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The Coloring Mechanism of Boehmite-treated Aluminum Foil

Toshiya ISHII* and Toshio OGAWA**

Abstract

Boehmite-treated aluminum foil was colored by a platinum coating, and its mechanism of coloring was investigated. Hydrated aluminum (boehmite (AlOOH)) was generated on the surface of aluminum foil. The color of the boehmite-treated surfaces did not change the metallic luster of the aluminum foil surface with treatment time. However, when the boehmite-treated aluminum foil surfaces were coated with platinum by magnetron sputtering, the color of the surface changed to several different colors based on the hydration time. This coloring mechanism was investigated by observation of surface structures and simulations of the reflectance of multilayer film interference. Boehmite develops as a porous needle shaped film on the aluminum surface. The deposited platinum coating is deposited in a similar manner. Therefore, the coloring mechanism of the boehmite films is thought to be due to the interference of multilayer films with varying degrees of thickness.

Key-words : Aluminum, Boehmite, Color, Platinum coating

1. Introduction

Aluminum foil surfaces treated in boiling distilled water result in the formation of hydrated aluminum on the surface of the aluminum foil. This hydrated aluminum is called boehmite (AlOOH). Boehmite-treated aluminum surfaces have been demonstrated to improve adhesion for paint, epoxy resins and low-density polyethylene¹⁻³⁾. A direct electric current in sulfuric acid solution is known to cause an anodic oxidation of aluminum, and thereby causing coloring. This anodized aluminum is called almite. The Asada method is generally employed to color almite, in which coloring is achieved by alternating the electric current⁴⁻⁶⁾. There are a number of other electrical and chemical methods to produce the colored aluminum used as construction materials such as aluminum sashes and the curtain walls⁸⁾. However, the coloring mechanisms have not

been elucidated.

Herein, boehmite-treated aluminum foil was colored by a platinum coating, and its mechanism of coloring was investigated. Aluminum foil was treated by immersion in boiling distilled water (electrical conductivity ; $0.05\mu\text{S/cm}$) at 100°C . Triethanolamine solution (0.3 wt %) served as a catalyst to the reaction. However, the boehmite-treated aluminum foil surfaces were not observed to change with treatment time ; the metallic color remained. Therefore, platinum films were deposited on the boehmite surfaces by magnetron sputtering. The platinum coated boehmite surfaces had various colors based on the hydration time. In an effort to investigate the mechanism of coloring of boehmite surfaces coated with platinum, surface structures were visualized and the reflectance of multilayer film interference was simulated. Results indicate that the porous needle shaped boehmite film directs platinum deposition in a similar manner. Thus, the multilayer film interference between the boehmite film and the platinum film is thought to be responsible for the coloring mechanism.

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* Material Analysis Research Laboratory, Technical Research Institute, Toppan Printing Co., Ltd., Sugito, Kitakatsushika, Saitama 345-8505, Japan

** Laboratory for Ecological Polymer Chemistry, Kanazawa Institute of Technology, Ohgigaoka, Nonoichi, Ishikawa 921-8501, Japan

2. Experimental

2.1 Boehmite treatment

Aluminum foil ($7\mu\text{m}$; thickness, purity; 99.4%, Toyo Aluminum, Japan) was used for the investigation. The aluminum foil was immersed in boiling distilled water at 100°C for predetermined times ranging from 15 to 120 s. The electrical conductivity of the distilled water used was $0.05\mu\text{S}/\text{cm}$. When aluminum foil was treated in boiling distilled water, hydrated aluminum was produced on the aluminum foil surface as by the following reaction⁸⁾.

Triethanolamine solution (0.3 wt %) was added to the solution as a catalyst.

2.2 Measurement of the thickness of boehmite film

The thicknesses of the boehmite films were measured by transmission electron microscope (TEM) observation (Hitachi H-8000, Japan) at an accelerating voltage of 200 kV. Epoxy resin was embedded in the sample, and the samples were placed in an oven at 60°C , for 12 hours until hardening. They were then sliced to a thickness of 80 nm at room temperature using an ultramicrotome diamond knife (Reichert ULTRACUT N, Nissei, Japan) in order to prepare them for TEM observation.

