

Development of Surface Treatment VACAL[®]-Z for Vacuum Equipment Using Corrosive Gases

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We have developed a method of micro arc oxidation treatment (VACAL[®]-Z) as a surface treatment for aluminum alloy used in vacuum equipment using corrosive gases, such as CVD equipment. The oxide layer formed by VACAL[®]-Z had a three layer structure of crystalline γ -alumina. In addition, we have devised and made possible a step processing method for treating the entire surface of large objects, such as vacuum production equipment for flat panel displays, by VACAL[®]-Z.

1. Introduction

In vacuum equipment that uses corrosive gas, such as chemical vapor deposition (CVD) and etching systems, the internal walls and internal parts require anti-corrosion treatment against various corrosive gases. The purpose of anti-corrosion treatment is to improve the durability of parts, to extend maintenance periods, and to suppress particle generation due to corrosion. In recent years, as displays and semiconductors have become more sophisticated, the continued miniaturization of their wiring has increased the importance of reducing particle generation. In CVD and etching systems, the main material used is aluminum alloy. And porous anodic oxidation treatment (Alumite) has been widely used as an anti-corrosion treatment on aluminum alloys. However, Alumite is known to have disadvantages: it increases the surface area, and the sealing process forms hydrates, increasing the amount of outgassing¹⁾. Furthermore, when alumite is used at high temperatures, cracks occur due to the difference in linear expansion coefficients between the base material and the Alumite. This causes a decrease in corrosion resistance and the generation of particles. We solved this problem using micro arc oxidation (MAO) treatment^{2,3)}. Fig. 1 shows a schematic diagram of the MAO treatment processing system and Fig. 2 shows the processing

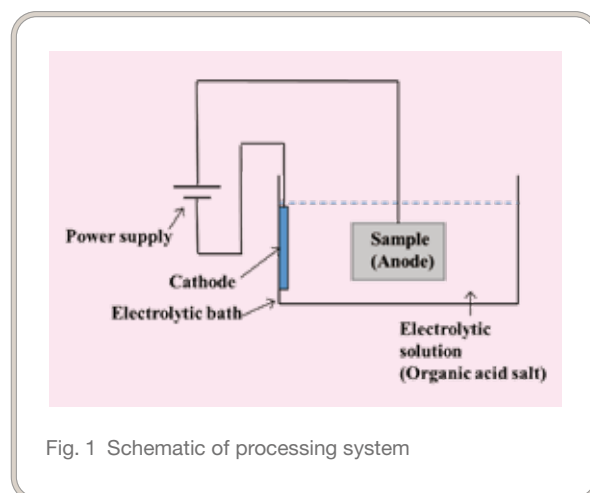


Fig. 1 Schematic of processing system

in progress. In MAO treatment, an oxide film grows by repeated melt and solidification while causing dielectric breakdown in the electrolytic solution. In addition, MAO treatment is known to grow crystalline oxide film because electrolysis is performed at high power. The crystalline oxide film is expected to have high corrosion resistance. In ordinary MAO treatment, alkali metal salts such as Na and K and phosphate chemicals are used in the electrolytic solution.

These components are said to be mixed into the oxide film. Surface treatments containing alkali metals, phosphorus, etc. cannot be placed in vacuum equipment because they have a bad affect the thin film to be deposited. We have developed the " VACAL[®]-Z " MAO process, which uses an electrolyte without alkali metal salts or phosphates. In this report, we present the evaluation results of the surface morphology, physical properties, and gas release characteristics of the

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Fig. 2 VACAL®-Z processing in progress

oxide film formed by the VACAL®-Z treatment. Furthermore, we describe the results of our development of a technique for processing large-scale products in their entirety by dividing them into multiple processing steps (step processing).

