Development of a Chromium-Free Post-Anodizing Treatment Based on 2-Mercaptobenzothiazazole for Corrosion Protection of AA2024T3

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The anticorrosion performance provided by new anodizing and sealing methods for the AA2024T3 aluminum alloy is discussed in this work. Two anti-corrosion post-anodizing treatments based on immersion in an ethanol solution containing 2-mercaptobenzothiazole (2-MBT) were applied. Both treatments consisted of the immersion of the anodized specimens in 2-MBT ethanol solution, but the second was followed by hydrothermal sealing in water. Electrochemical Impedance Spectroscopy (EIS) and an immersion test show that both treatments exhibited improved corrosion resistance compared with anodized AA2024-T3 that was only hot water sealed. Considering that these novel anti-corrosion methods appear to provide enhanced, long-term and stable corrosion resistance to the AA2024T3 aluminum alloy, the use of 2-mercaptobenzothiazole (2-MBT) is proposed as a promising inhibitor in sealing treatments.

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AA2024T3 aluminum alloy is widely used in the aerospace industry due to its high strength to weight ratio. However, high amounts of copper, together with magnesium and other alloying elements, generate second-phase particles that cause microgalvanic coupling in the presence of moisture or aqueous electrolyte, thereby reducing corrosion resistance.

Anodizing is an electrochemical method that converts the aluminum surface into a corrosion-resistant, durable oxide layer with a porous structure. The pore diameter, thickness, structure and morphology of the oxide layer depend on the applied anodizing conditions, such as anodizing potential, temperature and electrolyte.2 Traditionally, anodizing of aluminum alloys is usually performed in chromic acid electrolytes, and it is followed by sealing in dichromate solution. However, as a result of its toxicity, legislation will severely restrict the use of sodium dichromate, which has led to the development of alternative dichromate-free sealing treatments.3-6 The restriction on the use of chromium Cr (IV) compounds has also led to the development of alternative chromium-free anodizing methods, including the sulfuric–tartaric process (TSA), a typical anodizing method used in aerospace industries.7-10

In simple terms, the anodizing process is used to obtain a thick aluminum oxide layer with a porous structure, whereas the sealing process is used to close the pores with hydrated products, thereby further increasing the corrosion resistance. A detailed discussion of the complex effects of pore morphology, film thickness, sealing time and nature of the sealing solution can be found elsewhere and it is not reported in detail here.11-12 Different types of sealing methods have been studied, including dichromate sealing, hot water sealing, and nickel acetate sealing.13 Commonly quoted sealing treatments are hot water or aqueous nickel acetate, but neither is as good as hexavalent chromium-based processes; moreover, both are energy consuming as the sealing takes place at 95 °C. In addition, new sealing techniques such as cerium sealing have been developed during the last decade,14-17 with good results in terms of anticorrosion performance. A possible alternative route to incorporate corrosion inhibitors into the sealed anodic oxides is the immersion of the anodized part in an inhibitor-rich solution, which per se does not directly induce oxide hydration, followed by a subsequent hot-water sealing.6 The approach has been used previously to incorporate into sealed anodic layers the inhibitors imidazole, 1H-benzothiazole and 3,6-di-pyridyl-1,2,4,5-tetrazine, with promising results in terms of anticorrosion performance.6

Regarding the selection of corrosion inhibitors, nitrogen-rich compounds are popular corrosion inhibitors, thanks to their capability of binding with chlorides and preventing them to reach the metal surface.6 Further, compounds that contain nitrogen, such as benzothiazole and derivatives, have been proposed as corrosion inhibitors20 since they have strong affinity with copper and generally work well on pure copper or on those materials such as aluminum-copper alloys where the cathodic reaction is localized on the copper-rich intermetallics.21 The compound 2-mercaptobenzothiazole (2-MBT) can react with copper to form Cu-MBT complexes due to the polar functional groups in 2-MBT, which can form a film that restrains the cathodic reaction and subsequently protects the surface from further corrosion.22 This compound could therefore potentially be a corrosion inhibitor for protection of aluminum alloys with copper-rich particles as second phase.23 Using X-ray photo-electron spectroscopy (XPS), Chadwick and Hashemi have shown that 2-MBT forms a Cu(I)/MBT complex as a surface layer, which inhibits the corrosion of copper.24 Zhledkiveich et al. studied the inhibiting effect of triazole and thiazole derivatives (2-mercaptobenzothiazole for AA2024 T-3 aluminum alloy in neutral chloride solution).25 The results show that 2-MBT can significantly decrease the corrosion rate of the anodic reaction by forming a protective layer on the aluminum surface, as well as reducing the corrosion rate of cathodic reactions by restraining copper dissolution and dealloying of the intermetallic particles. Boisier et al. used post treatment to the anodizing process based on carboxylic acids before hot water sealing and achieved improved corrosion resistance on aluminum alloy.26 Balaskas et al. 2-MBT as a corrosion inhibitor for AA2024T3, showing that the presence of inhibitor in the aggressive environment effectively prevents corrosion initiation and propagation for hundreds of hours.

