High Corrosion and Weather Resistant Anionic Resin Coating for 2014 T6 Aluminum Alloys Which Maintains Mirror Luster

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A new surface treatment technology for 2014 T6 aluminum alloys that exhibits not only high corrosion and weather resistance but also good mirror luster has been developed. By using this new electrode-position coating process with anion resin, the resin can preferentially permeate into cavities that are formed by dissolving of the second phase particles during a general anodizing process. In order to maintain the excellent appearance, the thickness of the anodized layer and anion resin layer was optimized to make the layers as thin as possible while keeping the high corrosion and weather resistance. Thanks to this newly developed surface treatment technology, high strength aluminum alloys featuring high corrosion and weather resistance with mirror luster are now available for industrial products. [doi:10.2320/matertrans.47.2786]

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1. Introduction

Anodizing is one of the most common aluminum surface coating methods.^{1,2)} In the areas where appearance and functional aspects of aluminum products are important, a variety of ideas have been applied to surface treatment. Examples include the application of electro-deposition coating to the regular anodized surface; application of chromate or phosphate coating prior to anodizing process to improve wear resistance and corrosion resistance³⁾ and addition of agents to the electrolytic bath to decrease solar absorption index and increase infrared emissivity.^{4,5)} In recent years, many studies on the electrical insulation properties of tantalum, titanium, etc. within the anodized film have been carried out in the field of electronic materials,^{6–8)} and anodized aluminum is attracting a good deal of public attention as a clean, recyclable material.⁹⁾

While mirror luster and high corrosion resistance are required for products such as outdoor goods and high quality sporting goods to be used under a harsh environment, in reality, very few products have the required corrosion resistance and weather resistance while maintaining mirror luster. In addition, it is known that high strength aluminum alloys have many defects in which inter-metallic compounds of the substrate are dissolved and formed in the anodized film reducing corrosion resistance, and in particular, aluminum alloy $A2014^{10-12}$ is not suitable for the anodizing process. On the other hand, forming a thick anodized film or applying an electro-deposition coating after anodizing can maintain high corrosion resistance. However, this leaves the appearance of a coating and sacrifices the mirror luster unique to the metal, decreasing the surface reflectance. As a consequence, the appearance of high quality is lost and the product value will be decreased.

In order to provide A2014 alloy with high weather resistance and high corrosion resistance for outdoor use (CASS 3 cycle (172.8 ks); rating number 9.5 or greater), and good appearance with mirror luster unique to the metal

(reflectance of 50% or greater) without increasing cost, a new processing technique (hereinafter called "electrolytic permeation") that combines anodizing and electro-deposition coating techniques has been studied and developed. As a result, a surface of high corrosion resistance without damaging the good appearance of mirror luster¹³) was obtained by utilizing an electrochemical reaction for the existing anodizing and electro-deposition coating techniques.^{14,15})

2. Method of Experiment

2.1 Anodizing process

Aluminum alloy A2014 T6 (ϕ 40, t = 10) was used as the sample for this experiment. The surface of the sample was mirror-finished (Ra: 0.035 µm) with 1 µm alumina paste. As a pre-treatment, the sample was degreased with TOP AL-CLEAN (Okuno Chemical Industries Co., Ltd.) 50 g/L, acid cleaned with 30% nitric acid, and rinsed with water. The anodizing was performed with a commonly used electrolytic bath, which is a 12% sulfuric acid bath, at 298 K, and electric current density of 1.3 A/dm². Lead was used for the counter electrode. After the anodizing process, a nickel acetate sealing method¹⁶ in which samples can be continuously processed with existing inexpensive equipment, was applied.

2.2 Electrolytic permeation

After anodizing and nickel acetate sealing, the samples were degreased with TOP AL-CLEAN (Okuno Chemical Industries Co., Ltd.) 50 g/L, and acid cleaned with 3% dilute sulfuric acid. Subsequently, anionic electro-deposition was performed using acrylic-melamine anionic electro-deposition coating at 298 K, voltage 28 to 36 V, for 30 to 98s. As mentioned previously, this process is called electrolytic permeation. SUS316 was used for the counter electrode. The sintering process after permeation was carried out at 373 K for 0.6 ks, then at 463 K for 1.8 ks.



(c) After corrosion test

Fig. 1 The images of the top surface observed by an optical microscope: (a) after buffing and before anodizing; (b) after anodizing; and (c) after corrosion test (CASS test 3 cycles, 172.8 ks).

