Application of Inorganic Silicon Sealer to Anodic Oxide Coating

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The anodized film on aluminum-based materials can improve their corrosion resistance. Therefore, the surface treatment is very useful particularly for outdoor applications. When it is applied to some age hardened aluminum materials, the corrosion resistance is sometime deteriorated, and not improved by the conventional sealing. In this study, we applied an inorganic silicon sealer to anodized films for wrought Al-Cu, Al-Mg-Si and Al-Zn-Mg alloys and investigated their corrosion resistance by CASS test. Then we observed the corrosion characteristics by SEM-EDX etc. and discussed on the mechanism of corrosion and it's prevention by the silicon sealer.

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INTRODUCTION

Recently, the demand for high corrosion resistance of structural materials has been increasing each year. Various materials including weather resistant steels, hot galvanized steels, aluminium alloys etc. have been investigated. Particularly, aluminium alloys have high strength-to-weight ratios and have been applied to various conveyances such as aircrafts, automobiles, trains, bicycles etc. However, the surface treatment plays a very important roll to prolong their service lives, particularly when they are used in the open air. Anodic oxidation has been a powerful tool for the purpose, but unfortunately, it has not been adequate, since various deficiencies in anodic oxide films such as pin holes etc may decrease the corrosion resistance. Even though micro pores of the anodic oxide films were sealed in the hot water, the serious corrosion often occurs on the surfaces. Therefore, the overcoat by another ways would be a subsidiary protection way for those anodic oxide films.

There are many kinds of overcoats for anodic oxide films. They can be classified into two main groups. The one is organic. It can enhance the corrosion resistance. However, the stability has a serious problem under the ultraviolet light. On the other hand, the second group composed of inorganic compounds has higher stability in the open air, since the latter is relatively stable under the ultraviolet light. So we focused on an inorganic coating in this study and investigated the application to the anodic oxide films for aluminium alloys. We studied the corrosion characteristics of three kinds of aluminium alloys, when an inorganic coating was applied to anodic oxidized aluminium alloys.

EXPERIMENTAL

Specimens and sealers

Substrates used in these experiments were an Al-Cu alloy (JIS 2014), an Al-Mg-Si alloy (JIS 6151) and an Al-Zn-Mg alloy (JIS 7075). For the Al-Cu alloy and Al-Zn-Mg Alloy, the blocks (95 x 55 x 5 mm: 3.74in x 2.16in x 0.20in) were used. On the other hand, rods (the diameter 40mm: 1.57in. the length 5mm: 0.20in) were used for Al-Mg-Si alloys. For every kind of specimens, substrates were anodized. Anodizing treatments were carried out in the following way. The bath used for the purpose was 20% sulfuric acid. The treatment temperature was 25 centigrade Celsius (77 Fahrenheit) and the bath was agitated by a chemical pump. The anodic current density for the anodizing treatment was $1.3 A/dm^2$, and the treatment time was 450 sec. The film thickness was 2.5μm (9.84×10^{-7}in.). Then some of them were immersed in hot water to seal the surface pores of anodic oxide films. We call the process “conventional sealing” in this paper.

In addition, a silicon sealer[(1),(2)] was applied moreover to these anodized aluminum alloy specimens as occasion. The silicon sealer was one of alkoxysilane compounds (Rhombic Co., 1-69 Shiohama, Yokkaichi, Mie 510-0851, Japan) and it penetrated into the pores of coatings very easily due to its low viscosity (61.5mPa・s). After it interpenetrates into pores and coats the spray coating, it reacts with the moisture of the ambient atmosphere and hardens due to the formation of inorganic polymer. It is usually very stable under ultraviolet light. We coated these aluminium alloys with the silicon sealer, using small brushes, and in about five minutes after brushing, we blotted them by papers completely, so that we could check the effect of sealing for pores and defects of anodized films.

Specimens used in these experiments were summarized in table 1. We gave each of them a notation for convenience.

