An Optimized Trivalent Chromium Conversion Coating Process for AA2024-T351 Alloy

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In this work, a trivalent chromium conversion coating applied on AA2024-T351 alloy has been optimized for corrosion protection in sodium chloride solutions. Scanning electron microscopy, energy dispersive X-ray spectroscopy and electrochemical measurements were employed to characterize the coating. An immersion post-treatment of the coated alloy in 40°C deionized water for 120 s considerably enhanced the corrosion protection properties, compared with a post treatment at 20°C, or the absence of a post-treatment. Electrochemical noise measurements, combined with real time imaging, and potentiodynamic polarization experiments indicated a conversion treatment for 300 or 600 s provides optimal corrosion protection. Relatively long conversion treatments decreased the corrosion protection due to an increase in coating defects and cracks, especially around the second-phase particles.

Trivalent chromium conversion (TCC) coating processes are promising replacements for chrome conversion coating processes, which are highly regulated because of the toxicity and carcinogenic risks associated with chrome species.1–3 TCC coating formation is a pH-driven process and the coating formed on AA2024 alloy has a two-layer coating structure, with an outer Zr/Cr-containing oxide layer over a fluoroaluminate interfacial layer.4–6 With respect to the electrochemical behavior, Li et al.7 used electrochemical impedance spectroscopy (EIS) to reveal substrate-dependent corrosion resistances of TCC coatings formed for 600 s in 0.5 M Na2SO4 solutions. The difference of charge-transfer resistances between bare and coated specimens decreased in the following order: AA6061 > AA7075 > AA2024 alloys. In comparison with AA6061, copper-rich particles present in AA2024 alloys encourage the widespread formation of coating cracks, leading to a greater coating heterogeneity.8 As a consequence, a lower corrosion resistance and a higher porosity of the TCC coatings were revealed on AA2024 alloys.7

Therefore, surface pre-treatments of AA2024 alloys that remove the copper-rich particles are of great importance to improve the surface microstructure, coating formation and corrosion resistance.8–10 A pre-treatment of alkaline etching and nitric acid desmutting (HNO3-desmuttering method) is generally used to clean surface contaminations. However, it may not be fully effective in removing surface particles, as evidenced by the protruding particles which may remain after this pre-treatment. In contrast to the use of HNO3, an acid deoxidizer with addition of oxidants can significantly enhance deoxidation effect.8,9 In this regard, an Fe(III)-desmutting method (Oxidite D-30) has been reported to be more effective in removing etching products and surface particles.9,10 The improvement is attributed to the presence of Fe(III), which acts as an oxidizing agent that promotes the dissolution of nobler copper-containing precipitates.9 The resultant TCC coating provided a significant improvement in the corrosion protection properties in 0.05 M NaCl solutions.10 Thus, the present work applied this Fe(III)-desmutting method to AA2024-T351 alloys in an investigation of the TCC coating process, with consideration of the influence of the conversion treatment time and post-treatment procedures. The electrochemical behavior of TCC coated alloy was investigated using EIS, potentiodynamic polarization (PDP) and electrochemical noise analysis (ENA). Furthermore, high-resolution scanning electron microscopy (SEM), associated with energy dispersive X-ray spectroscopy (EDS), was used to understand the effects of the treatment processes on the corrosion protection and assist in optimizing the coating process for the AA2024 alloy.

Experimental

Specimens and reagents.—Specimens of AA2024-T351 alloy (4.65 wt% Cu, 1.54 wt% Mg, 0.52 wt% Mn, 0.21 wt% Fe, 0.088 wt% Si, <0.5 wt% other elements, bal. Al) were cut from panels of 1.5 mm thickness to dimensions of 30 × 24 mm. The surface pre-treatment procedure consisted of degreasing in ethanol for 15 s, abrad ing to a 4000 SiC grit finish, rinsing in deionized water (DI) water for 20 s, alkaline etching in 10 wt% sodium hydroxide solution at 60°C for 30 s and desmuttering in 15 vol.% Oxidite D-30 (MacDermid Corp.) solution at 30°C for 90 s. The desmutting solution contained nitric and sulfuric acid and a small amount of ferric salts. All treatments were followed by rinsing in DI water for 5 s.