2.3 Evaluation of properties

The surface and the segment of the prepared samples were observed by scanning ion microscopy (SIM). The prepared samples were cross-sectioned and the thickness were determined by microscopic measurement. The corrosion resistance was evaluated by a 172.8 ks copper-accelerated acetic acid salt spray test (CASS test) using a solution made by adding copper (II) chloride dihydrate to acetic acid sodium chloride (defined in JIS H8681). The weather resistance was evaluated by dew cycle testing (defined in JIS H8685) for 360 ks cycle between sunny at 336 K and 50% humidity for one hour and rainy at 303 K and 95% humidity for one hour using the sunshine carbon arc type weather resistance testing apparatus (rated as 50 V, 60 A).

3. Results of Experiment and Discussion

Microphotographs in Fig. 1 show the surface before and after the anodizing process observed by an optical microscope (a) after buff polishing, (b) after anodizing, and (c) after corrosion resistance test (3-cycle CASS testing; 172.8 ks). The inter-metallic compound CuAl₂ of the pre-anodized A2014 in (a) appears to have been dissolved or to have partially remained after anodizing as can be seen in (b). It is considered that these types of defective areas become the starting points for corrosion shown in (c).

Comparison was attempted for these post-anodized samples by quantifying the surface luster. To do this, the intensity was measured for each sample at the angle of incidence of 60° and the angle of reflectance of 60° . The reflectance of the



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Fig. 2 Relation between anodized film thickness and reflectance.

samples with varying anodized film thickness was measured by assuming that the reflectance of the pre-anodized, postmirror buffed sample (Ra: $0.035 \,\mu$ m) as 100%. The results in Fig. 2 show that as the anodized film thickness increases, the reflectance decreases. This agrees with the phenomenon that the metallic luster after mirror buffing is lost and clouded with increase in the anodized film thickness. The results suggest that metallic luster can be quantitatively expressed with reflectance values, which can be compared. From the observations above, it is clear that the decrease in reflectance after anodizing largely depends on the thickness of the anodized film. Accordingly, the thickness of anodized film was set at $1.5\,\mu\text{m}$ because the target reflectance is 50% or greater.

In the construction material industry, etc., sealing is carried out typically by electro-deposition coating after anodizing.^{17–19} Anodized film before sealing has greater electric conductivity than after sealing. Because of this, the mirror luster unique to the substrate metal is lost due to the electro-deposition coating resin, which is deposited thickly over the surface to be coated.²⁰⁾ Accordingly, in order to increase insulation, nickel acetate sealing was performed after anodizing, which was then followed by electrolytic permeation.

Although anodized film is considered to be almost the same as an insulator, $^{21,22)}$ as for H⁺ dissociated from water in the electrolytic permeation process, while the electric current that approaches the aluminum from the anodizing film as a result the proton current flows, current does not flow in the reverse direction because there is no supply of protons.⁶

Thus, the anodized film is suggested to control the flow direction in the manner that the electric current flows easily to the cathode direction.

Accordingly, an attempt was made to fabricate highly corrosion resistant combined type coatings by utilizing the rectifying capability of anodized coating. Generally, there are two types of electro-deposition coatings: cationic and anionic. In cationic resin, similarly to electroplating, both the normal areas and defective areas of the anodized film are deposited in the same manner, giving the coating appearance, which results in reduced reflectance. Therefore, it was intended to have the electro-deposition coating resin deposit onto the defective areas preferentially by utilizing the rectifying capability of anodized film. Specifically, by making the object to be processed an anode with the anionic electro-deposition coating technique so that the total amount of depositing resin is restricted and the resin is preferentially deposited onto the defective areas where the electric current readily flows towards the anode, an attempt was made to fabricate a combined type of coating featuring low coating appearance or high reflectance, and mirror luster unique to the substrate metal.

The correlation between the processing time and electrolytic permeation coating thickness at a given processing voltage was examined. The results in Fig. 3 show that the electricity increases as the processing voltage increases for a given process time, resulting in an increase in the electrolytic permeation coating thickness. Also, as processing time passes, the rate of increase in the coating thickness decreases. This phenomenon, which occurs when a certain level of electricity flows in the object to be processed and the resin is deposited over the surface of the object resulting in a restricted current, is also observed in regular electrodeposition coating.