2.3 Platinum coating

The platinum films were deposited on the boehmite surfaces using a magnetron sputtering system (Vacuum Devise MSP-10, Japan). Detailed sputtering conditions are as follows: gas pressure, 6 Pa; ion current, 30 mA; and sputtering rate, about 24 nm/min. Nitrogen gas was emitted into the chamber during deposition using a needle valve. The setting thickness of the

platinum film was approximately 12 nm.

2.4 Scanning Electron Microscope (SEM) Analysis

The microstructures of boehmite surfaces were observed using a Hitachi S-5200 Infield Field Emission scanning electron microscope (FE-SEM) at an accelerating voltage of 3 kV and at 100,000-fold magnification. The sample was secured to the SEM sample holder using conductive carbon tape. Samples taken after the following boehmite-treatment times were observed; 0 s (untreated), 15 s, 45 s, and 75 s.

3. Results and Discussion

3.1 Boehmite film thickness by TEM

The thicknesses of the boehmite films versus the treatment time in boiling distilled water are shown in **Figure 1**. The boehmite thickness was observed to increase up to a treatment time of 90 s. After a treatment time of 90 s, the thickness of the treated films was almost constant, indicating that the films grew slowly.

3.2 Colors of boehmite surface coated with platinum

Photographs of boehmite surfaces (A) and the boehmite surfaces coated with platinum (B) at different boehmite treatment times are shown in **Figure 2**. **Table 1** shows the color variation of boehmite surfaces coated with platinum as a function of treatment time in boiling distilled water. The boehmite-treated aluminum foil surfaces were not observed to change color with treatment time; the metallic color remained. On the other hand, boehmite films coated with platinum changed to a number of colors with treatment time.

3.3 Microstructures of boehmite surfaces coated with platinum

Figure 3 shows the SEM images of the aluminum

Fig. 1 The thickness of the boehmite films as a function of treatment time in boiling distilled water.

Fig. 2 Photographs of the boehmite surface (A) and the surface coated with platinum (B).

(See color photo on the first page)

Table 1 The color variation of boehmite surface coated with platinum as a function of treatment time in boiling water

Treatment time (s)	Color
0	Colorless
15	Light blue
30	Orange
45	Red
60	Purple
75	Blue
90	Pale green
105	Green
120	Olive green

Fig. 3 SEM images of the aluminum surface for various treatment time 0 (untreated) (A), 15 (B), 45 (C) and 75 (D) seconds.

surface for various treatment time 0 (untreated) (A), 15 (B), 45 (C) and 75 (D) seconds. The untreated surface was flat, and only had flaws formed upon rolling up the aluminum foil (3 A). As shown in Figures 3 (B)–(D), porous films were obtained after the aluminum foils were treated in boiling distilled water. The needle-like boehmite particles formed porous films covering the entire surface of the aluminum foil. The needles grew in a rhomboid crystalline shape as the treatment time increased. The width of the needles was about 5 nm, and the pore size was about 80 nm.

Figure 4 shows SEM images of the aluminum surface coated with platinum for various treatment time 0 (untreated) (A), 15 (B), 45 (C) and 75 (D) seconds. The width of the needles was 30 nm after the platinum coating, however the pore size was almost same as before the platinum coating.

3.4 The coloring mechanism

3.4.1 Measurement of refractive index of boehmite films

The refractive index of bulk boehmite was reported

Fig. 4 SEM images of the aluminum surface coated with platinum for various treatment time 0 (untreated) (A), 15 (B), 45 (C) and 75 (D) seconds. **Fig. 5** Reflectance curve of the boehmite films formed on the aluminum surface.

to be 1.65⁹⁾. However, a boehmite layer is porous, as shown in Figure 3. Therefore, the refractive index of porous boehmite differed from the refractive index of bulk boehmite. A Hitachi U-4000 Ultraviolet-visible spectrometer equipped with an integrating sphere attachment was used to investigate of the reflectance of boehmite films treated in boiling distilled water for 120 s. The reflectance curve of the boehmite films formed on the aluminum surface is shown in **Figure 5**. The integrated intensity of reflectance was high, about 55–70%. The refractive index of the boehmite film however, was unable to be estimated because the optical constant ($n-k$) of AlOOH is unknown. The constant n is the refractive index, and k is the extinction coefficient.

