

Improvement of Corrosion Resistance of Aluminum Alloy with Wettability Controlled Porous Oxide films

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The combined process of porous type anodizing and desiccation treatment was applied to improve wettability of A1050 aluminum alloy. The water contact angles of anodized samples were increased considerably with desiccation treatment. However, there was no considerable effect of polishing and anodizing time on water contact angle. The corrosion behavior with the treatments was investigated electrochemically. The corrosion resistance of the samples in 3.5 mass% NaCl solutions increased with higher contact angle. Anodized and desiccated samples showed better corrosion resistance than un-desiccated samples around rest potential region.

Keywords : aluminium, anodizing, wettability, desiccation

1. Introduction

There is a rising demand for improvements in the corrosion resistance of aluminum and its alloys. One of the techniques to improve corrosion resistance is control the wettability of surfaces^{1,2}. Recently, the organic coating processes have been employed as the main technique to reduce the surface wettability of metals and increase the corrosion resistance. Various kinds of chemicals, such as sodium laurate³, dodecanoic acid⁴, myristic acid⁵, and silane⁶ were used for the formation of a hydrophobic nanostructure, and some of the resulting surfaces shows both good anti-corrosion characteristics and self-cleaning properties. The organic coating techniques for fabrication of hydrophobic surfaces on aluminum, however, have disadvantages; the cohesive force between organic compounds and aluminum oxide is not stable, and the fabrication process is complicated. A simple method for fabrication of hydrophobic surfaces on aluminum without any organic coating would be attractive.

The porous type anodic oxide films can be formed on aluminum by anodizing in acid solutions, and the fabrication of different porous structures were reported in many investigations⁷⁻¹¹. Because of its special pore array morphology and physical properties, porous type anodic oxide films have been studied for many applications, especially as templates for organic and inorganic synthesis^{12,13}.

The similarity between the regular patterned uneven surfaces of porous type anodic oxide films and many natural or artificially created low-wettability surfaces appears to offer the potential for lowering surface wettability. However, porous type anodic oxide films prepared in acid solution generally display hydrophilic properties¹.

One of the authors reported that desiccation treatment at 373 K results in large increases in the water contact angle on anodic oxide films, requiring a fairly long time to achieve¹⁴. The anodizing solution is another important factor influencing surface wettability. Samples anodized in H₃PO₄, which have large pore diameters show lower wettability after desiccation than samples anodized in H₂C₂O₄¹. It was also reported that samples subjected to gradual heating and cooling in desiccation process show a larger contact angle than samples subjected to fast heating and cooling desiccation in an oven at the same temperature, and there is little change in the surface chemical composition before and after the desiccation treatment¹⁵. It is still not clear this technique can improve wettability of aluminum alloys and also improve corrosion resistance. The purpose of this study is to investigate the effect of mechanical polishing before anodizing and anodizing time on wettability of an A1050 aluminum alloy and corrosion behavior.

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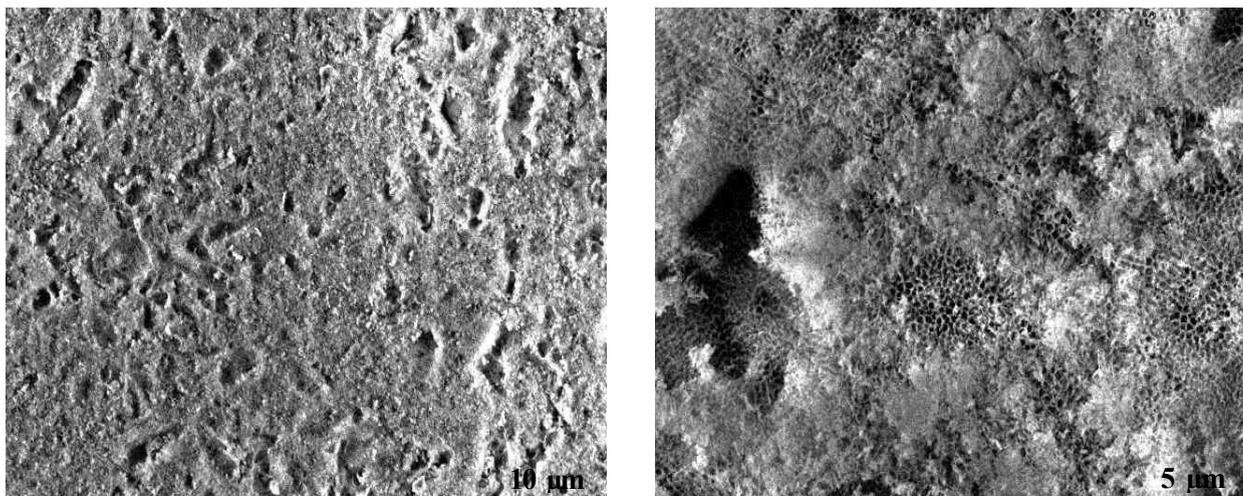


