 kmol/m^3 H_3BO_4 / 0.05 kmol/m^3 $Na_2B_4O_7$ solution with 0.01 kmol/m^3 NaCl. At t_i = 193ks, the potential and current PSD decrease with increasing frequency and the slopes are steeper than or equal to -1; at t_i = 213 ks, these is no clear dependence on the frequency. The potential PSD shifts to low frequencies and the impedance is also lower with longer immersion times.

Figure 8 shows the change in the mean value of the electrochemical noise impedance with time elapsed from the start of the localized corrosion (from end of incubation time) in 0.5 kmol/m^3 H_3BO_4 / 0.05 kmol/m^3 $Na_2B_4O_7$ solution with 0.01 kmol/m^3 NaCl. The impedance with the porous type anodic oxide film is higher than that of the barrier type film just after the localized corrosion has started. However, after some time, the impedance of the barrier type anodic oxide film specimens is higher than that of t_i = 120s porous type anodic oxide film. This may be because the dissolution area was covered with compact corrosion product. The impedance of the porous type anodic oxide film specimen increases with increasing anodizing time. These impedance values are in good agreement with the incubation period observed during the galvanic corrosion test. From the results, it may be concluded that the porous layer thickness affects the corrosion resistance of aluminum.

4. CONCLUSIONS

A new type of electrochemical noise analysis was applied to galvanic corrosion of two different types of anodic oxide film on aluminum specimens. The following conclusions may be drawn:

1) During an incubation period, the initial current and potential values change slightly only with

time. When localized corrosion has started, however, the values changed suddenly with continuous with fluctuations. The potential and the current fluctuations show a good correlation.

2) The slope of the current and potential PSD spectra of both types of anodized specimen is about minus one (-1) just after localized corrosion has started. After long immersion, the slope of the PSD of the porous type oxide film specimen becomes flatter.

3) The employed noise technique makes it possible to measure the electrochemical impedance during localized corrosion and the values do not change with frequency. The impedance of porous types anodic oxide film specimens decreases with immersion time and increases with increasing anodizing time.

Acknowledgements

The results here were originally presented at the 206th Meeting of The Electrochemical Society, Inc., 2004 Fall Meeting of The Electrochemical Society of Japan, and has appeared in The Electrochemical Society Proceedings Series, PV 2004-14, pp. 265-272.

References

1) K. Watanabe, M. Sakairi, H. Takahashi, S. Hirai, and S. Yamaguchi, J. Electroanal. Chem., 473, 250 - 255 (1999)

2) Y. Li, S. Shigyo, M. Sakairi, H. Takahashi and M. Seo, J. Electrochm. Soc., 144, 866 - 876 (1997).

3) M. Sakairi, P. Skeldon, G. E. Thompson, G. C. Wood, and K. Stevens, Proc. of ASST 2000, 410 - 415 (2000).

4) M. Sakairi, P. Skeldon, G. E. Thompson, G. C. Wood, and K. Stevens, Electrochem. Soc. Proc., 99-27, 171-180 (1999).

5) Y. Takashima, K. Miwa, M. Sakairi and H. Takahashi, J. Surf. Fin. Soc. Jpn., 51, 625 (2000).

6) M. Sakairi, Z. Kato, S. Chu, H. Takahahshi, Y. Abe and N Katayama, Electrochemistry, 71, 920 (2003).

7) M. Sakairi, J. Wakabasyshi, H. Takahashi, Y. Abe and N. Katayama, J. Surf. JPN., 49, 1227 (1998).

8) S. Z. Chu, M. Sakairi, H. Takahashi, and Z. X. Qiu, J. Electrochem. Soc., 146, 537 - 546 (1999)

9) S. Z. Chu, M. Sakairi, and H. Takahashi, J. Electrochme. Soc., 147, 1423 (2000).

10) S. Z. Chu, M. Sakairi, and H. Takahashi, K. Shimamura and Y. Abe, J. Electrochme. Soc., 147, 2181 (2000)

11) M. Sakairi, Z. Kato, S. Z. Chu, H. Takahashi, Y. Abe, and N. Katayama, Electrochemistory, 71, 920 (2003).