The aim of this work is to investigate new methods of improving the corrosion resistance of anodized aluminum alloys that are based on the use of 2-MBT and to reduce the energy demand associated with the surface treatment. The new treatment methods involve a post treatment in an ethanol solution of 2-MBT, with or without subsequent hydrothermal sealing.

Experimental

The nominal composition of AA2024T3 aluminum alloy is given in Table 1. Before anodizing, the specimens were first degreased in acetone using an ultrasonic bath for 5 minutes. Subsequently, they were etched in 10% sodium hydroxide (wt) for 30 s at 60 °C and desmutted in 30% nitric acid for 30 s at room temperature. The specimens were then rinsed in deionized water and finally dried under a cool air stream.

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Lacquer was used to cover the surface of the samples in order to leave 12.0 cm² of exposed area for anodizing and subsequent sealing.

All the electrochemical tests in this work were performed using a Solartron Modulab workstation. The anodizing solution was 0.46 M sulfuric acid and 0.53 M tartaric acid, which is the standard solution for the industrial TSA process and is used in numerous previous studies on the topic.28,29 As reference electrode, a saturated calomel electrode was employed, whereas the counter electrode was pure aluminum. The anodizing process was performed at 37 °C. The applied potential-time regime consisted in a 5 minutes initial voltage ramp from the open circuit potential to 14 V (SCE), followed by a potentiostatic hold at 14 V (SCE) for 20 minutes.

For the 2-MBT post-treatment, the anodized specimens were immersed for 30 minutes in 5% wt ethanol 2-MBT solution, in order to deposit the inhibitor within the porous skeleton. The compound 2-MBT from ACROS Organics (UK) (purity 98%) is a yellow powder to deposit the inhibitor within the porous skeleton. The compound 2-MBT is readily soluble in acetone and ethanol, but it has low solubility in water. After the 2-MBT post-treatment the specimens were not rinsed, but only dried under a cool air stream to allow for the evaporation of ethanol.

After the 2-MBT post-treatment, some of the specimens were then sealed in deionized hot water containing 1 g l⁻¹ of sodium sulfate, to improve the conductivity of the solution and enable reliable EIS measurements during sealing. Sulfuric acid was also added to adjust the pH at 6. The hot water sealing process took place at 96 °C for 30 minutes, during which an EIS measurement was performed every 5 minutes in the frequency range of 100 kHz to 20 mHz with an amplitude of 10 mV.

In order to evaluate the effect of the 2-MBT post-treatment on the AA2024T3 aluminum alloy specimens, four conditions were investigated. The first group comprised specimens that were only anodized, the second group comprised specimens that were anodized and post treated in 2-MBT, the third group comprised specimens that were anodized and sealed in hot water, and the fourth group comprised specimens that were post treated in 2-MBT and sealed in hot water.

A standard three-electrode arrangement was used for the EIS measurements, with the exposed surface of the AA2024T3 aluminum alloy specimen as working electrode, a saturated calomel electrode as reference electrode, and pure platinum as counter electrode. The specimens from the four groups were immersed in 3.5% sodium chloride solutions separately, and EIS tests were carried out after 2, 4, 8, 16, 26, 36 and 46 days of immersion. For the immersion test, four groups of samples were immersed in 3.5% NaCl solution with a camera acquiring images every 10 mins for 7 days.

Scanning electron microscopy was performed by using an EVO 50 instrument with an accelerating voltage of 20 kV.