Fig. 1. SEM surface images of polished, anodized for 7.2 ks and desiccated specimen. Left: Low magnification, Right: High magnification

2. Experimental Procedure

2.1 Specimens

The A1050 aluminum alloy sheets (11 x 11 x 2 mm) were used as specimens. The specimens were ultrasonically cleaned in ethanol and highly purified water for 300 s each. Some specimens were etched in 0.1 kmolm^{-3} NaOH for 180 s at room temperature, and mechanically ground by SiC paper up to #1200 under running water. The oxide films were formed by anodizing in 0.41 kmolm^{-3} H_3PO_4 at a constant current density of 100 Am^{-2} for 1.0 ks and 7.2 ks at room temperature, then rinsed with highly purified water. The anodizing time related to thickness of pore length in the formed oxide film, and the expected barrier layer thickness from anodizing voltage is about 150 nm. The specimens which were desiccated went through the following process¹⁵: Heating-up from room temperature to 423 K in 3.6 ks, followed by heating at constant temperature of 423 K for 50.4 ks, and then cooling down in the furnace to room temperature.

2.2 Wettability measurement

The water contact angle of different treated samples was measured by side view photographs of water droplets ($4 \mu\text{l}$ of highly purified water), and the average of contact angle at different area on each sample were used.

2.3 Electrochemical measurement

The corrosion behavior of the samples was examined by the rest potential and potentiodynamic polarization measurements. The experiment was performed in 3.5 mass% NaCl solutions at room temperature, with the anodized area of the sample dipped inside the electrolyte

solution. Rest potential measurement was carried out for 1.8 ks at room temperature. The potentiodynamic polarization tests were performed in a standard three-electrode cell at room temperature from -1.0 V to 0.0 V at a scanning rate of 50 mV/min. The Ag/AgCl sat. KCl electrode was used as the reference electrode.

2.4 Characteristic

The specimens' surfaces were observed by a scanning electron microscope (SEM, JEOL Ltd., JSL6510-LA). The surface films were analyzed by an X-ray photoelectron spectroscope (XPS, JEOL Ltd., JPS-9200) using an Mg $K\alpha$ X-ray source (1253.6 eV), and the area analyzed by XPS was $3 \times 3 \text{ mm}$ in all the experiments, without Ar ion sputtering.

3. Results and Discussion

3.1 Surface images and Water contact angle

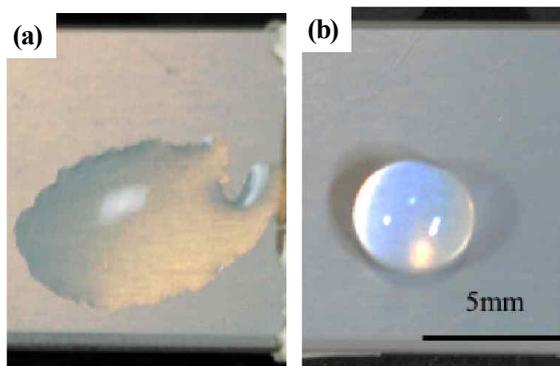


Fig. 2. Optical images of top view of water droplets on unpolished and 1.0 ks anodized samples, (a) before and (b) after desiccation treatment.

