

## Sealing Mechanism of Anodic Porous Oxide Films Formed on Aluminum in Lithium Hydroxide Solution

Sachiko ONO<sup>1</sup>, Masahiro OKURA<sup>1</sup>, Hidetaka ASOH<sup>1</sup>,  
Hiroomi TANAKA<sup>2</sup> and Tomoharu YAMAMOTO<sup>2</sup>

<sup>1</sup>Department of Applied Chemistry, Faculty of Engineering, Kogakuin University, 2665-1 Nakano, Hachioji, Tokyo 192-0015,

Japan <sup>2</sup>Suzuki Motor Corporation, 300 Takatsuka, Minami-ku, Hamamatsu 432-8611, Japan

A novel sealing process for porous anodic oxide films formed on aluminum using lithium hydroxide solution has been studied to clarify its mechanism. After sealing of anodic films in a lithium hydroxide solution at room temperature, platelet-like precipitates composed of  $\text{LiH}(\text{AlO}_2)_2 \cdot 5\text{H}_2\text{O}$  and hydrated alumina were formed on the surface as well as in the pores. Although the sealing temperature was lower and the treatment time was shorter than those of conventional hydration sealing or nickel salt sealing, comparable or rather superior corrosion resistance of the sealed anodic film treated in lithium salt was confirmed from the result of copper accelerated acetic acid salt spray test (CASS test). The sealing behavior was significantly dependent on the type of anodizing electrolyte used since the sealing proceeded through dissolution/precipitation stages of a pore wall of anodic oxide in which electrolyte anion species were incorporated.

**Keywords:** Aluminum, Anodic oxide film, Sealing, Corrosion resistance, Electrolyte anion.

### 1. Introduction

Anodization has been widely used as an excellent surface finishing process for aluminum to confer high corrosion resistance and fair appearance to the substrate surface [1-3]. To further improve the corrosion resistance, pores of the anodic film were sealed by treating the film in boiling water or hot steam to hydrate the oxide [4]. The mechanism of such hydration sealing was explained as a volume expansion of hydrated alumina that fills the pores [5-8]. These explanations were based on the uniform pore shrinkage during sealing treatment. Ono et al. [9, 10] reported hydration behavior through the dissolution of pore walls and the precipitation of platelet-like hydroxide in pores as well as on the top surface as determined by direct TEM observation of the cross sections of films. Consequently, a sealed film was found to be composed of an outer thick platelet hydroxide layer and an inner dense hydroxide layer with a porous layer filled with dense hydroxide.

Another sealing process that entails treating the porous oxide in a nickel salt solution including nickel ions [11] is also widely used. Recently, a novel sealing process [12] has been developed that entails dipping a specimen in a lithium hydroxide solution at room temperature for a short time. In this study, we investigated in detail the sealing mechanisms of porous anodic oxide films using lithium hydroxide solution as well as the mechanism of other conventional sealing processes.

### 2. Experimental

#### 2.1 Anodizing and sealing

High-purity (99.99%) aluminum sheets were electropolished in a 4:1 mixture of ethanol and 60% perchloric acid at 10°C. Anodization was conducted in 1.5 mol dm<sup>-3</sup> sulfuric acid solution (20°C) at 20 V for 10 min or in 0.3 mol dm<sup>-3</sup> oxalic acid (30 °C) at 40 V for 30 min to obtain an approximately 13 μm thick film. Sealing was performed in 0.24 mol dm<sup>-3</sup> lithium hydroxide solution at 25 °C for an adequate time. The pH of the lithium solution was about 13. Conventional sealing treatments by

dipping in boiling water for 10 min or in boiling commercially available nickel salt sealing bath (top seal) for 20 min were also conducted for reference.

## 2.2 Evaluation and characterization

Accelerated corrosion test by CASS was performed to evaluate corrosion resistance. The sealing process for each anodic film was examined using field emission scanning electron microscopy (FESEM) for morphological changes of the oxide cross section as well as EDX for compositional analysis and glow discharge optical emission spectroscopy (GDOES) for depth profiles of constituent elements.

