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Corrosion Resistance Improvement of Aluminum by Hydrophobic Anodic Oxide Film

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Diminishing surface wettability is an effective method to improve corrosion resistance of aluminum. Various techniques for preparing hydrophobic surface have been reported, most of which use organic coating as the final step. The key point to diminish surface wettability is to form a fine regular surface structure, and the porous type anodic oxide film (PAOF) has nano-pore structure, therefore promising for being utilized to develop hydrophobic surface combined with other treatment. In this study, a hydrophobic surface was prepared on aluminum sheet by constant-current anodic oxidation, followed by desiccation treatment. The surface morphology was investigated by SEM, and chemical composition was analyzed by AES and XPS measurement. The result showed that topside morphology of porous layer was greatly influenced by both desiccation time and temperature, without an evident change in chemical composition. Corrosion behavior of samples was investigated in 0.6 kmolm^{-3} NaCl solution in various immersion time. A decreasing quantum of corrosion products on anodized surface and hydrophobic surface indicated an improvement of corrosion resistance. Potentiodynamic polarization measurement was employed to confirm the corrosion resistance improvement of hydrophobic treatment in the same solution, and the result showed current density of anodized sample decreased more after desiccation process.

Keywords: *Hydrophobic, Aluminium, Corrosion inhibition, Anodizing, Desiccation*

1. Introduction

Wettability of metal surface is an important property, since it has a great influence on corrosion, adsorption, conductivity, optical and other performance [1]. Research in this field has aroused much attention recently, acorroding to its potential of wide practical application [2,3], and hydrophobic films have been successfully fabricated on various metallic and alloy substrates, such as Cu [4,5], Cu-Zn alloy [6], stainless steel [7].

Among metals, aluminum, because of its abundant content in lithosphere and easy-machining, represents a wide application area especially in electrical appliance, marine industry and aerospace industrial. Hydrophobic surface on aluminum has become an interesting topic and has been obtained through different kinds of treatment; the favourable corrosion resistance ability is also mentioned in some literatures [8-10]. However, almost every technique of aluminum-hydrophobization makes use of organic coating as the final step, which leads to some problem. For instance, the interface between organic layer and metal surface is not stable enough while in solutions. In this study, a simple and effective method was reported for the fabrication of hydrophobic film on aluminum, and its corrosion resistance capability was also investigated.

2. Experimental

2.1 Specimen

Aluminum sheets (99.99 mass %, 350 μm thickness) with an exposed area of 15 mm × 15 mm were used in this experiment. Before anodizing, the substrates were cleaned with ethyl alcohol in ultrasonic bath, and then electropolished in 13.6 kmolm^{-3} CH_3COOH / 2.56 kmol m^{-3} $HClO_4$ solution for 300 s at a constant voltage of 28 V at 283 K.

2.2 Hydrophobic films

Specimens were anodized in 0.41 kmolm^{-3} H_3PO_4 at a constant current density of 100 Am^{-2} for 7.2 ks at room temperature. Then the specimens were kept in the oven with various desiccation time and temperature. After cooling, the water contact angle of each sample was measured by side view of water droplet. Surface morphology was investigated by SEM and chemical composition was analyzed by AES and XPS.

2.3 Corrosion test

Immersion corrosion test was carried out by dipping untreated and treated samples (resin-sealed) in 0.6 kmolm^{-3} NaCl at room temperature, and surface morphology change was investigated by SEM. Potentiodynamic polarization tests were carried out in a standard three-electrode cell at room temperature, with the scanning rate of 0.83 mVs^{-1} in 0.6 kmolm^{-3} NaCl. The average current density in the anodic region was measured from the polarization curves.

3. Results and discussion

3.1 Wettability and microstructure of hydrophobic surface

Surface wettability of samples before and after different treating processes was compared. Figure 1 shows the side view photographs of water droplets on as-received aluminum (a), as-treated surfaces with electropolishing (b), anodizing (c) and desiccation (d), which demonstrates the change of wettability after each treating steps. As-received aluminum surface is a type of neither hydrophobic nor hydrophilic surface, showing a water contact angle of 63 degree. The electropolishing treatment shows little influence on wettability after which the water contact angle became 65 degree, although surface became smooth and bright. On the contrary, anodizing treatment in H_3PO_4 greatly diminished the contact angle to 29 degree, which exhibits hydrophilic property (Fig.1(c)). Then it is clearly shown that desiccation treatment is an effective method to improve hydrophobicity; the surface exhibits a high water contact angle of 114 degree by keeping in oven at 373 K for 1728 ks (Fig.1(d)).