2. Characterization of oxide film formed by VACAL®-Z treatment

2.1 Evaluation sample

To obtain the substrate to be treated, we cut a 40 mm × 40 mm square from a 2 mm thick sheet of rolled aluminum alloy A6061 (Si: 0.40 to 0.80%, Fe: 0.70% or less, Mn: 0.15% or less, Mg: 0.80 to 1.2%, Cr: 0.04 to 0.35%, Ti: 0.15% or less, Al: remainder). To make the electrolytic solution for the VACAL®-Z treatment, an organic acid salt containing no alkali metal salt or the like was dissolved in pure water. The sample was used as the anode, and a carbon plate was used as the cathode. Measuring the thickness of the formed oxide film with an eddy current film thickness gauge, we found that the oxide film had grown to a thickness of approximately 15 μm.

2.2 Oxide film morphology

Fig. 3-1 shows a surface scanning electron microscope (SEM) image of the VACAL®-Z treated sample. The surface of the VACAL®-Z treated sample has a bumpy, lava-like morphology. In addition, since the electrolytic treatment is accompanied by spark discharge, which is a feature of MAO treatment, there are holes of several μm in size across the entire surface. Fig. 3-2 shows a cross-sectional SEM image

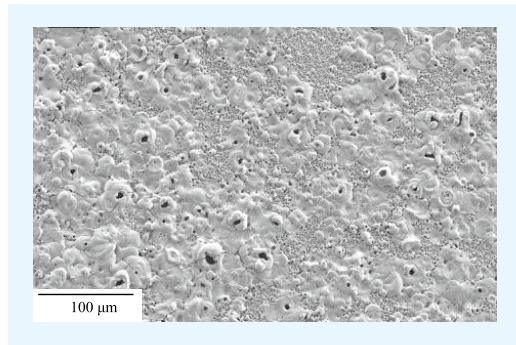


Fig. 3-1 Surface SEM image of VACAL®-Z oxide film

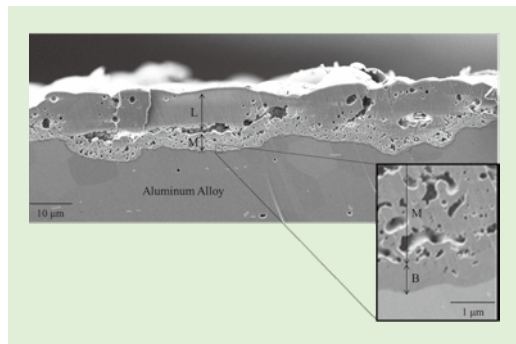


Fig. 3-2 Cross sectional SEM image of VACAL®-Z oxide film (L: Lava layer, M: Micro pore layer, B: Barrier layer)

of the VACAL®-Z treated sample. The film thickness varies from location to location and ranges from 10 to 17 μm. The oxide film formed by VACAL®-Z treatment has a three-layer structure. Starting from the outer surface, there is a lava-like layer with a thickness of less than 10 μm; a micro pore layer with a thickness of a few μm, containing small voids up to a few μm in size; and a barrier layer with a thickness of a few hundred nm formed at the interface with the base metal. The oxide film formed by VACAL®-Z treatment has voids of several hundred nm to several μm in size, but there are no voids or cracks extending from the surface to the base metal.

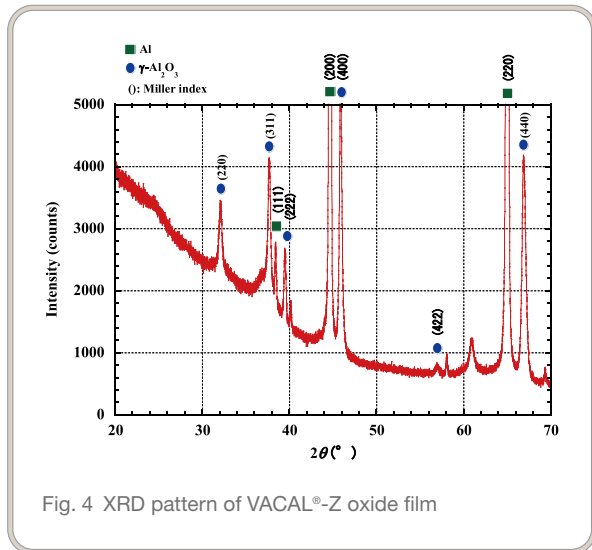
2.3 Changes in the oxide film due to heating and cooling