Commercial SurTec 650 chromitAL (Cr/Zr = ~0.7 atom%, SurTec Corp.) was diluted by DI water to prepare a 20 vol.% solution and the pH was adjusted to 3.9 by adding 1 wt% NaOH droplets. TCC coatings were formed by immersion of the alloy in the trivalent chromium bath at 40°C for 300, 600, 900, or 1800 s, followed by immersion in DI water (pH5) at either 20 or 40°C for 120 s, drying in a cool air stream and ageing in air for 24 h at ambient temperature. Immersion in DI water (pH5) at 40°C for 120 s, cool-air drying and overnight ageing in air is designated the standard post-treatment. Naturally-ared 0.05 M and 0.5 M sodium chloride solutions were used in electrochemical measurements. The dilute sodium chloride solution was less aggressive than the 0.5 M NaCl solution and was used to investigate the coating defects by EIS.11,12 In contrast, the latter electrolyte was used to investigate the longer term corrosion protection properties of the optimized TCC coating process.13

Characterizations.—A Zeiss Ultra 55 scanning electron microscope, operated at an accelerating voltage of 3 kV and associated EDS (15 kV), were used to investigate surface morphologies and compositions of TCC coatings before and after corrosion tests.

A three-electrode cell system was used for PDP and EIS measurements, which employed a Solartron electrochemical workstation with a ModLab software controller. The cell comprised a saturated calomel electrode (SCE, E° = 0.24 V vs. NHE), a platinum wire counter electrode and a working electrode consisting of the coated alloy. The exposed area of the coated specimens was ~2.25 cm².

The EIS and PDP scans in the naturally-aerated 0.05 M NaCl electrolyte proceeded as follows: (i) immersion at open-circuit potential
Figure 1. EC models used for fitting EIS data of the coated specimens, including electrolyte resistance ($R_e$), coating resistance ($R_{coat}$), Warburg resistance ($W_s$) and coating capacitance ($C_{coat}$), charge-transfer resistance ($R_p$) and capacitance of the coating/substrate interface ($C_{dl}$). EC abbreviation is (a) $R(Q(R(QR)))$ and (b) $R(Q(R(Q(WR))))$ respectively.

The real time corrosion performance of the coated specimens was investigated by image-assisted electrochemical noise analysis (ENA) in naturally-aerated 0.5 M NaCl solution. For ENA measurements, two identical specimens with exposed areas of $\sim 2.25$ cm$^2$, coupled by a 10 kohm resistor, were used, as described in detail in Ref. 17. A NI-SUB6009 (National Instrument) analogue-to-digital converter was employed to record the potential of the specimens relative to a SCE. The potential signals, with 1023 Hz segments of 1000 points at each iteration, were recorded by an in-house developed software, and averages of the 1000 values were used as a single value of potential acquired between the iterations. The final dataset of detected potential values was spaced by $1 \pm 0.05$ s in time. Assuming that negligible noise was present above 1023 Hz and below 0.5 Hz, ENA experiments between 0.5 and 1023 Hz can provide accurate potential signals at the frequencies of interest. In-house LabVIEW software was used to determine the time evolution of the low frequency noise resistance ($NR$), according to the mathematic procedure described by Curioni et al. In addition, real time imaging of the corroding surfaces during immersion in the corrosive electrolyte was carried out every 10 minutes using Maplin USB microscopes with an in-house developed software controller.