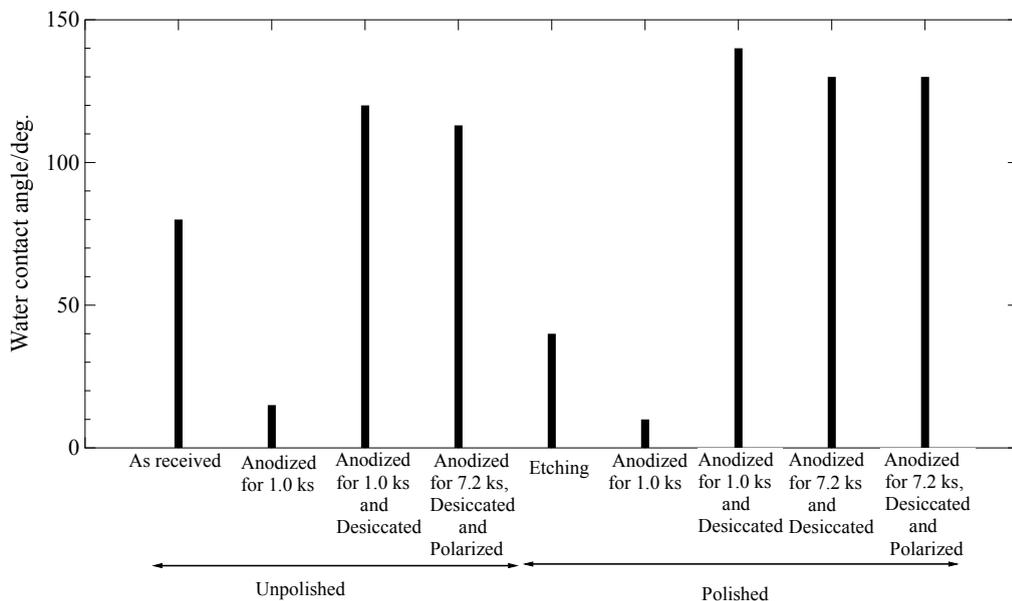


Fig. 3. Water contact angle of specimens after different treatments.

From observed voltage changes during constant current anodizing, both 1.0 ks and 7.2 ks anodizing made it possible to form ordered porous structure oxide films. Fig.1 shows SEM images of polished, anodized 7.2 ks and desiccated specimen surface. The left image is low magnification and right image is high magnification. There are feather or down like oxides layer on the porous layers (left image in Fig. 1), however, the ordered porous structure can be seen in the high magnification image (right image of Fig. 1).

Fig. 2 is the optical images of top view of water droplets on unpolished and 1.0 ks anodized samples, (a) before and (b) after the desiccation treatments. It is clearly seen that the desiccation treatment change the water contact angle of porous type anodic oxide film formed on aluminum alloy.

Fig. 3 represents changes of water contact angle with treatments. From Fig. 3, anodized samples not subjected to desiccation treatment show low water contact angle (lower than 20 deg.), while those subjected to desiccation after anodizing shows high contact angle larger than 130 deg. The water contact angle reduces considerably after etching in NaOH and polishing. It is also shown in the figure; the water contact angle of polished specimen with anodized and desiccated show slightly higher than that under similar conditions without polishing, hence exhibiting a comparatively lower surface wettability in the polished and anodized specimens. Longer anodizing time and polarization tests slightly reduce the water contact angle.

On the contrary, most of the hydrophobic surface (high water contact angle surface) produced by organic chemical coating will lose the hydrophobicity when immersed in aqueous solution. Therefore, the results of high water contact angle after polarization tests exhibit the high durability of proposed treatment (anodizing and desiccation treatments).