The VACAL®-Z treated specimens were repeatedly vacuum heated and cooled at 400°C for 3 h to check for cracks, which are the cause of the decrease in corrosion resistance. No cracks occurred in the VACAL®-Z treated

sample as a result of the heating and cooling, and there was no change in the surface morphology shown in Fig. 3-1. It is generally known that Alumite cracks when heated due to the difference in the coefficient of linear expansion between the base metal and the Alumite³⁾. This phenomenon applies to VACAL[®]-Z treatment as well. However, the reason why heating and cooling did not cause cracking in the oxide film formed by VACAL[®]-Z treatment is thought to be due to the stress relaxation caused by the distribution of voids of several hundred nm to several μm throughout the oxide film.

2.4 Crystallinity of the oxide film

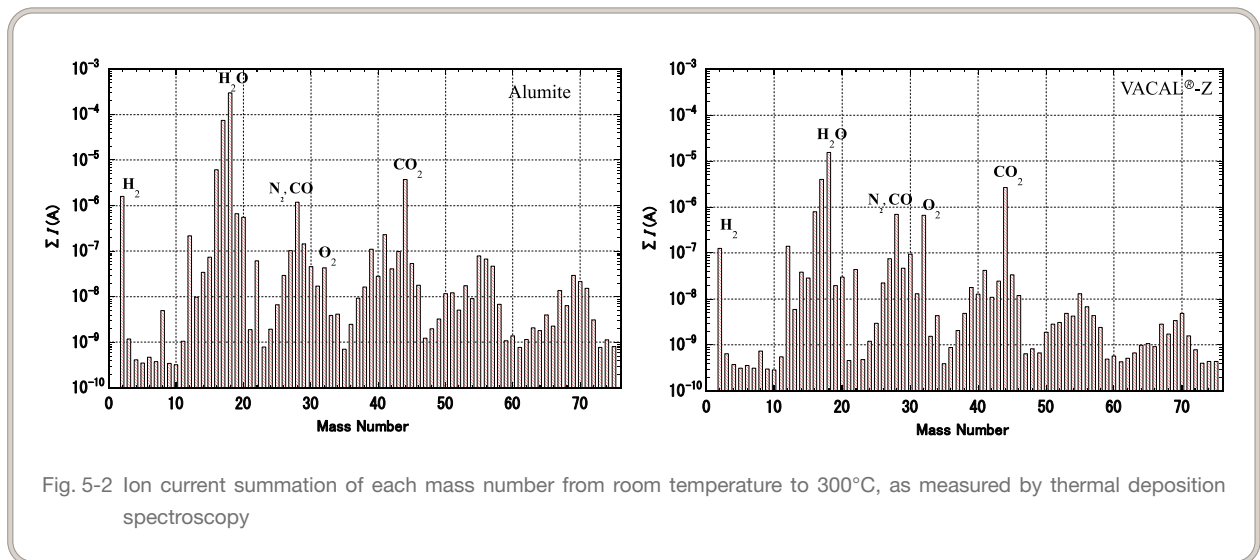
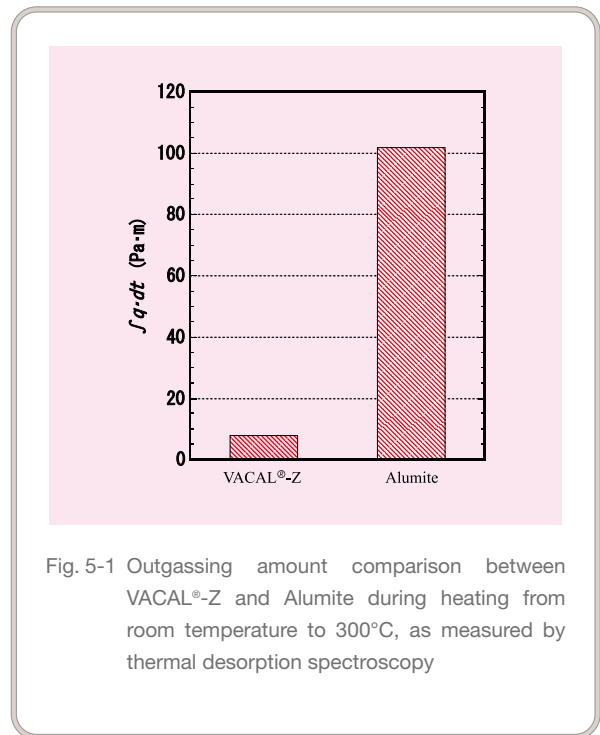
Fig. 4 shows the results of X-ray diffraction (XRD) measurements of the VACAL[®]-Z treated sample. Peaks of $\gamma\text{-Al}_2\text{O}_3$ were detected in the oxide film formed by VACAL[®]-Z treatment, indicating the growth of a crystalline oxide film. Since Alumite is an amorphous oxide film, no Al_2O_3 peaks