Results and Discussion

Effect of the temperature of post-treatment in the deionized water bath.—Figure 2 shows the influence of the DI water post-treatment
on (a) the impedance modulus-frequency plots of the alloy, after conversion treatment for 300 s, during the immersion in naturally-aerated 0.05 M NaCl solution. The freshly-formed specimens were post-treated with or without water immersion at 20 or 40 °C, and all were dried in a cool-air stream and aged overnight in the laboratory air. The plots of the coatings with a standard post-treatment were presented in a previous paper in Ref. 10. The steady OCPs of all specimens prior to the EIS measurements fit the EIS data using a R(Q(R(QR))) equivalent circuit for the condition, suggesting a stable solution/coating system during EIS measurements. TCC coatings formed for 1800 s suggested a less protective coating, which will be discussed later. A similar OCP was recorded before the PDP scan for this coating condition, suggesting a stable solution/coating system during EIS and PDP measurements. TCC coatings formed for 1800 s led to the lowest impedance modulus at 10^{-2} Hz (Fig. 4a). Correspondingly, the frequency-dependent phase angles displayed a single time constant (10^{-1} Hz, Fig. 4b). Furthermore, the frequency width of the phase angle peak of the specimens treated for 1800 s was the smallest, which also suggested reduced corrosion protection of the coating. In contrast, a higher impedance modulus at 10^{-1} Hz and the two time constants (10^{0} and 10^{-2} Hz) resulted with the coatings formed for 600 and 900 s; the data were fitted using the EC model of Fig. 4a. However, it was necessary to include a Warburg resistance in the EC to fit the impedance data (Fig. 1b) for the specimens treated for the longest time to account for the effect of a greater number of defects in the coating formed for 1800 s. The results of fitting the data are presented in Table II. $R_{\text{coa}}$ values increased in order: specimens without water immersion ($\sim 0.10 \Omega \text{ cm}^2$) < specimens with water immersion at 20°C ($\sim 0.17 \Omega \text{ cm}^2$) < specimens with water post-treatment at 40°C ($\sim 0.20 \Omega \text{ cm}^2$). Furthermore, the 40°C water treatment led to the maximum coating resistance (8230 Ω cm²) and a lower coating capacitance ($Q_{\text{coa}}$) in comparison with the first two cases. A higher temperature of DI water at 40°C has been previously associated with a reduced amount of oxides/hydroxides. 

| Specimens | No water | 20°C | 40°C |
|-----------|----------|------|------|
| $R_0$ / Ω cm² | 163 ± 1 | 199 ± 0.5 | 170 ± 5 |
| $R_{\text{coa}}$ / Ω cm² | 2848 ± 12 | 2810 ± 5 | 8230 ± 40 |
| $R_p$ / kΩ cm² | 97.0 ± 0.5 | 170.1 ± 0.4 | 203.2 ± 1.2 |
| $Q_{\text{coa}} (\times 10^{-6} \text{ cm}^2) | 8.8 ± 0.1 | 10.1 ± 0.1 | 8.9 ± 0.3 |
| $R_{\text{coa}}$ | 0.80 ± 0.01 | 0.81 ± 0.01 | 0.83 ± 0.01 |
| $Q_{\text{dl}} (\times 10^{-6} \text{ cm}^2) | 4.3 ± 0.1 | 5.2 ± 0.1 | 2.8 ± 0.4 |
| $R_d$ | 0.91 ± 0.01 | 0.93 ± 0.01 | 0.96 ± 0.01 |

**Figure 3.** Polarization scans at 1 mV/s starting from $-1 \text{ V}_{\text{SCE}}$ in 0.05 M NaCl solution for the bare alloy (orange) and the coated alloy, with coatings formed for 300 s followed by 20°C water post-treatment (red), 40°C water post-treatment (green) and no water post-treatment (black).

