Cold Sealing Mechanism Of Anodic Oxide Films on Aluminum Part I: Composition and Structure Of Cold-Sealed Oxide Films

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The composition and structure of cold-sealed anodic oxide films on aluminum formed in sulfuric acid solution were investigated by means of X-ray diffraction, infrared spectroscopy, thermogravimetry and differential thermal analysis. Oxide films are mainly composed of amorphous alumina, and also contain sulfate. Boehmite (AIOOH), nickel hydroxide [Ni(OH)₂], and aluminum fluoride (AIF₃) are formed in cold sealing. Finally, the mechanism of the cold sealing reaction is discussed.

nodized aluminum and its alloys are widely used in many fields, such as architecture, machinery, light industry, etc. The pore diameter and the porosity of anodic oxide film on aluminum formed in H₂SO₄, solution are approximately 120 Å and 10 percent, respectively. Corrosive media and environmental contaminants adhere easily to the surface of anodized aluminum, affecting not only the appearance, but attacking the film as well. Sealing treatment is therefore necessary. In 1929, Setoh'and Rohrig'reported that treating oxide films with heated steam and boiling water greatly reduces the sorptive characteristic of film and its susceptibility to chemical attack. After nearly 50 years, the techniques of hot sealing, which include hot water, steam and nickel salt, etc.,



have been almost perfected and the mechanism has been established also, but the high cost of energy for heating water is an economic burden aggravated by the long sealing time required. The hardness of the film decreases slightly after hot sealing and smut is easily formed on the surface.

Early in the 1980s, commercial scale cold sealing was first introduced in Italy. Cold sealing additives are mainly composed of metallic fluorides. Cold sealing overcomes many disadvantages of hot sealing, and its quality meets the ISO specification. It has been rapidly developed for anodized aluminum in recent years. Dito *et al.* investigated the effect of cold sealing conditions on quality .³The element distributions of the oxide film after cold sealing were determined by Short.⁴

Our purposes were to investigate the composition and structure of cold-sealed anodic oxide film on aluminum formed in sulfuric acid, and to discuss the mechanism of the cold sealing reaction.

Experimental Procedure

Commercial-purity aluminum foil (AI \ge 99 percent) specimens (2 x 0.5 dm²) were degreased, etched in 40 g/L NaOH solution (50 to 60 °C), and desmutted in 50-percent v/v HNO₃(room temperature). Subsequently, the specimens were anodized in 15-percent H₂SO₄(20 °C) at a constant current density of 1.5 A/ dm² for 30 min. The thickness of the oxide film was about 12 µm. The specimens were treated in BY02 sealing solution³ (30 °C, pH 6) containing 1.2 g/L Ni²⁺ for 15 min.

Additive developed by the General Research Institute for Non-Ferrous Metals, Beijing.



Fig. 2-Infrared transmission spectra of oxide films: (A) unsealed; (B) sealed



Fig. 3-Differential IR transmission spectrum (B - A) of oxide films.

The oxide film was separated from the aluminum substrate by using about five percent HgCl, solution, and used for X-ray diffraction (XRD) and infrared spectroscopy (IR) after drying and grinding. The oxide film powder scraped from the surface of the specimens was used for thermogravimetry (TG) and differential thermal analysis (DTA).

Results

XRD Analysis

Figure 1 shows XRD spectra of unsealed (A) and sealed (B) oxide films. All peaks are the diffraction bands of Hg₂Cl₂, which were obtained by reaction of film separation in HgCl₂ solution: ⁵

$$6$$
HgCl₂ + 2Al \rightarrow 3Hg₂Cl₂ + 2AlCl₂

There are convex bands in the range $2\theta = 20$ to 40° of two spectra, which means that anodic oxide film on aluminum is amorphous. Curve B does not show diffraction bands of cold-sealing reaction products. This suggests that sealing products are amorphous.