3.4.2 Estimation of the refractive index of boehmite film and reflectance for boehmite film coated with platinum

The width of the boehmite needles was about 5 nm and the pore size was about 80 nm. Therefore, the microstructures on the boehmite surface are smaller

than the wavelength of the visible light. Furthermore, the porous layer of the boehmite treated surface coated with platinum show similar optical properties. Therefore, the shape of the boehmite structures could not resolved in the wavelengths of visible light. The boehmite films coated with platinum were considered to assume two layers. The coloring mechanism was thought to be a result of the interference of the multilayer film between the boehmite and platinum film. The reflectance curves of multilayer films were simulated using Essential Macload software (Version 7.3 b, Thin Film Center Inc., USA). Reflectance curves for boehmite films coated with platinum at various thicknesses were simulated using the following model : Aluminum foil/boehmite films/platinum film ($n=2.00$ at 510 nm)/Air. The refractive index of boehmite film in this simulation was 1.65. The boehmite film thicknesses were 100 nm, 200 nm, 300 nm, 380 nm. The simulated reflectance curves are shown in **Figure 6**. The 100 nm, 200 nm, 300 nm and 380 nm boehmite films had peak maxima at wavelengths of 400 nm, 440 nm, 520 nm and 660 nm, respectively, and they were colored purple, blue, green and red, respectively. These results however,

Fig. 6 Reflectance curve of the boehmite film (refractive index 1.68, packing density 1.00) coated with platinum as a function of thickness.

Fig. 7 Reflectance curve of the boehmite film (refractive index 1.68, packing density 0.57) coated with platinum as a function of thickness.

were not in good agreement with the colors obtained as shown in Figure 2. Therefore, another simulation of the reflectance was carried out, in order to achieve resultant colors that corresponded to those shown in Figure 2. The refractive index used for the simulation was fixed at 1.65, and the packing density was varied since the boehmite film was porous. The new set of simulated reflectance curves is shown in **Figure 7**. The packing density of the porous boehmite film was estimated to be 0.57. The boehmite films with thicknesses of 200 nm, 300 nm and 380 nm had peak maxima at wavelengths of 600 nm, 440 nm and 500 nm, respectively, and resultant colors of orange, blue, and green respectively. These results were in good agreement with the colors shown in Figure 2. Therefore, porous boehmite films with a refractive index of 1.65 where the packing density of 0.57 were determined to correspond to the colors shown in Figure 2. In addition, layering of films with a refractive index of 1.65 and a packing density is 0.57 results in an actual refractive index of 1.38. This result is in good agreement with the refractive index of MgF_2 .

3.4.3 Reflectance for various thicknesses of boehmite films

In order to confirm that the color of the boehmite-treated surfaces were simulated in agreement with the color of the metallic luster color of aluminum foil, reflectance curves were estimated using the Al/boehmite model films ($n=1.38$)/Air. These curves are shown in **Figure 8**. The reflectances were determined to be about 80–90%, in the wavelength range of 400–700 nm, for all samples. The spectra did not have any sharp peaks, indicating that a peak did not exist at a specific wavelength. The human eye is unable to recognize a change in color induced by a change in thickness of the boehmite film in the surge of a spectrum of this level. Moreover, boehmite films are opaque; therefore, the color of boehmite-treated aluminum surfaces is described as having a metallic color.

Fig. 8 Reflectance curve of the boehmite film as a function of thickness.

Fig. 9 Reflectance curve of the platinum coated boehmite at different angles of incident light (treatment time 120 seconds).