**Effect of the time of conversion treatment on electrochemical behavior.** In order to determine the preferred time of conversion treatment of the alloy prior to the immersion step in DI water, EIS measurements were carried out in 0.05 M NaCl solution on specimens treated for 600, 900, or 1800 s followed by the standard post-treatment. Figures 4a and 4b show the resulting impedance modulus-frequency and phase angle-frequency respectively. The steady OCP values for specimens coated for 600, 900 and 1800 s were $-0.54, -0.55$ and $-0.7 \text{ V}_{\text{SCE}}$, respectively. The more negative OCP of the specimen treated for 1800 s suggested a less protective coating, which will be discussed later. A similar OCP was recorded before the PDP scan for this coating condition, suggesting a stable solution/coating system during EIS and PDP measurements. TCC coatings formed for 1800 s led to the lowest impedance modulus at $10^{-2} \text{ Hz}$ (Fig. 4a). Correspondingly, the frequency-dependent phase angles displayed a single time constant ($10^{-1} \text{ Hz}$, Fig. 4b). Furthermore, the frequency width of the phase angle peak of the specimens treated for 1800 s was the smallest, which also suggested reduced corrosion protection of the coating. In contrast, a higher impedance modulus at $10^{-1} \text{ Hz}$ and the two time constants ($10^{0} \text{ and } 10^{-2} \text{ Hz}$) resulted with the coatings formed for 600 and 900 s; the data were fitted using the EC model of Fig. 4a. However, it was necessary to include a Warburg resistance in the EC to fit the impedance data (Fig. 1b) for the specimens treated for the longest time to account for the effect of a greater number of defects in the coating formed for 1800 s. The results of fitting the data are presented in Table II. $R_{\text{coa}}$ values increased in order: $\sim 418 \Omega \text{ cm}^2$ for a treatment of 1800 s $< \sim 2327 \Omega \text{ cm}^2$ for a treatment of 900 s $< \sim 14336 \Omega \text{ cm}^2$ for a treatment of 600 s. The lowest charge-transfer resistance, $R_p$, was revealed in the specimen coated for 1800 s ($< 6.3 \times 10^{9} \Omega \text{ cm}^2$), which was reduced by $\times 50$ relative to the specimen coated for 600 s ($\sim 3.3 \times 10^{9} \Omega \text{ cm}^2$). It is concluded that increasing conversion treatment times can lead to a deterioration of the corrosion protection, especially for the specimen coated for 1800 s with an enlarged $Q_d$ and smaller exponent n_a. In addition, the presence of Warburg resistance of $\sim 6328 \Omega \text{ cm}^2$ in the coatings formed for 1800 s is attributed to diffusion of oxygen and metal ions through the defects in the coating, such as the coating cracks around the particles.

**Figure 5.** PDP scans from $-1.0$ to $+1.0 \text{ V}_{\text{SCE}}$ in 0.05 M NaCl solutions of the specimens coated similarly to those used in Fig. 4. In agreement with findings from EIS, PDP curvers of coatings formed for 1800 s displayed a reduced corrosion protection, evident from an increased current density in the anodic and cathodic branches of the curve. The occurrence of a peak was due to oxidation of copper ($\sim 0.2 \text{ V}_{\text{SCE}}$). The corrosion in the specimens coated for 1800 s are
Conversion treatment to 1800 s can encourage further fluorine enrichment at the coating/substrate interface, which can promote substrate dissolution around the cathodic particles.