3.2 XPS surface analysis

Fig. 4 is XPS wide scan spectrum of specimen with polished, anodized for 7.2 ks, and desiccated. From XPS wide scan spectrum of specimens, P, Al, O, and C peaks are observed. The peak of P may be incorporated from solution during anodizing, and C is related to contamination during sample preparation. Fig. 5 shows XPS narrow spectra of Al 2p and O 1s observed anodized for

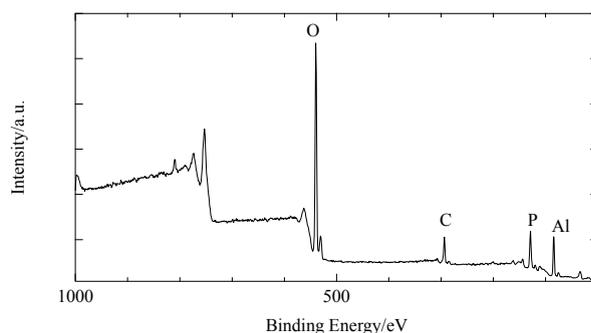


Fig. 4. XPS wide scan spectra of specimen with polished, anodized for 7.2 ks, and desiccated.

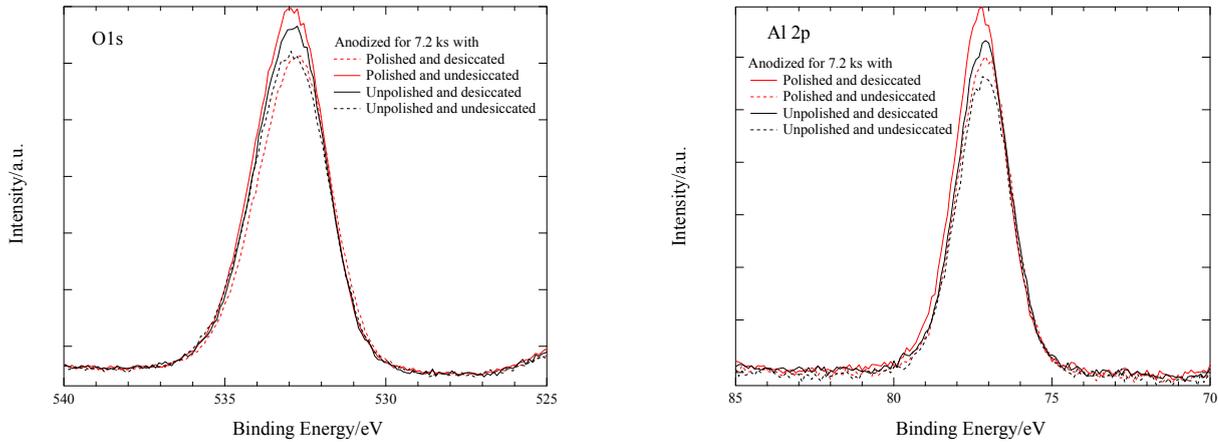


Fig. 5. XPS narrow spectra of Al 2p and O1s after anodizing for 7.2 ks with different treatment.

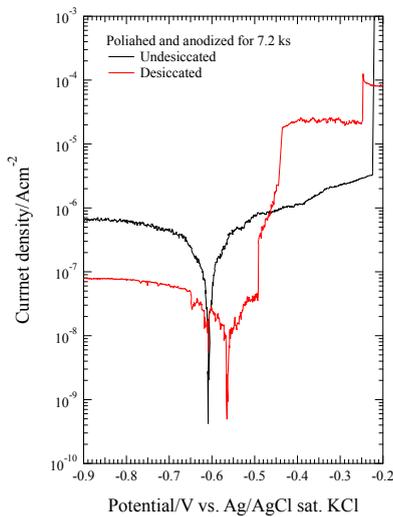


Fig. 6. Typical example of polarization curves of specimens with polishing and anodized.

7.2 ks with different treatments. The XPS narrow spectra in both Al and O indicate that chemical composition of formed films is Al₂O₃. The difference in the spectra with and without desiccation and polishing treatments hardly observe. Therefore, polishing and desiccation treatments have little or no effect on chemical composition of anodized films. As Zheng et al. mentioned¹⁵⁾, the contact angle change with desiccation treatment is mainly due to ordered pore structure, which was existed under the feather like oxide layer, appeared during desiccation. The results of SEM and XPS in the experiments are in good agreement with Zheng's results, therefore, the main reason to increase contact angle is ordered pore structure appeared during desiccation.