12) T. Kikuchi, M. Sakairi, H. Takahashi, Y. Abe, and N. Katayama, Surface and coatings technology, 169-170, 199 (2003).

13) T. Kikuchi, M. Sakairi and H. Takahashi, J. Electrochem. Soc. 150, C567 (2003).

14) T. Kikuchi, M. Sakairi, H. Takahashi, Y. Abe, and N. Katayama, J. Electrochem. Soc.,148, C740 (2001).

15) T. Yanagishita , Y. Tomabechi, K. Nishio, H. Masuda, Langmuir, 20, 554 (2004).

16) F. Matsumoto, K. Nishio, T. Miyasaka, H. Masuda, Jpn. J. App. Phys. 2-Letters & Express Letter 43 (5A), L640 (2004).

17) H. Masuda, F. Matsumoto and K. Nishio, Electrochemistry 72, 389 (2004).

18) U. Bertocci, C. Gabrielli, F. Huet and M. Keddam, J. Electrochem. Soc., 144, 31 (1997).

19) U. Bertocci, C. Gabrielli, F. Huet, M. Keddam and P Rousseau, J. Electrochem. Soc., 144, 37 (1997).

20) T. Tsuru and M. Yaginuma, Zairyo-to-Kankyo, 52, 488 (2003).

21) H. Yashiro, M. Kumagai and M. Kumagai, ibid, 52, 466 (2003).

22) Y. Ioti, S. Take and Y. Okuyama, ibid, 52, 471 (2003).

23) Y. Yoneda and H. Inoue, ibid, 52, 495 (2003).

Captions

Fig. 1 Anodizing curves of porous and barrier type anodic oxide films.

Fig. 2 Changes in the potential (a), and current (b), with time during galvanic corrosion of Al covered with barrier type anodic oxide film, E_a = 50 V, in 0.5kmol/m^3 H_3BO_3 / 0.05 kmol/m^3 $Na_2B_4O_7$ with 0.01 kmol/m^3 NaCl.

Fig. 3. Magnification of a part of the potential and current in Fig. 2.

Fig. 4 Changes in the potential (a), and current (b), with time during galvanic corrosion of Al covered with porous type anodic oxide film, t_a = 300 s, in 0.5kmol/m^3 H_3BO_3 / 0.05 kmol/m^3 $Na_2B_4O_7$ with 0.01 kmol/m^3 NaCl.

Fig. 5 Magnification of a part of the potential and current in Fig. 4.

Fig. 6 PSD of the potential (a), current (b), and impedance (c) in Fig. 2. For t_i = 43.7 ks just after localized corrosion has started and for t_i = 68.8 ks is just before the end of the experimental.

Fig. 7 PSD of the potential (a), current (b), and impedance (c) in Fig. 4. For t_i = 196 ks just after localized corrosion has started, and for t_i = 213 ks 20 ks after the start of localized corrosion.

Fig. 8 Changes in the electrochemical noise impedance of the anodic oxide film specimens with time elapsed after the start of localized corrosion (from end of incubation time).

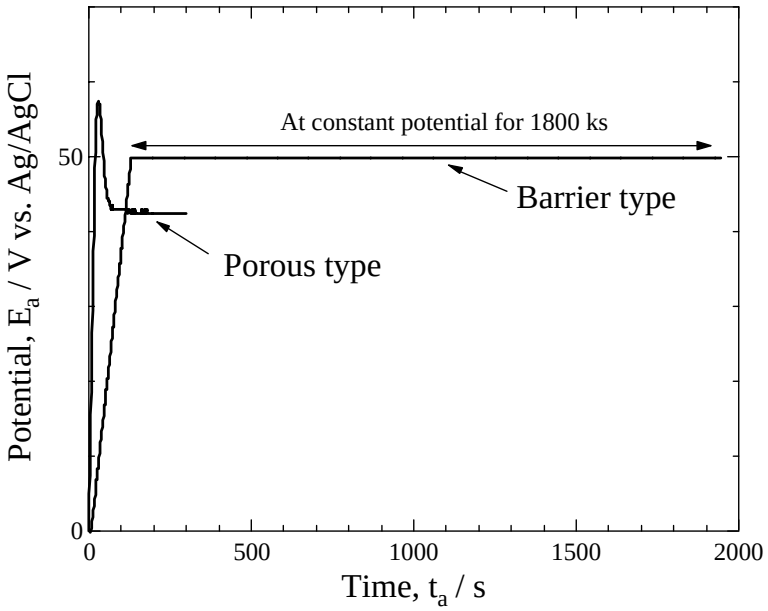

Fig. 1 Sakairi et al.