**Image-assisted electrochemical noise analysis.**—In order to assess the longer-term corrosion protection performance of TCC coatings in naturally-aerated 0.5 M NaCl solution, ENA measurements were undertaken, combined with in-situ imaging. Owing to the decreased corrosion resistances of specimens coated for 900 and 1800 s in the EIS and PDP tests, measurements were restricted to specimens treated for 300 and 600 s. The time evolutions of the low-frequency noise resistances (NRs) of the bare alloy and TCC coated alloy with the standard post-treatment are shown in Fig. 7a. Similar values of the NRs were found in the cases of the coatings formed for 300 and 600 s after exposure for 240 h, suggesting similar corrosion protection properties. The TCC coated specimens showed a × 6 increase in the NR relative to that of the bare alloy. Figure 7b displays the optical macrographs of the bare and coated alloys obtained during corrosion tests. On the bare alloy, corrosion products were generated after only 1 h (not shown here). Corrosion subsequently propagated to generate the dark pits after exposure for 60 h whereas no corrosion products were observed on specimens with treated for 300 and 600 s. However, bubbles formed on both coating surfaces after immersion for 10 min and their population increased to reach a stable level after 5 h. A greater number of bubbles was present on the coatings formed...
Figure 6. (a, b) Scanning electron micrographs of the coated specimens after conversion treatments for (a) 600 and (b) 1800 s, followed by the standard post-treatments, (c, d) SEM/EDS point analyses of the coated specimen formed for 600 and 1800 s above (c) the alloy matrix and (d) intermetallic particles corresponding to the star marked areas in (a) and (b) respectively. In addition, SEM/EDS point analyses of TCC coatings formed for 300 s above (c) the matrix and (d) intermetallic particles were also included.

Figure 7. (a) Time evolution of the electrochemical noise impedances (at 0.005 Hz) of the bare alloy and TCC coated alloys treated for 300 and 600 s, followed by the standard post-treatment, in 0.5 M NaCl solution. (b) Optical macrographs acquired during ENA measurements. For 600 s relative to that formed for 300 s, as shown in Fig. 7b. The bubbles would be attributed to hydrogen gas generated during corrosion events at coating defects, possibly indicated more localized corrosion. The greater number of bubble on the specimens treated for 600 s suggests a lower corrosion protection from the coating in the longer-term corrosion performance test.

Figures 8a and 8b show scanning electron micrographs of the corroded surface of the coatings formed for 300 s, with a standard post-treatment, at the end of ENA measurements at 240 h. Low-resolution imaging in Fig. 8a shows the presence of crystalline NaCl deposits (as labelled by “1” and “2”) and regions of partially-exposed substrates (as labelled by “3”), with compositions having been analyzed by SEM/EDS (not shown here). Figure 8b shows chloride-containing corrosion products accumulated around the regions of partially-exposed substrate of about 0.1 mm in diameter, which are about the size of hydrogen bubbles observed using the optical camera (Fig. 7b). With regard to the regions of exposed substrate, SEM/EDS point analyses shown in Fig. 8c revealed a large variation in the zirconium intensities between five examined spots (yellow stars, Fig. 8b). Some points indicated little or no coating remaining.

In summary, a standard immersion post-treatment in a DI water bath at 40°C for 120 s can enhance corrosion protection properties of TCC coatings formed on Fe(III)-treated AA2024 alloys, consistent with the literature. With regard to the effects of the conversion treatment time, increasing conversion treatment time up to 1800 s resulted in a reduction in the corrosion protection properties as evident from the results of EIS and PDP in 0.05 M NaCl. This phenomenon is attributed to the increased number of defects, e.g. cracks, in the coating, especially around the cathodic second phase particles. Simultaneously, fluorine accumulation in the coatings and copper enrichment at the coating base proceed with increasing TCC coating treatment duration. As a consequence, localized corrosion events
bubbles was observed on the surface coated for 600 s, which were associated with the local corrosion events. In this regard, the preferred coating process consists of surface pre-treatment (NaOH etching and D-30 desmutting), conversion treatment for 300 s and the standard post-treatment in the DI water at 40 °C, cool-air drying and overnight air ageing.

Conclusions

1. An immersion post-treatment in a DI water bath at 40 °C for 120 s can considerably enhance the coating corrosion protection properties of TCC coatings on AA2024-T351 alloy compared with the absence of a post-treatment or post-treatment at 20 °C.
2. Coatings formed for 900 and 1800 s revealed worse corrosion protection properties than coatings formed for 300 and 600 s due to an increase in the number of defects, such as cracks, especially around intermetallic particles.
3. Electrochemical impedance and potentiodynamic polarization measurements reveal that TCC coatings formed for 300 or 600 s with a standard post-treatment offer the best corrosion protection properties compared to the coatings formed for 900 and 1800 s.
4. Real time imaging of the coated surfaces reveals the presence of hydrogen bubbles due to the local corrosion events that appeared to be more numerous for the latter coating.