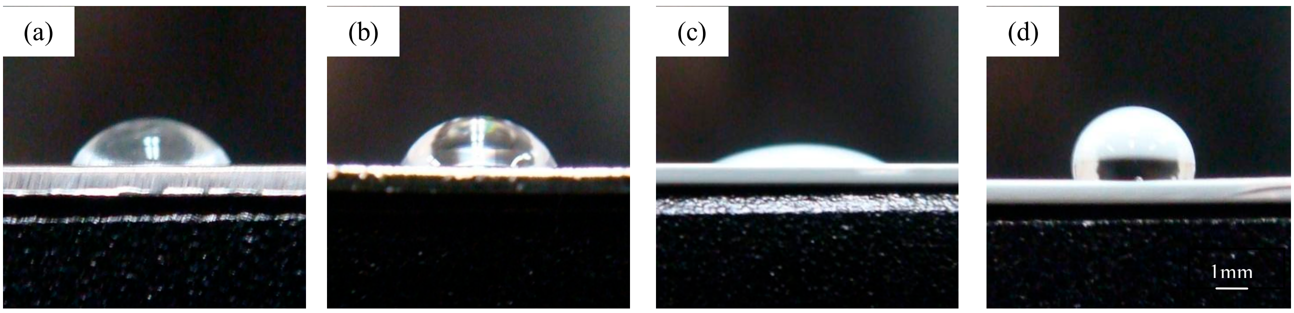

Fig. 1 Side view photographs of water droplet on as-received aluminum (a), as-treated surfaces with electropolishing (b), anodizing (c) and desiccation at 373 K for 1728 ks (d).

It is known that immersion of aluminum in aqueous solution at the initial period of anodizing results in the formation of hydroxide (white area in Fig. 2(a)), which remains on top of the oxide film as it grows continuously. Therefore, free water molecular adsorbed to hydroxide with physical force, makes a tridimensional hydrophilic property. During desiccation treatment, the hydrophilic layer may lose water gradually, leaving a relatively regular top layer known as porous type anodic oxide film (Fig. 2(b)). If it reaches an ideal diameter, the pores may easily act as pier to support droplet, and trap some gas inside the pores so that water can hardly reach the pore bottom. This may be the reason why contact angle increases with desiccation treatment.

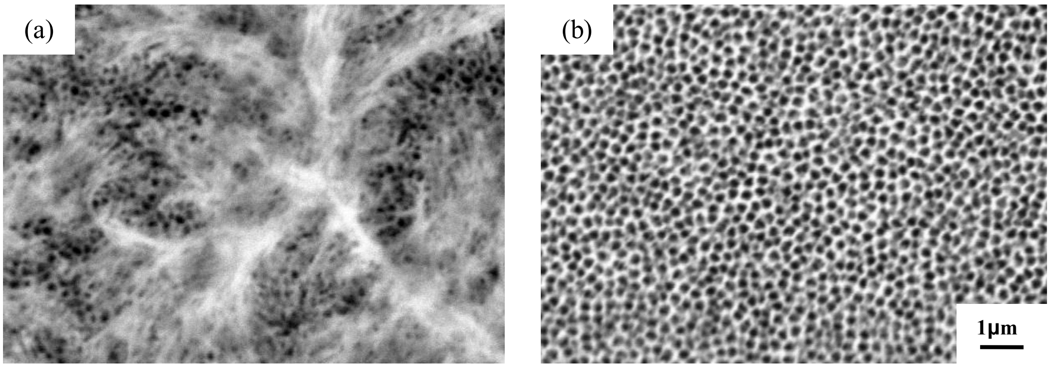

Fig. 2 SEM photos of sample surface after anodizing (a) and after desiccation at 393 K for 43.2 ks (b).