were detected in the XRD measurements.

2.5 Outgassing characteristics of the oxide film

Fig. 5-1 shows the amount of outgassing per unit area during heating from room temperature to 300°C. The amount of outgassing from the VACAL[®]-Z treated sample was no more than 1/10 of the amount from an Alumite sample. Fig. 5-2 shows the ion current summation value of each gas released from the VACAL[®]-Z treated sample and the Alumite sample from room temperature to 300°C. The main gases outgassing from the VACAL[®]-Z treated sample were hydrogen, water, nitrogen, carbon monoxide, oxygen,



and carbon dioxide, and water being the most commonly released gas. In terms of water release, the VACAL[®]-Z treated sample had an ion current summation value of about 1/10 that of the Alumite sample. This is thought to be due to the lack of fine holes like those in the Alumite sample and the lack of hydrate formation. In addition, the VACAL[®]-Z treated sample had a higher ratio of carbon dioxide and oxygen than the Alumite sample did. The large amount of carbon dioxide outgassing is thought to be due to the release of electrolyte anions incorporated in the oxide film. A large amount of oxygen was released because the electrolytic treatment was performed at a high voltage and a high current density, and as a result significant quantities of oxygen ions were incorporated into the oxide film.

2.6 Measurement of impurities in the oxide film

We used an electron probe micro analyzer (EPMA) to identify impurities in the oxide film formed by VACAL[®]-Z treatment. The elements detected in addition to Al and O were Mg, Si, Fe, Cr, and C. No elements other than those derived from the base metal were detected. In a typical MAO treatment, the electrolyte components Na, K, P, etc. enter the oxide film, and S does so in the Alumite. However, because our newly developed VACAL[®]-Z treatment uses organic acid salts as the electrolyte, these elements were not detected.

3. Technique for large-area VACAL[®]-Z treatment

3.1 Challenge: VACAL[®]-Z treatment of large shower plate

In the sections above, we described various characteristics of the oxide film formed by VACAL[®]-Z treatment, and we demonstrated that an oxide film with favorable characteristics