Table 1 Specimens used in this experiment and their notations.

	sealing in hot water	sealing by alkoxysilane	notations
Al-Cu	no	no	spec.A
Al-Cu	yes	no	spec.B
Al-Cu	yes	yes	spec.C
Al-Mg-Si	none	no	spec.D
Al-Mg-Si	yes	no	spec.E
Al-Mg-Si	yes	yes	spec.F
Al-Zn-Mg	none	no	spec.G
Al-Zn-Mg	yes	no	spec.H
Al-Zn-Mg	yes	yes	spec.I

Experimental Procedure

CASS tests

Corrosion characteristics were evaluated mainly by CASS tests. The solution used for the CASS test was composed of NaCl (50g/L), $CuCl_2$・$2H_2O$(0.26g/L) and acetic acid (1ml/L). The pH was adjusted to 3.0-3.2. The

CASS Test was carried out according to the Japanese Industrial Standard (JIS H8502: 1999). The temperature in the chamber was 50 degrees Celsius (122 degrees Fahrenheit), using the commercially produced apparatus (Suga, CAP-90). The amount of spray was 1.5/80cm^2/h and the compressed air pressure was 0.1MPa. The test term was 48 hours and then the surface conditions were observed by visual checks. Visual checks used in this investigation were classified into two types. One was the photos taken by a digital camera. The other was rating number technique prescribed by Japanese Industrial Standards (JIS) Z2371. For the latter, a certain area whose square measure was 5000 mm^2 (7.75 in^2) on each specimens after CASS tests was chosen for the evaluation. We call these measured areas “the effective surface”. The number and the shape of corrosive defects were compared with the appendix of the standard and the nearest numbers were fixed as rating numbers (RN). The RN has a certain relation to the corrosion area ratio shown in Table 2.

Table 2 Corrosion area rate and rating number.

Area(%)	0.00	<0.02	0.02-0.05	0.05-0.07	0.07-0.1	1-0.25	0.25-0.5	0.5-1.00	1.0-2.5	2.5-5	5-10	10-25	25-50	<50
RN	10	9.8	9.5	9.3	9	8	7	6	5	4	3	2	1	0

SEM observations

Surface Observation was done also by SEM-EDX. Each specimen before and after CASS tests was checked by naked eyes and the pictures were taken by a digital camera, as mentioned before. On the other hand, the cross sections of specimens’ surfaces were observed by a scanning electron microscope (SEM: Hitachi S-4300)-EDX (Horiba EMAX-7000). The acceleration voltage was 20kV and element mapping was carried out for cross sectional surface areas of the specimens.

RESULTS AND DISCUSSIONS

CASS Tests

(1) spec.A (2) spec.B (3) spec.C

Fig.1 Surface conditions of Al-Cu alloys after CASS tests.

CASS tests were carried out for all of specimens shown in Table 1. Fig.1 shows the surface conditions after CASS tests for Al-Cu alloys. Fig.1-(1) shows the surface of spec.A. Many corrosion pits and iron rust were observed on the surface and it indicates that anodized Al-Cu without any sealing was very corrosive. We presume that some inevitable defects in anodized film for Al-Cu alloy would induce serious corrosion. Fig.1-(2) shows the surface of spec.B. Many corrosion pits and red iron rust were still observed. But the extent of corrosion decreased than that of spec.A. Fig.1-(3) shows the surface of spec.C after CASS test. It indicates that the application of the silicon sealer enhanced corrosion resistance drastically. The number of corrosion pits decreased and there were few iron rust on the surface in this case.

(1) spec.D (2) spec.E (3) spec.F

Fig.2 Surface conditions of Al-Mg-Si alloys after CASS tests.

Fig.2 shows the surface of Al-Mg-Si alloys after CASS tests. Fig.2-(1) shows the result of spec.D. Many pits were found on the surfaces. However, the corrosion extent was not so high like spec.A. Fig.2-(2) shows the surface condition of spec.E. The amount of pits and corrosion sites decreased for the specimen, being compared with those of spec.D. The sealing of Al-Mg-Si in hot water increased the corrosion resistance. Fig.2-(3) shows the surface condition of spec.F. The extent of corrosion for this specimen was the least among these three Al-Mg-Si specimens. However, the differences of the corrosion among these three specimens were not so large than those for Al-Cu alloys.

(1) spec.G (2)spec.H (3)spec.I

Fig.3 Surface conditions of Al-Zn-Mg alloys after CASS tests.