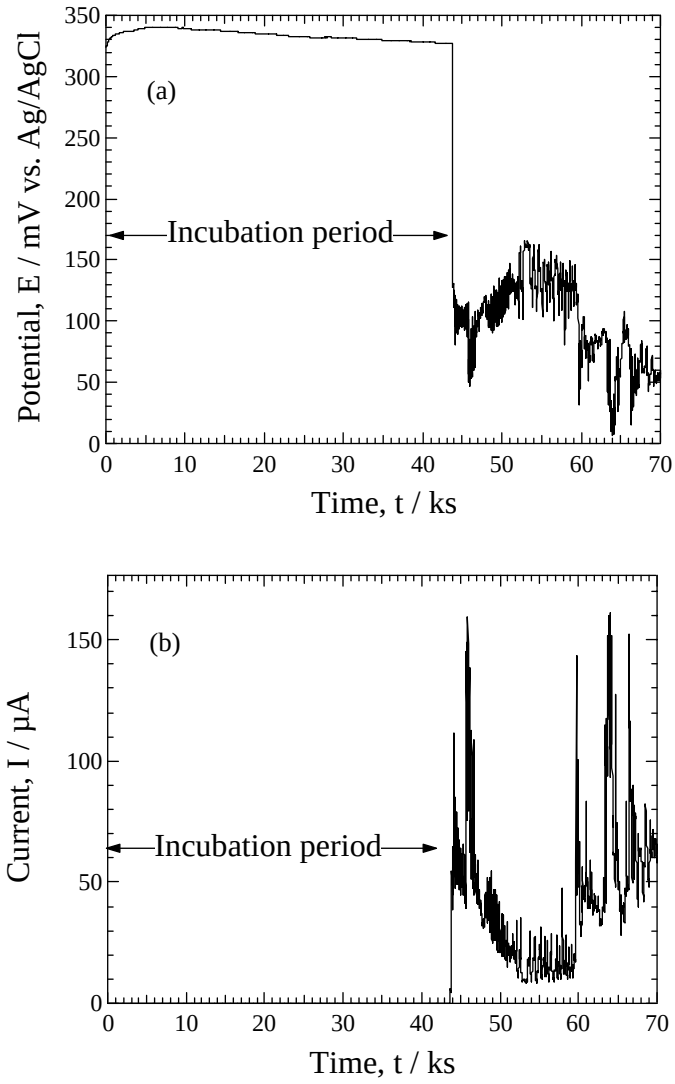

Fig. 2 Sakairi et al.

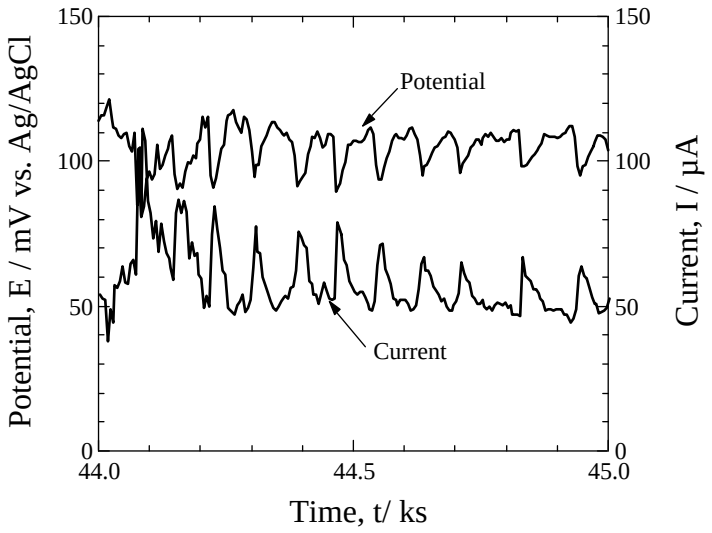

Fig. 3 Sakairi et al.