3.3 Electrochemical measurements

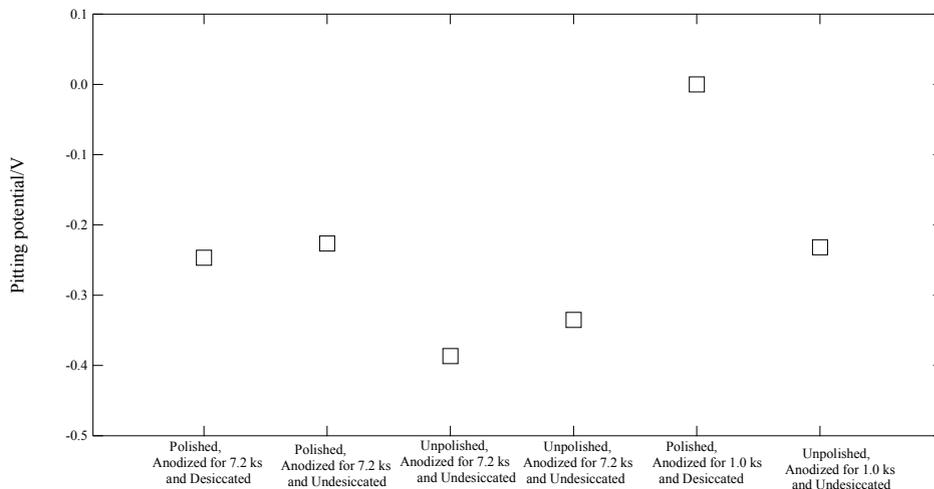


Fig. 7. Relationship between pitting potential, potential of current reached 1.0×10^{-4} Acm⁻² in polarization results, and treatments.

Fig. 6 shows typical example of polarization curves of specimens with polishing and anodized for 7.2 ks with and without desiccation. The desiccated specimens exhibit a higher corrosion potential and lower current density between -0.9 V and -0.45 V in Fig. 6. These results suggest that desiccation treatment improves corrosion resistant property of anodic oxide films. The behavior may be attributed by higher water contact angle surfaces with porous type anodic oxide films inhibit the intrusion of solutions to bottom of the pore, resulting decrease contact area of thin oxide layer (barrier layer) on specimen surface with solutions¹⁵. The reducing the area of electrochemical reaction such as Al dissolution, means reducing the measured current. This also means that improve the corrosion resistance of the treated specimens.

There is sudden current increase around -0.22 V, this is related to growth of pitting corrosion or localized corrosion. Hereafter, the potential at which current reached 1.0×10^{-4} Acm² is called as pitting potential. Fig. 7 shows relationship between pitting potential in observed polarization results and treatments. No significant difference is noticed in the pitting potentials of desiccated specimens and undesiccated specimens. The polarization behaviour at high overpotential region, especially pitting potential, shows some dispersion. Because pitting or localized corrosion are stochastic events. Therefore, not clear effect of desiccation treatment is observed in Fig. 7. From Fig. 7, pitting potential may affected by polishing treatment especially short anodizing time. However, the detailed mechanism is not clear. To elucidate the effect of polishing, further investigation in oxide film structure is required.

The results shown here, however, exhibit desiccation process play an important role for corrosion resistance of anodic oxide films.

4. Conclusions

The novel technique for improving of wettability by anodizing combined with desiccation was applied for improvement of corrosion resistance of A1050 aluminium alloy.

Following conclusions can be drawn.

- 1) The low wettability, high water contact angle, surface can be formed on A1050 aluminum alloy with anodizing in 0.41 kmolm^{-3} H₃PO₄ followed desiccation treatment. The largest water contact angle achieved in this work is 140 degree.
- 2) From XPS analysis, there was a very little or no

change in chemical composition of anodic oxide film between polished and unpolished specimens, and before and after the desiccation process.

- 3) With increasing the water contact angle, the corrosion resistance of the A1050 aluminum alloy increases in 3.5% NaCl solution. Therefore, anodized and desiccated specimens showed a better corrosion resistance as compared to the undesiccated ones.

Acknowledgments

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