Aging of Cold-Sealed Aluminum Oxide Films At Room Temperature and at 50 °C

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Post-sealing aging of anodic films subjected to cold sealing is of special interest because this type of finish does not meet quality standards immediately upon application. In this work, standard control tests and electrochemical impedance spectroscopy were used to investigate aging in anodic films subjected to no sealing, incomplete traditional hydrothermal sealing and cold sealing. The results reveal that the ingredients of the impregnation bath exert a catalytic effect on the aging process, which ensures fulfillment of quality standards within a few hours.

Anodizing of aluminum and its alloys is often done in sulfuric, phosphoric or oxalic acid in order to improve their aesthetic properties and corrosion resistance prior to use. Anodic oxidation in these electrolytes produces an oxide layer consisting of two substrates—one, internal, which is compact, adherent and only a few tenths of an angstrom thick (the barrier layer), and the other, external, porous and much thicker.¹



Fig. 1—Impedance diagrams for extreme conditions: (•) unsealed anodized aluminum. (•) anodized aluminum sealed by immersion in boiling water for 45 min.

For durability and aesthetic reasons, the porosity of these coatings is corrected by sealing, which has traditionally been accomplished by boiling in de-ionized water for 30–60 min for the usual thicknesses of architectural applications. The temperature and duration of this treatment, known as "hydro-thermal sealing" (HTS) make it rather expensive; in response, a variety of additives has been used to shorten the sealing time and, more recently, various cold sealing procedures have been developed for the same purpose.²⁻¹⁰ Compared to traditional HTS, cold sealing uses much less energy, avoids largely or completely the white dust typically formed on anodized aluminum by effect of HTS, significantly decreases the sealing time and avoids the typical vapor condensation problems associated with traditional baths.¹⁰

The cold sealing process, commonly known as "impregnation of anodic films," differs from traditional HTS not only in the lower temperature used, but, essentially, in the coprecipitation of Ni(OH)₂, Al(OH)₃ and AlF₃ as well, all in hydrated forms, within the outermost 3-4 μ m of the coating. Cold sealing is followed by a post-sealing or aging stage that involves hydration of the components of anodic films. This causes the pore contents to expand, the pores to be more tightly shut and, as a result, sealing quality to be improved.

This last step is very important because the finish resulting from cold sealing does not meet established standards immediately upon application. Depending on the type of test, the sealing may require as many as 30 days of aging to meet the standards originally developed for evaluating traditional HTS.^{2,3} This shortcoming can be circumvented, however, with a short post-treatment in hot (60–80 °C) NiSO₄ · 7H₂O solution.¹¹

The aim of this study was to increase available knowledge of the impregnation process during post-sealing. To this end, changes in cold-sealed anodized materials during aging in a



Fig. 2—Changes in water absorption during aging in a wet chamber at room temperature for cold-sealed, unsealed and incompletely sealed anodic layers in boiling water for 4 min.



Fig. 3—Changes in the dye drop during aging in a wet chamber at room temperature for cold sealed, unsealed and incompletely sealed anodic layers in boiling water for 4 min.

wet chamber at room temperature and 50 °C were analyzed. To acquire a global view of the aging process, which affects all sealed films, whatever the method used, autosealing (aging) in specimens subjected to anodization alone and others subjected to incomplete sealing in boiling de-ionized water for 4 min was also studied. Aging in properly sealed anodic films is of less interest, as they meet all quality standards immediately upon treatment.

Experimental Procedure

Materials

The working electrodes used were 5×10 cm aluminum plates of 99.5 percent purity, anodized under technical conditions in 18-percent sulfuric acid at 20 °C and 1.5 A/dm², followed by repeated washing and final drying with pressurized air. The oxide films obtained were about 20 μ m thick.

Working Conditions

Anodization was followed by one of the following treatments:

- (a) Impregnation in a cold sealing bath compliant with the specifications of the European Aluminium Anodisers Association (EURAS)¹¹ for 20 min.
- (b) Incomplete sealing (4 min) in boiling de-ionized water.

(c) No sealing.



Fig. 5—Changes in admittance during aging in a wet chamber at room temperature for cold-sealed, unsealed and incompletely sealed anodic layers in boiling water for 4 min.

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Fig.4—Changes in acid dissolution during aging in a wet chamber at room temperature of cold-sealed, unsealed and incompletely sealed anodic layers in boiling water for 4 min.

The specimens thus treated were subjected to aging in a wet chamber at room temperature or 50 $^{\circ}$ C.

Methods

The resulting anodized and anodized-sealed films were analyzed in terms of their water absorption capacity and by use of standard tests such as those of phosphochromic acid dissolution and the dye drop, in addition to 1 kHz admittance measurements, originally designed for conventional hydrothermally sealed anodized aluminum. The results obtained were supplemented by electrochemical impedance spectroscopy (EIS) measurements.