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References

1. F. Pearse steadin and V. S. Agarwal, Plat. Surf. Finish. 81, 50 (1994).
2. M. W. Kendall and R. G. Buchheit, Corrosion. 59, 379 (2003).
3. L. Xia and R. L. McCreery, J. Electrochem. Soc., 145, 3083 (1998).
4. Y. Gussaud and G. S. Frankel, Surf. Coat. Technol., 206 (2012).
5. L. Li, G. P. Swain, A. Howell, D. Woodbury, and G. M. Swain, J. Electrochem. Soc., 158, C274 (2011).
6. J. Qi, T. Hashimoto, J. Walton, X. Zhou, P. Skeldon, and G. E. Thompson, J. Electrochem. Soc., 163, C25 (2016).
7. L. Li, K. P. Doranand, and G. M. Swain, J. Electrochem. Soc., 160, C396 (2013).
8. A. E. Hughes, G. Theodossiou, S. Elliott, T. G. Harvey, P. R. Miller, J. D. Gormanand, and P. J. K. Paterson, Mater. Sci. Technol., 17, (2001).
9. S. K. Toh, A. E. Hughes, D. G. McCulloch, J. duPlessis, and A. Stohnam, Surf. Interface Anal., 36, (2004).
10. J. Qi, A. Némcová, J. R. Walton, X. Zhou, P. Skeldon, and G. E. Thompson, Thin Solid Films, 616, (2016).
11. ASTM, ASTM Standard G85-09. In Standard Practice for Modified Salt Spray (Fog Testing). ASTM: Philadelphia, PA, 2009.
12. M. García-Rubio, P. Ocón, M. Curioni, G. E. Thompson, P. Skeldon, A. Laviña, and I. García, Corros. Sci., 52, 2219 (2010).
13. Y. Gussaud and G. S. Frankel, Corrosion, 68, 045002-1 (2012).
14. K. Cho, V. Shankar Rao, and H. Kwon, Electrochim. Acta, 52, 4449 (2007).
15. J. Liang, P. B. Srinivasan, C. Blawert and, and W. Dietzel, Electrochim. Acta, 58, 6802 (2010).
16. A. C. Balaskas, M. Curioni, and G. E. Thompson, Surf. Interface Anal., 47, (2015).
17. M. Curioni, A. C. Balaskas, and G. E. Thompson, Corros. Sci., 77, 281 (2013).
18. A. C. Balaskas, M. Curioni, and G. E. Thompson, J. Electrochem. Soc., 161, (2014).
19. J. Qi, T. Hashimoto, J. R. Walton, X. Zhou, P. Skeldon, and G. E. Thompson, Surf. Coat. Technol., 280, 317 (2015).
20. J. Qi, T. Hashimoto, G. E. Thompson, and J. Carr, J. Electrochem. Soc., 163, C131 (2016).
21. C. A. Matzdorf, W. C. Nickerson, and E. Lipnickas, 2005 Tri-Service Corrosion Conference, NACE International: Orlando, Florida, U.S.A, (2005).
22. J. Creus, H. Mazzile, and H. Idrissi, Surf. Coat. Technol., 130, 224 (2000).
23. J. Qi and G. Thompson, Appl. Surf. Sci., 377, 109 (2016).
24. F. O. George, P. Skeldon, and G. E. Thompson, Corrosion., 65, 231 (2012).
25. H. Habazaki, K. Fushimi, K. Shimizu, and P. Skeldon and G. E. Thompson, Electrochem. Commun., 9, 1222 (2007).
26. Y. Liu, P. Skeldon, G. E. Thompson, T. Hashimoto, and C. J. E. Smith, Trans. Inst. Metal Finish., 83, (2005).