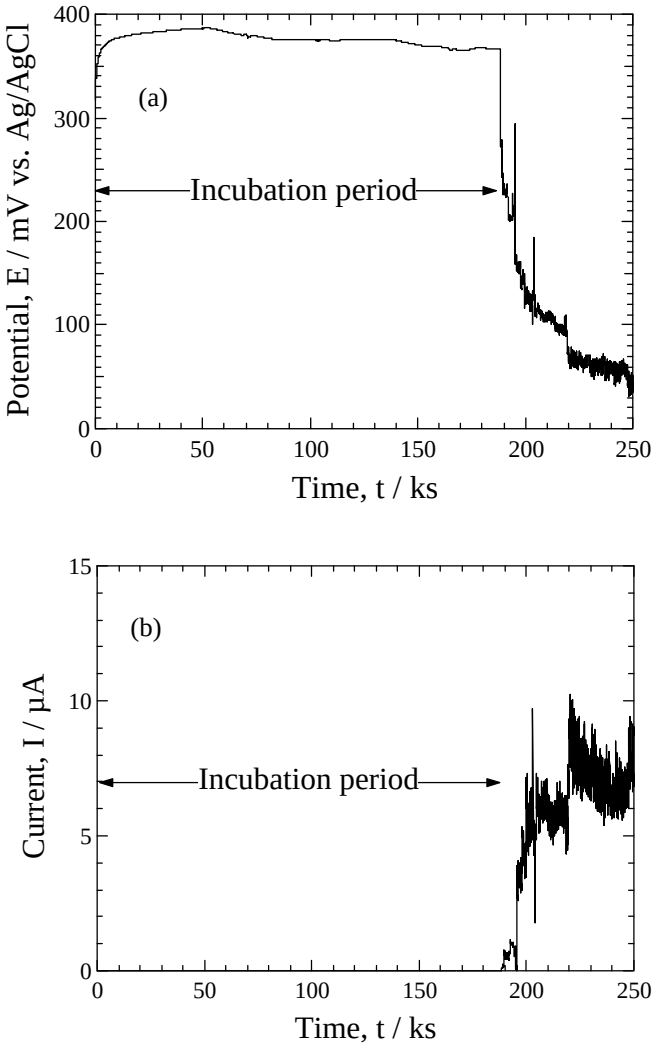

Fig. 4 Sakairi et al.

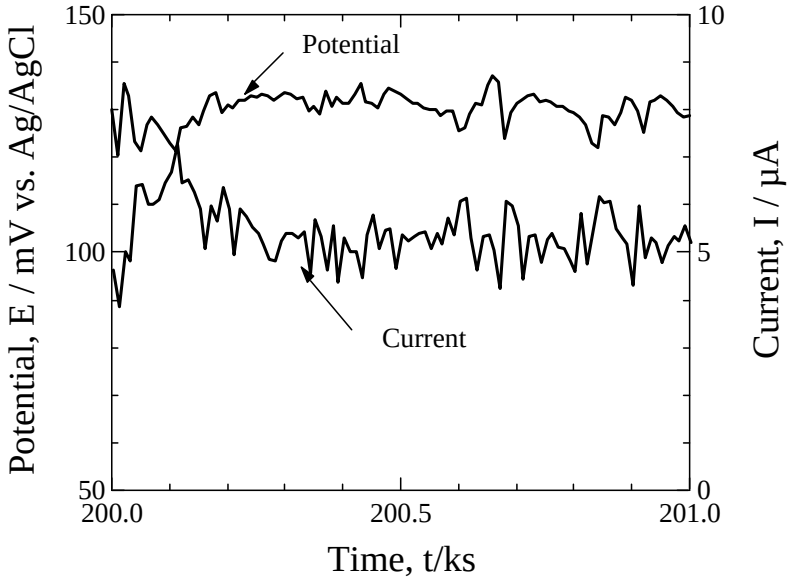

Fig. 5 Sakairi et al.