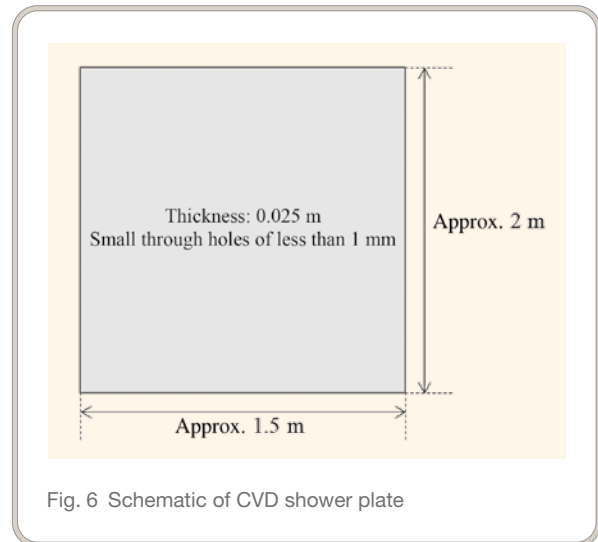


Fig. 6 Schematic of CVD shower plate

could be formed for use in CVD and etching systems. Current vacuum manufacturing equipment (especially for flat panel displays) is large. However, VACAL[®]-Z treatment requires high voltage for electrolysis, which means significant power is required for treatment of a large area. This makes it difficult to treat large components. This section summarizes the issues involved in VACAL[®]-Z treatment for shower plates used in CVD equipment, etc., which structurally have a high degree of difficulty in surface treatment among large parts. Fig. 6 shows a schematic of the shower plate to be treated. The first challenge, is that it is difficult in terms of electric power to process a large area at once. For this reason, we devised the step processing method described below, which enables treatment of the entire surface. The second challenge is the formation the oxide film at the corners. For example, in Alumite, since the growth direction of the oxide film is perpendicular to the surface, cracks are likely to form at sharp angles. The third challenge is the formation of the oxide film inside the fine holes. When treating a shower

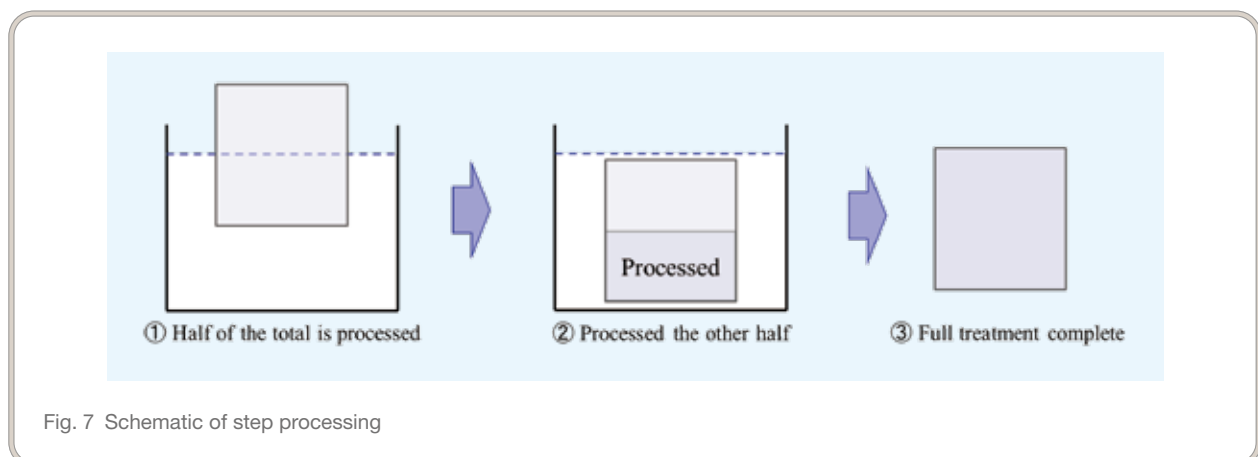


Fig. 7 Schematic of step processing

plate, an oxide film must be reliably formed even in holes of 1.0 mm or less in diameter and several dozens of mm in depth. This section shows the results of testing whether these challenges can be solved.

3.2 What is step processing?

Fig. 7 shows the procedure for step processing. The procedure shown here is for the case where the treatment of the entire surface is done in two steps. First, in order to treat half of the whole, half is immersed in the electrolytic solution and subjected to VACAL[®]-Z treatment. Next, in order to treat the remaining half, the entire surface is immersed and subjected to VACAL[®]-Z treatment. Since the VACAL[®]-Z treatment only grows an oxide film with a film thickness proportional to the treatment voltage, the oxide film does not grow above the film thickness determined by the treatment voltage. In other words, this method utilizes the fact that electrolytic treatment is preferentially performed in areas where the oxide film has not yet been formed. The method and step processing we devised ensure uniform VACAL[®]-Z treatment over the entire surface of the target.

3.3 Evaluation sample

The CVD shower plate shown in Fig. 6 was prepared as the evaluation sample. This shower plate was subjected to step processing four times to treat the entire surface. In addition to the above, to verify that there are no problems on morphology or composition, we obtained a 500 mm × 1000 mm × 3 mm sheet of aluminum alloy A6061 and prepared a sample that underwent the same step processing.