IR Analysis

Transmission IR spectra of unsealed (A) and sealed (B) oxide films are shown in Fig. 2. The table lists the wavenumber ranges of absorption bands and their vibration types.⁵⁷ The broadband from 3800 to 2800 cm-' represents the stretching vibration of the O-H bond, which indicates that there are OH groups in oxide films, or that water is absorbed. The band in the 1700 to 1600 cm-' represents the bending vibration of the O-H bond. The typical S-O bond of SO, groups corresponds to the band in the range 1200 to 1100 cm⁻¹. The absorption band within 950 to 500 cm' is related to the stretching vibration of the AI-O bond and is composed of three sub-bands. In spectrum B, the band at 450 cm-' represents the stretching of the Ni-O bond. To compare the differences in the compositions and structures of unsealed (A) and sealed (B) oxide films, the differential spectrum (B -A) from Fig. 2 is shown in Fig. 3. The sharp bands at 3640 cm² and 450 cm⁴ are specific bands of Ni(OH), corresponding to the O-H and Ni-O bonds, respectively. The absorption bands at 3280, 3040, 1150, 1100 and 950 t0 500 cm⁻¹ are specific bands of Boehmite (AIOOH), in which 3280 and 3040 cm³ represent the stretching vibration of the O-H bond; and 1150 and 1100 cm-i represent the bending vibration of the O-H bond.[®]The bend at 1220 cm¹ in Fig. 3 corresponds to the vibration of AIF₃. Accordingly, Ni(OH)₂, AlOOH and AlF₃ are formed in cold sealing.

Linear reflection measurement was used to investigate the surface of the oxide film at an infrared angle of incidence of 45°.



Fig. 4-Reflection IR spectra of oxide films: (A) unsealed; (B) sealed.

The results of unsealed (A) and sealed (B) oxide films are shown in Fig. 4. In curve B, the sharp band at 3640 cm⁻¹ corresponds to stretching vibration of the O-H bond in Ni(OH)₂; 3280 and 3040 cm⁻¹ represent stretching vibration of the O-H bond in AlOOH. These results further confirmed that Ni(OH)₂ and AlOOH are present in cold-sealed oxide film, and that they are distributed in the outer layer.

TG and DTA

Figure 5 shows TG and DTA curves of cold-sealed oxide films with total powder weight of 19 mg. The absorbing heat band near 100 °C in the DTA curve indicates vaporization of absorbed water, corresponding to weight loss at 100 to 200 °C in the TG curve. Dehydration of AlOOH is divided into two stages. First, a small amount of dehydration at 390 °C corresponds to obvious weight loss in the TG curve; then, more water is lost near 590 °C, leading to additional weight loss in the range 500 to 600 °C. Some aluminum substrate was taken into the powder as films were scraped; consequently, a heat-absorbing band of melting aluminum occurs at 680 °C in the DTA curve.

Discussion

Structure of Oxide Film

It was discovered that the absorption band in the range 950 to 500 cm⁻¹, related to stretching vibration of the AI-O bond, is composed of three sub-bands (Fig. 2) The band in the range of 950 to 750 cm⁻¹ corresponds to condensed tetrahedral AIO₄ groups; the band in the range 650 to 500 cm⁻¹ corresponds to condensed octahedral AIO₅ groups.³

In general, the wavenumber of molecular vibration depends on the binding constant, the mass of the atoms and the geometric shape of the molecule, etc., and can be expressed as

$$v = 1307 \sqrt{\frac{k}{\mu}}$$

where k is the binding constant in dynes/cm and

$$\mu = \frac{M_1 M_2}{M_1 + M_2}$$

is the reduced mass. For the groups of structural unit AlO_{α} , the coordination number α determines the wavenumber of vibration. The greater the α , the more reduced mass μ ; consequently, the smaller the wavenumber of vibration. From the



Fig. 5-TG and DTA curves of oxide films after cold sealing.