## 3. Results and discussion

### 3.1 Morphological change after sealing

SEM images of the surface and cross section of the anodic films formed in sulfuric acid at 20 V for 10 min after the various sealing treatments by dipping in (a) boiling water for 10 min, (b) boiling nickel salt solution for 20 min, and (c) lithium hydroxide solution at 25 °C for 1 min are shown in Fig. 1. In the case of the conventional hydration sealing (a), a platelet-like hydrated oxide layer with a thickness of 200-300 nm was found on the top of the oxide film. At the same time, thin platelet-like hydroxides were formed in the pores. In contrast, only a grain like precipitate was found in the pore as well as on the surface of the film after sealing treatment in the nickel salt solution (b). As clearly shown in Fig. 1(c), platelet-like hydroxide layer having a thicker and larger size than those observed in the water hydration sealing were found on the top surface of the film. Porous cells underneath the surface of the film also formed a dense aggregate of hydroxide platelets. These results suggest that different sealing processes have different sealing mechanisms.

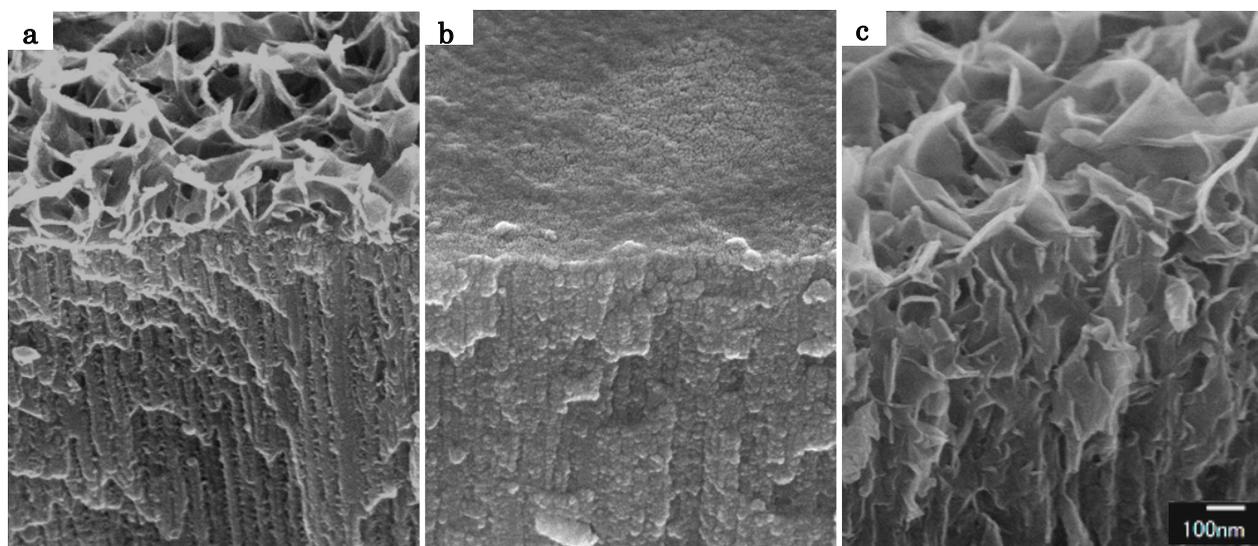


Fig. 1 SEM images of surface and cross section of anodic films formed in sulfuric acid at 20 V after sealing by dipping in (a) boiling water for 10 min, (b) boiling Ni-salt solution (top seal) for 20 min, and (c) lithium hydroxide solution at 25 °C for 1 min.

Then, the change in structure with sealing time in lithium hydroxide solution was examined and is shown in Fig. 2. By comparing the porous structure of the anodic film before sealing indicated in (a) with that of the film after 10 s sealing indicated in (b), it became clear that the pores were substantially widened within a short time by the dissolution of pore walls in the strong alkaline

lithium hydroxide solution. Although no SEM image of this is shown here, a small amount of platelet-like hydroxide was precipitated at the upper middle part of the film in this stage. After 30 s, however, the pores at the upper layer as well as on the surface were filled with platelet-like hydroxide; however, the bottom of the pores remained unsealed.