3.4 Verification of step processing

Fig. 8-1 shows a photograph of the CVD shower plate for

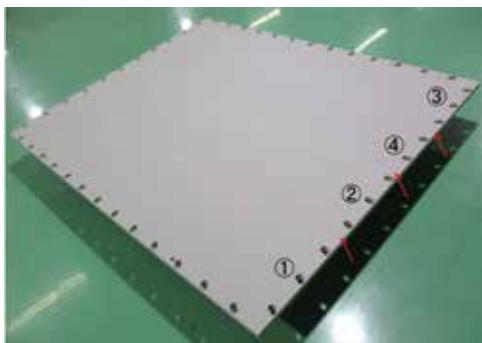


Fig. 8-1 Photograph of VACAL[®]-Z treated shower plate

Table 1 Component analysis of VACAL[®]-Z oxide film formed by step processing

Detected element	Fixed value(wt.%)	
	First	Border
O	62.4	63.4
Al	36.5	34.5
Mg	0.2	1.2
Si	0.3	0.1
Fe	0.1	0.2
C	0.5	1.2

which the entire surface was treated by step processing. The numbers in the photograph indicate the order (1, 2, 3, 4) in which the step processing was performed. Visual inspection revealed black streaks at the locations corresponding to the liquid surface of the electrolytic solution (red arrows), however an oxide film was formed on the entire surface. Fig. 8-2 shows the results of measuring the thickness of the oxide film using an eddy current film thickness gauge. The numbers in the photograph indicate the thickness of the oxide film at different locations, ranging from 13 to 15 μm. An oxide film of approximately the same thickness was formed at each step. Fig. 9 shows cross sectional SEM images of the first step and the border where the black streak appeared, and Table 1 shows the results of the component analysis of the oxide film performed by EPMA qualitative analysis. The results show that the border region formed by the step processing had an oxide film that was morphologically and compositionally equivalent to that of other regions.

3.5 Verification of oxide film formation at corners

Fig. 10 shows surface SEM images of two corners treated with VACAL[®]-Z treatment and Alumite, respectively.

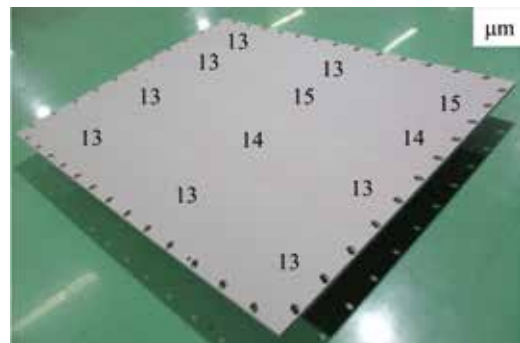


Fig. 8-2 Oxide film thickness of VACAL[®]-Z treated shower plate

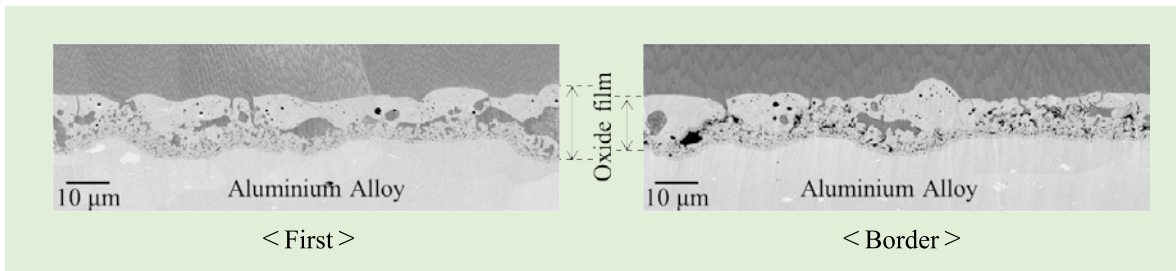


Fig. 9 Cross sectional SEM images of VACAL®-Z oxide film formed by step processing