AC impedance measurements were made in unstirred, aerated 3.5-percent (w/w) potassium sulfate solutions at 25 \pm 1 °C by exposing a surface of 1 cm². The cell and experimental set-up used are described in detail elsewhere.^{12,13}

Results

Possible Extreme Conditions

Figure 1 shows the impedance diagrams obtained for the extreme conditions of anodized aluminum—well-sealed, and anodized but not sealed. As can be seen, anodic films changed markedly by sealing in boiling de-ionized water for 45 min, which was long enough to meet the quality standards of traditional control tests. The purpose of these graphs was to facilitate comparison with the effects of traditional HTS.



Fig. 6—Changes in admittance during aging at room temperature and 50 $^{\circ}\!C$ after cold sealing.



Fig. 7—Changes in Bode diagrams during aging at room temperature following cold sealing. (\circ) 0 days, (+) 1 day, (\times) 3 days, (\square) 8 days, and (\bullet) 28 days.

Changes in Sealing with Aging in a Wet Chamber at Room Temperature or 50 $^\circ\mathrm{C}$

Figure 2 shows the mass gain resulting from water absorption during aging of cold-sealed, incompletely sealed and unsealed specimens in a wet chamber at room temperature. As can be seen, unsealed specimens took about 25 days to reach pore saturation with the water, compared to 10 days for incompletely sealed specimens and a shorter time (3-7 days) for cold-sealed specimens. Aging began, however, with halffilled pores in the latter two situations. Figures 3-5 show the sealing quality as estimated by the dye drop, acid dissolution and admittance tests, respectively, as a function of time in a very wet atmosphere at room temperature. As can be seen, the acceptance limits for all the standard tests were reached much sooner by the specimens that were impregnated in the cold sealing bath than by those that were subjected to sealing in boiling water for 4 min, which in turn evolved more rapidly than the unsealed specimens. Accordingly, cold-sealed specimens met the acceptance limit of the dye drop and acid dissolution tests after aging for 24 hr and reached the limit of the admittance test within 72 hr.

Changes were even faster if aging in the wet chamber took place above room temperature, as can be seen in Fig. 6, which compares aging at room temperature and 50 °C in cold-sealed specimens, as measured by the admittance test, the acceptance limit of which takes longer to reach.

Figure 7 shows the impedance diagrams obtained after aging in the wet chamber at room temperature for variable lengths of time following cold sealing. As aging develops, the



Fig. 8—Resistance of the porous layer, R_p , showing change much more rapidly during aging in a wet chamber after cold sealing than in unsealed or incomplete sealed specimens.

diagrams shift to higher impedances, which suggests the transformation of substances inside the original pores.

The horizontal portions of the impedance diagrams determines the porous layer resistance, R_p , because resistances are frequency independent. The larger R_p is, the better will be the sealing quality and, as can be seen in Fig. 8, R_p increases faster in cold-sealed specimens aged at room temperature than in those incomplete sealed or unsealed specimens, making this parameter useful as a measure of seal quality.

Discussion

Possible Extreme Conditions

As can be seen in Figs. 1 and 7, the transformations involved in sealing, whatever the working conditions, manifest in the medium- and high-frequency regions, approximately $1-10^3$ Hz and $> 10^3$ Hz, respectively, which are related to the properties of the porous layer (the only one that undergoes major changes as a result of sealing). Some frequency regions in these ranges reveal differences of 2-3 orders of magnitude between the responses of sealed anodized and those of unsealed anodized aluminum, which makes EIS a highly sensitive technique for assessing seal quality.

Taking into account that the resistance (impedance) of an ideal capacitor is inversely proportional to the frequency $(Z = 1/C\omega)$ and that a pure resistance is independent of this variable, the typical responses of unsealed, sealed and sealed-aged anodic films can be closely approximated by the equivalent circuits of Fig. 9. A more detailed analysis of EIS data obtained during sealing in boiling water allows interpretation of the morphological changes involved and monitoring of the course of the hydration process by means of equivalent circuits adapted to each stage of the process.¹⁴ The simplified circuits of Fig. 9, however, reproduce acceptably most practical situations and allow the more significant parameters for the anodic layers at the different sealing stages to be calculated.

The resistance of the porous film, R_p , can be used as a quantitative measure of the transformations occurring throughout the thickness of anodized coatings, particularly those with the original pores; in turn, such a measure can be an assessment of sealing quality.¹⁵ The quality levels established by the standards of the dye drop, acid dissolution and admittance tests are reached at R_p values equal to or greater than about 200 k $\Omega \cdot \text{cm}^2$. As can be seen from Fig. 8, this R_p value is surpassed after a period that is 10–20 times shorter in



Fig. 9—Equivalent circuits for the behavior of anodic layers (unsealed, fully sealed in boiling water, and sealed and aged for long times), including the approximate response for each situation. sealing.