Therefore, the process for sealing in lithium hydroxide solution is suggested as follows: First, the pore wall of an anodic film is dissolved, and subsequently, platelet-like hydroxide including lithium and aluminum precipitates in the pores. XRD analysis indicated that the sealed anodic film was composed of  $\text{LiH}(\text{AlO}_2)_2 \cdot 5\text{H}_2\text{O}$  and hydrated alumina. Next, as a result of the continuous dissolution of the oxide, hydroxide precipitates mainly near the surface region of the film followed by a significant growth at the outer surface. The reason for the delay of sealing at the lower part of the film could be the reduced alkaline strength of lithium solution caused by sulfate species incorporated in the anodic oxide film during anodization [13] since the circulation of the solution is limited when the pores at the upper part of the film are filled with hydroxide precipitates.

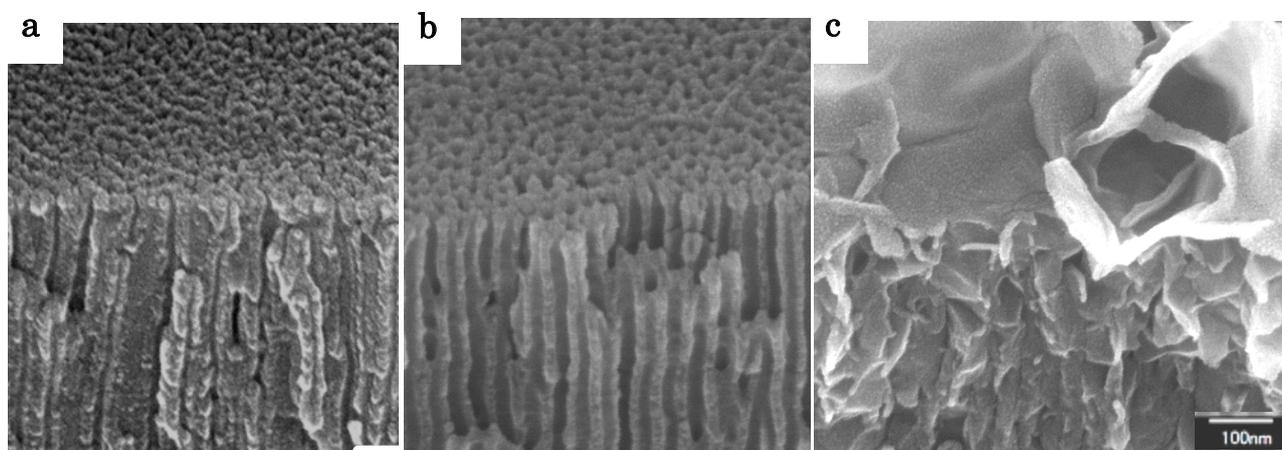


Fig. 2 SEM images of surface and cross section of anodic films formed in sulfuric acid after sealing by dipping in lithium hydroxide solution at 25 °C for (a) 0 s, (b) 10 s, and (c) 30 s.

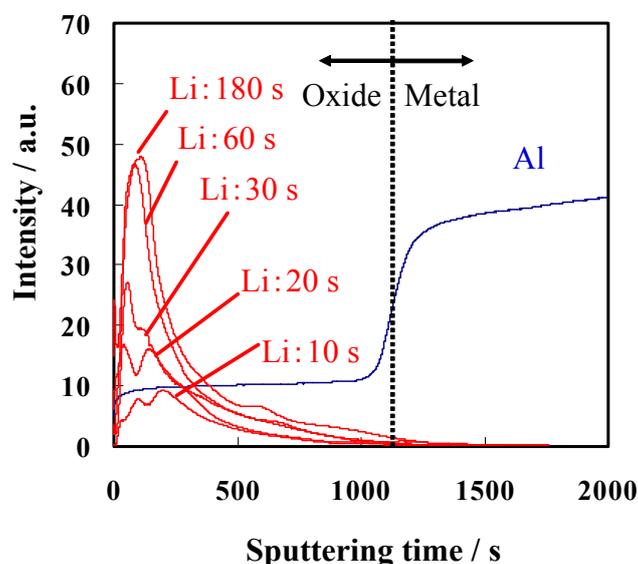


Fig. 3 Depth profiles of Al and Li in sealed anodic films formed in sulfuric acid at 20 V. Sealing was performed in lithium hydroxide solution for different times.