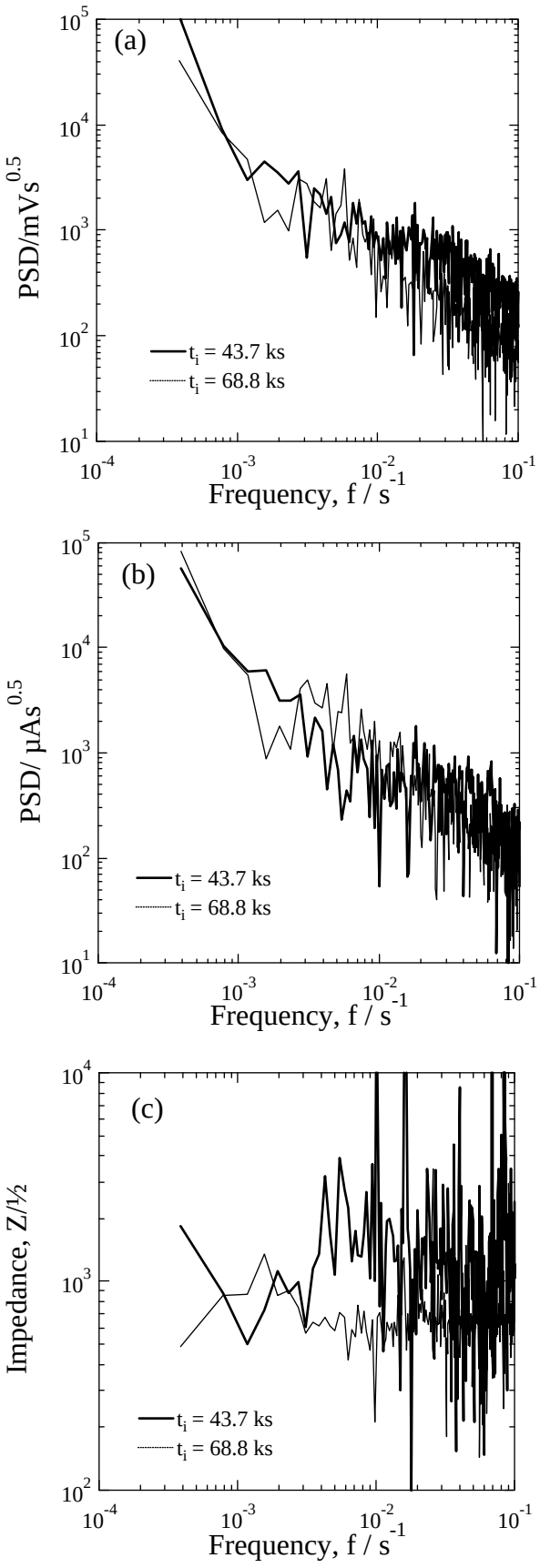

Fig. 6 Sakairi et al.