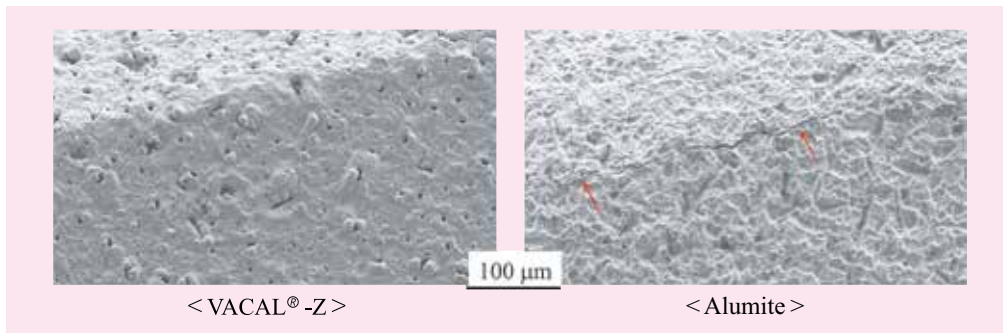


Fig. 10 Surface SEM images of VACAL®-Z oxide film and Alumite

Cracking is visible on the Alumite corner, whereas the corner receiving the VACAL®-Z treatment was covered with an oxide film. Alumite tends to crack at sharp angles such as corners because the oxide film grows perpendicular to the surface in the depth direction. It is thought that the VACAL®-Z treatment, in contrast, is able to form the oxide film uniformly without cracking, even in the corners, because the oxide film grows by repeated melt and solidification of the Al via electric discharge.

3.6 Verification of oxide film formation inside the fine holes

It is difficult to form an oxide film inside the fine holes in targets such as shower plates by means of anodic oxidation treatments such as VACAL®-Z treatment. The reasons for this are thought to be (1) it is difficult for the electrolytic solution to penetrate into the fine holes, and (2) bubbles generated by electrolysis inhibit the formation of the oxide film. We improved the immersion method to allow a sufficient amount of electrolytic solution to penetrate into the fine holes. To check the state of the oxide film inside a fine hole, we performed cross-sectional observation of

the oxide film at three locations around a fine hole: the shower plate surface (A), the fine hole opening (B), and the center of the interior of the fine hole (C). Fig. 11-1 shows the locations we inspected and Fig. 11-2 shows the cross-sectional observation results. On the shower plate surface, an oxide film of approximately 15 µm was formed. At the fine hole opening, no cracks were observed on the corner, and an oxide film equivalent to that on the surface was formed. At the center of the interior of the fine hole, an oxide film was formed, but the thickness was about 2/3 that of the surface film. In the VACAL®-Z treatment, an oxide film is formed in proportion to the treatment voltage, and areas where an oxide film is not formed, or where only a thin part is formed, are intensively processed. This is thought to enable the formation of oxide film even in fine holes of Ø1.0 mm or less, which are difficult to treat electrolytically.

4. Summary

Using VACAL®-Z treatment, we were able to grow an oxide film of about 15 µm on aluminum alloy A6061. We evaluated the morphology, physical properties, and

outgassing characteristics of the film, and obtained the following results⁴⁾:

- 1) The surface morphology of the formed oxide film was extremely bumpy and had holes of several μm . The cross-sectional morphology has a three-layer structure. Starting from the outer surface, there was a lava-like layer with a thickness of less than $10\ \mu\text{m}$ and voids a few μm in size; a micro pore layer with a thickness of a few μm and small voids a few hundred nm in size; and a barrier layer with a thickness of a few hundred nm at the interface with the base metal.
- 2) Repeated vacuum heating to 400°C and subsequent cooling did not cause cracking in the oxide film formed by VACAL[®]-Z treatment.
- 3) The oxide film formed by VACAL[®]-Z treatment was a crystalline oxide film containing $\gamma\text{-Al}_2\text{O}_3$.
- 4) The amount of outgassing from the oxide film formed by VACAL[®]-Z treatment was less than 1/10 that of Alumite, and the main gas released was water. In addition, the ratio of carbon dioxide to oxygen was higher than that of the Alumite.
- 5) In our component analysis of the oxide film formed by VACAL[®]-Z treatment, the elements detected in addition to Al and O were Mg, Si, Fe, Cr, and C. No elements other than those derived from the base metal were detected.