Fig.3 corresponds to the surface conditions of Al-Zn-Mg alloys after CASS tests. Fig.3-(1) shows the surface of spec.G after CASS test. There were lots of pits on the surface and it indicates that the specimen without any sealing was very sensitive to the corrosion. Fig. 3-(2) shows the result for spec.H, while Fig.3-(3) shows that for spec.I. The former was applied by the conventional sealing of anodic oxide film and the latter was coated by silicon sealer in addition. The extent of corrosion for both Fig.3-(2) and (3) were lower than that for Fig.3-1. However, the difference of corrosion extent was not so remarkable for this alloy. For all of specimens without any sealing, the corrosion resistance was lower, being compared with that of sealed specimens. It suggests that anodized oxide films on these aluminum alloys would have some defects vulnerable to corrosion. The sealing increased corrosion resistance to protect these defects. From the viewpoint, conventional sealing by hot water is not enough to protect the specimens against corrosion. When the silicon sealer is applied to aluminum alloys, their corrosion resistances are enhanced remarkably.

All of these corrosive conditions of specimens after CASS tests were evaluated by rating number technique according to Japanese Industrial Standard (JIS) Z 2371. The higher the rating number is, the more remarkable the corrosion condition of corresponding surface is. Fig.4 shows the rating numbers for all of these

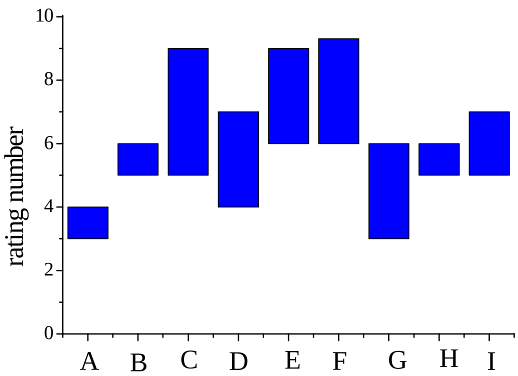

Fig.4 Rating numbers for all specimens used in this study after CASS tests.

specimens used in these experiments. For all aluminum alloys, the specimens without any sealing have the lowest rating numbers among the each same alloy group. When the specimens without any sealing are compared with each other, the rating number of spec.A (Al-Cu alloy) was the lowest. And it increased in this order: spec.G (Al-Zn-Mg alloy), spec.D (Al-Mg-Si alloy). It suggests that anodized Al-Si-Mg alloy was the most stable against corrosive CASS test. And the specimens with conventional sealing have the midst. For Al-Cu specimens, the rating number for spec.A was much lower than that of spec.B and C. It suggests that anodized Al-Cu has a lot of defects in their surface film and they can corrode during CASS test. Therefore, the sealing for the anodic film was effective and the application of both sealing techniques (conventional sealing and silicon sealing) increased corrosion resistance. When both type of sealing methods were compared with each other, the sealing by conventional sealing plus silicon sealer was more effective to prevent corrosion. For Al-Mg-Si specimens, the application of both sealing (conventional one and silicon sealer) increased the corrosion resistance almost to the same extent. On the other hand, the addition of silicon sealer was slightly more effective to increase corrosion resistance than only the conventional sealing for Al-Zn-Mg alloys. For both of Al-Mg-Si and Al-Zn-Mg alloys, the increases of corrosion resistance were not so remarkable than that for Al-Cu alloy, when silicon sealing was added to the conventional one. It suggests that the original anodizsed films on the formers were dense and anti-corrosive.

And Fig.5 shows the corresponding corrosion area ratios for all of specimens. The corrosion area ratios (A) are calculated from rating numbers (RN) by the following equation (1).

$$A = 10^{(2-RN/3)} \qquad (1)$$

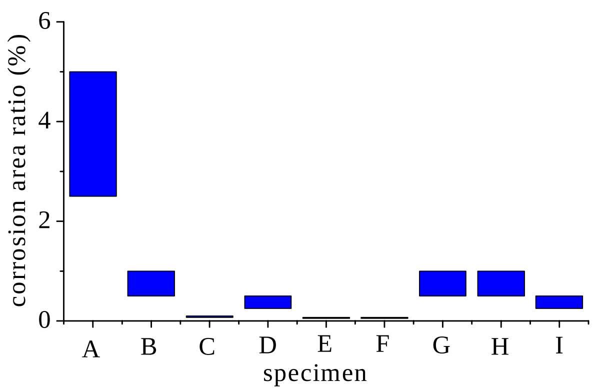

Fig.5 Calculated corrosion area ratio for all specimens used in this study.