Results and Discussion

Anodizing.—The applied potential and the current response observed during the anodizing process are presented in Figs. 2a, 2b. The potentiodynamic response presented in Fig. 2b shows two peaks at approximately 0 V and 4.5 V (SCE), indicating respectively the oxidation process of Al-Mg-Cu and Al-Cu-Fe second phase particles.30

Sealing.—EIS measurements during sealing in hot water.—In order to monitor and study the impedance change during sealing in hot water with and without 2-MBT post-treatment, EIS measurements were carried out every 5 minutes during sealing. Typical time series of impedance Bode spectra plots recorded for anodized AA2024T3 aluminum specimen two different treatment regimes (sealed in hot water only and sealed in hot water after 2-MBT treatment) are presented in Figs. 3a–3d. Figures 3a and 3c display the impedance Bode spectra obtained for anodized AA2024T3 aluminum specimens (with no 2-MBT post treatment) during hydrothermal sealing. It is evident that during sealing an increase in the low-frequency values of impedance modulus is observed, and such increase is more evident for the specimens that had undergone immersion in the 2-MBT ethanol solution prior to sealing.

Scanning electron microscopy.—The scanning electron micrographs of the surface of the specimens after the three treatments is presented in Fig. 4. In Fig. 4a, the surface morphology of the hot

Table I. Composition of 2024-T3 aluminum alloy.

| Element | Cu | Cr | Fe | Mg | Mn | Si | Ti | Zn | Other | Al |
|---------|----|----|----|----|----|----|----|----|-------|----|
| Concentration (wt%) | 3.8–4.9 | 0.1 | 0.5 | 1.2–1.8 | 0.3–0.9 | 0.5 | 0.15 | 0.25 | 0.15 | Balance |

Figure 1. Structure of 2-mercaptobenzothiazole(2-MBT).
A significant reduction in the impedance modulus at low frequency was observed throughout the whole time in 3.5% sodium chloride solution. In Fig. 5a, significant variations were presented in Figs. 5a–5h. Figures 5a and 5c show the impedance modulus and phase shift of anodized 2024 T3 aluminum specimen during hydrothermal sealing in hot water. (b, d) impedance modulus and phase shift during hydrothermal sealing of anodized 2024 T3 aluminum specimen immersed in the ethanol-2-MBT solution prior to sealing.

Figure 3. Typical impedance spectra obtained from 2024 T3 aluminum alloy specimens from different treatment regimes: (a, c) impedance modulus and phase shift of anodized 2024 T3 aluminum specimen during hydrothermal sealing in hot water. (b, d) impedance modulus and phase shift during hydrothermal sealing of anodized 2024 T3 aluminum specimen immersed in the ethanol-2-MBT solution prior to sealing.

Corrosion testing.—EIS measurements.—The time series of impedance spectra recorded for treated AA2024T3 aluminum alloy specimens during corrosion testing in sodium chloride solution are presented in Figs. 5a–5h. Figures 5a and 5c show the impedance modulus (a) and phase shift (c) spectra obtained from unsealed anodized only AA2024T3 aluminum alloy specimen as a function of exposure time in 3.5% sodium chloride solution. In Fig. 5a, significant variations in impedance modulus values can be observed throughout the whole frequency range with the increasing immersion times. A significant reduction in the impedance modulus at low frequency was observed at day 4, and the impedance decreased gradually over the remaining immersion time. The sharp decrease in impedance noted at day 4 indicates that corrosion had initiated. Furthermore, the impedance values in the medium frequency range also decreased significantly as a function of exposure time, indicating an increase in capacitance. Simultaneously, a phase angle shift to the left with increasing immersion time is observed in Fig. 5c. This suggests that the capacitance of the specimen increased, due to local rupture of the barrier layer and formation of active corrosion sites. Overall, the EIS spectra indicate that the unsealed anodized specimens were significantly corroded after 4 days of immersion in 3.5% sodium chloride solution.

The Bode plots shown in Figs. 5b and 5d were obtained for the anodized AA2024T3 aluminum alloy sealed in hot water. The impedance observed at low frequency was relatively high for the duration of the immersion test, showing only a minimal decrease over time. This means that the porous oxide layer sealed in hot water exhibits good corrosion resistance. In Fig. 5b, from the measurement obtained at day 2, the sealed sample exhibits a high low-frequency impedance modulus, close to $1.5 \times 10^6$ ohm cm$^2$, and about 15 times higher than that obtained by anodizing only (shown in Fig. 5a). Therefore, the additional contribution that the hot water sealing method alone makes to improve the corrosion resistance of the anodized AA2024T3 aluminum alloy sample is clearly evident. Interestingly, a second time constant appears in the high-frequency range for prolonged exposure times, and it is related to further hydration of the oxide forming the porous layer.