The effect of desiccation time and temperature on surface wettability is then studied. Figure 3 shows water contact angle as a function of time at various desiccation temperature, and Fig. 4 shows the change of water contact angle with desiccation time at 373 K. It is indicated that at desiccation temperature between 373 K and 393 K, the pre-fabricated alumina film exposes a regular porous structure as shown in Fig. 2(b), therefore water contact angle changes with temperature which also increased with desiccation time. While after desiccation at 423 K, surface exceptionally turned to hydrophilic and irregular morphology was observed by investigation of SEM. It is shown that the surface structure is not sufficiently stable to keep its regularity at a relatively higher temperature. 373 K is considered as the critical temperature to achieve hydrophobic surface, at which samples show a small water contact angle within 259.2 ks. However, by expanding desiccating duration at the same temperature, the water contact angle is also greatly improved after 864 ks, reaching a maximum value of 116 degree after 2160 ks. It was found that the chemical compositions of different treated samples were similar by AES and XPS measurement, which mainly consists of Al_2O_3. These results suggest that the change of tridimensional microstructure may be the main reason for achieving an excellent hydrophobic property of PAOF.

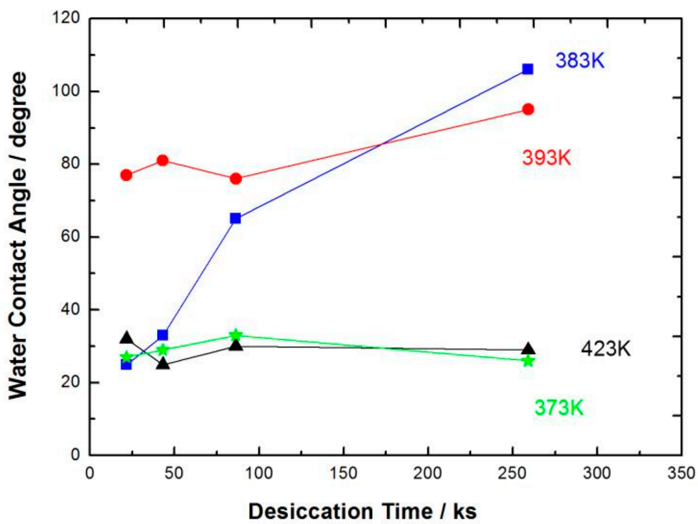

Fig. 3 Water contact angle as a function of time at various desiccation temperature.

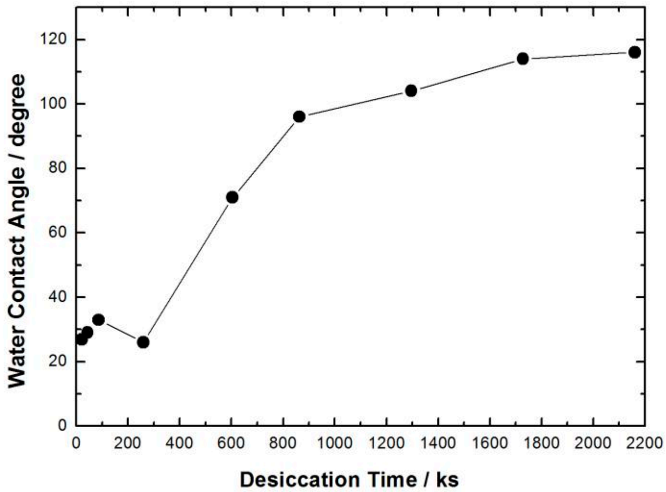

Fig. 4 Change in water contact angle with desiccation time at 373 K.

3.2 Corrosion resistance of hydrophobic film

Figure 5 shows the surface appearance of untreated and hydrophobic samples after immersion test, from 216 ks to 3628.8 ks. The circular white area where localized corrosion occurred is different from the area with metallic lustre on untreated aluminum plate. Evidently on untreated sample, some serious pitting corroded area appears after 604.8 ks, and the corroded area extends gradually with immersion time. On the other hand, no remarkable corroded area exits on the sample with hydrophobic film. The colour of hydrophobic specimen remains light blue after immersion corrosion test for 3628.8 ks, which is the characteristic colour of phosphoric anodic oxide film.

Figure 6 shows the hydrophobic surfaces observed by SEM after immersed in NaCl solution up to 3628.8 ks. The ordered porous structure can be seen on the sample surface after immersion corrosion test. It means the hydrophobic structure formed by desiccation treatment has a good stability and durability.