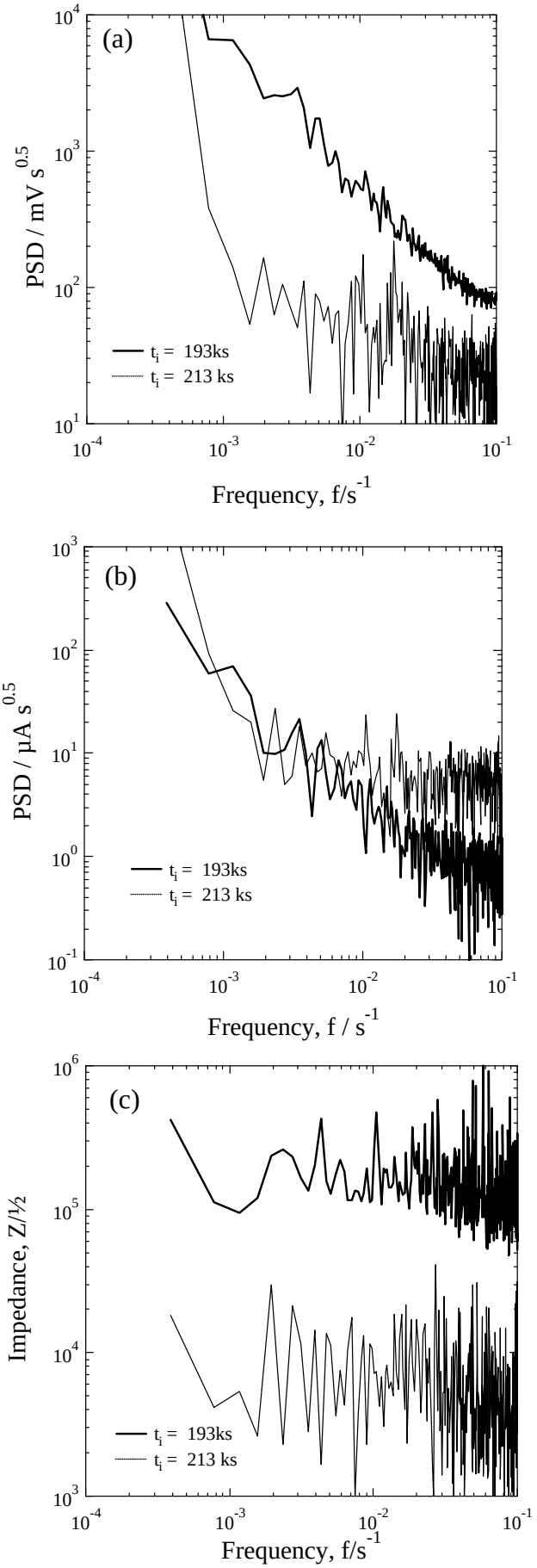

Fig. 7 Sakairi et al.

Incubation period

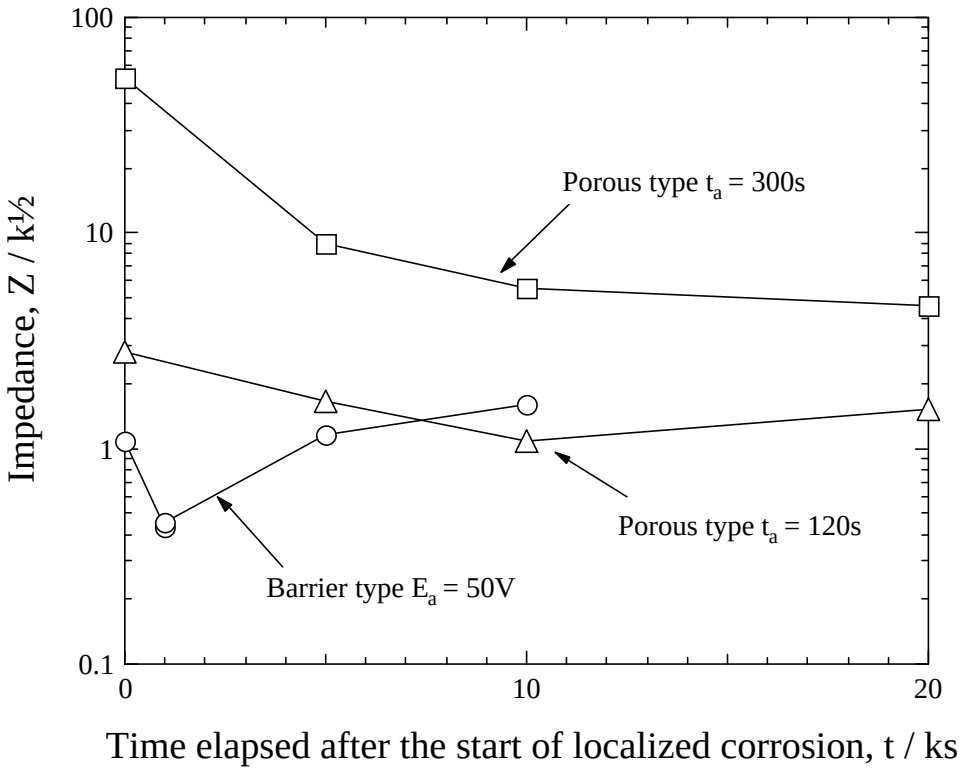

Fig.8 Sakairi et al.