We also applied VACAL[®]-Z treatment to the entire surface of large-scale products and a shower plate with fine holes and obtained the following results:

- 6) We were able to form an oxide film on the entire surface of large-scale products by applying step processing to treat them in multiple steps.
- 7) Using VACAL[®]-Z treatment, it was possible to form an oxide film that did not crack even at sharp corners.
- 8) Using VACAL[®]-Z treatment, it was possible to form an oxide film inside fine holes of $\text{Ø}1.0\ \text{mm}$ or less.

From these results, it can be deduced that the oxide film formed by the VACAL[®]-Z treatment we developed has high corrosion resistance and low outgassing performance when used as a surface treatment for CVD and etching processes that use corrosive gas. In addition, by using step processing, it was possible to form an oxide film even in products requiring large-scale treatment, such as vacuum manufacturing equipment for flat panel displays and products

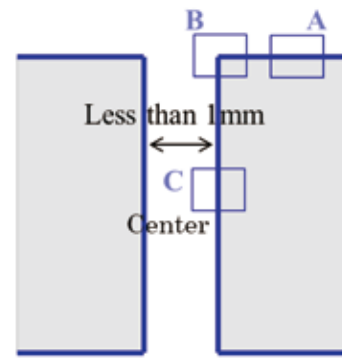


Fig. 11-1 Schematic of fine hole cross section

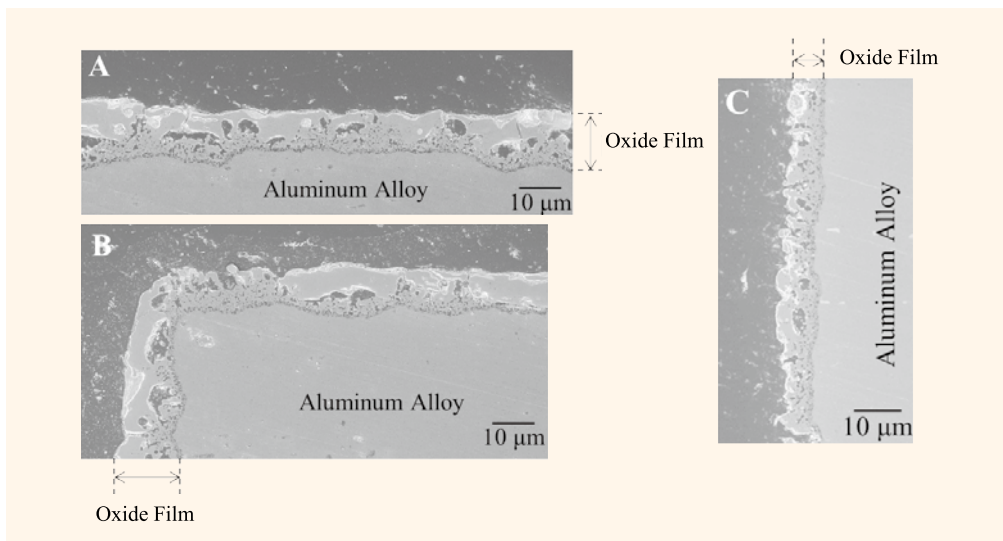


Fig. 11-2 Cross sectional SEM images of various parts of the fine hole

such as shower plates with fine holes deep enough to make surface treatment difficult. This VACAL®-Z treatment has been commercialized and is now used in our CVD systems.

*VACAL® is a registered trademark in Japan of ULVAC TECHNO, Inc., No. 4530221.

References

- 1) F. Ishigure and S. Inayoshi: J. Vac. Soc. Jpn., 58, 437 (2015)
- 2) S. S. Inayoshi and F. Ishigure: Shinku, 50, 205 (2007)
- 3) F. Ishigure and S. Inayoshi: Vacuum and Surface Science, 63, 61 (2020)
- 4) H. Sato, H. Nakamura, S. Tsukahara, Y. Ishikawa, S. Misawa, Y. Takahashi, and S. Inayoshi: Shinku, 45, 438 (2002)