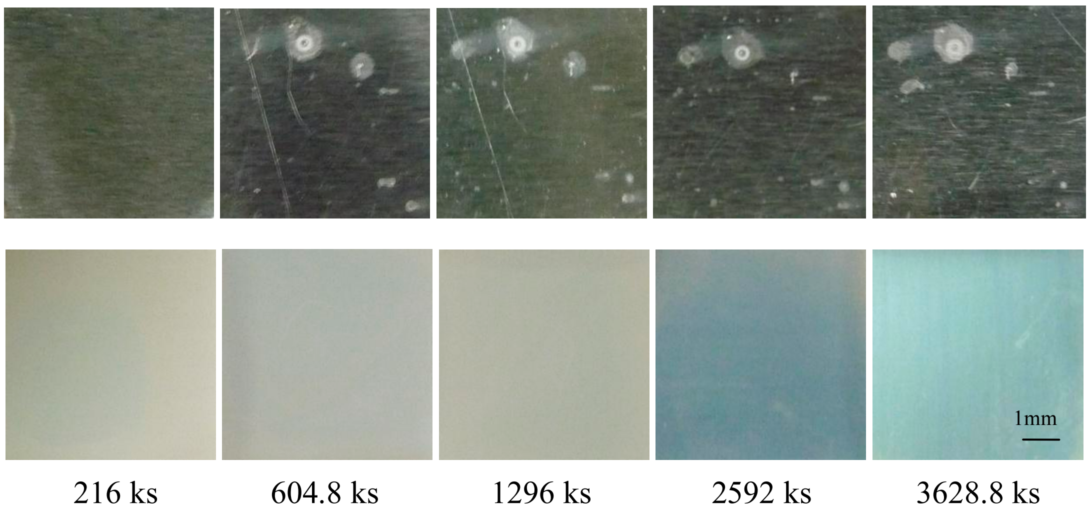

Fig. 5 The surface appearance of untreated sample (above) and hydrophobic sample (below) changes with immersion time in 0.6 kmolm^{-3} NaCl.

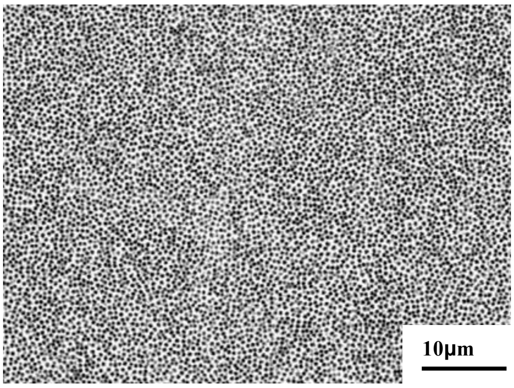

Fig. 6 SEM micrograph of hydrophobic sample after immersed in 0.6 kmolm^{-3} NaCl for 3628.8 ks.

The corrosion behavior of anodic oxide sample also had good corrosion inhibition during immersion test, which makes it difficult to distinguish the corrosion inhibition effect of hydrophobicity. Therefore, potentiodynamic polarization measurement was carried out in the same solution.

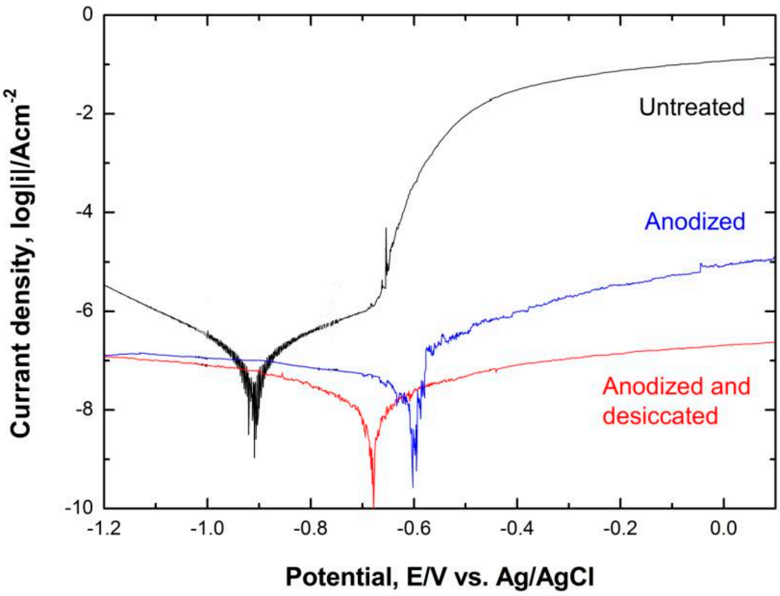

Fig. 7 Potentiodynamic polarization curves of three different treated samples in 0.6 kmolm^{-3} NaCl.