three sub-bands in the range 950 to 500 cm⁻¹, the coordination number of the middle Al-O absorption band in the range 750 to 650 cm⁻¹ is definitely higher than the 4 of the band from 950 to 750 Cr⁻¹ and lower than the 6 of the band from 650 to 500 cm⁻¹. Accordingly, it appears justified that the middle Al-O absorption band corresponds to the vibration of AlO_x(4< x < 6) groups. Because wavenumber and intensity of molecule vibration depend not only on symmetry and coordination number, but also on order, degree, etc., it is difficult to determine the precise coordination number of AlO_x, the value of which must be estimated.

The absorption bands of the condensed tetrahedral AlO₄ and octahedral AlO₆ groups indicate that the short range order structure is present in the oxide film. In this structure, there are not only distorted AlO₄ groups and AlO₆ groups, but non-stoichiometric AlO₄ (4 < x < 6) groups, and some free oxygen atoms as well.[®] It is thought that amorphous alumina resembling γ -Al₂O₃ is formed. XRD analysis also indicates that the oxide films are amorphous.

Mechanism of the Cold-Sealing Reaction

In hot-water sealing, the hydration reaction of alumina mainly transforms part of the oxide films into Boehmite (AIOOH), and the pores of the films are sealed through volume expansion." In nickel-salt hot sealing, hydrolysis of the nickel salt occurs, with formation of Ni(OH), precipitate within the pores, in addition to the above hydration reaction.¹² There are great differences in composition of solutions and technical conditions between hot and cold sealing. IR, TG and DTA results indicate that AIOOH, Ni(OH), and AIF₃ are formed in cold sealing. No diffraction bands of cold sealing products are observed in XRD analysis, however, and it is thought that they are amorphous.

Ni^a and F are the major ions in the cold-sealing solution and play a key role in the sealing reaction. Murphy thought that there is a double electrical layer at the film/solution interface during the anodizing process." Protons are adsorbed on the surface and pore walls of the oxide film. Accordingly, it is reasonable to believe that the oxide film retains an excess of positive charges. The aggressive fluoride anion easily adheres to the film/ solution interface during cold sealing and neutralizes the excess positive charges. The change in charge distribution at the interface is convenient for the sealing solution, especially cations, such as Ni², to be incorporated into the pores of the oxide film. AIF₃ is formed when fluoride reacts with the oxide film: $AI_2O_3 + 6F^2 + 3H_2O \rightarrow 2AIF_3 + 6OH$. At the same time, Ni²⁺ is incorporated in the pores of the oxide film, and hydrolyzes in the new, higher pH condition or reacts with the above OH formed, resulting in precipitation of Ni(OH),.

Through the actions of fluoride and other anions, the surface and pore walls of the oxide film are attacked. Dissolved aluminum ions are surrounded by six very tightly bound water molecules in the form of hydrated aluminum ions, $AI(H_2O)_{\epsilon}^{3\cdot e^{it}}$ When the concentration of these ions reaches a certain value, the ions combine, dehydrate and condense. With further sealing reaction, precipitation occurs because of constant dehydration. Finally, the ions are transformed to a steady phase containing one water molecule per molecule of AI_2O_3 : Boehmite, AIOOH (AI_2O_3 , H_2O).

To summarize, three kinds of sealing reactions are thought to occur during cold sealing:

- 1. A partial oxide film is transformed into AIOOH through a hydration reaction similar to hot sealing.
- Ni_a incorporated in the pores of the oxide film hydrolyzes to form a precipitate, Ni(OH)₂.
- 3. Chemical conversion reaction between F and the oxide film to form AIF₃.

Conclusions

Anodic oxide films on aluminum formed in H₂SO₂solution are mainly composed of amorphous alumina, and contain sulfate also. In cold-sealing treatment, AIOOH, Ni(OH)₂ and AIF₃ are formed by hydration, hydrolysis, and chemical conversion reactions, respectively.

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