3. 4. 4 Dependence of the viewing angle

The color of the boehmite films with coated platinum changed with the viewing angle. The reflectance of an Al/boehmite film (380 nm)/platinum film (12 nm)/Air model was simulated at different angles of incident light. These results are shown in **Figure 9**. The viewing angles of 0, 30, 60 and 80 degrees had peak maxima at wavelengths of 550 nm, 530 nm, 500 nm and 480 nm, respectively, and colors of green, almost green, malachite green and blue respectively. The angle of incident light on boehmite surfaces coated with platinum was thought to change because the optical path length in the boehmite films was longer than the appearance. The color of the boehmite films coated with platinum was therefore thought to change with the viewing angle.

4. Summary

The coloring mechanism of the boehmite-treated aluminum foil was investigated.

1) Boehmite films were opaque, whereas boehmite surfaces coated with platinum revealed various different colors depending on the thickness of boehmite film. Furthermore, the color of these surfaces also changed with viewing angles.

2) The boehmite-treated layer is porous, and boeh-

mite surfaces coated with platinum are deposited consistent with the boehmite shape. The microstructures on the boehmite surface are smaller than the wavelength of the visible light. Therefore, the shape of the boehmite structures could not be resolved in the wavelength of visible light. Platinum coated boehmite films were thought to form two layers.

3) Reflectance simulations were conducted in an effort to elucidate the coloring mechanism of platinum coated boehmite surfaces. The corresponding spectrum was obtained from simulations with a fixed refractive index at 1.65 and packing density changed from 1.00 to 0.57.

4) The coloring mechanism of boehmite surface coated with platinum was determined to be a result of multilayer film interference changes dependent on boehmite thickness.

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References

- 1) T. Ogawa, T. Tanaka, T. Hirai, T. Osawa, M. Shihozawa : *J. Adhes. Soc. Jpn.*, **33**, 47, (1997)
- 2) A. Rider : *J. Adhes. Soc. Technol.*, **15**, 395 (2001)
- 3) A. Stralin, T. Hjertberg : *J. Adhes. Soc. Technol.*, **7**, 1211 (1993)
- 4) T. Sato, T. Harizuka, A. Wada : *J. Met. Finish. Soc. Jpn.*, **27**, 542 (1976)
- 5) T. Sato : *J. Met. Finish. Soc. Jpn.*, **28**, 40 (1977)
- 6) T. Sato, T. Harizuka : *J. Met. Finish. Soc. Jpn.*, **28**, 117 (1977)
- 7) T. Sato : *ALUTOPIA*, **6**, 33 (1976)
- 8) T. Ishii, T. Ogawa, M. Saito : *Jpn. J. Polym. Sci. Technol.*, **58**, 353 (2001)
- 9) *The 22nd Edition of the Manual of Mineral Science* (after J. D. Dana). John Wiley & Sons, Inc. (New York), P 641 (2001)

ペーマイト処理アルミニウム箔を用いた発色機構の解析

石井敏也*・小川俊夫**

* 凸版印刷株式会社・総合研究所・物性評価研究所 埼玉県北葛飾郡杉戸町高野台南 4-2-3 (〒 345-8508)

** 金沢工業大学・環境高分子化学研究室 石川県石川郡野々市町扇が丘 7-1 (〒 921-8501)

要 旨

ペーマイト処理をほどこしたアルミニウム箔を用いた発色機構の解析を行った。ペーマイト処理は沸騰状態にした蒸留水でアルミニウム箔表面を処理する方法で、この処理によりアルミニウム箔表面にはペーマイト (AlOOH) と呼ばれる水酸化アルミニウムが生成される。このペーマイト処理表面は塗膜、エポキシ樹脂および低密度ポリエチレンなどに対して強い接着力を発現することが知られている。ペーマイト処理面はアルミニウム箔の金属光沢面とほとんど変わらない。この処理面に白金 (Pt) をコートしたところ、ペーマイト処理時間によってさまざまな色に発色した。この発色機構をしらべるため、処理面の形状観察と多層膜干渉の反射率シミュレーションを行った。その結果、ペーマイトは針状結晶の多孔質膜であり、Pt はこれらの形状に沿ってコートされていた。この発色機構はペーマイト層と Pt コート層の多層膜干渉によって説明できた。