Figure 5e shows a graph with the impedance modulus spectra obtained for the unsealed anodized AA2024T3 treated in 2-MBT. The shapes of the impedance modulus plots shown in Fig. 5e
in the phase angle spectra. It is interesting to notice that the second time constant appearing at high frequency, and associated with the self-sealing of the anodic oxide with increasing immersion time, is present for all the specimens that were post-treated after anodizing, but it is more pronounced when 2-MBT is present. This suggests that the presence of 2-MBT might enhance the self-sealing process during immersion.

**Comparison of EIS results obtained for the 4 different types of treated specimens.**—Typical sets of comparable results obtained from impedance Bode spectra recorded for AA2024T3 aluminum specimens from the four different treatment types: (i) anodized only, (ii) anodized and sealed in hot water, (iii) anodized and treated in 2-MBT, and (iv) anodized, treated in 2-MBT and sealed in hot water are presented in Figs. 6a–6d. These spectra were selected from results obtained at 2 specific times (2 days and 46 days). It is evident that the unsealed specimen displayed the lower values of impedance modulus at low-frequency at both times, whereas the specimens anodized and sealed in hot water displayed intermediate values. Both the specimens that were post-treated in the 2-MBT ethanol solution display higher values of low-frequency impedance, and they did not show a significant increase in capacitance over the entire exposure time. This suggests that utilizing 2-MBT as an anodizing post-treatment, with or without subsequent hot water sealing, greatly enhances the corrosion resistance.

**Immersion test.**—In order to evaluate the self-healing properties due to the post treatment in 2-MBT, immersion tests coupled with optical imaging were performed on specimens where an artificial defect was produced with a surgical blade. A cross shaped scratch of $1 \times 1 \, \text{cm}^2$ was manually produced on all specimen surfaces, and the specimens were immersed in the 3.5% NaCl solution.

Very clear differences were noted when comparing the optical images of the four specimens in terms of corrosion behavior (Fig. 7). For the unsealed anodized specimen, corrosion was substantial after 40 hours of immersion and continued until the end of the experiment. For the specimen anodized and sealed in hot water, small bubbles were observed on the surface of the specimen after 40 hours of immersion, likely resulting from hydrogen evolution. The scratched region was corroded and darkened with time, however the rest of the specimen displayed only minor pits for the whole duration of the test. For the anodized specimen treated in 2-MBT and sealed in hot water and for the one treated in 2-MBT but unsealed, only the scratched site was slightly corroded, whereas the rest of the specimen surface remained uncorroded during the whole 165 hours test.

**Conclusions**

In this work, two new protective post-anodizing treatments, based on immersing the anodized surface in a 2-MBT ethanol solution, were investigated. The first of the two treatments involved immersion in the 2-MBT solution only, while the second involved immersion in the 2-MBT solution followed by hydrothermal sealing in hot water. It was found that the anodized AA2024T3 aluminum alloy specimens post treated in 2-MBT and sealed in hot water show better corrosion resistance than the anodized specimens sealed in hot water only. Further, it was also found that the anticorrosion performance of the specimens treated in 2-MBT, with and without hot water sealing, is comparable. This was confirmed both from long term EIS measurements of undamaged specimens and from real-time imaging of the corrosion propagation on specimens where an artificial defect was created. SEM images indicate that for specimens treated in 2-MBT an excess of inhibitor was present on the surface in form of crystals, but for the specimens subsequently sealed in hot water such crystals were absent. Consequently, the improved corrosion resistance can be attributed to incorporation of inhibitor into the sealing products. The results indicate that a substantial improvement in the anticorrosion resistance compared to anodizing alone or anodizing followed by
Figure 5. Impedance spectra obtained from AA2024 aluminum alloy specimens after different treatment conditions during in 3.5% sodium chloride solution. (a, c) anodized only; (b, d) anodized and hot-water sealed; (e, g) anodized and 2-MBT treated; (f, h) anodized, 2-MBT treated and hot water sealed.
Figure 6. Comparison of sets of impedance spectra obtained from 2024 aluminum alloy specimens after different treatment conditions in 3.5% sodium chloride solutions at different immersion times: (a, c) after 2 days of immersion and (b, d) after 46 days of immersion.

Figure 7. Optical images of the corroding specimen surfaces during immersion test in 3.5% wt NaCl. Each image represents an area of approximately 3 \times 2 centimeters.
hydrothermal sealing can be achieved already by immersion in the 2MBT ethanol solution, even without the requirement of a subsequent step of hydrothermal sealing.

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