The change in reflectance when the anodized film thickness is uniform at $1.5 \,\mu\text{m}$ and the overlain electrolytic permeation coating thickness is varied is shown in Fig. 4. As in the case of anodized film, the reflectance decreases with increase in the electrolytic permeation coating thickness. Because the target reflectance is 50% or greater, the electrolytic permeation coating thickness is determined as $1.5 \,\mu\text{m}$.



Fig. 3 Relation between the processing time and coating thickness for electrolytic permeation over anodized film.



Fig. 4 Relation between electro-deposition coating thickness and reflectance of 1.5 µm anodized film formed specimens.

In the following step, the CASS test (defined in JIS H8681) was performed for 48 hours to evaluate the corrosion resistance for the samples that were electrolytically permeated at 32 V for 30s, which is the condition for the thickness of the electrolytic permeation coating reaching roughly 1.5 µm. The weather resistance was evaluated by the dew cycle test (defined in JIS H8685) performed for 360 ks. The results (Fig. 5) show that the samples without the electrolytic permeation process after 3 cycles of the CASS test (1 cycle: 57.6 ks) have the rating number of 7.0, while the samples with the electrolytic permeation process have the rating number of 9.5, maintaining a very high metallic luster. On the other hand, in a weather meter test, the color difference ΔE improved from 11.6 to 3.0. These results show that the electrolytic permeation technique adopted in this study provided the target reflectance of 50% or greater for the thin anodized film thickness of 1.5 µm, while improving corrosion



Fig. 5 Optical microscopy images of the surface of the anodized film and permeated samples after CASS test (172.8 ks) and dew cycle test (360 ks).

resistance. In addition, the results for the dew cycle test show that weather resistance against ultraviolet rays and water has also been improved.

An SIM image of the cross-section after electrolytic permeation is shown in Fig. 6. The image shows that the inter-metallic compounds are dissolved or fallen off due to anodizing, and the anodized film is formed in a concave manner. The thickness of the defective areas of anodized film in the concave locus is approx. $0.9 \,\mu\text{m}$, which is thinner than the thickness of the normal areas of 1.5 µm. Because many inter-metallic compounds, which cause defects, are present horizontally and vertically, and are precipitated on the surface of the pre-anodized samples, as well as in the direction of depth, defective areas are formed over the sample surface everywhere after anodizing. Depending on the size of the precipitated inter-metallic compounds, anodized film may hardly be formed in some areas, indicating that the substrate A2014 is possibly exposed on the surface. The subsequent electrolytic permeation covered the defective areas with a 1.9-µm-thick resin layer, while it formed a very thin, 0.6-µm-thick resin coating (electrolytic permeation coating) over the anodized film.



Fig. 6 An SIM image of cross section of the anodized coating and electrolytic permeation coating.

Carbon mapping

20 µm

Fig. 7 EPMA images (carbon mapping) of the top surface analysis at the initial phase of the electrolytic permeation process.

Figure 7 shows the carbon mapping by EPMA at the time of initial voltage application, in which electrolytic permeation coating is not continuous. The image shows that, by applying electrolytic permeation, preferential concentration of carbon, which is the main component of the resin, occurs in the deposited pits indicated by the red circles, indicating that the resin is filled in the pits. It is considered that the resin deposits and condenses selectively at the large defective areas of anodized film at the initial stage, and that the resin shifts to adhere to the smaller defective areas of anodized film as the time passes.

Electric current preferentially flows towards the anode in the areas where anodized film is thin or discontinuous, and thicker electrolytic permeation coating is preferentially formed in the defective areas, providing protection to the starting points of corrosion. Thus, a very thin electrolytic permeation coating was formed on the anodized film, resulting in a surface with mirror luster, which has little coating-like appearance.

Conclusion 4.

A new processing technique was studied that combines anodizing and electro-deposition coating techniques to give a good appearance without damaging mirror luster while maintaining a high corrosion resistance to aluminum alloy A2014, which had heretofore not been considered suitable for anodizing. As a result, the following became clear.

A combined type of anodized film (electrolytic permeation) was achieved by applying anionic electro-deposition coating after anodizing so that resin is preferentially deposited on anodized film to form a very thin resin-coating layer over the normal anodized film, taking advantage of the property that current flows towards the anode preferentially in the defective areas of anodized film based on the capability of anodized film to restrict electric current (i.e., restriction of current towards anode).

By performing electrolytic permeation, improved corrosion resistance and weather resistance while maintaining a high mirror luster was achieved for aluminum alloy A2014.

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