Figure 10—Proposed mechanism for cold sealing.

cold-sealed specimens aged at room temperature than in those previously sealed in boiling de-ionized water for 4 min, and about 50 times shorter than in unsealed specimens. In addition, R_p continues to increase above 200 k $\Omega \cdot \text{cm}^2$ in cold-sealed specimens and reaches values greater by about one order of magnitude after approximately one week.

Cold Sealing Followed by Aging in a Wet Chamber at Room Temperature and 50 $^\circ\mathrm{C}$

If high relative humidity is provided, pore saturation through water absorption takes place about 10 times faster in specimens previously impregnated in a cold sealing bath than in those exposed to the wet atmosphere with no pretreatment (Fig. 2). The times needed to meet the quality levels imposed by the dye drop (Fig. 3), acid dissolution (Fig. 4) and admittance tests (Fig. 5) are shortened in roughly the same proportion. Increasing the temperature to 50 °C considerably decreases the aging period of cold-sealed specimens (to less than 6 hr, Fig. 6). The specimens subjected to incomplete sealing in boiling de-ionized water and subsequently aged exhibit an intermediate behavior; this suggests that the transformations starting inside the pores may catalyze the subsequent stages of the process, even though not as efficiently as the ions present in the cold-sealing solution.

The fact that the mass gain continues to increase after the impregnation treatment in the cold sealing solution (Fig. 2) suggests that the solution does not saturate the pores. This,

together with the fact that none of the standard tests is passed immediately upon impregnation, reveals that pore filling is an essential prior stage to meet established sealing quality standards. No reaction (aging) with pore walls can take place if no solution is previously absorbed.

Aging is a natural, universal response of porous aluminum oxide films after the reactant solution fills the pores, whether partly or completely. For practical purposes, it would suffice to ensure that pores are filled and, consequently, that the absorption capacity of the anodic film is cancelled and any aesthetic alterations avoided to ensure an adequate service response. It is an indifferent matter whether the quality levels imposed by the acid dissolution or admittance tests are reached; provided the pores are filled, aging gradually increases the sealing quality as measured by the previous indices until the established levels are eventually surpassed. The usual practice of cold sealing in two steps can therefore be simplified. The second step, which involves immersion in a hot NiSO, \cdot 7H₂O solution, can be suppressed, provided the item in question is maintained in a wet atmosphere for a short time-until pores are saturated-following immersion in the cold-sealing solution.

Based on the results obtained in this study, the step sequence of the cold-sealing process may be somewhat different from that previously reported.⁷ The mechanism, schematically depicted in Fig. 10, may be as follows:

(1) The facts that water is absorbed at the beginning of aging

and that the dye drop reaches level 4 (close to 5, the maximum value) immediately after impregnation suggest that the solution that penetrates the pores during immersion occupies the bottom of the pores (see Fig. 10a).

 (2) The acidification inside the pores and the loss of SO₄⁻² ions suggested by Short and Morita^{4,5} may result from the following reactions (Fig. 10b): Al₂(SO₄)₃ + 6H₂O → 2Al(OH)₃ + 3SO₄⁻² + 6H⁺

 $F_{3}[Al(H_{2}O)_{6}] \rightarrow [Al(H_{2}O)_{3}(OH)_{3}] + 3F^{-} + 3H^{+}$

- (3) As pores are filled at the beginning of aging, the higher pH of the water absorbed causes Al and Ni ions to precipitate at pore mouths (see Fig. 10c) and form a mixture of aluminum hydroxy-fluorides and Al and Ni hydroxides.^{4,5} This process is also consistent with preferential accumulation of Ni and F in the outermost layer of anodic films.
- (4) As aging advances, anhydrous alumina continues to be hydrated and sealing to be perfected (see scheme in Fig. 10).

Conclusions

- Cold-sealed specimens meet the quality requirements of the dye drop and acid dissolution tests after aging at room temperature for less than 24 hr. Passing the admittance test takes 3 days of aging.
- Increasing the aging temperature to 50 °C leads to virtually instantaneous fulfillment of the quality standards of the dye drop and acid dissolution tests, and that of the admittance test, within 4-6 hr.
- The diffusion of some ingredients of the cold-sealing bath to the inside of the pores substantially accelerates the aging of anodic films, which proceeds much faster than in unsealed and incompletely sealed specimens.
- The rapid aging of anodic films impregnated in a nickel fluoride bath makes cold sealing in two steps redundant.
- Electrochemical impedance spectroscopy (EIS) is much more sensitive than standard control tests for studying the mechanism of the aging process and provides more detailed information about post-sealing transformations.

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