Figure 7 shows the potentiodynamic polarization curves of untreated, anodized and hydrophobic sample in 0.6 kmolm^{-3} NaCl. The rest potential shifts to higher potential after anodizing and desiccation treatment, because anodic oxide film inhibits the dissolution of aluminum substrate. Only the polarization curve of untreated sample shows a sudden increase at -0.7 V, for the reason of occurrence of pitting corrosion. Both anodic and cathodic currant is decreased with anodizing and desiccation treatment.

From three polarization curves, the average current density between -0.4 V and 0 V in Fig.7 is shown in Fig. 8. There is a sharp decline in current density between untreated sample and anodized sample, due to the existence of anodic oxide film. It is also found that after desiccation treatment, the average current density decreases more compared to anodic oxide aluminum. From polarization curves, hydrophobic sample shows a better corrosion inhibition than both untreated sample and anodized sample.

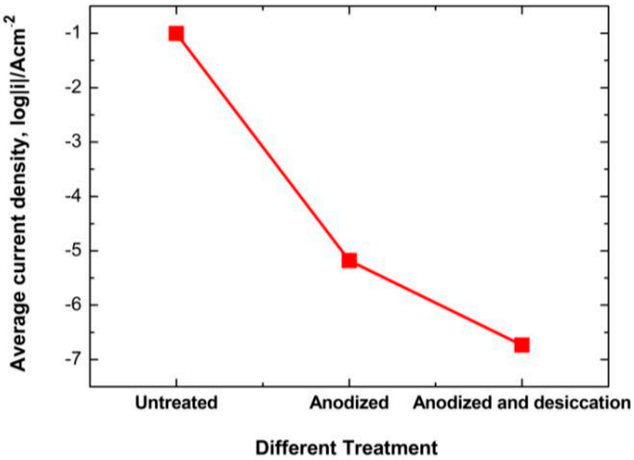

Fig. 8 Average current density between -0.4V and 0V of different treated samples in Fig. 7.

4. Conclusion

Electropolishing treatment has little influence on wettability, while anodizing treatment decreases water contact angle because of the formation of irregular morphology on the porous oxide layer. With desiccation temperature at 383 K and 393 K, the pre-fabricated PAOF loses adsorbed water and a regular porous structure is exposed, therefore water contact angle is increased, which mainly varies as desiccation time. Even at 373 K, hydrophobic property of PAOF is achieved after 1296 ks.

The hydrophobic film shows similar chemical composition of Al_2O_3 after different treatment, and the change of tridimensional microstructure may be the main reason for achieving an excellent hydrophobic property of PAOF.

Aluminum sheets with hydrophobic film exhibits higher corrosion resistance compared to untreated sample in immersion corrosion test. Pitting corrosion is evidently investigated on untreated sample, while hydrophobic sample keeps its porous structure. In the result of potentiodynamic polarization measurements, hydrophobic film exhibits a better corrosion resistance than anodic oxide film.

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References

[1] X. J. Feng and L. Jiang: Adv. Mater. 18 (2006) 3068-3071.
[2] R. Blossey: Nat. Mtaer. 2 (2003) 301.
[3] I. P. Parkin and R. G. Palgrave: J. Mater. Chem. 15 (2005) 1689.
[4] N. J. Shirtcliffe, G. Mchale, M. I. Newton and C. C. Perry: Langmuir. 21 (2005) 937-934.
[5] T. Liu, S. G. Chen, S. Cheng, J. T. Tian, X. T. Chang and Y.S. Yin: Electrochimica Acta. 52 (2007) 8003-8007.
[6] W. C. Wu, M. Chen, S. Liang, X. L. Wang, J. M. Chen and F. Zhou: Journal of Colloid and Interface Science. 326 (2008) 478-482.
[7] L. Chen, M. Chen, H. Zhou and J. Chen: Appl. Surf. Sci. 255 (2008) 3459-3462.
[8] H. Sakaue, T. Tbei, M. Kameda: Sensors and Actuators. 119 (2006) 504-511.
[9] Y. S. Yin, T. Liu, S. G. Chen, T. Liu, S. Cheng: Appl. Surf. Sci. 255 (2008) 2978-2984.
[10] T, He, Y. Wang, Y. J. Zhang, Q. Lv, T. Xu, T. Liu: Corrosion Science. 51 (2009) 1751-1761.