### 3.2 Change in depth profile of elements during sealing

The depth profiles of constituent elements were measured by GDOES with a change in sealing time from 10 s to 3 min in a lithium hydroxide solution. As shown in Fig. 3, lithium was found at the upper middle part of the film after 10 s and the intensity of lithium increased with increasing sealing time especially near the surface region. Lithium content saturated after 1 min, suggesting that the sealing was almost completed within a short time, i.e., 1 min. The sealing procedure revealed by the change in the depth profile of lithium with sealing time is consistent with the morphological changes observed by SEM.

In the film formed in oxalic acid (Fig. 4), Lithium was first found at the lower middle part of the film after 1 min of sealing unlike in the film formed in sulfuric acid. At this time, although no precipitation of platelet-like hydroxide at the top surface was observed by SEM, hydroxide precipitation was clearly observed at the lower part of the film. With increasing sealing time, the intensity of lithium increased at the middle part, and finally, after 3 min, it increased especially in the near-surface region, similarly to that in the film formed in sulfuric acid. Thus, the initial precipitation occurred at the bottom half in the film formed in oxalic acid. The difference in the initial precipitation position between both films could be related to the difference in the type of anion species embedded in the pore walls as well as the size of the pores.

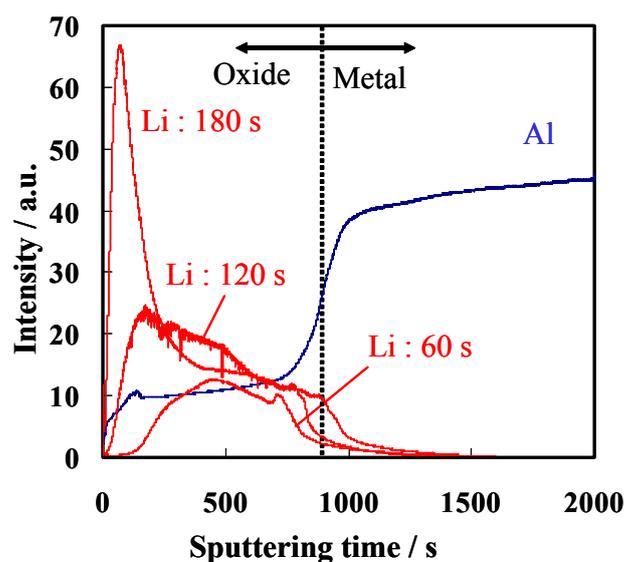


Fig. 4 Depth profiles of aluminum and lithium in the sealed anodic films formed in oxalic acid at 40 V. Sealing was performed in lithium hydroxide solution for different times.

### 3.3 Corrosion resistance

Figure 5 shows micrographs of the surface after the CASS test for 48 h of anodic films after sealing by dipping in (a) boiling water for 10 min, (b) boiling nickel salt solution for 20 min, and (c) lithium hydroxide solution at 25 °C for 1 min. The oxide film partly peeled off in the case of boiling water sealing. In the case of nickel salt sealing, the oxide film granularly detached from the substrate. In contrast, the oxide film remained on the substrate, although small cracks were found throughout the film. Therefore, it can be stated that the novel sealing process using lithium hydroxide solution result in a corrosion resistance comparable to or higher than those in the case of conventional sealing processes.

