

Evaluation of Anodized Aluminum Corrosion Resistance by Constant Current Anodic Polarization Test

Hideaki MIYASHITA¹Kohei TOMITA²Yuki YAMAGUCHI¹Takahiro KUWABARA¹

ABSTRACT

A method was developed that can estimate the corrosion resistance of anodized aluminum regardless of the aluminum material or treatment conditions. It was confirmed that the constant current anodic polarization method can be used to evaluate the state of voids and foreign matter in anodized aluminum and the corrosion resistance by measuring the initial potential increase rate when a constant current is applied to anodized aluminum.

In addition, the change in the initial potential increase rate showed that the factor lowering the corrosion resistance of anodized aluminum due to an increase in the amount of added contents in aluminum alloys is rooted in the change in the anodized aluminum structure.

This method can estimate the corrosion resistance of anodized aluminum in a short time, enabling determination of the specifications of anodized aluminum at an early stage.

1. Introduction

How to secure sustainable growth in consideration of the global environment is an ongoing issue, and calls for a transformation from a resource-wasting society to a recycling-oriented society⁽¹⁾.

Anti-corrosion technology is important for the effective use of limited resources. The actual loss amount due to corrosion in Japan varies depending on the calculation method, but it is estimated that the amount will exceed 4 trillion yen annually in 2015⁽¹⁾.

Anti-corrosion technology is also important for long-term effective use of automobiles. However, the application of aluminum, magnesium, and carbon-fiber reinforced plastics is increasing due to the shift to multi-material aimed at weight and cost reduction, and corrosion at contact points between different materials is also becoming an issue. Particular care is needed for aluminum, which is a metal with a relatively low natural potential that often promotes galvanic corrosion at contact points with different materials. Plating treatment and coating are often applied as countermeasures to enhance electrical insulating properties. However, there are an increasing number of

cases in which anodizing treatment is applied to provide electrical insulating properties by artificially forming a thick and stable oxide film on the aluminum surface by an electrochemical reaction.

Anodizing treatment is usually performed in the order of washing, electrolysis, and sealing. An oxide film composed of a barrier layer directly above the aluminum material and a porous layer having fine porous holes as shown in Fig. 1 is formed by electrolysis. Although the overall film thickness ranges from several μm to several tens of μm , the thickness of the barrier layer and the hole diameter and wall thickness of the porous layer are all on the order of several

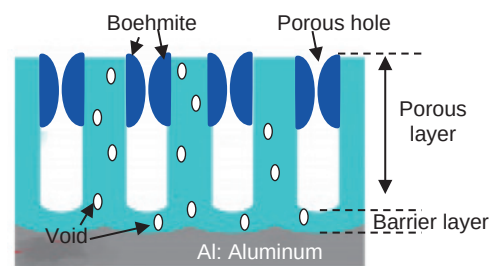


Fig. 1 Cross-sectional view of anodized aluminum

¹ Honda Motor Co., Ltd.

E-mail: hideaki_miyashita@jp.honda

² Material Research Center

tens of nm. In addition, fine voids are also generated from gases and impurities in the aluminum material^{(2), (4)}.

If porous holes and voids are present, moisture easily reaches the aluminum base material in a water-exposed environment, making it a challenge to obtain stable corrosion resistance. Therefore, corrosion resistance is enhanced by immersing the part in boiling water or nickel acetate solution, etc. after electrolysis to modify the surface of the oxide film into a hydroxide called boehmite by a hydration reaction, and applying sealing treatment to seal the porous holes and voids.

Previously, anodized aluminum often used A6061-T6 and AC4CH-T6 materials, which have fewer impurities, but use of recycled materials with greater amounts of impurities such as AC2B-T6 and ADC12-F materials is increasing, and anodizing treatment is increasingly applied to those materials.

However, when the corrosion resistance of anodized aluminum using various aluminum materials was actually evaluated, different anodizing treatment conditions and material composition resulted in different corrosion resistance, and there were cases where the target corrosion resistance could not be obtained. For this reason, the corrosion resistance of anodized aluminum has been evaluated and determined by subjecting the treated parts to long-term tests such as the cyclic corrosion test (CCT) and actual vehicle rust durability tests. However, these tests call for testing periods of tens of days to several months.