However, when RNs are from 9.3 to 9.8,

$$A = 1 - 0.1RN \qquad (2)$$

Fig.5 shows all of the tendencies in Fig.4 more saliently. The increase of corrosion resistance by the application of both sealing methods was the highest for Al-Cu alloy specimens. And for the Al-Cu alloy, the case for the application of both sealing methods was the most effective. And this figure also shows Al-Si-Mg alloy was the most anti-corrosive among all of specimens used in this study.

Fig.6 shows a cross section of spec.A's surface area observed by SEM. The corrosion pit was found in the vicinity of the surface. On the other hand, the sealed surface by the silicon sealer (Fig.7) was stable and not corroded, shown in Fig.6.

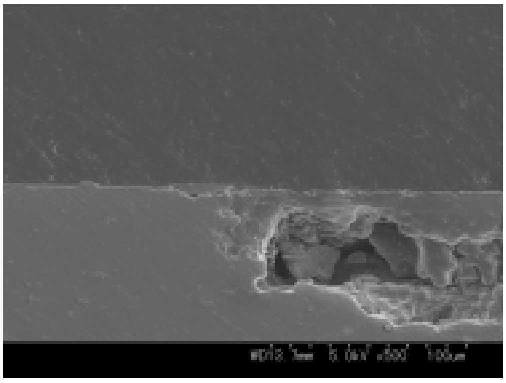

Fig.6 SEM photograph for the cross section of the surface (spec.A).

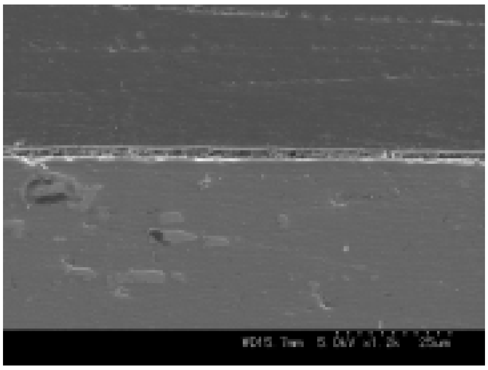

Fig.7 SEM photograph for the cross section of the surface (spec.C).

The anodizing and its sealing in the hot water give the aluminum alloys high corrosion resistance. However, they still have micro defects and the sites could be a starting point for corrosion. The silicon sealer can penetrate into such a defect very easily and after the reaction with the moisture in the air, and it can be hardened very rapidly, so that it protects the substrate and anodized films effectively. Since this silicon sealer is very stable against ultraviolet light, the sealed aluminum alloys by this silicon sealer will be powerful tools for the application of the aluminum alloys to the outdoor use.

CONCLUSIONS

The application of silicon sealer to some aluminum alloys to enhance the corrosion resistance of aluminum alloys was investigated. Anodized Al-Cu alloys, Al-Mg-Si alloys and Al-Zn-Mg alloys were used as specimens. The specimens without any sealing and those sealed in hot water were also investigated as reference. CASS tests were carried out as corrosion test. The corrosion surfaces were observed by visual check and scanning electron microscopy. The following results were obtained.

(1) Anodized Al-Cu alloy without any sealing was corroded severely by CASS test. The conventional sealing in hot water increased the corrosion

resistance of the alloy. And the application of the silicon sealer to the specimens with conventional sealing enhanced the corrosion resistance drastically.

(2) Al-Mg-Si alloys applied by silicon sealer did not show any remarkable difference from those sealed in hot water, even though the corrosion resistance of both were higher than that of the specimen without any sealing.

(3) For Al-Zn-Mg alloys, the results were very similar to those for Al-Mg-Si alloys. However, the effect of silicon sealer to enhance the corrosion resistance was higher for Al-Zn-Mg alloy than that for Al-Mg-Si alloy.

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