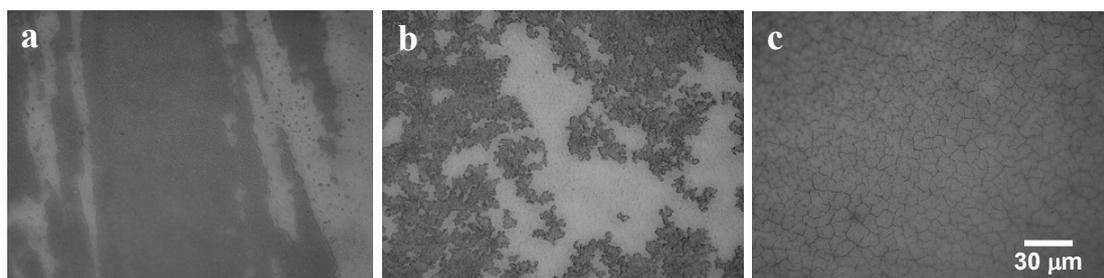


Fig. 5 Micrographs of the surface of sealed anodic films after CASS test for 48 h: (a) boiling water for 10 min, (b) boiling Ni-salt solution for 20 min, and (c) lithium hydroxide solution at 25 °C for 1 min.

#### 4. Conclusions

By applying a novel sealing process to anodic oxide films using lithium hydroxide solution, the mechanism of this novel sealing processes including conventional sealing processes has been investigated. After sealing anodic films in a lithium hydroxide solution at room temperature for 1-2 minutes, platelet-like precipitates composed of  $\text{LiH}(\text{AlO}_2)_2 \cdot 5\text{H}_2\text{O}$  and hydrated alumina were formed on the surface as well as in the pores. The sealing in lithium hydroxide solution is explained by dissolution/precipitation process at the pore wall of anodic oxide. First, the pore wall of anodic film is dissolved under highly alkaline condition, and subsequently, platelet-like hydroxide including lithium and aluminum precipitates in the pores. Next, as a result of the continuous dissolution of the oxide, hydroxide precipitates mainly in the near-surface region of the film followed by a significant growth of the precipitates at the outer surface in the case of the anodic film formed in sulfuric acid. In the case of the anodic film formed in oxalic acid, the initial precipitation of hydroxide occurred at the lower part of the film. Thus, the sealing behavior was significantly dependent on the type of anodizing electrolyte used since the sealing proceeded through dissolution/precipitation stages of a pore wall of an anodic oxide layer in which electrolyte anion species was incorporated. Although the sealing temperature was lower and the treatment time was fairly shorter than those of conventional sealing processes such as boiling hydration sealing and nickel salt sealing, a comparable or rather superior corrosion resistance of the anodic film treated in lithium salt was confirmed from the result of the CASS test.

#### Acknowledgements

Part of this work was financially supported by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science and the Light Metal Education Foundation of Japan. Thanks are also due to the “High-Tech Research Center” Project for Private Universities: matching fund subsidy from the Ministry of Education, Culture, Sports, Science and Technology.

#### References

- [1] K. Kujirai and S. Ueki: Japan Patent, 61920 (1923).
- [2] G. D. Bengough and J. M. Stuart: British Patent, 223994 (1923).
- [3] S. Ono and N. Baba: *Keikin-zoku*, **40** (1990) 729.
- [4] S. Setoh and A. Miyata: *Inst. Phys., Chem. Res.*, **17** (1932) 189.
- [5] T. P. Hore and G. C. Wood: *Proc. Conf. Anodizing Aluminium, Nottingham*, 1961, (1962) p.186.
- [6] R. C. Spooner and W. J. Forsyth: *Plating*, **55** (1968) 463.
- [7] K. Wefers: *Aluminium*, **49** (1973) 622.

- [8] M. Koda, H. Takahashi and M. Nagayama: J. Surf. Finish. Soc., **33** (1982) 242.
- [9] S. Ono, K. Wada, T. Yoshino, K. Wada and N. Baba: J. Surf. Finish. Soc. Jpn., **40** (1989) 1039.
- [10] S. Ono: J. Vac. Soc. Jpn., **52** (2009) 637.
- [11] T. P. Hore and G. C. Wood: Electrochim. Acta, **7** (1962) 333.
- [12] H. Tanaka, T. Yamamoto and M. Fujita: Japan Patent, 2010-77532 (2010).
- [13] S. Ono, K. Takeda and N. Masuko: Proc. of the 2nd Int. Symp. on Aluminium Surf. Sci. and Tech., (2000) pp.398-pp.403.