2. Development Goals

Figure 2 shows an example of observation of the vicinity of the barrier layer of a test piece using a transmission electron microscope (TEM). This test piece was made of A6063-T5 material, which is one of the A6000 series alloys that are said to have fewer impurities and more easily grow regular barrier and porous layers, and was anodized with oxalic acid.

The fine voids generated during electrolysis remain even after the sealing treatment, so it is presumed that moisture enters the interior through the gaps of these voids and porous holes and reaches the aluminum base material,

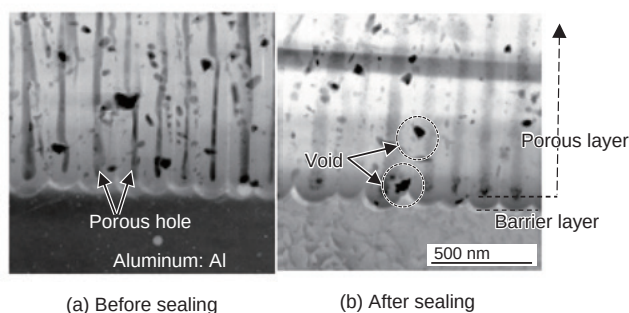


Fig. 2 Example of observation of anodized aluminum cross-section of A6063-T5 material using TEM

producing corrosion of the anodized aluminum.

Although the state of the voids and porous holes can be observed by TEM, only a narrow range can be observed at one time, and it is not easy to grasp the state of the entire anodized aluminum layer. Therefore, focus was placed on electrochemical testing as a method to evaluate the structure of the entire anodized aluminum layer⁽²⁾⁻⁽⁸⁾. Takahashi et al.⁽²⁾ stated that when a constant anode current is applied, the potential increases at a faster rate when there are smaller and fewer voids in the anodized aluminum, and more gradually as the size and number of voids increase. Therefore, it was thought that the constant current anodic polarization test could be used to evaluate the corrosion resistance of anodized aluminum, which is influenced by the size and number of voids.

3. Test Method

Anodized aluminum test pieces were fabricated using multiple aluminum materials. The potential behavior was measured by constant current anodic polarization tests, the rust occurred cycle was measured by CCT, and the relationship between the two was compared and evaluated.

3.1. Polarization Test

Figure 3 shows the polarization test device.

Current application and potential data recording used the HZ-7000 made by Meiden Hokuto Corporation.

The test piece was set so that it directly faced a platinum counter electrode at an interval of 10 mm as the anode, and the tip of a Luggin capillary into which the Ag/AgCl reference electrode was inserted was positioned between the two.

Past studies used a boric acid solution in many cases, but this test was conducted with the same 5% salt water as that used in the CCT test heated and held at 50°C in accordance with the corrosion test environment. After setting the test piece and holding for about 10 minutes, a constant anode current was applied, and the potential was measured every

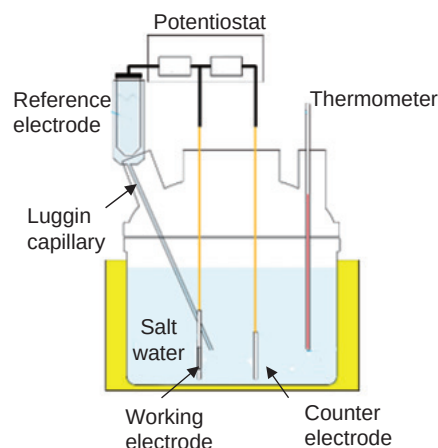


Fig. 3 Device of polarization test

0.01 seconds, which is the minimum measurement interval of the device. The anode current was set to $10 \mu\text{A}/\text{cm}^2$ so as not to exceed the $\pm 15\text{V}$ potential measurement range of the measuring instrument.

As the potential increases, some of the Al^{3+} and O^{2-} ions move from stable lattice positions to high-energy interstitial positions and the current flows more easily. As a result, a clear difference in potential behavior was observed immediately after current application⁽²⁾, and the initial potential increase rate (IPIR) was calculated by dividing the potential difference between 0.01 and 0.02 seconds by the time difference.

3.2. Test Pieces

Table 1 shows the added content of the four types of materials evaluated in this study. Test pieces were fabricated with these materials under different anodizing treatment conditions and evaluated.

Figure 4 shows the test piece shape before anodizing treatment.

The entire surface was milled to help reduce differences in anodized aluminum quality due to different surface shapes, and an M5 screw hole was provided in one corner for connecting to the anode.

Figure 5 shows a test piece used for the polarization test. The anodized test piece was cut to a size of $45 \times 45 \text{ mm}$, and the anodized aluminum in the part where the electrode rod was attached was peeled off with a router, etc.

Polyimide tape with a $30 \times 30 \text{ mm}$ range hollowed out

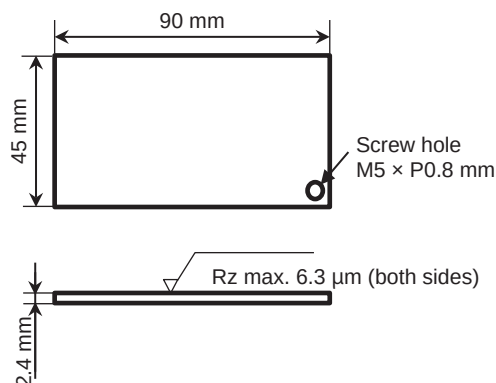


Fig. 4 Shape of aluminum test piece before anodizing treatment

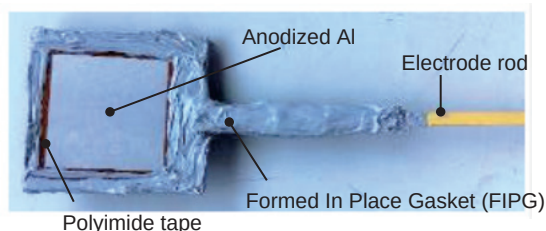


Fig. 5 Test piece for polarization test

Table 1 Added content of anodized Al materials

Material	Added content (wt%)				
	Cu	Si	Mg	Zn	Fe
ADC12-F	1.8	10.1	0.21	0.63	0.77
AC2B-T6	3.0	7.0	0.31	0.01	0.16
AC4CH-T6	0.02	6.9	0.33	0.004	0.08
A6061-T6	0.19	0.48	0.98	0.01	0.46

Table 2 Anodizing treatment conditions

No.	Electrolyte	Current density (A/dm^2)	Minimum thickness (μm)	Sealing treatment
1	Sulfuric acid	2.0	3.0	Nickel acetate
2			1.5	
3			8.0	
4			20.0	
5			3.0	None
6	Oxalic acid	4.0		Water
7				Nickel acetate

was attached in the center, and a copper electrode rod with a resin-coated alligator clip was attached to the part where the anodized aluminum was peeled off.

After that, a Formed In Place Gasket (FIPG) was applied to areas except for the opening of the polyimide tape and dried at room temperature until it was no longer sticky as waterproofing.

3.3. Anodizing Treatment Conditions

Table 2 shows the anodizing treatment conditions. When corrosion resistance is emphasized, the No. 1 condition is often selected: after degreasing and washing, electrolysis is performed in a sulfuric acid solution to provide a film thickness of at least $3 \mu\text{m}$, and finally sealing treatment is performed with a nickel acetate solution. Therefore, using this as the basic condition, test pieces were fabricated with different electrolyte, film thickness, and sealing treatment.

The film thickness and sealing treatment were selected as evaluation parameters because they were thought to influence the time it took for salt water to enter the anodized aluminum layer and reach the aluminum base material. The film thickness was adjusted by the electrolysis time.

It is known that when oxalic acid is used as the electrolyte, the barrier layer and porous walls are thicker than when sulfuric acid is used, and it was thought that this could help reduce the impact of the voids and enhance corrosion resistance, so it was also selected as an evaluation parameter. In that case, the anodized aluminum does not grow at the same current density as with sulfuric acid, so electrolysis was performed with the current density changed to $4 \text{ A}/\text{dm}^2$.

After cutting and polishing the center part of the test

piece, it was observed with an optical microscope, and the film thickness of the thinnest part was used as the typical value.

3.4. Corrosion Test

The back surface and a range of about 5 mm around the outer circumference of the anodized test piece were masked with polyester tape, and the test piece was placed in the CCT tester so that it was 70 degrees to the horizontal. The CCT was conducted under Honda's original conditions of 24 hours per cycle combining salt spray, wet, dry, and keeping at low temperature, and the progress was observed.

The JIS H8679-1 Rating Number Method⁽⁹⁾ was used to determine corrosion resistance, and the number of CCT cycles at which corrosion corresponding to a rating number (RN) of 9.8 occurred was set as the Rust Occurred Cycle (ROC).

4. Test Results and Discussion

4.1. Impact of Anodizing Treatment Conditions

The impact of anodizing treatment conditions on IPIR and ROC was verified using AC4CH-T6 material, which is often applied to aluminum wheels and power unit parts due to the ease in obtaining the anti-corrosion effects of anodized aluminum.

Figure 6 shows the constant current anodic polarization curves for No. 1, No. 5, and No. 7, which exhibited greatly different ROC.

The larger the ROC and the higher the corrosion resistance, the larger the slope of the initial potential increase, which suggests a faster IPIR.

Table 3 and Fig. 7 show the results of calculating the IPIR for each condition and comparing it with the ROC. IPIR and ROC were positively correlated for all samples with different anodizing treatment conditions, and results enabling evaluation of the corrosion resistance of anodized aluminum by the constant current anodic polarization method were obtained.

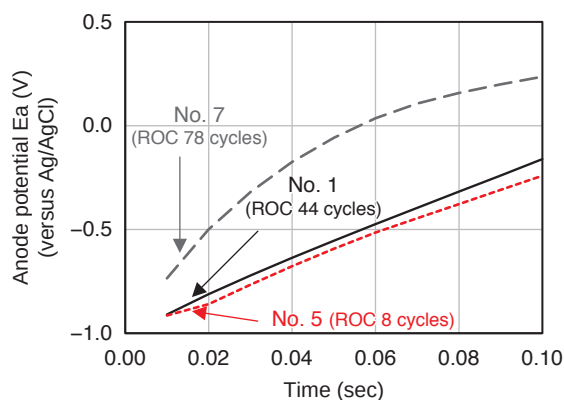


Fig. 6 Relationship between anode potential E_a and polarization time of No. 1, No. 5, and No. 7

Table 3 Evaluation results of AC4CH-T6 anodized test pieces

No	Differences from condition No. 1	IPIR (V/sec)	ROC (n)
1	—	9.4	44
2	Thin	6.6	11
3	Thick	13.9	60
4	Very thick	17.0	80
5	No seal	5.4	8
6	Boiling water seal	8.2	14
7	Using oxalic acid	17.2	78

Table 4 Evaluation results of each test piece under anodized condition No. 1

No.	Material	Subtotal of added content (wt%)	IPIR (V/sec)	ROC (n)
1	ADC12-F	13.51	3.9	5
2	AC2B-T6	10.48	7.1	20
3	AC4CH-T6	7.33	9.4	44
4	A6061-T6	2.12	18.3	72

4.2. Impact of Aluminum Material Composition

Test pieces were fabricated by anodizing ADC12-F, AC2B-T6, and A6061-T6 materials in the same manner as AC4CH-T6 material and evaluated.

Table 4 shows the relationship between the subtotal of added content, IPIR, and ROC for each material anodized under condition No. 1 in Table 2.

Figure 8 shows the relationship between IPIR and ROC. A positive correlation was observed between IPIR and ROC, and it was confirmed that the corrosion resistance of anodized aluminum differs greatly depending on the material composition even with the same anodizing treatment conditions.

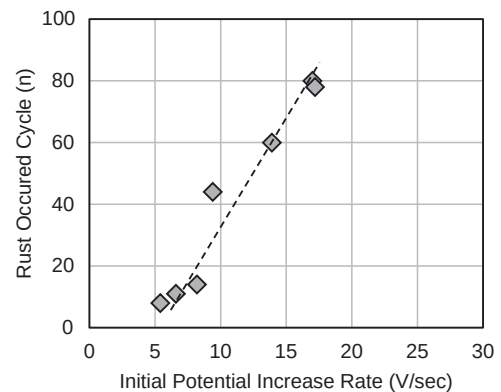


Fig. 7 Relationship between Rust Occurred Cycle and Initial Potential Increase Rate of anodized AC4CH-T6

Figure 9 shows the relationship between the amount of added content and IPIR. In this case, a negative correlation was observed between the amount of added content and IPIR.

Figure 10 shows the results of observation of the anodized aluminum cross section of A6061-T6 and ADC12-F materials using an optical microscope.

In the ADC12-F material, voids and Si that is thought to have remained in the anodized layer without dissolving

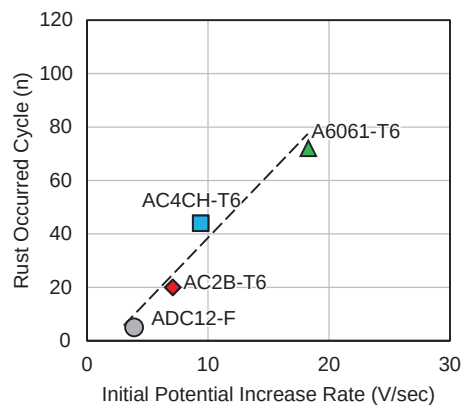


Fig. 8 Relationship between Initial Potential Increase Rate and Rust Occurred Cycle under condition No. 1

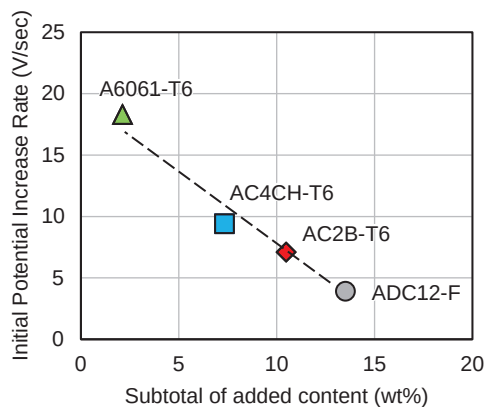


Fig. 9 Relationship between Initial Potential Increase Rate and subtotal of added content under condition No. 1

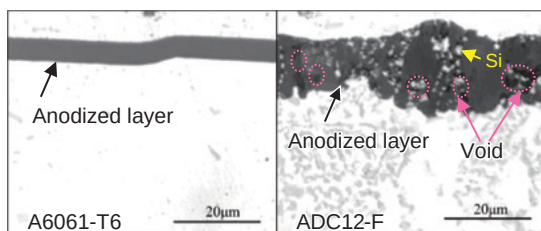


Fig. 10 Cross-sectional structure of A6061-T6 and ADC12-F test pieces anodized under condition No. 1

during electrolysis are present at a level that can be confirmed even with an optical microscope. Si itself has high electrical resistance and does not allow current to flow easily, and it is thought that like voids, Si remaining as foreign matter in anodized aluminum lowers the quality of the anodized aluminum.

This showed that the reason why IPIR and ROC differ greatly depending on the aluminum material composition is that the added content not only forms voids but also exists as foreign matter in the anodized aluminum, and their impact can be evaluated by the constant current anodic polarization method.

This result is thought to show the validity of the estimation mechanism whereby the IPIR obtained by the constant current anodic polarization method is an indicator of the state of voids and foreign matter in anodized aluminum, and that moisture reaches the aluminum base material via those voids and foreign matter and corrosion occurs.

Figure 11 shows the relationship between IPIR and ROC for all anodized test pieces fabricated in this study. The larger the IPIR value, the larger the ROC, which confirmed a strong positive correlation.

From this, it was found that measurement of IPIR by the constant current anodic polarization method enables evaluation and estimation of the corrosion resistance of anodized aluminum regardless of differences in anodizing treatment conditions and material composition.

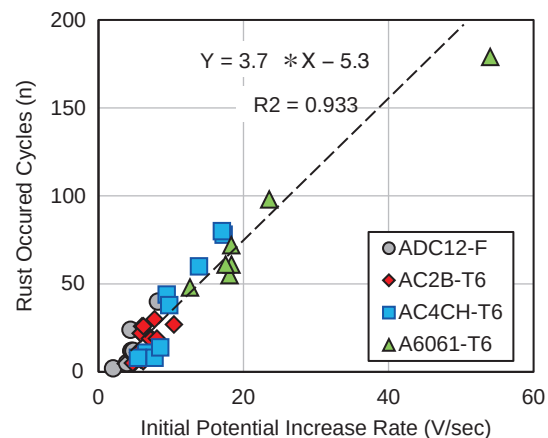


Fig. 11 Relationship between Initial Potential Increase Rate and Rust Occurred Cycle of all anodized test pieces

5. Conclusion

The following results were obtained by fabricating anodized test pieces from multiple aluminum materials under various conditions, and measuring, comparing, and verifying the potential behavior obtained by the constant current anodic polarization method and the rust occurred

cycle in CCT.

- (1) When anodized aluminum is treated by constant current anodic polarization, the potential increase behavior immediately after current application changes according to differences in the aluminum materials and the anodizing treatment conditions.
- (2) There is a strong positive correlation between the IPIR and the ROC in CCT, and the corrosion resistance of anodized aluminum can be estimated based on the differences in the anodizing treatment conditions and aluminum materials.
- (3) The change in the IPIR showed that the factor lowering the corrosion resistance of anodized aluminum due to an increase in the amount of added content in aluminum materials is rooted in the change in the anodized aluminum structure.
- (4) It was found that by measuring IPIR, the time needed to evaluate the corrosion resistance of anodized aluminum, which previously took up to several months, can be shortened to about one or two days. This enables determination of the specifications of anodizing treatment at an early stage.

References

- (1) Committee on Cost of Corrosion in Japan, Japan Society of Corrosion Engineering, Japan Association of Corrosion Control: Cost of Corrosion in Japan, Zairyo-to-Kankyo, Vol. 69, No. 11, p. 283-306, (2020) (in Japanese)
- (2) Takahashi, H., Fujiwara, K.: Electrochemical Analysis of Imperfections in Anodic Oxide Films on Aluminum, Hyomen Kagaku, Vol. 15, No. 7, p. 433-439, (1994) (in Japanese)
- (3) Yamada, M., Kikuchi, T., Sakairi, M., Takahashi, H.: Breakdown of Anodic Oxide Films on Aluminum, Journal of The Surface Finishing Society of Japan, Vol. 58, No. 6, p. 331-336, (2007) (in Japanese)
- (4) Ono, S.: Structure and Growth Mechanism of Anodic Oxide Films Formed on Aluminum and Their Gas Emission Property in Vacuum, Journal of the Vacuum Society of Japan, Vol. 52, No. 12, p. 637-644, (2009) (in Japanese)
- (5) Masuda, T.: Anodo Sanka Porasu Arumina no Bisai Kozo Hyouka to Netsu shori ni yoru α - Arumina Menburen no Sakusei, Doctoral dissertation of Kogakuin University, 145p., (2015) (in Japanese)
- (6) Asoh, T., Ono, S.: Fundamental Technology that Support Functionalization of Alumite, Journal of The Surface Finishing Society of Japan, Vol. 65, No. 9, p. 406-413, (2014) (in Japanese)
- (7) Takahashi, H., Kumagai, H., Nagayama, M.: Estimation of the Microstructure of Anodic Porous Oxide Films on Aluminum by the Pore-filling Method I. Analysis of Film Structure Formed by Two-Step Anodizing, Journal of the Metal Finishing Society of Japan, Vol. 36, No. 11, p. 478-482, (1985) (in Japanese)
- (8) Ono, S., Masuko, N.: Dissolution behavior of the barrier layer of porous anodic films formed on aluminum studied by pore-filling technique, Journal of Japan Institute of Light Metals, Vol. 43, No. 9, p. 447-452, (1993) (in Japanese)
- (9) JIS H 8629-1: Anodizing of aluminium and its alloys --Rating system for the evaluation of pitting corrosion-- Part 1: Rating number method, (2013)

■ Author ■



Hideaki MIYASHITA



Kohei TOMITA



Yuki YAMAGUCHI



Takahiro KUWABARA